Remediation of Arsenic from Groundwater Containing Organic Compounds by Ion Exchange Media

A K M Saiduz Zaman

A Thesis
in
The Department
of
Building, Civil, and Environmental Engineering

Presented in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy (Civil Engineering) at
Concordia University
Montreal, Quebec, Canada

April 2006

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-16283-5
Our file Notre référence
ISBN: 978-0-494-16283-5

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Abstract

Remediation of Arsenic from Groundwater Containing Organic Compounds by Ion Exchange Media

A K M Saiduz Zaman, Ph.D.
Concordia University, 2006

This research work was dedicated to the problem arising from the coexistence of arsenic and organic substances principally in the US (the Superfund Sites) and Bangladesh. Dissolved organic ions are strong competitors to arsenates, and because of their large size and slow kinetics, arsenic removal becomes problematic. Macroporous ion exchange media can remove both arsenic and organic pollutants efficiently while preserving exchange capacity and effluent quality.

The novelty of this work is characterized by the determination of interpendence of important factors influencing the sorption of arsenates and organic substances by macroporous ion exchange media. Exchange capacities of these resins in both chloride and hydroxyl forms in acidic media as well as the chloride-form operating in weakly basic medium were investigated. The investigations were focused on factors such as the effects of pH, influent concentration of dissolved organic matter (DOM) and filtration velocity. Interaction of these effects was also investigated. Reducing the pH from 10.4 to 7.0 increased the arsenate-exchange capacity from 28 meq/kg to 63 meq/kg (a 35 meq/kg increase).

Optimum conditions for regeneration of macroporous media have been determined such as a NaCl consumption of 300 kg/tonne, a concentration of NaCl solution of 10%, a ratio of NaCl concentration to that of NaOH in regenerant of 10, a regeneration rate of 4 m/h, and a temperature of 40° C.

Waste handling processes have been developed to treat and reuse spent regeneration solutions as well as to detoxify the solid waste containing arsenic and organic matter. A reagent based technology for the treatment of spent regeneration solutions by $Ca(OH)_2$ and $MgCl_2$ (or $MgSO_4$) has been devised.

Based on the results, appropriate decontamination schemes have been developed for groundwater contaminated with arsenic and organic impurities. The benefit of these schemes is guidance for the organization of the treatment process depending upon the levels of mineralization and concentration of DOM as well as the conditions for the implementation of the process (for an existing or new treatment unit to be designed).

Acknowledgments

I dedicate this research work to my passed away wife Late Sarah Sadia Noor.

As with any other research, the number of individuals who have made it possible far exceeds my name alone. At the hazard of leaving someone out, I would like to explicitly thank the following individuals for their contribution.

First and foremost I want to express my gratitude to Professor Catherine Mulligan, and Professor John Hadjinicolaou, who did the bulk of the thinking: analyzing, predicting, formulating innovative ideas, and guiding all the way up to the end of this research.

I am grateful to Professor Heidi M. Muchall for her helping me to understand the behavior of organic molecules and their functional groups, which constitutes, in fact, the bulk of this research.

I am also thankful to Professor Ted Stathopoulos for his helping me to understand the importance of "design of experiments" in engineering statistics and Professor Amruthur Ramamurthy for his guiding in hydraulic calculations.

To Mr. Ron Parisella, who is known to be the father of graduate students, our esteemed teacher in the lab, I offer sincere appreciation for his help and assistance in carrying out the research.

I am thankful to a number of co-workers and friends: Drobotea Elena, Yuan, Azita, Behnaz Dahr Azma, Ilya Kaplun, Monem Elzeftawny, Hafez Massara, Suiling Wang, Ali Mahmood and many others for their encouragement and keen interest in this new environmental trend – the utilization of arsenic contaminated groundwater in potable water supply. To them a hearty thank you!

And last, but certainly not least, I wish to thank my family: my daughter Nuwaira Hiam, my father A K M Hamiduzzaman, my mother Begum Mahmuda Mirza, my younger brother Dr. Hadiuz Zaman and my wife Humaira Haroon, who have put up with the nonsense of my being a full-life student.

Table of Contents

LIST OF FIGURES

List of Tables

List of abbreviations used

3FI	3 Factor Interaction
Adeq Precision	Adequate Precision
Adj R-Squared	A measure of the amount of variation around the mean explained by the model, adjusted for the number of terms in the model.
ANOVA	Analysis of variance
As	Arsenic
BAT	Best available technology
CI	Confidence Interval
CM	Carboxylmethylcellulose
COD	Chemical oxygen demand
CV	Coefficient of variation
D	Decarbonizer
DEAE	Diethylaminoethylcellulose
DF	Degree of freedom
DOE	Design of experiments
DOM	Dissolved organic matter
DVB	Divinylbenzene
IX	Ion exchange
MF	Mechanical filter
O&M	Operation and maintenance
O	Oxidizing filter
Obs	Number of observations obtained for a response.
POTW	Publicly Owned Treatment Works
Pred R-Squared	A measure of the amount of variation in new data explained by the model.

PRESS	Predicted Residual Error Sum of Squares
PV	Permanganate value
R-squared	The multiple correlation coefficient computed as 1-[SSresidual/(SSmodel + SSresidual)]
R3FI	Reduced 3 Factor Interaction model
SBR	Strongly basic anion exchange resin
Std	Standard
STW	Shallow tube well
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
TCW	Tank for clarified water
TDW	Tank for decarbonized water
TOC	Total organic carbon
Tonne	Metric Ton
TRRS	Tank for recovered regeneration solution
TRS	Tank for regeneration solution
TSW	Tank for softened water
WBR	Weakly basic anion exchange resin
VIF	Variance inflation factor

1. INTRODUCTION

The development of industry and the growth of the population are greatly related to the increase in demand for water supplies. Increasing levels of demand on natural fresh water resources have made more urgent the task of supplying potable water derived from groundwater, which can be highly contaminated with such toxic pollutants as arsenic and a number of dissolved organic substances.

The use of groundwater as a source of potable water supply presents serious problems in many countries including US, Bangladesh, India, Thailand, Japan, China, and Canada, amongst others. Until recently, these countries have been in a very privileged position in their use of high-quality groundwater supplies for drinking purposes. This was helpful because it was believed that in most cases, the groundwater is pure enough for drinking. Although the groundwater is pure enough, the surface waters must be treated (purified) before drinking to remove suspended or dissolved material that makes it unsuitable for health or esthetic reasons. The existence of arsenic and other groundwater issues in these countries have changed things dramatically.

Groundwater has been considered so clean that traditionally, water preparation for domestic supplies includes only softening, which is, by definition, the reduction in hardness caused by calcium and magnesium salts. Typical processes include lime softening and sodium cation exchange, hydrogen-sodium cation exchange, sodium cation exchange with acidification, and sodium chloride ion exchange. If potable water is to be prepared from contaminated groundwater then the treatment process should include chemical treatment; the removal of all salts in water to standard maximum allowable concentration levels. Chemical treatment processes include distillation (thermal method), ionic exchange (ion exchange media method) and electrodialysis (electro-chemical method).

It is EPA's belief that arsenic may be mobilized from naturally occurring arsenic in contact with organic rich leachate, thus causing contamination of the groundwater in the area surrounding many superfund sites in the US such as the Coakley landfill (Saalfield et al., 2005). Review of the data indicates the occurrence of arsenic above the detection limit typically coincides with elevated organic material and iron concentrations. Aboveground treatment of the groundwater by macroporous ion exchange media can be a solution to this problem.

Remediation of arsenic from groundwater in Bangladesh has been thorny because of both technical and socio-economic difficulties: arsenic contamination of aquifers where waters are anoxic, particularly where organic matter is abundant which is contributed by the degradation of human organic waste in latrines and fermentation of buried peat deposits. Besides there are widespread public concerns, varying conditions within the affected areas and the overall poverty of the country. Therefore, despite large-scale research in the fields of arsenic removal from groundwater and many well-established technologies, their potential for use in Bangladesh has not previously been studied. Along with the above, there is a psychological barrier based on the fact that local engineers have no clear idea of the available technologies and the properties of groundwater or the possible extent to which it can be treated, and on the arbitrary interpretation of sanitary and hygienic criteria for its utilization. These deficiencies are supplemented in a number of cases by inertia of thinking, and narrow-mindedness, as well as failure to comprehend the evident truth that water is an invaluable creation of nature required for the preservation of life. Attempts are often made to switch to other sources of water supply ignoring the fact that of all water sources, groundwater is still the most reliable and inexpensive supply source. In a preliminary study of arsenic pollution in Bangladesh drinking water sources, Duke University hydrologists have found evidence that surface waters can also be contaminated with arsenic. Thus, say the scientists, abandoning polluted wells in favor of ponds and surface reservoirs, as is advocated by the World Health Organization (WHO) and the Bangladeshi government, will not always solve the problem (Rojstaczer et al., 2004).

Because of all this, Bangladesh, amongst others, has fallen behind the best foreign practice, where many years' experience has been gained in removing arsenic from groundwater. It is very indicative that, up to now, only a few tubewells in Bangladesh has been subjected to arsenic removal treatment.

An extensive literature review and a deeper study of the issues has indicated the viability of combining well-established technologies while efficiently removing the complex and peculiar components of groundwater, arsenic and dissolved organic substances, compounds of nitrogen, surfactants, etc. To remove a high concentration of arsenic alone is quite hard, removal of dissolved organic matter is even harder, and the hardest of all is to remove both simultaneously. While employing conventional arsenic removal technology e.g. ionic exchange, dissolved organic substances are capable of worsening the operating parameters of anionic exchange media by fouling them. The residual concentration of DOM may not only exceed the potable water standard but also in certain technologies e.g. distillation, may cause foaming and discharge of toxic organics into the steam line.

In Bangladesh, the degradation of human organic waste in latrines and fermentation of buried peat deposits created a background contamination analogous to that of tertiary treated domestic wastewater. Safiulla et al. (International Farakka Committee, 2003) have found in their survey that total organic carbon (TOC) in sediment may be as high as 7.8%. Similarly, Nickson (International Farakka Committee, 2003) has obtained a present value of 6% for Gopalgonj (a district in Bangladesh) samples. Dissolved organic carbon in groundwater was found to be as high as 5 mg/L (TOC). This concentration was higher than the 0.2-0.7 mg/L typically found in unpolluted groundwaters, which contain mostly humic substances, such as fulvic and humic acids (Jonsson et al., 2004).

In this regard, when removing arsenic by any of the technologies, correction or addition is required to the existing technology in order to remove DOM. In water and wastewater treatment practices, this problem is traditionally solved by sorption on activated carbon. However, the development of macro and iso-porous ion exchange media, their relatively low cost, acceptable exchange cycle capacity, sorptive capacity, degree of sorption, and the simplicity of regeneration make them competitive in comparison to activated carbon. Because of this, the task of using macro-porous ion exchange media, with a view to removing arsenic from groundwater containing organic substances efficiently, has been urgent. The case of Bangladesh was used in this work as an application and not the main focus on the identification and solution to their main problem.

Proceeding with the information cited above, this research work aimed at the investigation of the pattern of co-sorption of mineral and organic ingredients of groundwater, on macro-porous ion exchange media, in the schemes of softening and chemical arsenic removal. This included:

- Determination of sorption and regeneration rates
- Development of an effective technology for regeneration and utilization of spent regeneration solutions, and
- Evaluation of technical, economic and environmental efficiency of the proposed schemes.

1.1 Research rationale

The rationale directing this inquiry stems from the need to develop and apply a technically sound and environmentally safe method for arsenic removal in the presence of dissolved organic matter. Arsenic is a common contaminant throughout the US, including nearly one third of superfund sites (Saalfield et al., 2005). 45/97 sites have been reported to be contaminated with arsenic that comes from nonanthropogenic sources. 42/45 arsenic sites are also contaminated with organic matter. Many of these landfill superfund sites have been contaminated with a number of toxic metals (e.g., As, Cr, Pb, Ni, Zn) and aromatic hydrocarbons such as benzene. Long-term monitoring indicates that the concentration of most of these contaminants have decreased as a result of treatment by monitored natural attenuation; however, dissolved arsenic levels increased modestly over the same interval. This increase is caused by the microbially intervened reductive dissolution of arsenic-bearing iron oxides. This reduction is advanced by the presence of landfill-derived organic matter. In fact, decreasing the part of organic concentrations that was caused by microbial decomposition is highly correlated to the degree of arsenic release from the sediments into groundwater. Overall, the potential of organic matter decomposition to stimulate the release of natural arsenic have become an issue for the potential of monitored natural attenuation for site remediation (Saalfield et al., 2005).

It has been proposed that organic carbon in buried peat in the Bengal basin was the driver of microbial reduction of FeOOH in the sediments, and that human organic waste in latrines might locally contribute to As release by providing point-sources of organic matter to enhance local reduction of FeOOH (Mc Arthur et al., 2004). The global rise in sea level between 18 and 6 ka (ka is a thousand years ago), created settings worldwide for As-enriched aquifers to form. The rates of sea level rise and sediment supply have been the primary controls on wetland formation, where organic-rich muds and alluvial or deltaic sands are closely juxtaposed (Banerjee et al., 2004). Dissolved organic matter has become a vital problem in arsenic removal.

This information implies not only the need to identify alternative technological paths to remove arsenic in the presence of DOM, but also to find approaches capable of integrating various perspectives and knowledge. In Bangladesh, widespread water quality problems attributable to farm operations and domestic settlements require an expanded suite of solutions. This thesis explores the technical capabilities of ion exchange treatment in arsenic removal along with DOM. Although ion exchange is a well-studied process, scientific investigations of its capacity and dependencies have not previously been studied. This lack is due primarily to the fact that arsenic occurrence in the presence of DOM was new and unusual until recently (Banerjee et al., 2004). Little research has been conducted to identify the barriers and opportunities related to the implementation of ion exchange to remove arsenic and DOM and few studies in Bangladesh have fully documented case studies.

There are a number of standard technologies that efficiently remove arsenic from groundwater. Coagulation, adsorption, ion exchange, and some emerging technologies such as low-cost column filter and SAFI filters are claimed to be in use in some restricted regions of Bangladesh. According to Safiulla et al (International Farakka Committee, 2003), a total of 500 arsenic removal units were distributed among affected individuals. This is of course appreciable. Nevertheless, this number is not significant while over 40 million people are reported to be arsenic affected. Millions of tubewells still need to be taken care of. Literature review and personal survey indicate that none of the mitigation measures has taken the presence of dissolved organic species into account. However, it is the existence of a variety of impurities in the polluted ground waters, which distinguishes them from natural waters. The problem of soluble arsenic alone in drinking water has well been addressed worldwide. Natural organic matter places a substantial restriction to most of the technologies established so far. It must be emphasized that this demands changes to the conventional technology of arsenic removal and conditioning, and the development of new variations of the conventional processes of coagulation, filtration, adsorption, ion exchange and distillation. Hering et al. (1997) studied such an issue relating to arsenic removal from drinking water during coagulation. The presence of sulfate (at pH 4 and 5) and natural organic matter (at pH 4 through 9) adversely affected the efficiency of arsenic (III) removal by ferric chloride. Arsenic (III) could not be removed from source waters by coagulation with alum. Similarly, organic fouling of ion exchange resins is quite well known. Therefore, the presence of dissolved organic matter in groundwater destined to arsenic removal is a vital problem. At present, this is one of the most important problems, the immediacy of which is indicated by the fact that significant concentrations of DOM (5 mg/L of TOC) (Jonsson et al., 2004) have been found in Bangladeshi groundwater. The role of the dissolved organic matter is to inhibit the sorption of arsenic by gel-type resins. This problem exists not only in a number of regions of Bangladesh but also in many other countries including the US. The alternative is the use of macrporous ion exchange resins instead of gel-type resins.

This study involved investigations of arsenic and organic removal from drinking water by ion exchange. Since this is neither a feasibility study nor an engineering project, emerging technologies offered to Bangladesh and their many drawbacks including waste disposal were not investigated. It is noteworthy that waste disposal issues are strongly dependent on the technology chosen.

The main concern was about the effect of interventions such as pH, initial concentrations of arsenic and DOM, filtration velocity etc. The sole purpose of the performance and analysis of the experiments was the drawing of inferences about the effects of treatments. A number of regression equations derived in this research are such statistical inferences.

The main disadvantages of using experimental method to study ion exchange are that it is labor intensive, provides limited information and may yield results which can only be applied under the conditions obtaining in a given experiment with respect to given parameters. Such parameters include the regeneration regime, ion exchange rate, influent water quality, type and fractional composition of the exchange media, column parameters, conditions of supply for regenerant and so on. None of these parameters is constant during actual operation. Therefore, a design based solely on experimental data can result in substantial failures. Subsequently, in order to avoid such failures those elements of the scheme on which its reliability depends are over-designed. This is apparent in the installation of additional filters, and the excess consumption of feed materials and reagents, with consequential increases in the volume of wastewater and costs of operation. The main difficulty in the optimization of ion exchange treatment for potable water supply lies in the large number of interrelated parameters, which characterize the process. The most rational research method is the application of a mathematical model that will allow the optimum operating parameters to be determined by calculation. The use of a computer for these calculations greatly enhances solution of the problem and allows wide ranges to be considered for large numbers of parameters. Within relatively short periods of time one can estimate the optimal levels for the process under study, or in other words, set up the optimum values of all the variables, thereby achieving the extreme values of the selected criterion.

1.2 Objectives

In light of the rationale outlined above, the goal of this research was: **to investigate the effect of interrelated parameters, which characterize the ion exchange process when removing arsenic in the presence of DOM**. To achieve this goal, the following objectives were established:

- To develop a statistical relationship that will allow the optimum operating parameters to be determined by calculation for the removal of As in the presence of DOM onto macro-porous ion exchange media in chloride form and the development of optimum conditions for their regeneration.
- To optimize the operating parameters of macroporous ion exchange media used in a two-stage deionization system, comparison of the sorption regimes of organic and mineral impurities, and the solution in this respect of the practical problems of determining the limit of duration of filter cycles and the need to include an adsorption unit in the process sequence.

The scope of this research included:

- Chromatographic separation and identification of the organic content of influent water contaminated with As and DOM
- Selection of the principal factors that significantly affect ion exchange capacity and residual concentrations of arsenic in the presence of DOM
- Running preliminary experiments in order to determine and justify the intervals and levels of various concentration factors as well as hydrodynamic factors.

- Determination of optimal conditions for regeneration of exhausted ion exchange media
- Determination of the dependences of ion exchange capacity and residual concentrations
- Statistical analysis of the experimental results while formulating desirable regression equations

The thesis is organized in the following way. Chapter 2 provides a literature review and will discuss general characteristics of organic impurities in ground waters, sorption of dissolved organic substances on cationic and anionic exchange media, methods of arsenic removal from groundwater containing organic impurities, and existing technologies for arsenic removal. Chapter 3 provides an overview of the methodology and methods utilized for the investigations. Chapter 4 presents the analyses of the data generated in the four different studies that were investigated during this research. Profiles detailing each study can be found at the beginning of these sections. Chapter 5 provides a synthesis of the findings that were established during the analysis including technical, economic, and environmental parameters of several proposed schemes as well as waste handling. Chapter 6 includes conclusions and interpretations of the findings, summarizes the contributions of the research and presents recommendations for further research.

2. LITERATURE REVIEW

2.1 General characteristics of organic impurities in groundwaters

Arsenic is a common contaminant throughout the US and Bangladesh. In the deltaic plain of the Ganges-Meghna-Brahmaputra Rivers in Bangladesh, arsenic concentrations in groundwater commonly exceed regulatory limits. FeOOH becomes microbially reduced, and it releases its sorbed load of arsenic to groundwater. The most intense reduction is driven by microbial degradation of buried deposits of peat. Concentrations of ammonium up to 23 mg/L come from microbial fermentation of buried peat and organic waste in latrines (McArthur et al., 2004). Concentrations of phosphorus of up to 5 mg/L come from the release of sorbed phosphorus when FeOOH is reductively dissolved, and from degradation of peat and organic waste from latrines (McArthur et al., 2004).

All natural waters contain organic substances. The occurrence of organic substances in the groundwaters of Bangladesh most likely comes from weathering of peat and organic waste from latrines. Unlike inorganic substances, they have high molecular mass, take part in reactions more frequently in the molecular form than in the ionic, are the source of food for animals, and are degraded by micro-organisms.

One of the most widespread classes of natural organic compounds are humic substances. They enter the groundwaters because of the weathering of peat and other organic matter. High concentrations of organic substances in groundwater occur also because of the degradation of organic waste from latrines. Degradation of such waste may cause formation of relatively stable compounds analogous to humic compounds. Organic substances entrained into groundwater may be colorless or colored. The main sources of color of such ground waters are the humic acids, which contain 60-80% of dissolved organic substances.

Humic acids are of high molecular weight; tend to associate with metals, and polydisperse polyfunctional ligands, which are close, in chemical nature, to polyoxypolycarbonic acids. There is information in the literature that these compounds are formed because of polycondensation of flavanoids, lignins and tannins. A simplified structure for humic acid has been proposed by certain workers and is given in Figure 2.1-1 (Purolite, 1999). However, more recent evidence suggests a more complicated structure that can have heavy metals complexed with the groups attached to the aromatic structure, as can be seen, in Figure 2.1-2. "Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide, 1992). In cooperation with the U.S. Environmental Protection Agency, the ATSDR (Agency for Toxic Substances and Disease

Registry) has compiled a Priority List for 2001 called the "Top 20 Hazardous Substances." The heavy metals arsenic (1), lead (2), mercury (3), and cadmium (7) appear on this list. Notwithstanding arsenic is widely referred to as a heavy metal (Kogel-knabner et al., 1988; USEPA, 2003; USDHHS, 2005), its being a heavy metal can well be disputed since arsenic is not always a metal.

It can be appreciated from both Figure 2.1-1 and especially from Figure 2.1-2 that this complex molecule when absorbed onto an anion resin will not only cause potential organic fouling but also is likely to deposit heavy metals within the resin matrix which cannot be removed by caustic soda regeneration.

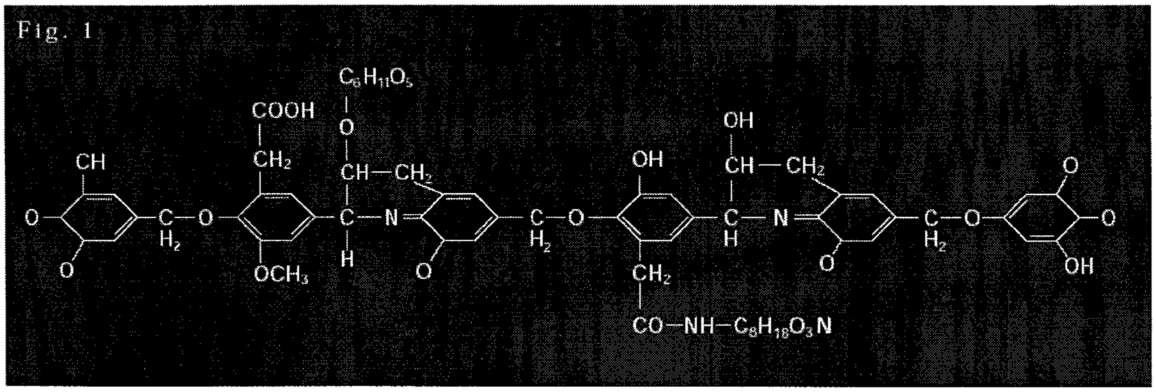


Figure 2.1-1 Simplified structure for humic acid (courtesy of Purolite International Limited).

Fig. 2.

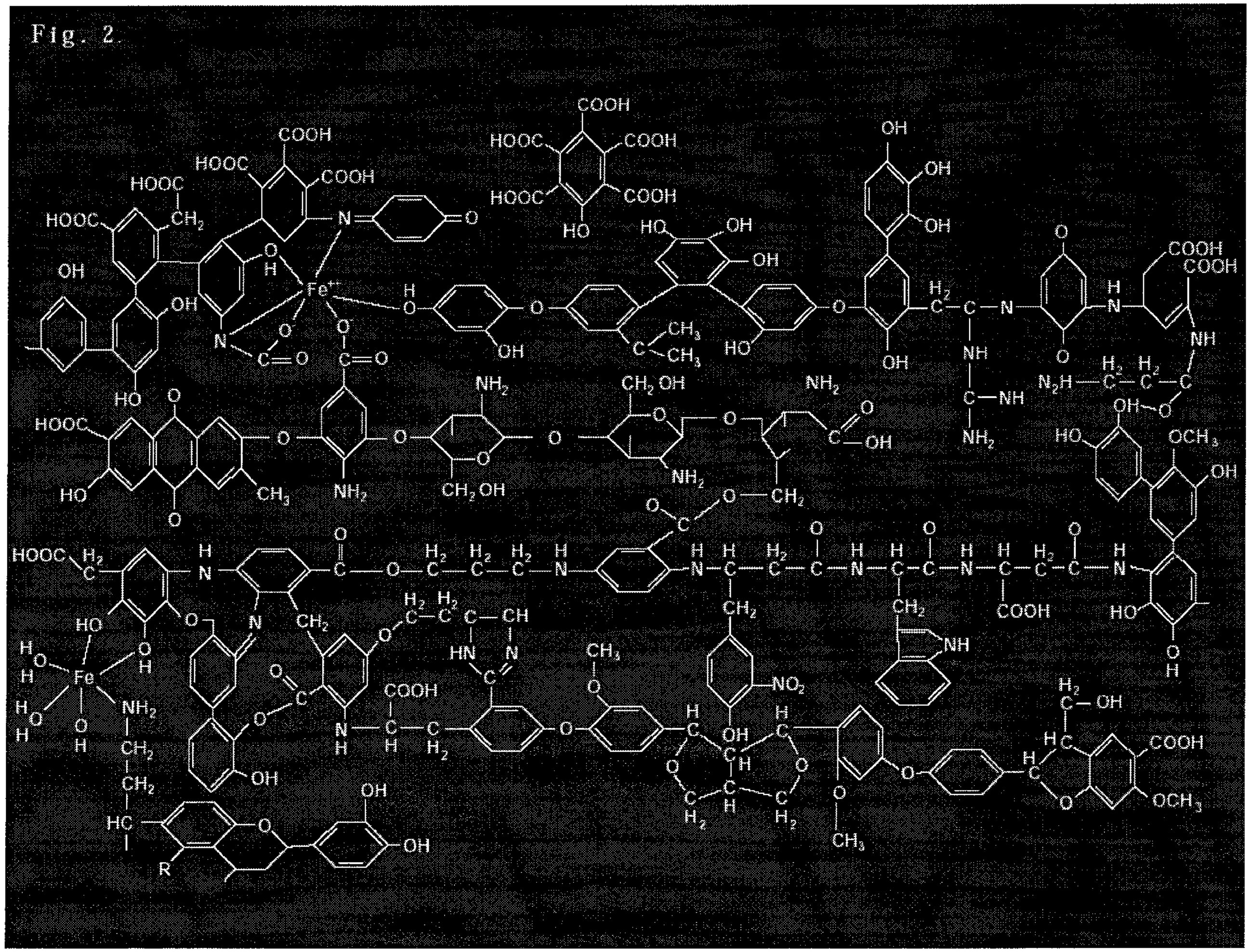


Figure 2.1-2 Structure for humic acid that can have heavy metals complexed with the groups attached to the aromatic structure (courtesy of Purolite International Limited).

As can be seen, the structure of humic acid includes a number of oxygen-containing functional groups: carboxyl groups, phenolic and alcoholic hydroxyls, carbonyl groups, enolic, quinoid, lactonic and etheric groups. The acidity of humic substances is caused by numerous carboxyl groups as well as by phenolic and enolic hydroxyls.

The fulvic acid type structure has not been as well defined as the humic acid but it is thought to be smaller. Fulvic acids are more water-soluble. For them, higher degree of oxidizability and higher content of carbonyl and hydroxyl groups are characteristic. Analysis of humic acids and fulvic acids testifies of the significant contribution of oxygen in their structure (for fulvic acids it is up to 51%). Humic acids are usually found in groundwater in the colloidal state, and only at high pH values do they transform into the dissolved state. Fulvic acid may simultaneously exist both in colloidal and dissolved states. The molecular mass of these compounds ranges from hundreds to 200,000 g/mole (Gjessing, 1970).

The hydrogen in the carboxyl groups may be displaced by cations, forming humate salts. Phenolic oxy-groups also contribute to the formation of humic acids complexed with ions of metals. Due to the presence of these two functional groups in the structure of humic acids, the latter plays an important role in dissolution, transport and deposition of metals. Humates of alkaline metals and ammonia are soluble in water but humates of calcium, magnesium, and iron are almost insoluble. Due to the higher solubility, fulvic acids comprise the bulk of DOM in ground waters. As a rule, the content of fulvic acids exceeds that of humic acids and constitutes 1-100 ppm (Hand et al., 1999). Salts of fulvic acids with Na^+, K^+, NH_4^+, and Fe^{2+}, are soluble in water. Fulvic acids are classified as crenic and apocrenic acids according to the extent of the solubility of their barium salts. Crenic acid is a complex of the least oxidized humic compounds; its barium salts are water-soluble. Apocrenic acid is a mixture of more oxidized humic compounds. Its barium salts are insoluble in water (Hand et al., 1999). The chemical stability of humic compounds to oxidizers and adsorbents increases in the following sequence: humic acids – colloidal fulvic acids – dissolved fulvic acids. Therefore, when designing a technological unit for the removal of arsenic and DOM, it is necessary to consider not only their concentration but also the fractional composition of humic compounds. Thus, the predominance of dissolved fulvic acids decreases significantly the efficiency of coagulation, despite small concentrations of organic compounds in natural waters (Nicholadze, 1987).

The contamination of surface and ground waters with domestic and industrial wastes has already led, in a number of cases (e.g. Bangladesh), to such state, that they can only formally be considered natural, but as a matter of fact they are diluted city wastewaters (surface water COD values reported to be on average 178 mg /L (Gray et al., 2004), and ground water has as high a COD value as 15 mg /L) (Jonsson et al., 2004).

Wastewater from latrines and kitchens enters, via groundwater, the community groundwater treatment units. People often build latrines near a tubewell, do their laundry and wash their cookware all near a tubewell. Shallow water table, poorly constructed wells are all favorable for wastewater to get into the groundwater. Therefore, existing schemes and water-preparatory equipment designed for the use of ground water polluted with arsenic alone, in such cases, may not provide the required degree of arsenic removal.

The most typical components of domestic wastewaters are dissolved, biogenic, organic compounds. Their analytical determination and identification in wastewaters can be very difficult because of their complex and variable composition, and because some individual compounds are only present in minute quantities.

Domestic wastewater can be considered as a dilute mixture of bath and laundry effluents (hygienic processes and laundering), kitchen effluents (cooking and washing-up), urine and feces. Bath and laundry effluents are essentially colloidal suspensions of detergents. Their composition includes substantial amount of matter of organic and inorganic origin (greases, organic acids, urea, ammonia, etc.) as well as suspended particles of cloth, hair and skin. It is because of the presence of soap and protein, and lipid compounds, which form part of human excretions, that these solutions are colloidal. Their overall composition depends, primarily, on the volume of water used for the particular hygienic procedure, as well as on the amount and composition of the detergent.

Table 2.1-1 summarizes the data on the composition and main organic components of bath and laundry effluent, kitchen wastes, urine and feces;

the prime pollution of domestic effluent (Abdullaev et al., 1992). These are generalized data, applicable to any nation, independent of the geographical location.

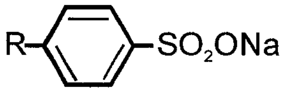
Table 2.1-1 Content of organic species in effluent streams combining to form domestic waste water (Abdullaev et al., 1992).

Organic species	Content of organic species, mg/L	Content of organic species, %
Fats:		
Oleic acid	21.6	8.7
Palmitic acid	13.6	5.5
Stearic acid	2.7	1.1
Soaps:		
Sodium stearate	46.3	18.7
Fatty acids	7.0	4.8
Urea	93.5	37.9
Creatinine	3.4	1.4
Organic acids:		
Hippuric acid	3.5	1.4
Uric acid	1.9	0.8
Other amino acids	0.6	0.2
Citric acid	1.6	0.6
Phenols	0.6	0.2
Starch (as glucose)	13.5	9.2
Fixed fatty acids	22.2	9.2
Total	232	100

Note: the concentrations given in this table are based on the following volumetric assumptions: bath and laundry effluent 120; kitchen wastes 3; urine 1.2; (in units of liters per head per day).

There are usually no significant differences in the proportions of these compounds due to either dietary protein intake or changes in water availability. However, some developed countries may claim the use of more environmentally friendly detergents and soaps.

This literature review leads to the conclusion that the principal components of organic materials in bath and laundry effluents are detergent agents (soaps) in solution at, typically, 120 ppm and greases at 58 to 80 ppm (Malakhov et al., 1988). These concentrations relate to the standard water consumption for bathing and laundering of 120 liters per head per day. About three quarters (72%) of the soaps used for bathing and laundering are sodium stearate, $C_{17}H_{35}COONa$, based. Recently, synthetic detergents have become more widely used, and detergents are now found in bath and laundry effluents, which represent a mixture of sodium salts, sulfuric esters and alcohols. The principal organic component of synthetic detergents, amounting to some 15 to 20% of their mass, is sulphonate. Figure 2.1-3 shows the structural formula of sulfonate.



Where R = C_8 to C_{15}.

Figure 2.1-3 Structural formula of sulfonate (Malakhov et al., 1988).

The composition of kitchen-derived effluents is mainly determined by the food processed in the kitchen. The main components of such effluents tend to be animal fats and vegetable oils, which are typically present at concentrations in the range 600 to 2000 ppm on the basis of a consumption of 3 liters per head per day.

The most common acid in natural fats is oleic acid, which is comprised of more than 50% of the overall acid weight. Palmitic acid is also present in all of the fats to the extent of about 35% by weight. Stearic acid is less common, making up around 10% of the total by weight (Malakhov et al., 1988).

Human excretions, urine and feces, form the greater part of domestic wastewater. Typical daily human diuresis is between 800 and 1800 mL. Urine, because of its chemical composition, is the worst pollutant in domestic effluent; it is made up of some 229 compounds including 103 nitrogen-containing substances, 30 electrolytes, 22 vitamins, 38 hormones, and 10 enzymes, as well as organic acids, lipids and carbohydrates (Kim et al., 1998).

The organic components of urine are mainly nitrogenous compounds – various functional groups with NH_2, NH, etc. The major part (55%) is carbamide, i.e. urea, the concentration of which is between 15.6 and 32.9 g/L in domestic effluent. Amongst other organic compounds are creatinine at 0.42 to 1.33 g/L, amino acids including – alanine, glycine, histidine and glutamine in substantial amounts – (0.17 g/L), hippuric acid (0.07 to 1.75 g/L), uric acid and phenols (0.01 to 0.3 g/L) (Kang et al., 1989).

Feces are characterized by a variety of chemical, biochemical and microbiological components at high concentrations. Typical daily human fecal production is around 100 to 300 g. The main components are fats such as stearic acid, (27.7 to 32.8 g/L), soaps (6.5 to 11.75 g/L), starches (1.5 to 33.75 g/L) and fixed fatty acids (28.75 g/L) (Sannolo et al., 1981).

Untreated domestic wastewater, entering groundwater, deteriorates the chemical composition of groundwater by the components cited above. Villagers tend to build their latrines near a newly installed tubewell, do their laundry and wash their cookware all near a tubewell. It is the shallow water table and poor construction of wells that allows wastewater to get into the groundwater. Such cases are quite common in Bangladesh. The organic impurities in groundwater, entering the arsenic removal units, to a significant extent, complicate the normal operation of ion exchange units. If organics are allowed to accumulate on a resin, the following effects can be observed:

- Reduction in water quality
- Lower operating capacity

- Higher rinse requirements

If the exchange sites on an anion resin are partially screened by large organic molecules, the rate of exchange of inorganic arsenate ions from the water onto the resin will be slower. Therefore, it is urgent to study the sorption of DOM on traditionally used gel-type ion exchange media in arsenic removal such as Purolite A-300 and its analogue macro-porous anionic exchange medium such as Amberlite IRA-910. A strong-base anion exchange resin (SBA) in either chloride or hydroxide form can remove As (V) (Wang et al., 2000). Purolite A-300 is such a strong base anion exchange resin. Amberlite IRA-910 is also strongly basic anion exchange resin with macroporous structure. Macroporous resins are more appropriate to prevent organic fouling (Purolite, 1999).

Determination of the chemical composition of organic matter can be very difficult because of its over all complexity and the presence of some compounds in microquantities. If groundwater, containing DOM, is to be prepared for use in the arsenic removal unit, it is important that the composition of the organic load be determined accurately. This is necessary in order to predict both the extent of treatment needed to remove the organic impurities at various arsenic removal stages and the influence of the individual organic components on the water condition in the arsenic removal systems. Concentration and fractionation techniques are used extensively in the organic analysis of wastewater (Leenheer, 1996).

The standard methods of analyzing dissolved organic materials have a number of disadvantages. These include losses due to compound volatility, the salting out of high molecular weight materials, and changes to the natural organic compounds arising in the process of separation. Many of these disadvantages do not arise if the organic materials are separated by chromatographic fractionation using cellulose based ion exchange media (Abdullaev et al., 1992). This technique makes it possible to extract the dissolved organic substances and classify them as acidic, basic or neutral. The sorption of organic compounds takes place chiefly on the fiber surfaces of ion exchange cellulose media, which makes them suitable for the separation of organic substances. Other advantages are the rate of the sorption process, and the ease and completeness of subsequent desorption for analysis; it is also possible to concentrate the materials under investigation.

The quantitative and qualitative analysis, presented above, of the composition of organic impurities enables the organization of the investigation of ion exchange processes of such waters, allows the evaluation of the intensity and nature of the fouling of ion exchange media, the expediency of the addition of organic removal units in the arsenic removal process sequence, the development of a technology to desorb organic materials from ion exchange media, and the prediction of the arsenate-exchange processes depending on the concentration of DOM in the influent water.

2.2 Sorption of dissolved organic substances on cation exchange media

When using ion exchange in groundwater treatment and the influent water is contaminated with not only arsenic but also DOM, one of the most important issues is the study of the impact of DOM on the operating parameters of ion exchange media. The “poisoning” impact of DOM is determined by the nature of dissolved organic substances and their concentration in influent water. Proteins polyelectrolytes, detergents and certain saccharides can foul cation resins (Keller et al., 2005).

In the practice of chemical treatment of natural waters, containing organic contamination, serious deterioration of the operating capacity is often observed. Reduction in the operating capacity of ion exchange filters, deterioration of the quality of filtrate, increase in the consumption of regeneration reagents and wash water, reduction in the exchange cycle of ion exchange media are caused by the sorption of organic substances on the surface and deep into the volume of the beads of the synthetic resin. Allowable concentrations of DOM in the influent water of a treatment unit must not exceed 2 mgO_2/L, determined by the permanganate value (Popov et al., 1977). While supplying domestic wastewater for stable performance of cation exchange and anion exchange media, it is necessary to provide a reduction in COD to 10 to 12 mgO_2/L. The recommended values are applicable only to chemical treatment systems and limited, first, to the presence of anionic filters in the scheme (Popov et al., 1977). Malakhov et al [85] showed stable performance of the sodium form of cation exchange medium when treating water, containing as high a concentration of DOM as 30 to 60 mgO_2/L as COD (8 to 14 as PV). Permanganate value is a measurement of organic materials in water often called oxidizability. PV is measured by Kubel's method, which is accepted internationally to be the standard method for the measurement of organic substances (UNEP, 2004). PV is the amount of potassium permanganate consumed in the chemical oxidation of organic substances contained in water, this amount being quoted in mg/L $KMnO_4$ as well as in mgO_2/L as the corresponding oxygen equivalent.

Organic ions differ from each other by size, form and molecular mass. They are weakly hydrated, have one or several functional groups that are capable of dissociation and have hydrophobic aliphatic or aromatic composition. The mechanism of their sorption on ion exchange media is highly complicated. Their sorption is determined not only by electrostatic and chemical interaction with the fixed ions and effect of difference in hydratability in the solution and on the phase of ion exchange media, but also by non-electrostatic sorption forces (blocking of electronic clouds of π-bonds) between the ions being sorbed and the structural section of the matrix (London forces). Nonpolar molecules are attracted to each other by temporary dipoles, which are called London or dispersion forces. Deformation of the electron clouds surrounding the molecules creates temporary dipoles. With more electrons, the electron cloud is deformed more easily and more greatly; thus, the dipoles are larger and the attraction is greater. In some cases, formation of hydrogen bonds takes place between the matrix and polar groups of organic ions (Ashirov, 1983).

Inadequate porosity of gel-type ion exchange media hinders the effective desorption of organic molecules. In the course of time, organic substances enter so deep into the resin beads, that extraction of them in the regeneration stage becomes very difficult (Mc Nully et.al.,1986). Sorption of organic ions is characterized by strong manifestation of the steric factor, the factor (always less than one) that reflects the fraction of collisions with orientations that can produce a chemical reaction: sorbed large ion shields other functional groups, narrows the channels and pores down, obstructs them and hinders further penetration of ions from the solution into the resin. In this regard, exchange capacity of ion exchange media tends to be used up incompletely (Ashirov,1983).

Recent understanding is that the deterioration of the operating characteristics of ion exchange media is caused by the reduction in the diffusion rate in resin beads (Pashkov et.al.,1972). The increase in ion exchange rates can be achieved by the use of ion exchange media of special structure: macro and iso-porous resins. Macroporous resins are opaque because they contain as much as 20% divinylbenzene in the polymer matrix. They are not simply gel resins with additional crosslinking since the interior of a gel with 20% DVB (Divinylbenzene) would be inaccessible (Alain,1988). Macroporous resins are produced from a styrene-divinylbenzene copolymer to which has been added a non-polymerizable diluent that volatilizes leaving discrete macro pores throughout the bead. These pores are considerably larger than those found in gel resins and, as such, allow the accessibility of large molecules. Due to the increased amount of DVB in the macroporous resins (i.e. higher degree of crosslinking), little volume change is exhibited in any solvent. Therefore, they may be successfully used in non-polar solvents since the matrix is non-collapsible (i.e. does not shrink). Macroporous resins are also frequently used where rigorous conditions are encountered since the increased crosslinkage permits resistance to resin degradation caused by such factors as osmotic shock, attrition and oxidation. The cited above peculiarities provide easy access to the reacting substances to the active centers and stable sorption as well as desorption processes of organic substances (Payne, 1990; Dal, 1974).

Popular macroporous cation exchange media are as follows: Amberlite 200, 200 c, 252 and 15 A (ROHM and HAAS Company), Duolite c26, Duolite C 464 and C 433 (ROHM and HAAS Company), Zerolite c 625 and C 226 (LOBA CHEMIE PVT. LTD.), Dowex MS C1 (The Dow Chemical Company USA), strongly acidic sulphonated cationic exchange media KU-23, weakly acidic carboxylic cation exchange medium KB-2-7P, KB-2-10P, KB-4-10P (Aj Inc.), Tulsion T 42 MP (LOBA CHEMIE PVT. LTD.) (Ashirov, 1983).

The following are examples of the interaction between DOM and cationic exchange media with a view to clarifying the mechanism of the sorption of dissolved organic substances. The consideration of the sorption of individual organic substances by cationic exchange media enables the prediction of analogous processes when applying cation exchange in groundwater softening in the presence of multi-component DOM. The literature review of the sorption of individual DOM is applicable to the gel-type as well as macroporous cation exchange media in sodium and hydrogen forms. This selection was based on the fact that the sodium ion is the operating form for chemical softening while the hydrogen form is for a thorough chemical treatment.

In the sorption of phenols by gel-type cationic exchange media such as Tulsion T 42, T 40, Ku-2, Ku-1, sulphonated coal, ionic exchange practically does not take place (Yamasaki, 2004), their removal is caused by molecular sorption, efficiency of which depends on:

- The nature of the ion exchange medium,
- The structure of the hydrocarbon skeleton,
- Nature and concentration of the ionogenic (capable of ionizing) groups,
- Location and nature of benzene ring substitutes (Yamasaki, 2004).

The sorption of phenols increases as the salting out effect on phenols in the phase of ion exchange media decreases and as the content of sulfonic groups in the resin decreases.

Sorption of nitrophenols by sulfonic cation exchange media is determined by the following factors (Korenman et.al, 1989):

- Their solubility in the pore water of the resin

- Influence of salting out
- Influence of polar attraction forces and dispersion forces
- Operating form of cation exchange media (sodium form, practically does not sorb nitrophenols)

Better results were achieved when concentrating nitrophenols on macroporous cation exchange medium Amberlite 200 C (Korenman et.al.,1989). The content of divinylbenzene in the matrix of Amberlite 200 C and porosity greatly influence the sorption of alkylphenols. Sorption of alkylphenols depends on the ionic form of cation exchange media and decreases when switching from the sodium form to the hydrogen form. Sorption capacity increases as the length of hydrocarbon chain increases in the following sequence: methyl - < ethyl - < propyl -<butyl -<amylphenol. In addition to the interaction between sorbent and sorbate, the interaction among sorbed alkylphenol molecules influences the sorption process: an increase in the degree of their spreading through the resin substantially increases the sorption process (Alimova et.al., 1981).

Pochhali et al. (1977) studied the mechanism of the sorption of aliphatic carbonic acids onto cation exchange medium Amberlite IRA 120. It was shown that both molecular sorption and ionic exchange take place at the same time. When used in the H-form, the efficiency of molecular sorption increases as the length of the carbonic acid chain increases in the following sequence: formic<acetic<propionic<n-butanoic acid. Molecular sorption of carbonic fatty

acids is a function of chain length as well as dissociation constant. Carbonic acids having a higher constant of dissociation are hardly adsorbed by cation exchange media. On the contrary, with an increase in the constant of dissociation of carboxy acids, ionic exchange increases.

Pavlovich et al. (1985) studied molecular sorption of normal fatty acids (butanoic, valeric, caproic acids) from aqueous and aqueous-organic solvents (aqueous-acetonic, aqueous-methanolic and aqueous-ethanolic mixtures) by the hydrogen form cation exchange media. It was shown that, the distribution coefficients of these acids and the selectivity of sorption, increases with an increase in the dielectric permittivity of the solvent.

Davidov et al. (1987) and Bidnaya et al.(1986) studied sorption of aromatic amines by cation exchange media. As an instance of the sorption of chloroaniline and diethylparaphenylendiamine from a mixture of acetic acid with water by sodium-form cation exchange media (Davidov et al.,1987), it was shown that the nature of the kinetic curves of the sorption of organic ions being investigated corresponded to the sol-gel mechanism at a content of acetic acid in water up to 0.6 molar fractions. With an increase in its concentration, the speed of sorption decreases, which can be explained by a decrease in the extent of swelling of the cation exchange media, as well as the formation of ionic associates in the solution (due to the reduction in dielectric permittivity of the solvent) (Levchenko et al.,1982). Significant sorption of the amines of bases is possible by means of an acid-base reaction between the sulfone groups of the sorbent and amines

(Bidnaya et al., 1986).

The capability of aliphatic amines of being sorbed by cation exchange media Tulsion T 40 and Ku-2 in hydrogen and sodium forms was examined using representative diethylamine and ethanolamine (pushnyak et al., 1989). The sodium form of cation exchange media takes these amines up by means of molecular sorption. Ionic exchange, in this condition, was not observed. Being strong bases, aliphatic amines were sorbed well by ionic exchange when using cation exchange media in the hydrogen form (Phillppov et. al., 1986).

Sorption by sulfonic cationic exchange media was studied for alcohols and ethers (methanol, ethanol, n-butanol, isopentanol, allyl alcohol, methoxyethanol, ethylene chlorohydrin, ethyl acrylate, and butyl acrylate (Philippov et.al., 1986). An excess of the equimolar ratio was observed for hydroxyl containing sorptive materials at one sulfonic group (up to 18 molecules of sorptive materials). Obviously, oxygen atoms of sulfonic and hydroxyl groups take part in the reaction of organic ions and cation exchange media (in addition to the formation of one hydrogen bond between the proton of sulfonic group and oxygen of hydroxyl group. Besides, successive formation of several monolayer sorptive molecules occurs due to intermolecular hydrogen bonds. Complex etheric molecules do not have active protons. Therefore, their capability of being sorbed does not exceed the equimolar quantity of sulfonic group of cation exchange media. Sorption is caused only by the presence of one hydrogen bond between the proton of sulfonic groups and carbonyl oxygen. A significant increase in the sorption capacity, particularly by complex ethers can be achieved when using macroporous cation exchange media (Levchenko et. al., 1982).

Generalized data from various sources is presented in Table 2.2-1, which enables the prediction of the sorption pattern of multi-component systems of DOM by cation exchange media in the scheme of softening (Na-filters) as well as that in the scheme of chemical treatment (H-filters).

From the above analysis of the mechanism of sorption of individual DOM by cation exchange media, the conclusion can be drawn that in the sodium form mainly molecular sorption takes place while in the hydrogen form both molecular sorption and ionic exchange take place.

Abdullaev et al. (1980) showed that the results of fractionation of DOM are presented as three groups (acidic, basic and neutral). The conditions for sorption and desorption of multi-component systems of organic substances are also given by the mentioned generalized parameters.

In the experiments with the sodium form of cation exchange, in the scheme of chemical softening, physico-chemically treated domestic wastewater was used. The concentration of DOM was comprised of 30 to 60 mgO_2/L as COD. The acidic group was sorbed mainly, the content of which in the composition of DOM, may reach 70 to 80%, by the sodium form of cation exchange media.

The basic group of DOM was also sorbed. The initial content of which was insignificant (from 2 to 4%). Neutral compounds, which constitute 20 to 30% of the total quantity, are not sorbed at all by fresh sodium form cation exchange media. However, as it is shown in the report of Malakhov et al. (1987), after the sodium form of the cation exchange medium has sorbed acidic and basic groups, the sorption of the neutral group also takes place. It was shown experimentally that the sorption of the latter takes place by the compounds of other groups, sorbed earlier.

Total sorption of DOM by Na-filters in the scheme of two-stage softening when using treated municipal wastewater constituted: 27 to 31% (in the 1st stage, load KU-2) and 15 to 24% (in the 2nd stage, load sulfonated coal) of initial, for each stage, quantity (Abdullaev et.al., 1980). The exchange capacity of KU-2 was reduced to 13% after 1000 BV, while that of sulfonated coal practically did not change. The irreversible sorption of DOM, in the sodium form, bears a weak pronounced nature.

In the experiments with the hydrogen-form of cation exchange, in the scheme of chemical treatment, biologically treated domestic wastewater subjected to tertiary treatment by coagulation and mechanical filtration was used. The concentration of DOM was comprised of 7.5 to 9 mgO_2/L as COD. Reduction in the concentration of DOM, on average per exchange cycle, constituted: 25 to 30% (in the 1st stage, load KU-2) and 15 to 18% (in the 2nd stage, load KU-2) of initial, for each stage, quantity (Malakhkov et.al., 1988). During the regeneration, the bulk quantity of organic substances was desorbed by acid; nearly 20 to 30% was irreversibly sorbed.

Table 2.2-1 Sorption of DOM of wastewater by cation exchange media in the schemes of two-stage softening and two-stage chemical treatment

Substance category	Substance	Capacity	Resin brand	References
Phenols	Phenol	2 eq/L resin	DOWEX G-26 (H)	(DOW Corp, 2002)
	Alkylphenol		KU-23	(Manza et al.,1983)
Aliphatic amines	Diethylamine, ethanolamine	Not mentioned	Wofatit EP61, EP62, Y59 &Y77	(Heitzsch et.al.,1994)
Alcohols	Primary alcohols	Not mentioned	PRP-X400	(McCarthy et. al.,1992)
Aliphatic acids	Formic, acetic acids	3705 mg/L	Home-made NDA-999	(Pan et.al.,1999)
	Butanoic, valeric, caproic acids	5 g/L	Styrosorbs 1(XDC),Styrosorbs 1BP & Amberlite XAD-2	(Tsyurupa et.al.,1974)
Aromatic amines	3,4- dichloropropionaniline, 3,4 – dichloroaniline	Not mentioned	Amberlite series	(Carlyle, 1982)
	Aniline, α-naphthylamine	2-10 mmol/L; 50-524 mmol/L	Lewatit EP63	(Azanova, 1999)
Aliphatic	Diethylamine, triethylamine	Not mentioned	Amberlite series	(Payne, 1990)

Substance category	Substance	Capacity	Resin brand	References
	Ethanolamines	Not mentioned	Amberlite IR 118H	(Miller et.al.,2004)
Alcohols and ethers	Methanol	Throughout the aqueous solubility range	Amberlite series	(Simpson et.al.,1996b)
	Ethanol	Throughout the aqueous solubility range	Amberlite series	(Simpson et.al.,1996b)
	Propanol, n-butanol, isopentanol, allyl alcohol, methoxyethanol, ethylene chlorohydrin, ethyl acrylate, butyl acrylate	Not mentioned	Amberlite series	(Maity et. al. 1991)

2.3 Sorption of dissolved organic substances on anion exchange media

Many researchers point out the unstable performance of anionic exchange media compared to that of cationic exchange media, when using ion exchange in groundwater treatment and influent water which is contaminated with not only arsenic but also DOM (Rutsch et. al.,1999; Popov et. al., 1977; Levchenko et.al., 1982; Abrams, 1982; Mc Nully et.al.1986; Bullock,2002). Partly this is caused by the fact that, in traditional water treatment, liming is used as a pretreatment, which results in passing the bulk of the dissolved organic species through the cationic exchange media. These are organic acids with carboxylic and phenylhydroxyl groups, dissociated and easily soluble.

Organic species trapped by cationic exchange media can be subjected to destruction by oxidation, since the sulfonic groups are quite stable with weak oxidizing agents (Loraine 2002). However, anionic exchange media can only in exceptional cases and under certain conditions, be subjected to oxidizing reactions. The “poisoning” of anionic exchange media occurs due to the blocking of ionogenic groups as well as due to chemical reactions between functional groups of resins and organic substances being sorbed.

Macroporous ion exchange media have significant competitive advantages against gel-type ones when treating water that is contaminated with organic substances. As it was mentioned earlier (in section 2), their structures increase the rate of the ion exchange process up in the intradiffusion area. This enables the achievement of a significant reduction in the poisoning of anion exchange media by organic substances.

Popular macroporous anion exchange media are as follows: weakly basic Lewatite MP 60 (Bayer Bitterfeld), Amberlite IRA-96 (ROHM and HAAS Company); strongly basic Amberlite IRA-910, Duolite A 161 (ROHM and HAAS Company), Zerolite MPF and KMP (LOBA CHEMIE PVT. LTD), Dowex MSA 1 (The Dow Chemical Company USA), AB-17-10P (Aj. Inc.) (Ashirov, 1983).

A significant amount of research has been dedicated to the "poisoning" of anion exchange media by humic and fulvic acids in natural waters (Mc nully et. al.,1986; popov et al., 1977; Dal, 1974). High molecular mass, the presence of condensed aromatic cycles and aliphatic chains, and the presence of carboxyl, hydroxyl, amino and other functional groups cause the deterioration of ion exchange characteristics by sorption of humic acid. Fulvic acids in natural waters are not individual substances either, but a mixture of aliphatic and aromatic amino acids. Moreover, because of the greater concentration, greater solubility, smaller sizes and sorption of fulvic acids exceeds that of humic acids. For assessment of the poisoning of anion exchange media by these acids, model organic compounds are frequently used. Functional groups of these models simulate those of natural humic and fulvic acids (Levchenko et. al. 1982).

The consideration of the sorption of individual organic substances by anionic exchange media enables the prediction of analogous processes of anion exchange of wastewaters that are characterized by multi-component composition of DOM.

The following literature review is applicable to the gel-type as well as the macroporous anion exchange media in the hydroxyl and chloride forms. This selection was because the hydroxyl form is the operating form for chemical treatment systems while the chloride form is for combined softening and chemical treatment. In the latter case, the use of macroporous resin is only for the purpose of removing DOM before gel-type anion exchange media i.e. in acidic medium.

The mechanism of the sorption of phenols by macroporous anion exchange media (Amberlite IRA-910) is complex: during the beginning of exchange cycle, ion exchange takes place and molecular sorption thereafter. Anion exchange media in the hydroxyl form sorb phenol more intensively compared to those in the chloride form. This can be explained by the formation of hydrogen bonds of phenols with hydroxyl groups (Alimova et. al., 1989).

The gel-type anion exchange media have less capacity with respect to phenols than the macroporous ones do. To use them is particularly unprofitable when phenol concentrations are low and when large volumes of regenerant are required to recover resins having a relatively low exchange capacity.

Sorption of nitrophenols onto macroporous anion exchange media occurs by an ionic exchange mechanism. This is confirmed by a decrease in its efficiency at low pH levels, at which the degree of ionization of nitrophenols is insignificant (Alimova et. al.,1989).

Sorbability of cresols, onto anion exchange media such as Amberlite IRA 910, is determined by the position of the CH_3 groups. The least soluble n-cresol is marked with the greatest sorbability, which indicates the molecular character of sorption (Levchenko et.al., 1982).

Altshuler et al. (1989) and Tsitovich et al. (1988) studied the sorption of aromatic acids by anion exchange media. Nicotinic acid served as the representative of aromatic acids. It was shown that in addition to the ionic exchange mechanism, the reaction of the nonpolar part of anions with the resin matrix also takes place. Selectivity of sorption of organic ions from water depends on dispersion and Coulombic forces as well as on the steric effect. Anionic sorption of aromatic monocarboxylic acids grows with an increase in the pH values of the solutions being treated, which can be explained by the increase in concentration of ionic forms of these acids. Comparative analysis of the mechanism of sorption of benzoic and salicylic acids by macroporous and gel-type anion exchange media indicates nonionic sorption for the first and anionic exchange for the second. The following sequence of sorbability onto gel-type anion exchange media in the chloride form was established: sulfosalicylate ion>anion of benzene sulfonic acid > benzoate ion (Tsitovich, 1988).

Tsitovich et al. (1988) and Selemenov et al. (1982) studied sorption of aliphatic acids by anion exchange. A joint mechanism, ionic exchange and molecular sorption, was marked, seldom with ion exchange alone. The lower the constant of dissociation of the acid and the greater the length of hydrocarbon chain in its molecule, the higher is the molecular sorption. Because of this, the selectivity of ion exchange of these acids grows with an increase in the number of chlorine atoms in the molecule, while molecular sorption falls in the order – monochloroacetic > dichloroacetic > trichloroacetic. For a number of acids (from formic to butanoic) effective sorption by anion exchange media in chloride form was observed (Lecchenko et. al., 1982).

Accompanied by ion exchange, molecular sorption of amber acid, fumaric acid, malenic acid, oxalic acid and other aliphatic oxyacids can be explained by not only Van der Waal's forces but also by the formation of the hydrogen bond between functional groups of ion exchange media and sorbed molecules, the appearance of stable coordination and covalent bonds of ion exchange media with substances being sorbed (Selemenov et. al. 1982).

Sorption of aromatic amines was studied by Dore et al. (1975) and determined by the same factors as the sorption of aromatic acids. It was established that distribution coefficients of aniline and its derivatives depends little on the concentration and always higher on weakly basic than on strongly basic anion exchange media.

Tsitovich et al. (1988) investigated the sorption of 3,4-dichloropropionanilide and 3,4-dichloroaniline by strongly basic gel-type and macroporous anion exchange media in chloride form. As a whole, molecular sorption of macroporous media reached the highest values. In static conditions, these substances were sorbed poorly, but under dynamic conditions, their molecular sorption grows by factors of tens and hundreds of fold. With an increase in the concentration of the solutions being investigated, molecular sorption grew continuously, which is obviously caused by the formation of polymolecular layers of sorbate in resin beads.

Starobinets et al (1986) investigated sorption of aliphatic amines represented by nonionic sorption of the chlorides of primary aliphatic amines. The constant of distribution of a number of chlorides of aliphatic amines (methyl-, isoamyl, heptyl-, undecyl-, and octadecylamine) between anion exchange media and solution increases as the number of carbon atoms in the radical increases, which is caused by hydrophobic reactions.

Levchenko et al. (1982) studied sorption of proteins represented by tryptophan, albumin, and pepsin. With an increase in the concentration of proteins, their adsorption increases on anion exchange media. In addition to electrostatic factors, sorption of proteins is significantly influenced by configuration, structure of lateral chains, pH of solution, and quantity of water bound with anion exchange media and proteins.

Generalized data from the cited above and other sources are presented in Table 2.3-1, which enables the prediction of the sorption pattern of multi-component systems of DOM by anion exchange media for softening (Cl-filters), two-stage chemical treatment (OH-filters) and in the precluded (before

OH-filters) Cl-filters of a treatment plant with a gel-type anion exchange media.

From the above analysis of the mechanism of sorption of individual DOM by anion exchange media, the conclusion can be drawn that in the hydroxyl and chloride forms, a total process, determined by molecular sorption and ionic exchange, takes place. Abdullaev et al. (1992) presented the results of investigation with regards to the sorption of DOM from biologically treated wastewater after tertiary treatment by coagulation and mechanical filtration, onto a gel-type anion exchange media. The initial concentration of DOM constituted from 7.5 to 9 mgO_2/L. Reduction of DOM in one exchange cycle on average constituted from 45 to 50% (stage 1) and from 70 to 80% (stage 2) of the influent for each stage. In the regeneration process, DOM was desorbed by alkali. The quantity of irreversibly sorbed DOM reached 30% of the sorbed quantity. In stage 2, 50% of sorbed DOM per exchange cycle was desorbed (Malakhkov et.al.,1988). Sorption of arsenate in the presence of DOM on Cl-anion exchange media has not been investigated previously. However, sorption of some other metals or salts in the presence of DOM is being studied seriously. The effects of aquatic humic substances on the bioavailability of the lipophilic metal complexes towards freshwater algae are an example of such investigations (Boullemant et. al., 2004). The uptake kinetics of cadmium diethyldithiocarbamate, Cd (DDC) 20, was studied. It was shown that this lipophilic complex was taken up much faster than the free Cd^{2+} ion (up to 70 times faster at comparable total dissolved Cd concentrations) in the presence of DOM. However, there has been no discussion about the regeneration kinetics. Desorption rate is even more important than sorption rate. The regeneration stage is affected more in the organic fouling than the sorption stage. Slow desorption kinetics, in fact, leads to the irreversible fouling of sorbents.

Table 2.3-1 Sorption of DOM of wastewater by anion exchange media in chloride form in the scheme of softening, precluded chloride filters in arsenic removal with gel-type resins, and OH-form filters in the scheme of two-stage chemical treatment

Substance category	Substance	Capacity	Resin brand	References
Phenols	Phenol	50 g/Lof resin, <200 mg/L	Purolite A-100, Amberlite XAD-4, DOWEX MSA-1	(Hand et. al., 1999)
Phenols	Nitrophenol, cresol	40 to 70 % , Not mentioned	MIEX®, Dowex 1	(Cornel et. al., 1986)
Aromatic acids	Benzoic acid	8-25 mmol/L	Reillex-425	(Gusler et. al., 1993)
Aromatic acids	Chlorobenzoic acid	0.05-5 mmol/L	Reillex-425	(Gusler et. al., 1993)
Aromatic acids	Nitrobenzoic acid	639 mg/L	CHA-111	(Zhang et. al.,1997)
Aromatic acids	Aminobenzoic acid	0.09-10 mg/L	Lewatit EP63	(Frimmel et. al.,1999)
Aromatic acids	Salicylic acid	8-25 mmol/L	Reillex-425	(Gusler et. al., 1993)

Aromatic acids	Sulfosalicylic acid	1.2 meq/ml of resin	Dowex 1-X8 resin, Dowex 2-X8 resin	(Daniels et. al., 1965)
Aromatic acids	Benzenesulfonic acid	Not mentioned	Amberlite XAD-2	(Weber et. al.,1981a)
Aromatic acids	N-toluenesulfonic acid	Not mentioned	Amberlite XAD-2	(Weber et. al.,1981a)
Aromatic acids	Sulfonylic acid	Not mentioned	Amberlite IRC-718	(Daniels et. al., 1965)
Aromatic acids	Nicotinic acid	3.5 mmol g resin	Amberlite IRA-900	(Ian et. al., 2002)
Aromatic acids	Chlorophenoxyacetic acid	3705 mg/L	Home-made NDA-999	(Pan et. al.,1999)
Aliphatic acids	Formic acid	55%, 50 g/L resin	DOWEX M-43, Purolite A103S	(DOW Corp., 2002)
Aliphatic acids	Acetic acid	Not mentioned	Dowex 1-X8 resin, Dowex 2-X8 resin	(Daniels et. al., 1965)
Aliphatic acids	Chloro-substituted acetic acid	Not mentioned	Dowex 1-X8 resin, Dowex 2-X8 resin	(Daniels et. al., 1965)
Aliphatic acids	Butanoic acid	Not mentioned	Amberlite IRA-938	(Ayten et. al., 2004)
Aliphatic acids	Tartaric acid	80%	Amberlite series	(Bullock, 2002)
Aliphatic acids	Lactic acid	90%	Purolite A-100, Amberlite IRA 900	(Moldes et. al., 2001)
Aliphatic acids	Citric acid	90%	Amberlite IRA 900	(Moldes et. al., 2001)

Aromatic amines	3,4 – dichloroaniline	2-10 mmol/L;50-524 mmol/L	Amberlite XAD-4, LewatitEP63	(Azanova et. al.,1999)
Aromatic amines	3,4-dichloropropionanilide	Not mentioned	Amberlite series	(Carlyle, 1982)
Aliphatic amines	Trimethylammonium hydroxide,	Not mentioned	Amberlite series	(Hartmeier, 1992)
Aliphatic amines	Trimethylammonium chloride	Not mentioned	Amberlite XAD-2	(Weber et. al., 1981a)
Proteins	Tryptophan, albumin, and pepsin	0.75-0.90 meq/g resin	DEAE 23 SH	(Servacel, 2004)

2.4 Methods of arsenic removal from groundwater containing organic impurities

Several common treatment technologies are used for removal of inorganic contaminants, including arsenic, from drinking water supplies. However, above ground arsenic removal in the presence of dissolved organic matter has not been identified. Large-scale treatment facilities often use conventional coagulation with alum or iron salts followed by filtration to remove arsenic. Lime softening and iron removal also are common, conventional treatment processes that can potentially remove arsenic from source waters. In small communities, small-scale systems often use IX adsorption because of their ease of handling and sludge-free operations (Wang et. al., 2000). Treatment options identified by the EPA include ion exchange, reverse osmosis, activated alumina, nano-filtration, electrodialysis reversal, coagulation/filtration, lime softening, greensand filtration and other iron/manganese removal processes, and emerging technologies not yet identified (Clifford, 1998). Pre-oxidation technology includes chlorination, potassium permanganate, and ozone, although aeration over a significant time is also possible (Wang et. al., 2000).

Ion exchange (IX) can effectively remove arsenic using anion exchange resins. It is recommended as a BAT (best available technology) primarily for sites with low sulfate because sulfate is preferred over arsenic. Sulfate will compete for binding sites resulting in shorter run lengths (Clifford et. al., 1998).

Activated Alumina (AA) is an effective arsenic removal technology. However, the capacity of activated alumina to remove arsenic is very pH sensitive. High removals can be achieved over a broad range of pH, but shorter run lengths will be observed at higher pH. Because arsenic is strongly adsorbed to the media, only about 50-70% of the adsorbed arsenic is removed. The brine stream produced by the regeneration process then requires disposal (Ghurye et.al.,1998).

Reverse osmosis (RO) can provide removal efficiencies of greater than 95% when the operating pressure is ideal. Water rejection (on the order of 20-25%) may be an issue in water-scarce regions and may prompt systems employing RO to seek greater levels of water recovery. Water recovery is the volume of drinking water produced by the process divided by the influent stream (product water/influent stream). Increased water recovery is often more expensive, since it can involve recycling of water through treatment units to allow more efficient separation of solids from water. This can also produce more concentrated solid wastes. However, the waste stream will generally not be as concentrated as anion exchange brines, so it should be easier to dispose of. It should be noted that while reverse osmosis is listed as a BAT, it was not used to develop national costs because other options are more cost effective and have much smaller waste streams (Clifford, 1998).

Modified coagulation/filtration (C/F) is an effective treatment process for removal of As (V) according to laboratory, pilot-plant, and full-scale tests. The type of coagulant and dosage used affects the efficiency of the process. Below a pH of approximately 7, removals with alum or ferric sulfate/chloride are similar. Above a pH of 7, removals with alum decrease dramatically (at a pH of 7.8, alum removal efficiency is about 40%). Other coagulants are also less effective than ferric sulfate/chloride. Systems may need to lower pH or add more coagulant to achieve higher removals (Clifford, 1998).

Modified lime softening (LS), operated within the optimum pH range of greater than 10.5 is likely to provide a high percentage of As removal. Systems operating lime softening at lower pH will need to increase the pH to achieve higher removals of arsenic (Clifford, 1998).

Electrodialysis reversal (EDR) can produce effluent water quality comparable to reverse osmosis. EDR systems are fully automated, require little operator attention, and do not require chemical addition. EDR systems, however, are typically more expensive than nanofiltration and reverse osmosis systems.

It should be noted that while electrodialysis reversal is listed as a BAT, it was not used to develop national costs because other options are more cost effective and have much smaller waste streams (Clifford, 1998).

Oxidation/filtration (including greensand filtration) has an advantage in that there is not as much competition with other ions. Arsenic is co-precipitated with the iron during iron removal. Sufficient iron needs to be present to achieve high arsenic removals. One study recommended a 20:1 iron to arsenic ratio. Removals of approximately 80% were achieved when iron to arsenic ratio was 20:1. When the iron to arsenic ratio was lowered (7:1), removals decreased to below 50%. The presence of iron in the source water is critical for arsenic removal. If the source water does not contain iron, oxidizing and filtering the water will not remove arsenic. When the arsenic is present as As(III), sufficient contact time needs to be provided to convert the As(III) to As(V) for removal by the oxidation/filtration process (Clifford, 1998).

Ion exchange is a physical/chemical process in which ions held electrostatically on the surface of a solid phase are exchanged for ions of similar charge in a solution (i.e., drinking water). The solid is typically a synthetic anion exchange resin, which is used to preferentially remove particular contaminants of concern. Ion exchange is commonly used in drinking water treatment for softening (i.e., removal of calcium, magnesium, and other cations in exchange of sodium), as well as removing nitrate, arsenate, chromate, and selenate from municipal water (USA EPA, 2003). Ion exchange is a low-cost alternative but has problems with the presence of sulfate. Sulfate will tie up the exchange media before removal of arsenic and release any arsenic that has been removed by the media (Clifford, 1986). Bangladesh groundwater contains very low levels of sulfate (from less than 0.2 to 20 ppm) and nitrate (from less than 0.01 to 5 ppm). Selenate has also been detected in low levels (less than 0.2 ppb) only in deep tubewell water (Kinniburgh et. al., 2001). There are, however, problems with the presence of dissolved organic matter at levels of 15 ppm of BOD_{20}.

Ion exchange does not remove As (III) because As (III) occurs predominantly as an uncharged ion (H_3AsO_3) in water with a pH value of less than 9.0 (kang et. al.,2000) . The predominant species of As (V), $H_2AsO_4^-$ and $HAsO_4^{2-}$, are negatively charged, and thus are removable by ion exchange (IX). If As(III) is present, it is necessary to oxidize As(III) to As(V) before removal by IX (Kang et. al., 2000).

To remove arsenic from drinking water, water is passed through one or more IX resin beds. Arsenate ions ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and several other anions (most notably sulfate and DOM) are preferentially removed according to the order of preference for exchange. When all available sites on the resin have been exhausted, the bed is regenerated with a brine solution (chloride exchange).

The efficiency of the IX process for arsenic removal is strongly affected by competing ions, such as total dissolved solids (TDS), DOM and sulfate (EPA, 2000). Other factors affecting the use of the IX process include empty bed contact time (EBCT) and spent regenerant disposal. Competition from background ions for available IX-sites greatly affects the technical and economic efficiencies of IX systems. The level of these background ions often determines the applicability of the IX process at a particular site. The following selectivity sequence was established for SBA (A strongly basic anion exchange resin in the chloride form that consists of a copolymer of styrene and divinylbenzene with quaternary ammonium functional groups) resins (USA EPA, 2003):

$$SO_4^{2-}>NO_3^{-}>HAsO_4^{2-}>NO_2^{-},Cl>>H_2AsO_4^{-},HCO_3^{-}>>Si(OH)_4,H_3AsO_4$$

It has been shown that the naturally occurring organic substances have affinities for the resin similar in degree to sulfate (Michael, 1993). Therefore, high sulfate and DOM levels can significantly reduce arsenic removal efficiency. In general, the IX process is not economically efficient if the source water contains high TDS (>500 mg/L) and sulfate (>150 mg/L) (Wang et. al., 2000). Also, the presence of Fe (III) in feed water can affect arsenic removal by forming Fe (III)-arsenic complexes, which cannot be removed by IX resins (Tripp et. Al., 1998). Using solid-phase oxidation by Filox-R, which has widely been used for iron removal purposes, can solve this. Filox-R column serves as mechanical filter blocking any iron breakthrough into anion exchange filter. Sulfate is, by no means, a concern because of its very insignificant concentration (from <0.2 to <50 ppm) in Bangladesh groundwater.

Summarizing this section, the following conclusions can be drawn. There are still many problems, which have yet to be solved. Such problems are the effect of dissolved organic species on sorption capacity and the development of waste handling techniques.

Organic fouling of ion exchange resins is not new. However, organic fouling in an arsenic removal process is new and critical. This is partially because until recently the reduction of FeOOH and release of arsenic to groundwater was thought to be driven by mechanisms other than the degradation of organic material. Therefore, the DOM concentrations in groundwater were never measured before. The wastes produced by these processes present even more problems. Therefore, the effects of DOM on arsenic removal and technically sound waste handling methods need to be investigated.

2.5 Effect of pH

One of the most important variables affecting the sorption process is the pH value of the solution. Arsenic is sensitive to mobilization at pH values typically found in groundwater, i.e. pH 6.5-8.5, and under both oxidising and reducing conditions (Kinniburgh et. al., 2001). Figures 2.5-1 and 2.5-2 show the fraction diagrams for As (III) and As(V) as a function of pH.

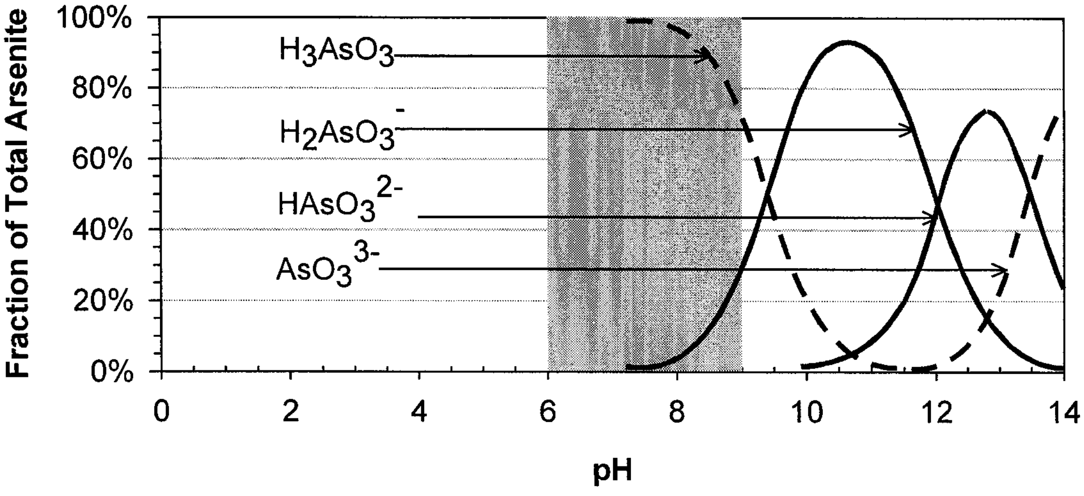


Figure 2.5-1 Dissociation of arsenite [As (III)] (USA EPA, 2003).

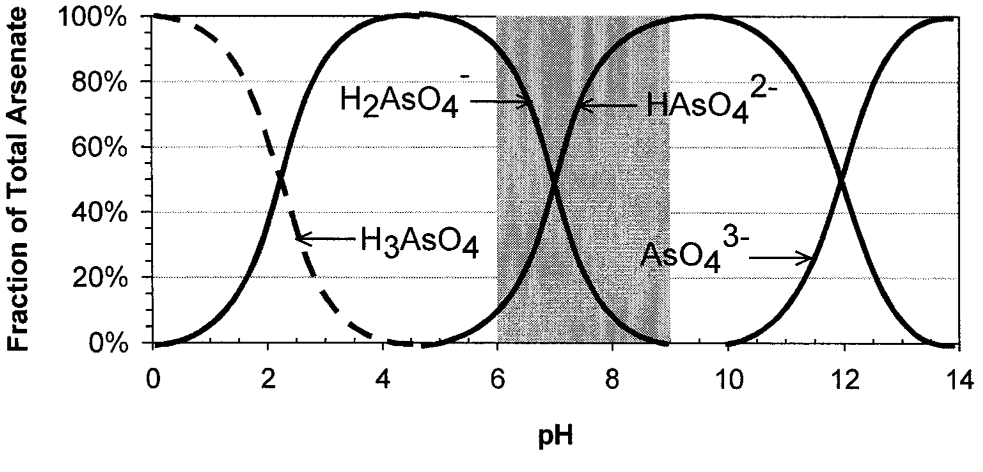


Figure 2.5-2 Dissociation of arsenate [As (V)] (USA EPA, 2003).

As can be seen in Figure 2.5-3, arsenic contaminated groundwater has been found to be contaminated with dissolved organic species also. Water samples were taken from various sediments with differing colors and textures. The water samples from the black sediments contain high levels of arsenic. The red, off-white and white sediments contain lesser amounts of arsenic. A lot of organic material indicates oxygen deficiencies and reducing conditions, which explains why As is abundant in the water from black sediments (Jonsson et. al., 2004).

Only chemicals that tend to ionize are much affected by pH, the only influence on neutral molecules would be the change in the character of the surface. For example, at low pH, humic materials are nearly neutral and more hydrophobic. Changes in pH will dramatically affect organic acids and bases by changing their solubility. Cations resulting from the protonation of an organic base, for example, may more strongly sorb to resins than the neutral species. As pH changes, the surface charge also changes, and the sorption of charged

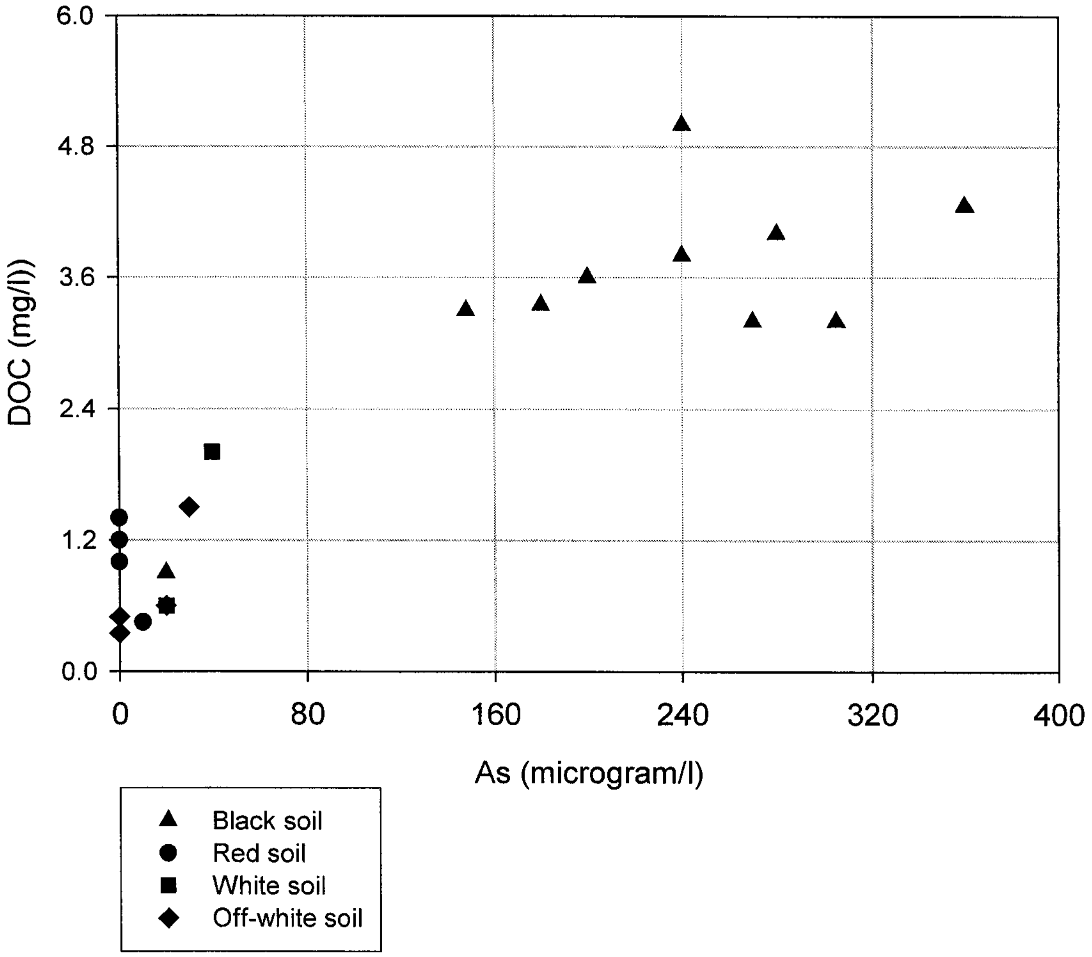


Figure 2.5-3 Presence of dissolved organic matter in arsenic-rich groundwater (Jonsson et. al., 2004)

Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, the resin capacity depends in part on the solution pH. Figure 2.5-4 shows that a typical weak acid resin has a limited capacity below a pH of 6.0.

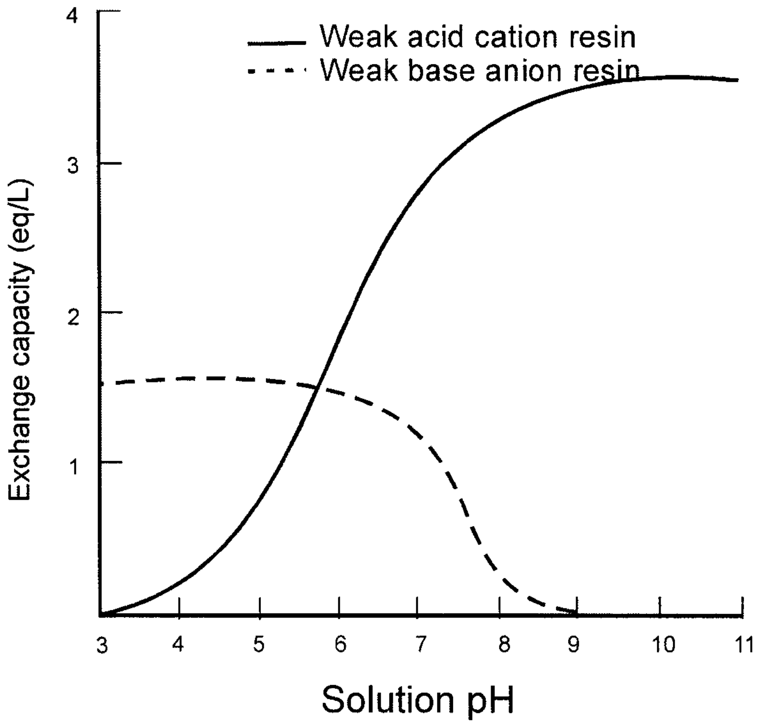


Figure 2.5-4 Exchange capacity of weak acid cation and weak base anion resins as a function of solution pH (Schreiber, 2001).

Weak base anion resins are like weak acid resins in that the degree of ionization is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0 (Figure 2.5-4). A reaction (Schreiber, 2001) between the resin in the free base form and HCl would proceed as follows:

$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3Cl$

These resins merely sorb strong acids: they cannot split salts. In an ion exchange wastewater deionization unit the wastewater would pass first through a bed of strong acid resin. Replacement of the metal cations (Ni^{2+}, Cu^{2+}) with hydrogen ions would lower the solution pH. The anions (SO_4^{2-}, Cl^-) can then be removed with a weak base resin because the entering wastewater will normally be acidic and weak base resins sorb acids. Weak base resins are preferred over strong base resins because they require less regenerant chemicals.

Existing technologies for arsenic removal in Bangladesh

With aid from the Dutch Government, the Department of Public Health Engineering of Bangladesh has built three arsenic removal plants in small towns (Johnston et. al.,2004). These plants are principally iron removal plants, and add no chemicals, but pump groundwater over a series of cascades to aerate the water. Filtration then removes the subsequent iron and arsenic precipitate, and the water is chlorinated and stored in a tower for distribution. Water stored in the tank is from time to time used to backwash the filters. The wastewater is stored in sludge ponds, and sludge is removed once or twice per annum. Arsenic removal effectiveness varies noticeably, and improves with higher iron levels. Although removal rates are not very high, in all cases it is effective enough to comply with the Bangladesh drinking water standard of 50 µg/L. Plant managers carried out trials with addition of coagulants (4 mg/L $FeCl_3$) and oxidants (0.9 mg/L bleaching powder), but found that arsenic removal efficiency was not appreciably improved.

Precipitation-Coagulation Method

Sorption of arsenate onto the oxyhydroxides of iron and aluminum has been reported to be a potential technology for arsenic removal in Bangladesh (International Farakka Committee, 2003). Oxidation of As^{+3} to As^{+5} by bleaching powder, air, or photochemical oxidation (sunlight) in the presence of air has been discussed. The presence of a sufficient quantity of iron has been emphasized for effective removal of arsenic along with ferric oxyhydroxide. The need for safe sludge disposal has been pointed out. However, the report does not indicate any implementation of this process in Bangladesh.

Adsorption-Filtration Method

Various materials have been reported to be in use for arsenic removal (International Farakka Committee, 2003). However, it is not clear whether these materials are used in Bangladesh at full scale or if they are still under laboratory investigations. Such materials are hydrated ferric oxide (HFO), magnetite (Fe_2O_3/Fe_3O_4), activated charcoal, silica based mesoporous material, and modified Fe_2O_3/MnO_2-laterite soils. Various waste handling techniques seem to be in the proposal stage. These include:

(i) the generation of appropriate pore size and active surface area.

(ii) the chemical incorporation of all the active removal species in the composite structure of the material.

(iii) the creation of highly oxidizing surfaces and cavities to retain the bound arsenic under extreme changes of redox and pH.

Geochemical Intervention in the Aquifer

The introduction of oxygen/ ozone/H_2O_2 is being proposed to mitigate the arsenic problem if the reducing environment in the aquifer proves to be the determining factor (International Farakka Committee, 2003).

Low-Cost Column Filter

Originally, a composite column of sand, Fe_2O_3/MnO_2 and laterite soil (locally available) was prepared. Arsenic was claimed to be removed totally by passing contaminated water (0.05-2 ppm) through such a column (International Farakka Committee, 2003). One such filter costs $1.56. About 500 units were distributed among the affected people of certain region. A mixture of laterite soil-Fe_2O_3-MnO_2 was thermally treated to produce the porous bricks. The removal efficiency of such columns is claimed to be 100%. Exhausted media was subjected to the toxicity leaching procedure tests (International Farakka Committee, 2003).

(iii) Development of a Domestic Filter (SAFI Filter)

Safiullah (International Farakka Committee, 2003) developed an arsenic removal domestic filter in 1997. HFO (hydrous ferric oxide) was deposited on composite porous ceramic configured to a porous ceramic candle.

The HFO based system named 'SAFI Filter' had been used in arsenic removal for the last five years. The filter is reported to remove arsenic above 0.5 mg/L, and deliver arsenic free water at a rate of 100 liters per day for more than one year. Exhausted media was reported to pass the toxicity leaching procedure tests.

Critique/recommendation

The above-mentioned description of the status of arsenic issues in Bangladesh indicates various deficiencies. None of the technologies considered the presence of organic matter in Bangladesh groundwater. The reagent doses seem to be quite low. There is no data available on COD, As, and suspended solids levels. The reagent doses can be as high as 910 mg/L of lime and 220 mg/L of ferric chloride (as anhydrous $FeCl_3$) (Abdullaev et. al., 1992).

Hering et al., (1997) showed that the presence of natural organic matter (at pH 4 through 9) adversely affected the efficiency of arsenic (III) removal by ferric chloride. Arsenic (III) could not be removed from source waters by coagulation with alum. Safiullah et al. (2004) reported the presence of organic matter in Bangladesh groundwater. One then would conclude that “precipitation-coagulation method" is restricted to a narrow region in Bangladesh where groundwater is free of organic species.

The low-cost column and SAFI filters are both promising but there is no data available whether these filters remove dissolved organic species as well.

3. MATERIALS AND METHODS

3.1 Materials used for the various investigations of arsenic removal by ion exchange media

Filox-R, a MnO_2 based material was used as the oxidizing medium and was regenerated by a potassium permanganate solution. FILOX-R™ is the raw, unrefined ore used in the manufacture of FILOX® filtration media. Chemically, FILOX-R (Raw) is a naturally occurring ore that has been properly screened and sized. FILOX-R media is stable within a range of pH 5.0 to 9.0. However, the generally acceptable range for drinking water is pH 6.5 to 8.5. At extreme ranges of pH (both low and high), contaminant removal and bed stability are adversely affected. This should be considered in applications operating at the high and low ends of FILOX-R's pH 5.0 to 9.0 range. The maximum acceptable TDS level for drinking water is 500 ppm. FILOX-R media may be successfully applied at levels exceeding 1100 ppm TDS (Water, 2001). This material was purchased from Magnor Inc., Boucherville, Quebec.

Purolite A-300 is a Type II, strongly basic gel anion exchange resin. The Polymer Matrix Structure is a polystyrene crosslinked divinylbenzene. The functional groups are $R(CH_3)_2(C_2H_4OH)N^+$. Its total exchange capacity in the Cl- form is 1.45 - 1.6 eq/L min. Whole bead counts are a minimum of 92% clear beads with mechanical strengths ranging over 300 grams. Particle size ranges from +16 mesh<5% to 50 mesh<1% [Purolite A-300 data sheet]. It is unaffected by dilute acids, alkalies, and most solvents. This material was purchased from Magnor Inc., Boucherville, Quebec.

The arsenic detection kit, Hach – 28228-00, was used for the analysis of most samples. It was purchased from Anachemia Canada Inc. The kit included reaction vessels, chemical reagents (sulfamic acid and powdered zinc) and test strips.

MasterFlex L/S pump with a controller was purchased from Labcor. This was used to maintain co-current downflow ion exchange process and its regeneration.

Chemicals used were H_3AsO_3, $FeCl_3.6H_2O$, $Al(SO_4)_3.14H_2O$, $MnSO_4.H_2O$, NH_4NO_3 , Na_2SO_4 , NaF , and distilled water (pH 6.8). These were used to prepare the influent test water. Sorption of arsenic by a gel-type resin in the absence of DOM was first investigated to see if the resin is capable of removing high concentrations of arsenic. There are some regions where the concentrations of organic material are absent but the water is still contaminated with inorganic arsenic (anthropogenic source of arsenic contamination). Such a case should not be ignored. Most investigations carried out earlier did not consider organics when investigating the sorption of arsenic at relatively lower concentrations (up to 150 ppb). This is why only gel-type resins were studied by other researchers for arsenic removal. However, predictive models for the gel-type resins were not developed by them. This necessitated the investigation of the sorption of arsenic with no organics to develop predictive model for waters contaminated with arsenic but not contaminated with organics. Therefore, organics were not used to make up arsenic polluted water to run this section of experiments.

Influent water for the rest of the experiments (the main part of the work) was formulated using treated domestic wastewater containing organics. Samples of treated wastewater from the **MUC Wastewater Treatment Plant,** Montreal (Quebec), Canada, was obtained and As was added to them. To resemble the real composition of Bangladeshi groundwater, the MUC samples with the St. Lawrence River water were diluted, and further treated by coagulation and filtration. The residual concentration of DOM in the treated wastewater constituted 5.1 to 16 mgO_2/L as Permanganate value or 20-40 mgO_2/L as COD. Arsenic concentration was in the range of 500 to 1600 ppb. The indices of PV and COD were determined by a modified Kubel method and standard methods (UNEP, 2004). Water contaminated with arsenic and organics was used to investigate the sorption of arsenic by two usual methods of ion exchange: **softening** and **deionization**.

It was necessary to optimize the regeneration conditions for an exhausted chloride form macroporous anion exchange resin. Since the influent water, entering the chloride anion column of the softening unit is alkaline, it was necessary to investigate the sorption of such alkaline water. Water pH was varied between 7 and 10.4. These necessitated two sets of experiments: optimization of chloride form macroporous resin and the sorption of arsenates from alkaline water.

Next the investigation was focused on the ion exchange method "deionization". Since the cation exchange resin of a deionization unit is in the hydrogen ion form, the effluent is acidic. This effluent then enters the anion exchange column with macroporous resin in the hydroxide form. Since ion exchange is also dependent on the strong acid anions, the water was modified by dilution to have the content of strong acid anions less than 6 meq/L. The water was passed through a two-stage deionization system. The results from this section of investigation necessitated a more thorough investigation to examine the sorption of mineral components relative to that of organics.

Next considering the relatively higher capacity of a strongly basic anion exchange resin in the chloride form one more investigation was carried out. The purpose of this last experiment was to examine the usefulness of a SBA in the chloride form in a two-stage deionization system. Water was made acidic with a pH range from 2 to 7 to investigate the sorption of arsenates from acidic water.

Anionic-exchange media Amberlite IRA-910 is a strongly basic type II Cl-form macroporous anion exchange resin. It has a Styrene-DVB matrix, macroporous structure. Particle size ranges from 16 to 50 mesh (0.94 mm to 0.25 mm). Its total exchange capacity in the Cl- form is 1.3 eq/L. It is stable but heat sensitive. Operating temperature must not exceed 40^0C. This material was purchased from Sigma-Aldrich, Oakville, Ontario. CM cellulose microgranular form is an insoluble, stable white solid fibrous powder. This material was purchased from Sigma-Aldrich, Oakville, Ontario. DEAE cellulose anion exchanger is an insoluble, stable white solid powder. This material was purchased from Sigma-Aldrich, Oakville, Ontario. Reflux condenser, water bath, boiling stones, sulfuric acid, oxalic acid and potassium permanganate solution were used to determine the influent and effluent permanganate values of water being investigated.

Ammonia-Nitrogen SMART (LaMotte Company product code: 3642-SC), chloride (Chloride spectrophotometric tablets, product code: 3693-SC), nitrate (product code: 3689-SC), nitrite (product code: 3650-SC), phosphate (product code: 3653-SC), silica (product code: 3687-SC), and sulfate reagents (product code: 3665-SC); Hardness Spectrophotometric Grade Tablet (product code 3691-SC); COD test kit. These materials were purchased from V.W.R. International, Montreal.

Amberlite – 200 C is a strongly acidic macroporous cationic exchange medium. Its total exchange capacity in the H- form is 1.3 eq/L. This material was purchased from SIGMA-ALDRICH. Amberlite IRA 96 is a free base macroporous anion exchange medium. Its total exchange capacity is 1.4 eq/L. This material was purchased from SIGMA-ALDRICH.

3.2 Methodology

Figure 3.2-1 shows the investigation steps carried out in this study.

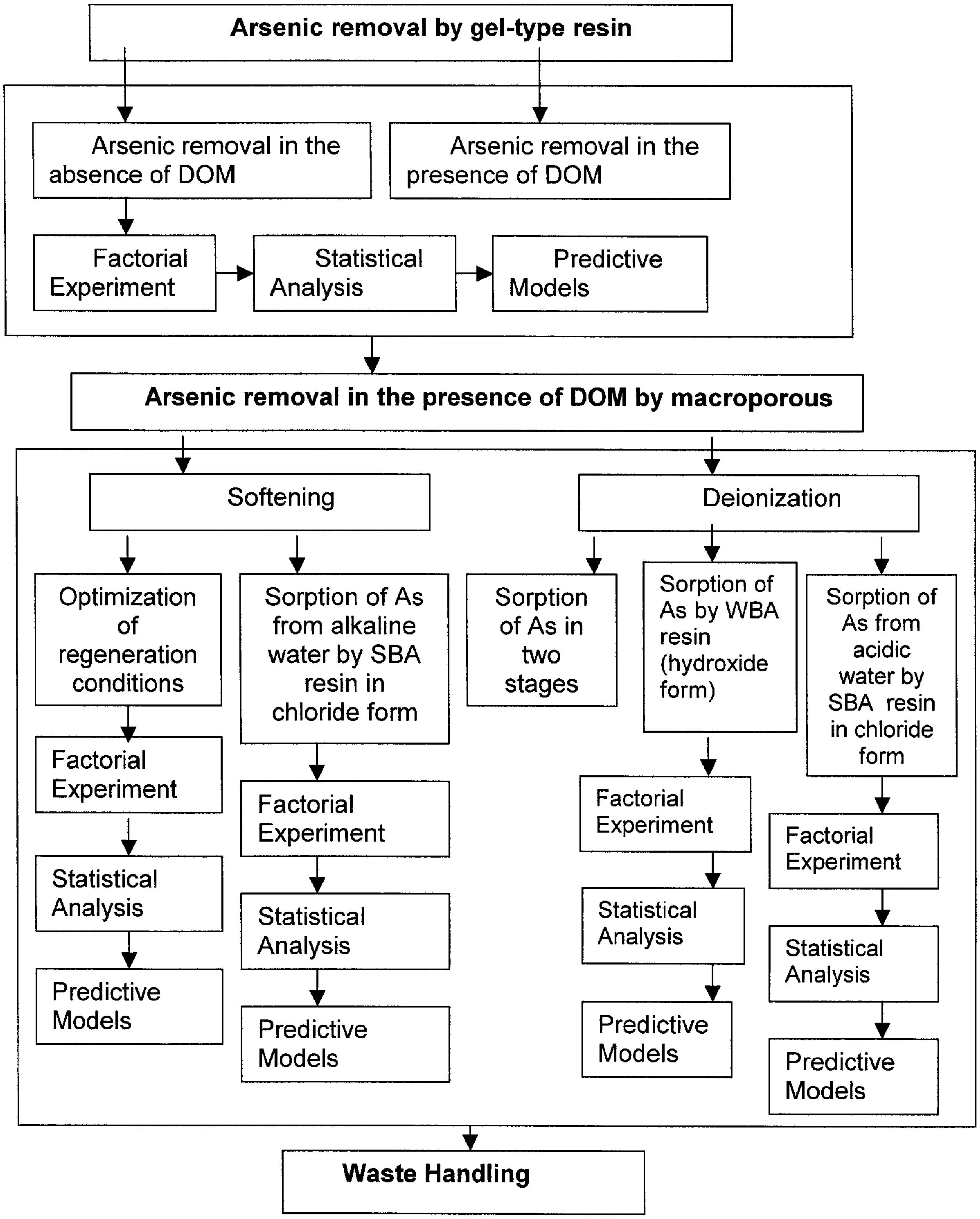


Figure 3.2-1 Sorption processes of arsenic and DOM: investigation steps

3.2.1 Preliminary tests for arsenic removal by anion exchange media Purolite A-300

The treatment process consists of an oxidizing filter followed by an ion exchange column. The effect of pH, arsenate concentration and filtration velocity were examined using a simulated Bangladeshi groundwater.

The investigation procedure was as follows. The investigation was carried out in the laboratory on a fixed unit incorporating dynamic columns with Filox-R and the anionic-exchange media Purolite A-300 (chloride ion form) serving as oxidizing and ion-exchanging filters respectively. Thus, an oxidizing filter was used followed by an anion filtration system. Figure 3.2-2 is a schematic diagram of the treatment process used, which consists of the following major elements:

Influent water

Raw water was pumped from a three-liter flask and flowed downward through the oxidizing filter. A MasterFlex L/S pump with a controller was used. Flow rates (1 mL/min to 3 mL/min) were adjusted with the speed control potentiometer as well as an additional flow meter.

Oxidizing Filter

A plastic syringe was installed, which served as the oxidizing filter column, to oxidize As (III) to As(V). The oxidizing filter column was a 6.5 cm high ten-milliliter and 1.4 –cm-diameter plastic column. Six mL of oxidant were used.

Ion Exchange System

After passing through the oxidizing filter, water flowed into a plastic column filled with the anion exchange resin Purolite A-300. The ion exchange column had the same size as the oxidizing filter and the resin bed was 6 cm^3.

Regeneration/Backwash

The oxidizing filter was regenerated with potassium permanganate (133 mg/L) for 30 min at a flow rate of 3 mL/min. This was followed by a slow rinse of 54 mL for 18 min at 3 mL/min and then a fast rinse of 90 mL for 10 min at 9 mL/min. This regeneration is not usually required unless the Filox performance is reduced. The ion exchange filter (Figure 3.2-3) was regenerated with the 100 mL solution made of potassium chloride (2 M) and NaOH (0.2 M) for 33 min at 3 mL/min followed by a slow rinse at the same flow rate for 18 min. Finally a fast rinse was used for 10 min at 9 mL/min. The small amount of NaOH was used in combination with salt during the regeneration in order to enhance the resin operation. This addition gives a higher operating capacity.

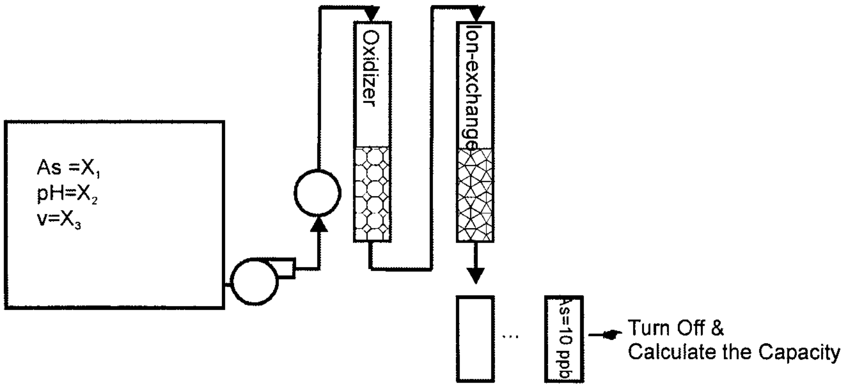


Figure 3.2-2 Schematic diagram of the ion exchange system

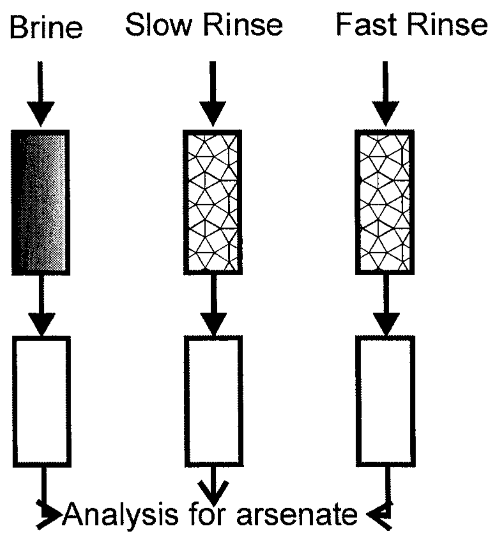


Figure 3.2-3 Regeneration of the exhausted resin

3.2.1.1 Water composition

The influent water was made to resemble the real composition of Bangladeshi groundwater (Kinniburgh et. al., 2001) as shown in Table 3.2-1. Concentrations of arsenic were varied between 500 ppb and 1600 ppb. The pH values were varied as well between 6.5 and 8.5 adjusting with 0.10 M NaOH or HCl as needed.

Table 3.2-1 Composition of water investigated based on water analyses data from British Geological Survey reports (Kinniburgh et. al.,2001).

Type of tube well	STW*
As(III) (ppb)	1600
Fe^{3+} (ppm)	0.15
Al^{3+} (ppm)	0.0014
Mn^{2+} (ppm)	0.001
Na^{+} (ppm)	0.26
NH_4^{+} (ppm)	0.001
SO_4^{2-} (ppm)	2.9
NO_3-N (Nitrate) (ppm)	0.004
F^{-} (ppm)	0.22
pH	6.8

STW* stands for shallow tube well

Solutions of known concentration were prepared by combining the weighed solutes with distilled water according to the methods described by Kotz and Treichel (1999). Stock solutions were then diluted with distilled water to prepare solutions of the required concentration levels.

3.2.1.2 Experimental procedure

The determination of arsenate-exchange capacity of strongly basic gel-type anion exchange media, initially thought to be influenced by influent arsenic concentration, pH values and filtration velocity required a well-designed experiment. Response surface method (RSM) design was selected because it quantifies the relationships between one or more measured responses and the vital input factors. The first step in creating a response surface design is to select a RSM design. A three level factorial design was selected. Full factorial 3-level design was chosen for 3 factors. The number of experiments will be 3^k plus some replicates of the center point. Since there are only 3 levels for each factor, the appropriate model is the quadratic model. For 3 factors this design requires to run 27 experiments and 5 replicates of the center point to estimate the coefficients in a quadratic model. Unlike fractional factorial a full factorial design means an experimental design, which includes all possible combinations of the factors chosen at their designated levels. This is not to mean that all possible factors have been chosen. A fractional factorial design is an experimental design, which includes only a subset of all possible combinations of factor levels, causing some of the effects to be confounded.

The number of factors and levels was limited to three because one of the disadvantages from a practical point of view, of factorial experiments is that the number of treatment combinations increases rapidly as the number of factors and/or levels increases. A rough estimate shows that it would take 1051 days (24 hours/day), if four-level experiments were to be considered.

A design matrix was prepared before running the experiment; results were recorded as every run was completed. Design matrix is an array of values presented in rows and columns. The columns usually represent design factors. The values in the rows represent settings for each factor in the individual runs or experiments of the design.

Analysis of the results was then done to obtain an equation that describes the dependence of arsenate-exchange capacity on the various factors. Analysis of Variance (ANOVA) is a method, based on the F-distribution, for testing the null hypothesis of no treatment effects. It is a statistical technique, which subdivides the total variation of a set of data into component parts associated with specific sources of variation for testing a hypothesis on the parameters of a model.

The system was turned off as a 10 ppb breakthrough occurred. The ion exchange column was regenerated and the spent regenerant analyzed to determine the amount of arsenate the resin sorbed in the sorption process as well as the amount of arsenate that was possible to desorb from the exhausted resin in the regeneration stage. This analysis determined the nature of the sorption process, i.e. whether the process was reversible. The quantity of arsenic sorbed on the Cl-form resin was recorded to be 2,810 μg. The quantity of arsenic desorbed from the resin by normal regeneration was recorded to be 2,725 μg. The close proximity of these values indicates, in fact, two things. First, the sorption mechanism is anionic exchange. It is because almost all of the arsenates sorbed on to the resin in the ion exchange process appeared to be displaced by chlorides in the regeneration process. Second, this displacement process is exactly the reverse of the sorption process and termed as regeneration. If the regeneration process involved something other than the use of brine, such as thermal extraction, a non-ionic and irreversible mechanism could then be appropriate but this was not the case. Since 97% of arsenates was possible to desorb from the resin by NaCl solution, the ionic exchange process is considered reversible.

The treatment system was turned off at a given concentration breakthrough as stated above. This is why there were residual concentrations of arsenate in the filtrate. This necessitated the analysis of how residual concentrations were dependent on the various factors.

In this section of investigations, dependences of arsenate-exchange capacity and residual arsenate concentration on three various factors were studied. The exhausted Cl-form anion exchange resin was regenerated as 10 ppb breakthrough occurred. Since this research did not involve an equilibrium study, it was not necessary to let the resins become fully exhausted. In case of the absence of a tank for clean water, at a complete exhaustion of the resin, the effluent water would have as high a concentration as 1600 ppb of arsenic. In such a case, a huge tank is necessary so that the mixed diluted effluent water may have the 10 ppb concentration. The whole purpose of treatment is to provide people with drinkable water that contains no more than 10 ppb of arsenic. However, a complete breakthrough curve (only one) is necessary in the designing stage of an ion exchange unit. The designing stage should only be approached when a satisfactory flow rate has been selected (Reynolds et. al., 1996). This is the reason why the Langmuir isotherm, which represents adsorption equilibrium, was not used. A satisfactory flow rate should be selected by using the statistical relationships between the interrelated factors and the responses. Scale-up or kinetic design approaches require one single breakthrough curve obtained from a test column, run under selected optimum operation conditions. The optimization stage would produce 32 different breakthrough curves. A breakthrough curve at the complete exhaustion of the resin has been presented in the "Results and discussion" chapter.

Independent factors were chosen as follows: A – arsenate concentration, ppb; B - pH values of water being treated; C – linear velocity of filtration, cm/min. Arsenate-exchange capacity was chosen as the target function Y_1 and residual arsenate concentration as Y_2.

Preliminary tests determined the levels and intervals of the factors. The concentration range of arsenate of 500-1600 ppb is typical of groundwater in Bangladesh (Kinniburgh et. al., 2001).The pH range of 6.5-8.5 is the drinking water standard. The velocity range of 0.65-1.94 cm/min (EBCT range of 2-6 min) (Abdullaev et. al., 1992) is typical for most ion exchange filters. Initial data and the designing matrix are given in Tables 3.2-2 and 3.2-3 respectively. ANOVA tables are provided in the results chapter.

Table 3.2-2 Initial data for the design of the response surface experiment

Study Type	**Initial Design**	**Design Model**	**Experiments**	**Blocks**			
Response Surface	3 Level Factorial	Quadratic	32	No Blocks			
Response	**Name**	**Units**	**Number of Observations**	**Minimum**	**Maximum**	**Transformation**	**Model**
Y_1	As-capacity	meq/g	32	0.0092	0.0385	None	R2FI
Y_2	Effluent As	ppb	32	2.1	8.5	None	Linear
Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Low Coded**	**High Coded**
A	Input As	ppb	Numeric	500	1600	-1	1
B	pH		Numeric	6.5	8.5	-1	1
C	v	cm/min	Numeric	0.65	1.94	-1	1

Table 3.2-3 Planning matrix for the determination of the dependence of exchange capacity and residual concentration on various factors

Std	Run	Factor 1 A:Input As (ppb)	Factor 2 B:pH	Factor 3 C:v (cm/min)	Response 1 As-capacity (meq/g)	Response 2 Effluent As (ppb)
28	1	1050	7.5	1.295	0.02	5.40
13	2	500	7.5	1.295	0.01	3.65
29	3	1050	7.5	1.295	0.02	5.35
17	4	1050	8.5	1.295	0.01	6.50
24	5	1600	7.5	1.94	0.02	7.60
15	6	1600	7.5	1.295	0.03	7.00
6	7	1600	7.5	0.65	0.03	6.40
7	8	500	8.5	0.65	0.009	4.00
5	9	1050	7.5	0.65	0.02	5.10
26	10	1050	8.5	1.94	0.01	7.20
19	11	500	6.5	1.94	0.02	3.50
4	12	500	7.5	0.65	0.01	3.00
21	13	1600	6.5	1.94	0.03	6.70
10	14	500	6.5	1.295	0.02	2.90
1	15	500	6.5	0.65	0.02	2.10
2	16	1050	6.5	0.65	0.03	4.30
14	17	1050	7.5	1.295	0.02	5.30
20	18	1050	6.5	1.94	0.03	5.30
11	19	1050	6.5	1.295	0.03	4.60
16	20	500	8.5	1.295	0.009	4.70
30	21	1050	7.5	1.295	0.02	5.60
23	22	1050	7.5	1.94	0.02	6.30
22	23	500	7.5	1.94	0.01	4.20

27	24	1600	8.5	1.94	0.02	8.50
31	25	1050	7.5	1.295	0.02	5.66
18	26	1600	8.5	1.295	0.02	8.00
3	27	1600	6.5	0.65	0.03	5.50
8	28	1050	8.5	0.65	0.02	5.85
25	29	500	8.5	1.94	0.009	5.30
12	30	1600	6.5	1.295	0.03	6.30
9	31	1600	8.5	0.65	0.03	7.30
32	32	1050	7.5	1.295	0.02	5.70

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

Formulated water made up of 500 ppb of arsenic III, pH 6.5 and other anions as shown in Table 3.2-1, was passed through the oxidizing filter, which was initially saturated with arsenic III (from preliminary tests) and could no longer sorb any of arsenic present in water but oxidize arsenic III to arsenic V. The removal of arsenic V took place in the ion exchange column. Regeneration schedules of the oxidizing media and IX media are given in Tables 3.2-4 and 3.2-5.

Table 3.2-4 Regeneration schedule of the oxidizing media

Regeneration Step	Volume of liquid, (ml)	Concentration, (mg/L)	Quantity of $KMnO_4$, (mg)	Flow direction	Duration (min)	Flow rate (ml/min)
Backwash	360	-		Upflow	18	20
$KMnO_4$ solution	90	133	12	Downflow	30	3
Slow rinse	54	-		Downflow	18	3
Fast rinse	90	-		Downflow	10	9

Note: Regeneration of Filox is normally not required as arsenic, iron and manganese are oxidized on the surface of the media and the media contains 80 % manganese dioxide. When the oxidizing power of Filox is reduced, the bed has to be regenerated with the solution of potassium permanganate thus restoring its oxidizing capacity.

Table 3.2-5 Regeneration schedule of the ion exchange media

Regeneration Step	Volume of liquid (mL)	Concentration (M)	Quantity of KCl (gram)	Flow direction	Duration (min)	Flow rate (mL/min)
Backwash	-	-	-	Upflow	-	-
Brine	100	2	14.9	Downflow	33	3
Slow rinse	54	-	-	Downflow	18	3
Fast rinse	90	-	-	Downflow	10	9

3.2.1.3 Batch experiments

As part of the field work required for this research, some batch experiments were conducted onsite in a remote village southwest of Bangladesh called Nakol, which is located on the bank of the Garai River. Water was sampled from 12 tube wells in this area. Total arsenic concentrations, pH and oxidizability index were measured immediately using a portable pH meter, Hach Arsenic kit and reflux condenser. The analytical procedures for the determination of arsenic concentrations and permanganate value are described in sections 3.2.1.4 and 3.2.2.4, respectively.

One g of air-dried Filox-R was suspended in 100 mL of freshly drawn groundwater in 150-mL glass tubes. The tubes were hand shaken to equilibrate for 30 minutes. The (pre-oxidized) filtered water was then mixed with 10.0 mg (0.01 g) of the air-dried exchange resin Purolite A-300 in 150-mL glass tubes. The same procedure was followed with macroporous anion exchange resins Amberlite 910 and Amberlite IRA 96 activated in chloride and hydroxyl forms respectively. The tubes were hand shaken to equilibrate for 30 minutes. The exchange capacity of each of the resins was determined from the difference of arsenic concentration in the original and treated final water.

The exchange capacity of the media was calculated as:

$$s_{arsenate} = \sum \frac{\overline{V} \cdot \gamma_i \cdot (C_{o,i} - C_{f,i})}{MW_i . m} \qquad (3.2\text{-}1)$$

where:

s_i = Sorption capacity of media for species *i* (eq/g resin)

$\overline{V}$ = Volume of solution added (L)

γ_i = Normality of species *i* (eq/mole)

m = Mass of media added (g)

MW_i = Molecular weight of species *i* (mg/mole)

$C_{o,i}$ = Initial Concentration of Species *i* (mg/L)

$C_{f,i}$ = Final concentration of species *i* (mg/L)

The US EPA arsenic treatment technology design guidance was followed (UNEP, 2004). Table 3.2-6 and Figure 3.2-4 provide values for use in equation 3.2-1. An example of media capacity evaluation by EPA method is given below. Representative data for Purolite A-300 capacity is shown in Table 3.2-7.

Table 3.2-6 Constants for exchange capacity calculations (UNEP, 2004)

Species	Molecular Weight (mg/mole)	Normality (eq/mole)
Hydroxide	17	1
Sulfate	32.06 as S	2[1]
Arsenate	74.922 as As	Use Figure 3.2-4

[1] For pH > 2

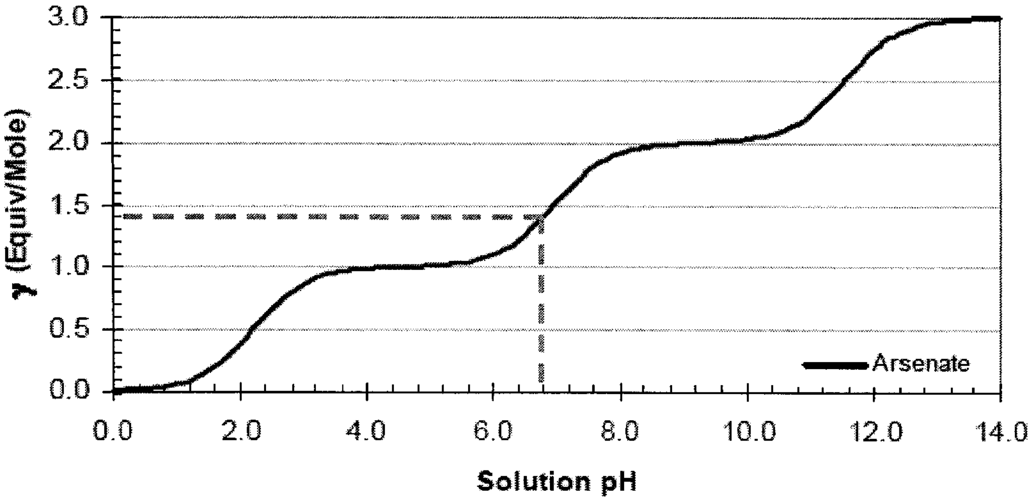


Figure 3.2-4 Normality of arsenate versus pH (UNEP, 2004).

Table 3.2-7 Data for media capacity.

Parameter	Experimental Results	
	Start	End
Solution pH	7	6.8
Arsenic	0.45 mg/L as As	0.1 mg/L as As

The sorption capacity was calculated for arsenate as follows:

$$s_{arsenate} = \sum \frac{\overline{V}.\gamma_i.(C_{o,i} - C_{f,i})}{MW_i.m}$$

$$\therefore s_{arsenate} = \frac{(0.1\,\text{L}).(0.45 - 0.1\,\text{mg/L})(1.4\,\text{equiv/mole})}{(74{,}922\,\text{mg/mole}).(0.01\,\text{g})} = 6.5\times10^{-5}\ \text{eq/g resin}$$

3.2.1.4 Analytical procedures

The chemical analysis of the samples was done by a colorimetric method

(Hach method) for the detection of arsenic of 0-500 ppb. Sulfamic acid and powdered zinc react to create strong reducing conditions in which inorganic arsenic is reduced to arsine gas (AsH_3). The arsine gas then reacts with mercuric bromide impregnated test paper to form mixed arsenic/mercury halogenides (e.g. AsH_2HgBr). These compounds discolor the test strip depending upon the concentration of the arsenic in the sample. The color change is from white to yellow to tan to brown.

Most tests for arsenic, including the Hach method, rely on the conversion of arsenic to arsine gas.

$As_2O_3+6Zn+12HCl \rightarrow 2AsH_3+6ZnCl_2+3H_2O$

$H_3AsO_4+4Zn+8HCl \rightarrow AsH_3+4ZnCl_2+4H_2O$

The liberated arsine gas is then reacted with a detector paper that has been impregnated with mercuric bromide. As the reaction above indicates, arsine gas is commonly generated by reduction with zinc metal and hydrochloric acid. The zinc powder and all other reagents in the Hach method were packaged in unit dose form for convenience and to minimize handling. The mercuric bromide test paper was on the end of a long plastic strip to eliminate the need to be exposed to the mercuric bromide.

The strips were all photographed and digitized by a Canon Power Shot S200 Digital Elph camera. Representative samples of influent and effluent water were analyzed by the company Body Cote using ICP-MS at the detection limit of 1 ppb to double check the reproducibility of the analytical results. No difference was observed.

3.2.2 Procedure for the determination of sorption and desorption of arsenates in the presence of DOM

The investigation procedure was as follows. The investigation was carried out in the laboratory on a fixed unit incorporating dynamic columns with Filox-R and the anionic-exchange media Amberlite IRA-910 (chloride ion form) serving as oxidizing and ion-exchanging filters, respectively. Thus, an oxidizing filter was used followed by an anion filtration system. The treatment process used, consisted of the following major elements:

3.2.2.1 Influent water

Raw water was pumped from a three-liter flask and flowed through the oxidizing filter. A Master Flex L/S pump with a controller was used. Flow rates were adjusted with the speed control potentiometer as well as an additional flow meter.

3.2.2.2 Oxidizing filter

A glass tube was installed, which served as the oxidizing filter column, to oxidize As (III) to As(V). The oxidizing filter column was a 16 mm-internal-diameter glass column and 100 cm high. The BV (bed volume) was 200 ml. A MnO_2 based material (Filox-R) was used as the oxidizing medium and was regenerated by a potassium permanganate solution.

3.2.2.3 Ion exchange system

After passing through the oxidizing filter, water was pumped into a glass column filled with anion exchange resin Amberlite IRA-910. The ion exchange column had the same volume as the oxidizing filter and the resin bed (200 mL). The oxidizing filter was regenerated with potassium permanganate (133 mg/L) for 30 min at a flow rate of 3 mL/min. This was followed by a slow rinse of 54 mL for 18 min at 3 mL/min and then a fast rinse of 90 mL for 10 min at 9 mL/min [153] This regeneration is not usually required unless the Filox performance is reduced (when the oxidation is less than 100%).

3.2.2.4 Water composition

Samples of treated wastewater from the **MUC Wastewater Treatment Plant,** Montreal (Quebec), Canada, was obtained and As was added to them. To resemble the real composition of Bangladeshi groundwater, the MUC samples with the St. Lawrence River water were diluted, and further treated by coagulation and filtration. The residual concentration of DOM in the treated wastewater constituted 5.1 to 16 mgO_2/L as Permanganate value or 20-40 mgO_2/L as COD. Arsenic concentration was in the range of 500 to 1600 ppb. The indices of PV and COD were determined by a modified Kubel method and standard methods (UNEP,2004).

Kubel method (Oxidizability):

Procedure:

1. 5 mL of sulfuric acid, H_2SO_4, c = 1.27 mole/L was added to 100 mL of the sample in an Erlenmeyer flask. Two boiling stones were added. The mixture was heated rapidly to boiling.

2. 15 mL of potassium permanganate solution, $KMnO_4$, c = 0.002 mole/L was added immediately to the boiling solution with the aid of a burette. The solution was kept boiling for exactly 10 minutes under reflux from the time at which boiling commenced.

3. If, during the boiling process, the colour of the solution became brownish, the analysis had to be repeated with a smaller amount of the water sample made up with diluting water to 100 mL. This dilution of the water was taken into account in the calculation.

4. After boiling for 10 minutes, 15 mL of oxalic acid solution, $(COOH)_2$, c = 0.01 mole/L was added. If the solution did not become colourless immediately, it had to be heated again for a short time.

5. The hot solution was then back titrated with potassium permanganate solution, $KMnO_4$, c = 0.002 mole/L until a barely visible pink colouration appeared and remained for at least 30 seconds.

1 mL of 0.002 mole/L $KMnO_4$ corresponds to 0.316 mg $KMnO_4$

1 mL of 0.002 mole/L $KMnO_4$ corresponds to 0.08 mg oxygen

Guiding value for drinking water: 2 mg O_2/L = 8 mg/L $KMnO_4$ - consumption

Limiting value for drinking water: 5 mg O_2/L = 20mg/L $KMnO_4$ – consumption

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is a measure of organic matter in water, which is susceptible to oxidation by chemical oxidants. COD can be empirically related to the Biological Oxygen Demand (BOD) and organic carbon content of a specific source of water. This correlation must be determined experimentally for each source of water. The Montreal MUC wastewater samples were tested for both PV and COD values. The results were then put together to compare one against another. A correlation of PV:COD of 1:3 was observed consistently.

Water samples were added to the standard tube, which contained 7.5 mL of the digestion solution (LaMotte company product code: 0077-SC). Dichromate in the presence of silver salts, at high temperature in a closed system, oxidizes most organic compounds to 95-100% of the theoretical amount. This process is called digestion. As dichromate oxidizes the organic compounds, a green complex is formed. The concentration of the green complex was measured at 605 nm and was directly proportionate to the COD of the sample.

Potassium hydrogen phthalate (KHP) of known COD value (500 mg O_2/L) was used as the standard. A COD heater block was preheated to 150±2°C. The COD tube vial was held at a 45° angle. 2.0 mL sample water was added carefully allowing the sample to run down the side of the vial. Vials were capped and mixed thoroughly. The outside of the vial was rinsed with distilled water and wiped dry with a paper towel. These steps were repeated using 2.0 mL KHP solution. This was the reagent blank. Vials were placed in a preheated COD block heater and kept at a temperature of 150±2°C for two hours. At the end of the heating period the heater was turned off. 20 minutes were allowed for the vials to cool to 120°C or less. Vials were removed from the block heater, inverted several times to mix and allowed to cool to room temperature. The vials were then tested using a Perkin-Elmer Lambda 2S spectrophotometer. A reagent blank was run with each set of samples and with each lot of reagents. For greater accuracy, a minimum of three repetitions was performed and the results were averaged.

AMMONIA-NITROGEN

Ammonia nitrogen is present in various concentrations in many surface and ground waters. Any sudden change in the concentration of ammonia nitrogen in a water supply is a cause for suspicion. A product of microbiological activity, ammonia nitrogen is sometimes accepted as chemical evidence of pollution when encountered in natural waters.

Special bacterial groups that produce nitrite and nitrate rapidly oxidize ammonia in natural water. This oxidation requires that dissolved oxygen be available in the water. Ammonia is an additional source of nitrogen as a nutrient, which may contribute to the expanded growth of undesirable algae and other forms of plant growth that overload the natural system and cause pollution.

The Nesslerization Method was used to measure ammonium concentration in the water samples. Salicylate and ammonia react at high pH in the presence of a chlorine donor and an iron catalyst to form a blue indophenol dye, the concentration of which is proportional to the ammonia concentration in the sample. A Perkin-Elmer Lambda 2S spectrophotometer was used. A clean tube was rinsed with sample water. It was filled to the 10 mL line with sample. The tube was inserted into the spectrophotometer chamber and scanned (BLANK). The tube was removed from the spectrophotometer and 8 drops of Ammonia Nitrogen Reagent #1 (V-4797) were added. The tube was then capped and mixed. 1.0 mL of Ammonia Nitrogen Reagent #2 (V-4798) was added and mixed. 5 minutes were allowed for maximum color development. At the end of the 5-minute waiting period, the tube content was mixed, inserted into the chamber and scanned.

The following formula was used to express the results as Ionized Ammonia (NH_4^+):

ppm ionized ammonia (NH_4^+) = ppm ammonia-nitrogen (NH_3–N) x 1.3

For the best possible results, a reagent blank was determined to account for any contribution to the test result by the reagent system. To determine the reagent blank, a distilled water blank was scanned. The distilled water sample was the reagent blank.

HARDNESS

Hardness refers to the total amount of calcium and magnesium in the water. All water contains some natural hardness that will vary regionally and from source to source within a region. If there is too little hardness, the water is considered soft and tends to be corrosive. If the water hardness level is too high, the calcium and magnesium may come out of solution and form scale deposits. Hard water will also reduce the ability of soap to form lather. The control of hardness is an important step in many domestic and industrial water systems.

The phthalein purple method was used to measure hardness. Calcium and magnesium ions react with phthalein purple at a pH of about 9 to form a purple color in proportion to the hardness concentration. A tube was rinsed with sample water and filled to 10 mL with sample. The tube was then inserted into the spectrophotometer chamber and scanned. The tube was then removed from the spectrophotometer and one Hardness Spectrophotometric Grade Tablet was added. The tablet was crushed using a crusher. The tube was then capped, shaken for 10 seconds and allowed a 1-minute waiting period. The tube was inserted into chamber and scanned. Result in ppm hardness was recorded. For best possible results, a reagent blank was determined to account for any contribution to the test result by the reagent system. To determine the reagent blank, distilled water blank was scanned. This test result was the reagent blank.

NITRATE

Nitrogen is essential for plant growth, but too much in water supplies can result in nutrient pollution. Nitrates, and phosphate, stimulate the growth of algae creating water quality problems. Nitrogen compounds may enter water as nitrates or be converted to nitrates from agricultural fertilizers, sewage, industrial and packinghouse wastes, drainage from livestock feeding areas and manure. Nitrates in large amounts in drinking water can cause “blue baby syndrome” (methemoglobenemia) in infants in less than 6 months of age and other health problems. US Public Health Service Drinking Water Standards state that 44 ppm nitrate should not be exceeded. To the sanitary and industrial engineer, concentrations of less than 4 ppm are acceptable.

The zinc reduction method was used to measure nitrate. Zinc is used to reduce nitrate to nitrite. The nitrite that was originally present, plus the reduced nitrate, reacts with chromotropic acid to form a red color in proportion to the amount of nitrite in the sample. A tube was rinsed with sample water and filled to 10 mL with the sample. The tube was inserted into the chamber and scanned. The tube was then removed from the spectrophotometer and one Nitrate Spectrophotometric Grade Tablet (3881) was added. The tube was capped and inverted 60 times each minute for 2 minutes (one inversion equals 180°). Following a waiting time of 5 minutes, the tube was inserted into chamber and scanned. The result in ppm nitrate was recorded. For best possible results, a reagent blank was determined to account for any contribution to the test result by the reagent system. A distilled water blank was scanned. This test result was the reagent blank. To convert nitrate (NO_3) results to nitrate-nitrogen (NO_3-N), divide by 4.4.

NITRITE

Nitrite represents an intermediate stage of the nitrogen cycle, usually resulting from the bacterial decomposition of compounds containing organic nitrogen. Under aerobic conditions bacteria oxidize ammonia to nitrites; and under anaerobic conditions, bacteria reduce nitrates to nitrites. Nitrites are often used as food preservatives. The nitrite concentration of drinking water rarely exceeds 0.1 ppm.

The diazotization method was used to measure nitrite concentration in water samples. The compound formed by diazotization of sulfanilamide and nitrite is coupled with N-(1-naphthyl)-ethylenediamine to produce a reddish purple color in proportion to the nitrite concentration. A clean tube was rinsed with sample water and filled to the 10 mL line with sample. The tube was then Inserted into chamber and scanned as blank. It was removed from the spectrophotometer and 5 mL was poured off into a graduated cylinder. The remaining sample was discarded. The 5 mL sample from the graduated cylinder was poured into the colorimeter tube. A graduated cylinder was used to measure 5 mL of the Mixed Acid Reagent (V-6278) and was added to the tube. The tube was capped and mixed. A 0.1 g spoon was used to add two measures of the Color Developing Reagent (V-6281). It was then capped and mixed by gently inverting for 1-minute. 5 minutes was allowed for maximum color development. At the end of the 5-minute waiting period, the tube content was mixed, inserted into chamber and scanned. Result was then recorded. Nitrite-nitrogen (NO_2–N) results were multiplied by 3.3 to convert to ppm nitrite (NO_2) results.

PHOSPHATE

Phosphorus is an important nutrient for aquatic plants. The amount found in water is not more than 0.1 ppm unless the water has become polluted from wastewater sources or excessive drainage from agricultural areas (LaMOTTE COMPANY, 2003). When phosphorus is present more than the concentrations needed for normal aquatic plant growth, a process called eutrophication takes place. This creates a favorable environment for the increase in algae and weeds. When algae cells die, oxygen is used in the decomposition and fish kills often result. Rapid decomposition of dense algae scums with associated organisms causes foul odors and hydrogen sulfide gas.

Ammonium molybdate and antimony potassium tartrate react in a filtered acid medium with dilute solution of PO_4^{3-} to form an antimony-phosphomolybdate complex. This complex is reduced to an intense blue colored complex by ascorbic acid. The color is proportional to the amount of phosphate present. Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid digestion. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion. A clean tube was rinsed with sample water and filled to the 10 mL line with sample. The tube was then inserted into chamber and scanned as blank. The tube was then removed from the spectrophotometer. 1.0 mL of the Phosphate Acid Reagent (V-6282) was added and mixed. One measure of the Phosphate Reducing Reagent (V-6283) was added using the 0.1 g spoon. The tube was capped and shaken until the powder dissolved. Five minutes were allowed for full color development. Solution will turn blue if phosphates are present. At the end of a 5-minute waiting period the tube content was mixed, inserted into chamber and scanned. The result was then recorded.

SILICATE

Silicon dioxide, SiO_2, commonly known as silica, occurs in all natural water. Silica may be present as suspended, insoluble particles in a colloidal or polymeric state. It may also be present in a reactive form as silicic acid or silicate ions. Silica is a major nutrient for diatoms. A silica cycle occurs in many bodies of water containing organisms, such as diatoms, that use silica in their skeletal structure. The silica removed from the water may be slowly returned to solution by the decomposition of the dead organisms. The major source of silica in natural water is from the decomposition of silicate minerals in the drainage basin from which the waters flow.

The presence of silica is objectionable in water used for boiler feed water purposes, as it may cause formation of a hard, dense scale, which has an unusually high resistance to heat transfer. Serious loss of turbine efficiency results from insoluble silica turbine blade deposits caused by vaporization of silica from the boiler water.

Reactive silica forms a complex with ammonium molybdate in an acidic solution to produce a yellow-green color in proportion to the amount of silica present. Phosphate also reacts with molybdate but adding oxalic acid eliminates the molybdophosphoric acid complex. This silica molybdate complex is then reduced by ascorbic acid to produce an intense blue color. A clean tube was rinsed with sample water and filled to the 10 mL line with sample. The tube was then inserted into the chamber and scanned as blank. The tube was then removed from the spectrophotometer. Six drops Silica Reagent #1 (V-4466) were added, capped and inverted to mix. Twelve drops of Silica Reagent #2 (V-4467) were then added, capped and mixed. Five minutes was allowed to wait. Eight drops of Silica Reagent #3 (V-4468) were then added, capped and mixed. A 2-minute wait period was allowed. One measure of the Silica Reagent #4 (V-6284) was then added by using the 0.1 g spoon (0699). The tube was capped and mixed gently until the powder dissolved. 5 minutes were allowed to wait for full color development. At the end of 5-minute waiting period, the tube content was mixed, inserted into the chamber and scanned. The result was then divided by 0.3 and recorded as silicate (mg/L).

For best possible results, a reagent blank was determined to account for any contribution to the test result by the reagent system. A distilled water blank was scanned. This test result was the reagent blank.

SULFATE

The most common mineral forms of sulfur are iron sulfide, lead sulfide, zinc sulfide and as calcium sulfate and magnesium sulfate (LaMOTTE COMPANY, 2001). In most fresh waters, the sulfate ion is the second or third most plentiful anion, being exceeded only by bicarbonate and, sometimes, silicate. Sulfur, in the form of sulfate, is considered an important nutrient. Mineral springs are rich in sulfate and feed large quantities of this ion to the watershed. Acid mine water drainage is a form of pollution that may contribute large amounts of sulfate content to natural waters. Other sources of sulfate include waste material from pulp mills, steel mills, food processing and municipal wastes. Many bacteria obtain sulfur from sulfate for the synthesis of amino acids. In lakes and streams low in oxygen, this process of sulfate reduction causes production of hydrogen sulfide, with its characteristic offensive odor. Calcium sulfate and magnesium sulfate contribute significantly to the hardness of water. Under natural conditions, the quantities are normally expected in lakes to be between 3 and 30 parts per million (LaMOTTE COMPANY, 2001).

Sulfate ion is precipitated in an acid medium with barium chloride to form a barium sulfate suspension in proportion to the amount of sulfate present. Barium Chloride Method was used to measure sulfate concentration in water samples. A clean tube was rinsed with sample water and filled to the 10 mL line with sample. The tube was then inserted into the chamber and scanned as blank. The tube was then removed from the spectrometer. One measure of Sulfate Reagent (V-6277) was then added by using the 0.1 g spoon. The tube was capped and mixed gently until the powder has dissolved. 5 minutes was allowed to wait for full color development. At the end of the 5-minute waiting period, the tube content was mixed, inserted into the chamber and scanned. The result was then recorded. For the most accurate results, samples and reactions should be at 25±4°C.

ALKALINITY–UDV

Alkalinity is a measure of the acid-neutralizing capacity of water that enables it to resist abrupt changes in pH. It is the sum of all titratable bases. Alkalinity is significant in maintaining proper pH levels in natural water; water used for irrigation, swimming pools, industrial processes and wastewater treatment processes.

The presence of buffering materials in natural waters helps to neutralize acids as they are added to, or created in, the water ecosystem. A Total Alkalinity of 100 to 200 ppm will stabilize the pH level in a stream (Exploring the Environment, 2003). In swimming pools, total alkalinity is commonly known as a pH stabilizer because, when the alkalinity is at a proper level, a consistent pH level can be maintained while treatment chemicals or fresh make-up water is added. In industrial situations, alkalinity is an important factor in preventing fluctuating pH levels that can damage equipment and corrode pipes. The sample is added to a buffered indicator reagent. The color that develops, ranging from yellow to blue, will indicate the amount of alkalinity in the sample.

The unit dose vials method was used to measure alkalinity. A 10 mm square cell adapter was used. A clean vial with sample water was rinsed with sample water. A syringe was used to add 3 mL of sample to the vial. The vial was then inserted into chamber and scanned as blank. The tube was then removed from the spectrometer. A 3 mL of sample was added to an Alk UDV vial (4318). A 2 minute waiting period was used. The vial was inverted 3 times to mix. The tube was inserted into chamber and scanned. The result was then recorded. For best possible results, a reagent blank was determined to account for any contribution to the test result by the reagent system. A distilled water blank was scanned. This test result was the reagent blank.

CHLORIDE

Chloride is one of the major anions found in water and sewage (Alken, 2003). The presence of chlorides in large amounts may be because of the natural process of water passing through salt formations in the earth. It may also be evidence of the intrusion of seawater or pollution from industrial processes or domestic wastes. The salt content of water affects the distribution of plant and animal life in an aquatic system, based on the amount of salt they can tolerate.

Silver nitrate reacts with chloride to form turbid silver chloride in proportion to the amount of chloride in the sample. Chloride Spectrophotometric Grade

Tablets (argentometric method) were used to measure chloride concentration. A tube was rinsed with sample water and filled to 10 mL with sample. The tube was inserted into the chamber and scanned. The tube was then removed from the spectrometer and one Chloride Spectrophotometric Grade Tablet was added. The tube was capped and inverted 2 times and then there was a 3 minute wait. The tube was inserted into the chamber and scanned. The result in ppm chloride was recorded. For best possible results, a reagent blank was determined to account for any contribution to the test result by the reagent system. A distilled water blank was scanned. This test result was the reagent blank.

Acidity

Acidity was measured by the titration method (American Society of Testing and Materials, 1984). 5.8 mL of water sample were poured into a square bottle for mixing. One drop of phenolphthalein indicator solution (1g/L) was added to the mixing bottle and swirled to mix. If the water remained colorless the sodium hydroxide standard solution (0.035 N) was added drop by drop. Each drop was counted as it was added. Drops were added until the sample just began to turn slightly pink. The acidity of water, expressed in mg/L as calcium carbonate is equal to the number of drops of sodium hydroxide standard solution used times 20.

3.2.2.5 Chromatographic fractionation for organic compounds in effluent municipal wastewater using ion exchange processing techniques

In the chromatographic separation of the organic content of MUC wastewater, diethylaminoethylcellulose (DEAE) and carboxylmethylcellulose (CM) resins were used (Abdullaev et. al., 1992). Fig. 3.2-5 is a schematic diagram of the fractionation of dissolved organics in wastewater.

The water sample being analyzed was passed, in series, through the columns containing DEAE and CM; the column diameter was 23 mm, the charge depth was 75 mm, and the batch size was 6.0 g. The columns were then washed with 15 to 20 ml of double distilled water, and the wash waters were added to the filtrate. Desorption of organic species from the anionic and cationic exchangers was carried out using 2 BV of 0.1 M NaOH containing 0.5 M NaCl. The columns were then washed with 0.5 M NaCl alone and further washed with the solution of 0.1 M HCl containing 0.5 M NaCl.

Each sample yields three groups of compounds on fractionation – an acidic group including humic and fulvic acids, low molecular weight amino acids, and phenols, etc; a basic group including proteins, amines, carbonyl compounds, and the like; and a neutral group containing free reducing sugars, polysaccharides, ethers, and so on. This is based on chromatographic fractionation using DEAE and CM ion exchange cellulose. The presence of humic and fulvic acids, amino acids, phenols in the effluents of urban wastewater plants is well documented

(Abdullaev et. al., 1980). Proteins, amines, and carbonyl compounds are the bases that remain in the effluent even after various treatment processes in city wastewater works (National Guidelines and Standards Office, 2005). Reducing sugars, polysaccharides, and ethers that are neutral organic species have been frequently reported to be present in the effluent of domestic wastewater plants (Sannolo et. al., 1981).

The quantity of organic material in the initial, unfractionated samples of wastewater, and in some fractions containing separated groups, was found by the determination of both the chemical oxygen demand (COD) and permanganate value (PV).

The samples of wastewater were collected at the MUC Wastewater Treatment Plant. The plant is located at 12001, Maurice Duplessis, Montreal. The samples were effluent final water and were supplied by the plant personnel. H_2SO_4 was added to adjust the pH to less than 2 and the samples were refrigerated and analysed within 7 days. Some of the samples were filtered immediately and refrigerated for the determination of phosphate, sulfate, nitrate, nitrite, acidity, and alkalinity. After recovery of the coarse particulate and colloidal impurities by filtration through membrane filter, the organic materials were classified into acidic, basic, and neutral groups as follows. As ion exchange cellulose absorbs the acidic group, organic compounds, the DEAE filtrate contains only organic compounds from the basic and neutral classes; passing the filtrate over a cation exchange medium, which will retain only neutral organic matter, can separate these. Analysis of the filtrates and sorbates from both columns enabled the percentage composition of the various organic fractions in the MUC wastewater. Both COD and permanganate values were measured. The determination of the composition of organic fractions was necessary to see which of the fractions dominates in the influent water and to determine whether any sorbent can sorb selectively the dominating fraction of organics. The schematic diagram of the fractionation process is shown in Figure 3.2-5.

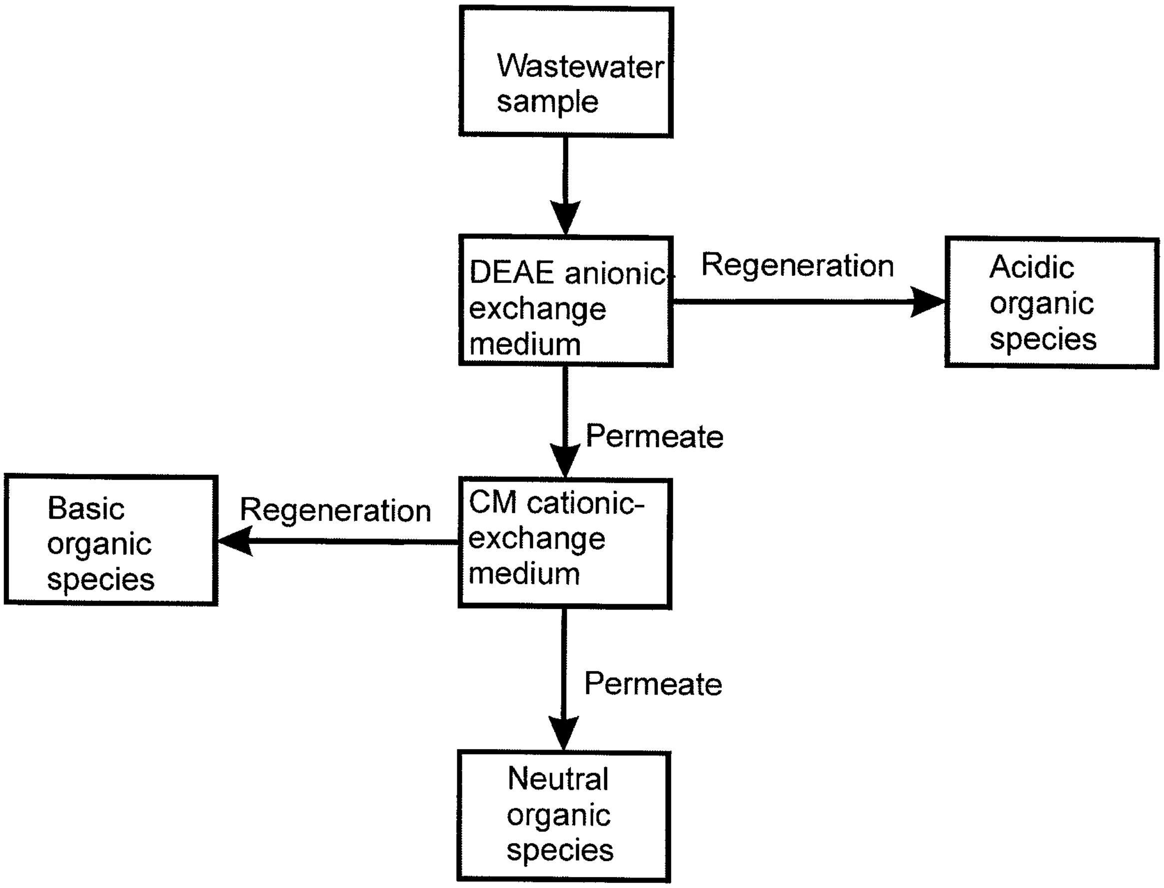


Figure 3.2-5 Schematic diagram of the fractionation process for organic compounds in municipal wastewaters using ion exchange processing techniques

As can be seen in Table 4.2-7, the bulk part of DOM belongs to acidic organic species, which can efficiently be sorbed onto the macro-porous anion exchange media. The acidic organic species are the major competitor of arsenate ions. While carrying out the investigation of the regeneration process, the resin bed was brought to equilibrium exhaustion (when the effluent concentrations reached those of the influent water) in terms of both arsenate and

DOM. This enabled the determination of the impact of any factor on regeneration efficiency, due to the concentration of arsenate and DOM in spent regeneration solution. The exhausted resin was divided into equal weights, which were regenerated under various conditions: temperature regime, consumption and concentration of brine, content of NaOH in the regenerant for enhancing the regenerating properties in relation to arsenate and DOM, and the regeneration rate. While conducting an investigation of the sorption process (after having found the optimum regeneration conditions), the resin bed was brought to the given breakthrough of 10 ppb and 2 mgO_2/L of arsenate and DOM respectively. Based on the nature of the sorption of DOM, its impact on arsenate removal, and the necessity to reduce the entrance of acidic organic species into potable water, the filter was turned off as the concentration of acidic organic species reached 2 ppm, which was determined by means of separation and identification of filtrate samples during all exchange cycles. The concentration of 2 ppm of DOM corresponds to the quality of unpolluted natural water and thus stops interfering with the conventional arsenic removal process. Since the presence of DOM necessitates the use of macroporous media, the removal (or significant reduction) of DOM will allow the use of traditional gel-type ion exchange media.

3.2.2.6 Experimental procedure for the determination of the optimum regeneration conditions, desorption and sorption processes

The DOE and analyses were performed using Design-Expert version 6.0.11. The software was bought from Stat-Ease, Inc., Minneapolis, USA. In this section, desorption and sorption processes of arsenic in the presence of DOM and on the macroporous chloride form media were investigated. Table 3.2-8 shows the design layout for optimum regeneration of macroporous anion exchange media. A full-factorial experiment was carried out in the laboratory to study three factors thought to influence the optimum regeneration conditions of a strongly basic anion exchange media. The factors chosen were specific consumption of salt per unit weight of dry resin (G_s), brine concentration (C_s) and the concentration ratio of salt to alkali ($C_{s/a}$).

Table 3.2-9 summarizes the experimental design in more details. As can be seen three-factor interactions were investigated at three levels. At each combination of these settings, the amount of arsenates desorbed per unit weight of dry resin was recorded. The goal was to maximize the desorption rate and also try to determine the conditions that would allow maximum regeneration efficiency.

Table 3.2-8 Design layout for the optimum regeneration of macroporous anion exchange media

Std	Run	Factor 1 A:Gs(kg/tonne)	Factor 2 B:Cs(%)	Factor 3 C:Cs/a	Response 1 (meq/kg)
32	1	200	7.5	6	229.0
19	2	100	5.0	10	156.0
24	3	300	7.5	10	326.0
11	4	200	5.0	6	229.0
4	5	100	7.5	2	131.0
22	6	100	7.5	10	163.0
1	7	100	5.0	2	159.0
27	8	300	10.0	10	370.0
5	9	200	7.5	2	212.0
28	10	200	7.5	6	230.0
21	11	300	5.0	10	283.0
29	12	200	7.5	6	229.5
30	13	200	7.5	6	229.0
15	14	300	7.5	6	310.0
17	15	200	10.0	6	228.0
2	16	200	5.0	2	239.0
23	17	200	7.5	10	245.0
7	18	100	10.0	2	102.0
31	19	200	7.5	6	229.5
14	20	200	7.5	6	229.0
16	21	100	10.0	6	136.0
20	22	200	5.0	10	220.0

26	23	200	10.0	10	270.0
10	24	100	5.0	6	158.0
8	25	200	10.0	2	186.0
25	26	100	10.0	10	171.0
3	27	300	5.0	2	319.0
6	28	300	7.5	2	294.0
12	29	300	5.0	6	301.0
18	30	300	10.0	6	319.0
9	31	300	10.0	2	269.0
13	32	100	7.5	6	147.0

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

Table 3.2-9 Design summary of the experiments with respect to optimum regeneration of macroporous anion exchange media

Study Type	**Initial Design**	**Design Model**	Experiments	**Blocks**			
Response Surface	3 Level Factorial	Quadratic	32	No Blocks			
Response	**Name**	**Units**	**Number of Observations**	**Minimum**	**Maximum**	**Transformation**	**Model**
Y1	Response 1		32	102	370	None	RCubic
Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Low Coded**	**High Coded**
A	Gs(kg/tonne)	kg/tonne	Numeric	100	300	-1	1
B	Cs(%)	%	Numeric	5	10	-1	1
C	Cs/a		Numeric	2	10	-1	1

Table 3.2-10 shows the design layout for the determination of the arsenate exchange capacity of a macroporous anion exchange resin in alkaline medium. A full-factorial experiment was carried out in the laboratory to study three factors thought to influence the arsenate exchange capacity . The factors chosen were influent concentration of dissolved organic matter (C_{DOM}), pH and filtration velocity.

Three-factor interactions were investigated at three levels. At each combination of these settings, the exchange capacity per unit weight of dry resin was recorded. The goal was to maximize the exchange capacity and also try to determine the conditions that would allow maximum exchange capacity.

Table 3.2-10 Design layout for the determination of the dependence of the arsenate-exchange capacity in the presence of DOM (using macroporous exchange media, MTO-AMBERLITE IRA-910)

Std	Run	Factor 1 A:C_{DOM} (mg/L)	Factor 2 B:pH	Factor 3 C:v (m/h)	Response 1 Arsenate capacity (meq/kg)	Response 2 Residual As Concentration (ppb)
9	1	11.2	10.4	10	34.0	12.0
20	2	7.4	7.0	30	65.0	8.5
4	3	3.6	8.7	10	78.0	6.0
7	4	3.6	10.4	10	66.0	7.0
21	5	11.2	7.0	30	62.0	11.0

5	6	7.4	8.7	10	62.0	8.0
13	7	3.6	8.7	20	69.0	7.0
15	8	11.2	8.7	20	49.0	11.0
24	9	11.2	8.7	30	46.0	12.0
23	10	7.4	8.7	30	53.0	10.0
32	11	7.4	8.7	20	56.5	8.0
26	12	7.4	10.4	30	38.5	11.5
3	13	11.2	7.0	10	65.0	8.5
27	14	11.2	10.4	30	27.0	14.0
30	15	7.4	8.7	20	59.0	8.5
16	16	3.6	10.4	20	59.0	8.0
28	17	7.4	8.7	20	57.0	9.0
22	18	3.6	8.7	30	60.0	8.0
2	19	7.4	7.0	10	75.0	6.5
1	20	3.6	7.0	10	87.0	4.0
8	21	7.4	10.4	10	49.5	9.5
12	22	11.2	7.0	20	65.0	10.0
18	23	11.2	10.4	20	34.0	13.0
6	24	11.2	8.7	10	52.0	10.0
10	25	3.6	7.0	20	78.0	5.0
11	26	7.4	7.0	20	73.0	7.5
14	27	7.4	8.7	20	57.00	9.0
17	28	7.4	10.4	20	46.0	10.5
29	29	7.4	8.7	20	58.0	8.0
31	30	7.4	8.7	20	56.0	9.0
19	31	3.6	7.0	30	68.0	6.0
25	32	3.6	10.4	30	50.0	9.0

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

3.2.3 Methods for the investigation of the processes of sorption and desorption of DOM and other impurities by two-stage treatment

The investigation was carried out on a fixed unit incorporating dynamic columns with Amberlite –200 c (hydrogen ion form) exchange resin in both stages, and the anionic-exchange media Amberlite IRA-96 and MTO-Amberlite IRA-910 (hydroxyl ion form) in stages I and II respectively.

Domestic waste water (effluent) from the Montreal municipal treatment works was further coagulated with lime (150 mg-CaO/L) in the lab, diluted to the sum of strong acid anions ≤ 5 meq/L with natural water from the Saint Lawrence River, As(V) was added, after which the concentration of organic matter in the treated water (with respect to COD) was within the recommended limits (residual COD of less than 30 to 40 ppm) and the total anionic content of 5 meq/L (Keller et. al., 2005).

3.2.3.1 Chromatographic fractionation of DOM in highly mineralized and diluted tertiary treated domestic wastewater

Along with the mineral composition including arsenate, dissolved organic substances of domestic wastewater of the city of Montreal that served the influent water in this investigation were also studied. The organic materials were separated by chromatographic fractionation using cellulose based ion exchange media. This technique makes it possible to extract the dissolved organic substances and classify them as acidic, basic, or neutral. In the chromatographic separation of the organic content into acidic, basic and neutral groups, diethylaminoethylcellulose (DEAE) and carboxymethylcellulose (CM) were used. Results of the fractionation are shown in Table 4.3-2. Analysis of DOM was conducted by various methods such as Kubel's method (Permanganate value), the COD test, and the determination of TOC value by using PV.

3.2.3.2 Experimental procedure for a two-stage system to remove mineral and organic contents

The design layout and design summary are presented in Tables 3.2-11 and 3.2-12 respectively. This is a three-level three-factor interaction model. The type of analysis is numeric rather than categoric. Actual and coded values of the main factors are also given.

The design layout is set for the determination of the arsenate exchange capacity of a macroporous weakly anion exchange resin . A three-level response surface experiment was carried out in the laboratory to study three factors thought to influence the arsenate exchange capacity . The factors chosen were influent concentration of dissolved organic matter (C_{DOM}), NaOH consumption for regeneration per unit weight of dry resin and the concentration ratio of sulfate to chloride.

Three-factor interactions were investigated at three levels. At each combination of these settings, the exchange capacity per unit weight of dry resin was recorded. The goal was to maximize the exchange capacity and also to determine the conditions that would allow maximum exchange capacity.

Table 3.2-11 Design layout of the response surface experiment, for the determination of the dependence of the arsenate-exchange capacity in the presence of DOM

Std	Run	Factor 1 A:C_{DOM} (mg/L)	Factor 2 B: G_{NaOH} (kg/tonne)	Factor 3 C: $C_{\frac{SO_4^{2-}}{Cl^-}}$, eq/eq	Response 1 As-exchange capacity (meq/kg)
24	1	7	50	3	136.00
17	2	5	60	2	149.13
25	3	3	60	3	162.00
10	4	3	40	2	136.88
18	5	7	60	2	141.38
8	6	5	60	1	144.00
30	7	5	50	2	139.00
9	8	7	60	1	136.00
5	9	5	50	1	131.00
6	10	7	50	1	122.00

2	11	5	40	1	117.00
3	12	7	40	1	107.00
14	13	5	50	2	139.00
27	14	7	60	3	146.00
31	15	5	50	2	139.00
13	16	3	50	2	147.00
12	17	7	40	2	115.38
28	18	5	50	2	139.00
21	19	7	40	3	125.00
20	20	5	40	3	136.00
29	21	5	50	2	139.00
19	22	3	40	3	147.00
15	23	7	50	2	131.00
23	24	5	50	3	145.00
22	25	3	50	3	154.00
16	26	3	60	2	156.88
1	27	3	40	1	127.00
7	28	3	60	1	152.00
11	29	5	40	2	126.13
32	30	5	50	2	139.00
26	31	5	60	3	154.00
4	32	3	50	1	140.00
$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$					

Table 3.2-12 Design summary of the investigation of the dependence of arsenate exchange capacity on influent organic concentration, NaOH consumption and the ratio of sulfate to chloride concentrations

Study Type	**Response Surface**	**Design Model**	**Experiments**	**Blocks**			
Initial Design	3 Level Factorial	Quadratic	32	No Blocks			
Response	**Name**	**Units**	**Obs**	**Minimum**	**Maximum**	**Trans**	**Model**
Y1	Response 1		32	107	162	None	R2FI
Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Low Coded**	**High Coded**
A	C_{DOM}	mg/L	Numeric	3	7	-1	1
B	NaOH	kg/tonne	Numeric	40	60	-1	1
C	sufate/chloride		Numeric	1	3	-1	1

3.2.4 Methods of the investigation of the sorption process of arsenic from acidic water onto macroporous anion exchange media

Sorption of a macroporous resin was studied in acidic medium. Table 3.2-13 shows the design layout for the determination of the arsenate exchange capacity of a macroporous anion exchange resin in acidic medium. A response surface experiment was carried out in the laboratory to study three factors thought to influence the arsenate exchange capacity . The factors chosen were influent concentration of dissolved organic matter (C_{DOM}), pH and filtration velocity.

The design summary is given in Table 3.2-14. Three-factor interactions were investigated at three levels. At each combination of these settings, the exchange capacity per unit weight of dry resin was recorded. The goal was to maximize the exchange capacity and also try to find conditions that would allow maximum exchange capacity.

Table 3.2-13 Design layout of the response surface experiment, for the determination of the dependence of the arsenate-exchange capacity and effluent arsenic concentration in the presence of DOM

Std	Run	Factor 1 A:Input DOM (mg/L)	Factor 2 B:pH	Factor 3 C:v (m/h)	Response 1 As-capacity (meq/kg)	Response 2 Effluent As (ppb)
32	1	5	4.5	20	228.60	8.00
20	2	5	2.0	30	228.56	8.40
5	3	5	4.5	10	244.95	7.00
28	4	5	4.5	20	228.00	8.00
7	5	3	7.0	10	264.71	5.50
27	6	7	7.0	30	185.11	11.50
12	7	7	2.0	20	221.09	8.70
26	8	5	7.0	30	196.69	10.00
13	9	3	4.5	20	252.42	6.50
31	10	5	4.5	20	228.70	8.30
15	11	7	4.5	20	205.15	9.75
18	12	7	7.0	20	189.21	11.00
19	13	3	2.0	30	240.14	7.40
25	14	3	7.0	30	208.26	8.30
14	15	5	4.5	20	228.79	8.00
1	16	3	2.0	10	296.59	4.70
30	17	5	4.5	20	228.80	8.00
2	18	5	2.0	10	260.89	6.30
4	19	3	4.5	10	280.65	5.00
3	20	7	2.0	10	225.19	8.00
9	21	7	7.0	10	193.31	10.00

11	22	5	2.0	20	244.72	7.50
17	23	5	7.0	20	212.85	8.85
22	24	3	4.5	30	224.20	7.90
21	25	7	2.0	30	216.99	9.50
8	26	5	7.0	10	229.01	7.80
29	27	5	4.5	20	228.50	8.20
24	28	7	4.5	30	201.05	10.60
16	29	3	7.0	20	236.49	7.00
23	30	5	4.5	30	212.62	9.10
10	31	3	2.0	20	268.36	6.00
6	32	7	4.5	10	209.25	9.00

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

Table 3.2-14 Design summary of the response surface experiment, for the determination of the dependence of the arsenate-exchange capacity and effluent arsenic concentration in the presence of DOM (using macroporous exchange resin) in acidic medium.

Study Type	**Initial Design**		**Design Model**	**Experiments**	**Blocks**		
Response Surface	3 Level Factorial		Quadratic	32	No Blocks		
Response	**Name**	**Units**	**Observations**	**Minimum**	**Maximum**	**Trans**	**Model**
Y1	As-capacity	meq/kg	32	185.11	296.59	None	R2FI
Y2	Effluent As	ppb	32	4.70	11.50	None	R2FI
Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Low Coded**	**High Coded**
A	Input DOM	mg/L	Numeric	3	7	-1	1
B	pH		Numeric	2	7	-1	1
C	v	m/h	Numeric	10	30	-1	1

3.2.5 The utilization of the spent regeneration solutions

The utilization of spent regeneration solutions from Na-Cl ionization softener unit equipped with a macroporous anion exchange media chloride filter is described as follows. The sodium-cationic exchange media was activated with a 15% NaCl solution and the chloride anionic exchange media with a 10% to 15% NaCl solution in a mixture with 1% to 1.5% NaOH solution respectively.

The concentrated part of the spent solutions from sodium and chloride filters was collected and supplied to a clarifier. A half percent magnesium chloride solution was used as the coagulant. The solution in the clarifier was tested periodically for magnesium concentrations. $MgCl_2$ was dosed into the clarifier to keep Mg^{2+} concentration adequate in the clarifier. The precipitates of the Ca and Mg compounds were removed by filtration.

NaCl was added up to the initial concentration, after Ca and Mg compounds were removed thereby restoring the softened solution. This was then divided into two volumes. One of them was assigned for the regeneration of the Na-cationic filter. The residual concentration of alkalinity in the recovered regeneration solution was neutralized by adding 0.1 N HCl. The 2nd volume was assigned for the regeneration of chloride-form anion exchange media. NaOH alkali was added to the initial concentration of 1% to 1.5%, thereby restoring the regeneration solution.

The utilization of the spent regeneration solution from the chemical treatment unit with macroporous ion exchange media is described as follows. The spent regeneration solutions from the H-cationic and OH-anionic filters were collected in a clarifier. The spent regeneration solutions were collected in a clarifier and treated with $Ca(OH)_2$ and Mg_2SO_4. The dose was chosen on the basis of the specific sorption capacity of $Mg(OH)_2$ with respect to DOM i.e. 3 mg of oxidizability for 1 mg of precipitate.

The spent regeneration solutions were concentrated in a vapor diffusion apparatus. The concentrate (NaCl) was recycled for the regeneration of the Na-cationic filters of both initial water treatment and spent regeneration solution treatment columns.

The utilization of spent regeneration solutions from the additional filter with macroporous media is described as follows. The spent regeneration solution was collected in a clarifier. A reagent treatment was conducted in two stages. In stage 1, the spent regeneration solution was treated with ferric chloride in the quantity equivalent to the quantity of hydroxyl ions. The precipitate was separated and the solution was treated with $Ca(OH)_2$. In this stage, the sulfate ions were removed and the pH was adjusted in the range of 10.5 to 11.0 with $Ca(OH)_2$, thereby recovering the initial hydroxyl ions.

The precipitates from all the proposed schemes were collected in a pressure vessel, heated and then subjected to the EPA recommended TCLP test.

3.2.6 TCLP Tests

The schematic of ion exchange with regeneration and waste treatment is shown in Figure 3.2-6. TCLP extraction tests were conducted on solid-phase residuals. Extractions were done in accordance with EPA Method 1311, as outlined in the Federal Register (1990). Extraction fluid # 1 was prepared by adding 5.7 mL glacial acetic acid to 500 mL of double distilled water, adding 64.3 mL of 1N NaOH, and diluting to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05. The pH of the solution was measured and recorded to be 4.94.

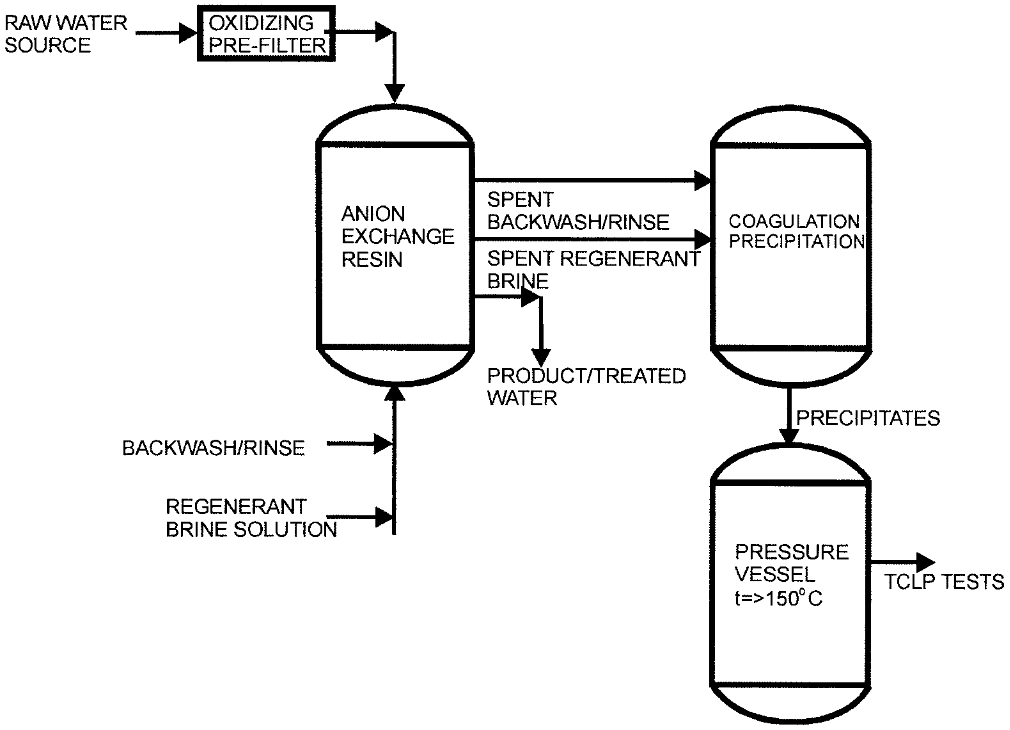


Figure 3.2-6 Schematic of ion exchange with regeneration and waste treatment

Extraction fluid # 2 was prepared by diluting 5.7 mL glacial acetic acid with double distilled water to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05. The pH of the solution was measured and recorded to be 2.9.

The residual samples generated in precipitation and crystallization tests were filtered through a glass fiber filter in a pressure filter device. A domestic steam cleaner (Shark) boiler was used to produce scorodite. An extraction was performed on the solids (plus filter). The extract and filtrate were subsequently combined for arsenic analysis. The extraction fluid used was determined based on the pH of each sample by combining 5 g of the sample with 96.5 mL of double distilled water. This solution was vigorously stirred for 5 min using a magnetic stirrer. If the pH was less than 5.0, an extraction fluid (#1) with a pH = 4.93 ± 0.05 was used. If the pH was greater than 5.0, then 3.5 mL of 1 N hydrochloric acid (HCl) was added to the solution, it was heated to 50°C and then was held for 10 min. After the solution was cooled, if the resulting pH was less than 5.0, extraction fluid #1 was used. If the pH was greater than 5.0, an extraction fluid (#2) with a pH = 2.88 ± 0.05 was used.

The solid media samples plus a volume of extraction fluid equal to 20 times the weight of the sample were added to an extractor vessel, secured in a rotary agitation device and rotated at 30 ± 2 rpm for 18 ± 2 hrs. The extract was acidified with nitric acid to a pH less than 2.

4. RESULTS AND DISCUSSION

4.1 Preliminary tests for arsenic removal by gel-type anion exchange media

Initial tests were performed to determine if As(III) could be removed by the ion exchange media without oxidation. Using an influent concentration of 1600 ppb As(III) into the ion exchange column, it was shown that the concentration of As(III) in the column effluent was approximately the same as the influent, indicating negligible removal of this form of arsenic. This is demonstrated in Figure 4.1-1. Subsequently, the oxidizing media was evaluated for its ability to remove As (III). The results are shown in Figure 4.1-2. They indicate that the removal of the As (III) was complete until saturation of the column started to occur at 250 mL (10 ppb breakthrough). After 1860 mL of water had passed through, the column exhaustion occurred. Therefore, the use of the oxidizing media is a requirement for the eventual removal of As (III) as arsenic III needs to be converted to arsenic V prior to treatment. Ion exchange does not remove As (III) because As (III) occurs predominantly uncharged (H_3AsO_3) in water with a pH value of less than 9.0 (Kang et. al., 2000). The predominant species of As (V) are $H_2AsO_4^-$ and $HAsO_4^{2-}$, which are negatively charged, and thus are removable by ion exchange. If As(III) is present, it must be oxidized to As(V) before removal by ion exchange (Wang et. al., 2000). The regeneration schedule of the oxidizing media and that of the ion exchange media are shown in Tables 3.2-4 and 3.2-5 respectively.

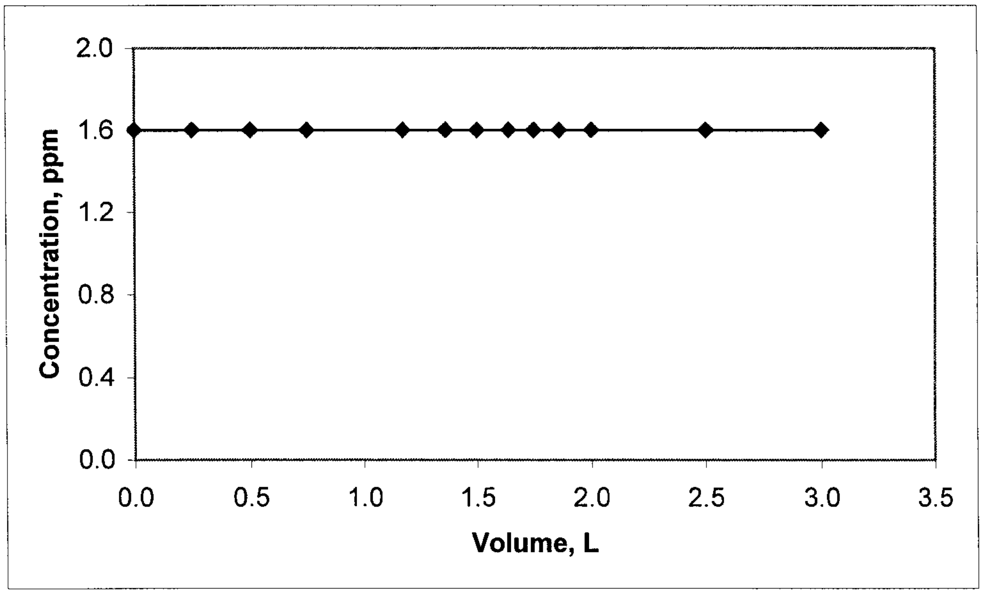


Figure 4.1-1 Concentration of arsenic III in the effluent of the ion exchange column

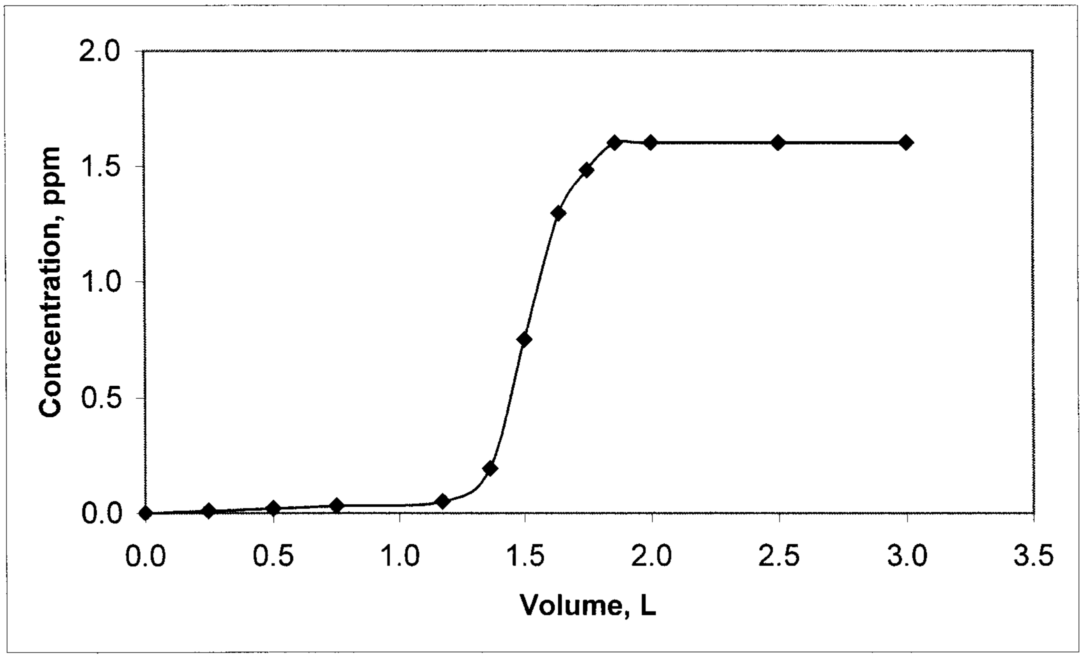


Figure 4.1-2 Concentration of arsenic III in the effluent of the solid phase oxidizing media

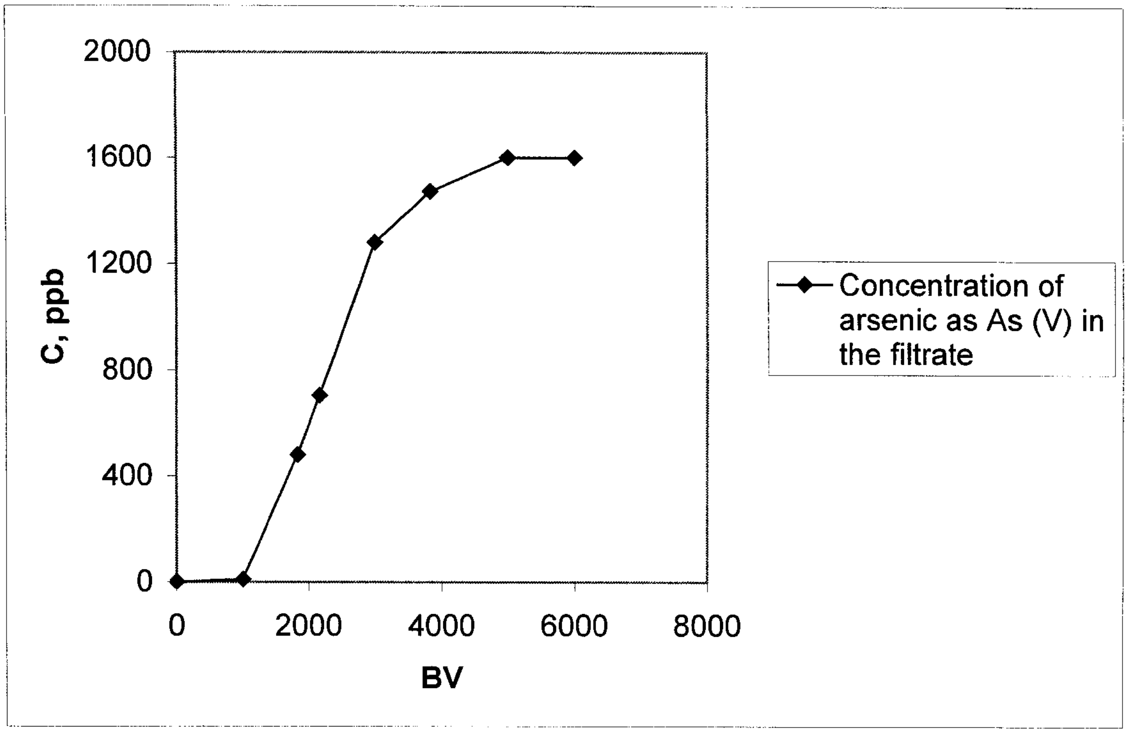


Figure 4.1-3 Sorption of As (V) onto gel-type chloride form ion exchange media Purolite A-300

Experimental results of one of the runs carried out in this section have been given in Table 4.1-1. As can be seen, 97% of arsenates were desorbed from the exhausted resin. Effluent concentration was as low as 2.4 ppb. As can be seen from Figure 4.1-3 the breakthrough of arsenic started to occur at 2947 ml and the 10 ppb breakthrough had occurred at 5647 mL (maximum allowable concentration of 10 ppb). The filter was stopped at this point. The results of this run are presented in Table 4.1-1.

Table 4.1-1 Sorption and desorption of arsenate from the ion exchange column

Item	Value
Water treated, mL	5647
Water treated, BV	941
Influent concentration, ppb	500
Amount of arsenic in raw water, µg	2823.5
Residual concentration in the filtrate, ppb	2.4
Quantity of arsenic in the treated water, µg	13.55
Quantity of arsenic sorbed on the resin, µg	2810
Concentration of arsenic in the spent regeneration solution including wash water, ppm	11.2
Quantity of arsenic desorbed, µg	2725
Total volume of brine and wash water, mL	244
As(V) removal by regeneration, %	97

Note: 1 equivalent of arsenate equals 139.9/2 = 69.95 grams

ANOVA for the determination of arsenate exchange capacity of gel-type anion exchange resin Purolite A-300 is shown as follows. ANOVA for Response Surface Reduced 2FI Model is given in Table 4.1-2.

Table 4.1-2 Analysis of variance table [Partial sum of squares] for the determination of arsenate exchange capacity by gel-type chloride-form anion exchange resin.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remarks
Model	0.001718	5	0.000344	1242.945	< 0.0001	significant
A	0.000673	1	0.000673	2434.867	< 0.0001	
B	0.000834	1	0.000834	3016.776	< 0.0001	
C	5.82E-05	1	5.82E-05	210.4814	< 0.0001	
AB	0.000112	1	0.000112	406.4367	< 0.0001	
AC	4.04E-05	1	4.04E-05	146.1642	< 0.0001	
Residual	7.19E-06	26	2.76E-07			
Lack of Fit	6.52E-06	21	3.1E-07	2.322793	0.1778	not significant
Pure Error	6.68E-07	5	1.34E-07			
Cor Total	0.001725	31				

The Model F-value of 1242.94 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 2.32 implies the Lack of Fit is not significant relative to the pure error. There is a 17.78% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.1-3 Summary of adequacy test for the determination of arsenate exchange capacity by gel-type chloride-form anion exchange resin.

Std. Dev.	0.000526		R-Squared	0.995834
Mean	0.025551		Adj R-Squared	0.995033
C.V.	2.057864		Pred R-Squared	0.993927
PRESS	1.05E-05		Adeq Precision	129.6341

The "Pred R-Squared" of 0.9939 is in reasonable agreement with the "Adj R-Squared" of 0.9950. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 129.634 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.1-4 Main and interaction factors for the determination of arsenate exchange capacity by gel-type chloride-form anion exchange resin

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.025551	1	9.3E-05	0.02536	0.025742	
A-Input As (ppb)	0.006115	1	0.000124	0.005861	0.00637	1
B-pH	-0.00681	1	0.000124	-0.00706	-0.00655	1
C-v (cm/min)	-0.0018	1	0.000124	-0.00205	-0.00154	1
AB	0.00306	1	0.000152	0.002748	0.003372	1
AC	-0.00184	1	0.000152	-0.00215	-0.00152	1

Table 4.1-5 Diagnostics case statistics for the determination of arsenate exchange capacity by gel-type chloride-form anion exchange resin

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	0.028	0.029	-0.0003	0.36	-0.87	0.07	-0.86	15
2	0.035	0.034	0.0008	0.14	1.73	0.08	1.80	16
3	0.038	0.039	-0.0005	0.36	-1.30	0.16	-1.32	27
4	0.018	0.019	-0.0005	0.22	-1.07	0.05	-1.08	12
5	0.028	0.027	0.0006	0.08	1.29	0.02	1.31	9
6	0.035	0.035	-0.0003	0.22	-0.64	0.02	-0.64	7
7	0.009	0.009	-0.0001	0.36	-0.31	0.009	-0.30	8
8	0.021	0.020	0.0004	0.14	0.94	0.02	0.93	28
9	0.031	0.031	-5.3E-05	0.36	-0.12	0.001	-0.12	31
10	0.028	0.029	-0.0004	0.22	-0.87	0.03	-0.86	14
11	0.033	0.032	0.0006	0.08	1.27	0.02	1.29	19
12	0.035	0.035	-0.0001	0.22	-0.24	0.002	-0.24	30
13	0.019	0.019	-0.0002	0.08	-0.46	0.003	-0.46	2
14	0.025	0.025	0.0001	0.03	0.28	0.0004	0.28	17
15	0.031	0.031	-0.0006	0.08	-1.32	0.02	-1.34	6
16	0.009	0.009	-0.0003	0.22	-0.79	0.03	-0.79	20

17	0.019	0.018	0.0006	0.08	1.31	0.02	1.33	4
18	0.027	0.027	-0.0004	0.22	-0.90	0.03	-0.90	26
19	0.029	0.029	-0.0001	0.36	-0.33	0.01	-0.32	11
20	0.031	0.030	0.0006	0.14	1.42	0.05	1.46	18
21	0.031	0.031	-0.0001	0.36	-0.24	0.005	-0.23	13
22	0.019	0.019	-0.0004	0.22	-1.02	0.05	-1.02	23
23	0.024	0.023	0.0002	0.08	0.49	0.003	0.48	22
24	0.027	0.028	-0.0005	0.22	-1.15	0.06	-1.16	5
25	0.009	0.009	-0.0004	0.36	-0.96	0.08	-0.96	29
26	0.018	0.016	0.0010	0.14	2.16	0.12	2.34	10
27	0.024	0.024	-0.0002	0.36	-0.68	0.044	-0.67	24
28	0.025	0.025	0.0001	0.03	0.28	0.0004	0.28	1
29	0.026	0.025	0.0004	0.03	0.86	0.004	0.86	3
30	0.025	0.025	-0.0005	0.03	-1.06	0.006	-1.06	21
31	0.025	0.025	0.0001	0.03	0.28	0.0004	0.28	25
32	0.026	0.025	0.0004	0.03	0.86	0.004	0.86	32

As a result of the statistical treatment, as shown above, including the elimination of insignificant coefficients by Student's criterion and adequacy test by Fisher's criterion, the following regression equation was obtained. The predictive model is listed in both actual and coded terms. The coded equation is useful for identifying the relative significance of the factors by comparing the factor coefficients. This comparison cannot be made with the actual equation because the coefficients are scaled to accommodate the units of each factor. The equations give identical predictions.

$$\text{As-capacity} = 0.026+6.115\text{E-}003*A-6.807\text{E-}03*B-1.798\text{E-}003*C+3.060\text{E-}003*A*B-1.835\text{E-}003*A*C \qquad (4.1\text{-}1)$$

A, B, and C are the coded factors representing influent arsenic concentration, pH, and filtration velocity respectively. Statistical analysis of this equation revealed that pH has the largest impact on Y_1. With an increase in the pH, the arsenate-exchange capacity decreases. This situation can probably be explained as follows. The hydroxyl ions present both on the surface of the resin and in water compete with arsenate ions. The second, in terms of the extent of impact on arsenate-exchange capacity, is the initial arsenate concentration. The dependence between Y_1 and A is proportional: with an increase in initial arsenate concentration, the arsenate-exchange capacity of the resin increases. Hydroxyl ions guard against the contracting effect of strong brine on the functional groups. This accommodates more sites for the arsenate ions to be sorbed onto. The negative sign of the linear coefficient at C indicates that, with an increase in the velocity of filtration, arsenate-exchange capacity decreases. The positive sign of the double interaction coefficients AB shows that an increase in Y_1 is achieved by a simultaneous increase in the values of the factors A and B, but the negative sign of the double interaction coefficients A and C shows the reverse dependence. Interaction coefficient of the factors A and B insignificantly exceeds that of A and C.

Equation 4.1-1 in the natural scale is as follows:

$$\textbf{As-capacity} = \mathbf{0.10 - 2.39106E\text{-}005 * \text{Input As} - 0.01 * \text{pH} + 2.64E\text{-}003 * v +}$$
$$\mathbf{5.56E\text{-}006 * \text{Input As} * \text{pH} - 5.17E\text{-}006 * \text{Input As} * v} \qquad (4.1\text{-}2)$$

Graphical interpretation of this equation is made in Figure 4.1-4. This figure shows the dependence of arsenate-exchange capacity of Purolite-A300 on initial arsenate concentration in water and pH values at EBCT of 2, 4 and 6 minutes.

As can be seen from this figure, larger values of arsenate-exchange capacity are achieved on the lower border of pH range, i.e. in weakly acidic and weakly basic medium. Particularly pH has a strong impact in the area of lower arsenate concentration (here divergence of lines is observed. The pH is constant). It is most probably because the hydroxyl ions are in a better environment to inhibit the arsenate ions in the presence of a lower concentration of arsenic. This counter ion effect decreases with an increase in the arsenate concentration.

Likewise a regression equation was obtained that depicts the dependence of residual arsenate concentration (Y_2) on the same factors (Tables 3.2-2 and 3.2-3). ANOVA for the determination of residual arsenic concentration by gel-type anion exchange resin Purolite A-300 is shown in as follows. Analysis of variance is given in Table 2.1-6.

Table 4.1-6 Analysis of variance table for the determination of residual arsenic concentration by gel-type anion exchange resin Purolite A-300

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	71.10	3	23.70	882.81	< 0.0001	significant
A	49.83	1	49.83	1856.08	< 0.0001	
B	14.49	1	14.49	539.69	< 0.0001	
C	6.78	1	6.78	252.65	< 0.0001	
Residual	0.75	28	0.02			
Lack of Fit	0.60	23	0.02	0.88	0.6266	not significant
Pure Error	0.14	5	0.02			
Cor Total	71.85	31				

The Model F-value of 882.81 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 0.89 implies the Lack of Fit is not significant relative to the pure error. There is a 62.66% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit indicates that the model fits.

Table 4.1-7 Summary of adequacy test for the determination of residual arsenic concentration by gel-type anion exchange resin Purolite A-300.

Std. Dev.	0.163856		R-Squared	0.989538
Mean	5.462813		Adj R-Squared	0.988417
C.V.	2.999476		Pred R-Squared	0.986512
PRESS	0.96921		Adeq Precision	109.6117

The "Pred R-Squared" of 0.9865 is in reasonable agreement with the "Adj R-Squared" of 0.9884. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 109.612 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.1-8 Coefficient estimate for the determination of residual arsenic concentration by gel-type anion exchange resin Purolite A-300

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	5.46	1	0.02	5.40	5.52	
A-Input As (ppb)	1.66	1	0.03	1.58	1.74	1
B-pH	0.89	1	0.03	0.81	0.97	1
C-v (cm/min)	0.61	1	0.03	0.53	0.69	1

Table 4.1-9 Diagnostic case statistics for the determination of residual arsenic concentration by gel-type anion exchange resin Purolite A-300

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	2.10	2.29	-0.19	0.20	-1.28	0.10	-1.30	15
2	4.30	3.95	0.35	0.14	2.30	0.22	2.50	16
3	5.50	5.62	-0.12	0.20	-0.79	0.04	-0.78	27
4	3.00	3.19	-0.19	0.14	-1.22	0.06	-1.23	12
5	5.10	4.85	0.25	0.09	1.60	0.06	1.65	9
6	6.40	6.51	-0.11	0.14	-0.74	0.02	-0.74	7
7	4.00	4.08	-0.08	0.20	-0.56	0.02	-0.55	8
8	5.85	5.75	0.10	0.14	0.68	0.02	0.68	28
9	7.30	7.41	-0.11	0.20	-0.75	0.03	-0.74	31
10	2.90	2.90	0.00	0.14	-0.01	0.00	-0.01	14
11	4.60	4.57	0.03	0.09	0.22	0.00	0.22	19
12	6.30	6.23	0.07	0.14	0.46	0.01	0.46	30
13	3.65	3.80	-0.15	0.09	-0.95	0.02	-0.95	2
14	5.30	5.46	-0.16	0.03	-1.01	0.01	-1.01	17

15	7.00	7.13	-0.13	0.09	-0.81	0.02	-0.80	6
16	4.70	4.70	0.00	0.14	0.03	0.00	0.02	20
17	6.50	6.36	0.14	0.09	0.89	0.02	0.89	4
18	8.00	8.02	-0.02	0.14	-0.16	0.00	-0.15	26
19	3.50	3.52	-0.02	0.20	-0.11	0.00	-0.10	11
20	5.30	5.18	0.12	0.14	0.79	0.03	0.79	18
21	6.70	6.84	-0.14	0.20	-0.98	0.06	-0.98	13
22	4.20	4.41	-0.21	0.14	-1.40	0.08	-1.43	23
23	6.30	6.08	0.22	0.09	1.43	0.05	1.45	22
24	7.60	7.74	-0.14	0.14	-0.93	0.04	-0.92	5
25	5.30	5.31	-0.01	0.20	-0.07	0.00	-0.07	29
26	7.20	6.97	0.23	0.14	1.49	0.09	1.52	10
27	8.50	8.64	-0.14	0.20	-0.94	0.05	-0.94	24
28	5.40	5.46	-0.06	0.03	-0.39	0.00	-0.38	1
29	5.35	5.46	-0.11	0.03	-0.70	0.00	-0.69	3
30	5.60	5.46	0.14	0.03	0.85	0.01	0.85	21
31	5.66	5.46	0.20	0.03	1.22	0.01	1.23	25
32	5.70	5.46	0.24	0.03	1.47	0.02	1.50	32

$$\text{Effluent As} = 5.46 + 1.66 * A + 0.90 * B + 0.61 * C \qquad (4.1\text{-}3)$$

Unlike Equation 4.1-1 in Equation 4.1-3, the dependence Y_2, on factors B and C, shows a direct proportional character. With an increase in pH value and filtration velocity, the residual concentration of arsenic, in the treated water, increases. Influent arsenate concentration has the largest impact on Y_2.

The maximum deviation of experimental and estimated values does not exceed 7.5%. Equation 4.1-3 in the natural scale is as follows:

$$\textbf{Effluent As} = \mathbf{-5.67 + 3.02E\text{-}003 * Input\ As + 0.89 * pH + 0.95 * v} \qquad (4.1\text{-}4)$$

Graphical interpretation of this equation is made in Figure 4.1-5. It shows the dependence of residual arsenate concentration in the filtrate on initial arsenate concentration in water and pH values at velocities of 0.65 cm/min, 1.295 cm/min and 1.94 cm/min. As can be seen from this figure, the lowest values of residual arsenate concentration are achieved on the lower limit of intervals of all three factors. Figure 4.1-6 shows the effect of pH on removal efficiency. Figure 4.1-7 shows a 3D graph of the optimization of arsenic removal from groundwater by the gel-type SBA in chloride form. The numerical optimization was based on an objective function called desirability (Montgomery, 1996). The overall desirability (D) is the geometric (multiplicative) mean of all individual desirabilities (d_i) that range from 0 (least) to 1 (most): The variable goals were set to "maximum," and “in range”. The desired goal for each factor and response was chosen. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only).

A minimum and a maximum level were provided for each parameter. A weight was assigned to each goal to adjust the shape of its particular desirability function. The "importance" of each goal was set to be equally important at a setting of 3 plusses (+++).

The goals were combined in an overall desirability function. The goal seeking began at a random starting point and proceeded up the steepest slope to a maximum. By starting from several points in the design space chances improved for finding the "best" local maximum. 3D surface plots of the desirability function for each optimum were used to explore the function in the factor space.

The material balance of the sorbed (sorption stage) and desorbed (regeneration stage) arsenate was determined. The ion exchange column was regenerated and the spent regenerant analyzed to determine the amount of arsenate the resin sorbed in the sorption process as well as the amount of arsenate that was possible for desorption from the exhausted resin in the regeneration stage. This analysis determines the nature of the sorption process, i.e. it indicates whether the sorption process is indeed ion exchange and is reversible. An equal amount of arsenate sorbed and desorbed shows that the sorption process is reversible. In the sorption stage arsenate ions displaced chloride ions but in the regeneration stage chloride ions displaced almost all the arsenate ions and thus recovered the resin as seen in Table 4.1-1. This shows the exchange part as well. As the definition suggests, ion exchange is a **reversible process** where ions in a solution are exchanged with similarly charged ions attached to a solid medium (a resin) (Marchand , 1995). Ion exchange reactions are stoichiometric and reversible. Once the sorption mechanism is proven to be of ionic exchange, the nature of the sorption cannot be other than reversible.

Summarizing the results of the investigations carried out in this section, the following conclusions can be drawn. There are still many problems that have yet to be solved, such as the effect of sulfate, nitrate and nitrite on sorption capacity and the minimization of the wastes produced during the regeneration of the ion exchange column. Therefore, attention can be drawn to the following preliminary conclusions of this research.

- Removal of high levels of arsenic concentration at higher than 98% removal was obtained for all conditions evaluated
- Sorption mechanism is anionic exchange for arsenate ions
- Arsenite cannot be removed without oxidation to arsenate
- Increasing the pH from 6.5 to 8.5 decreases sorption capability of the resin
- Polynomial dependencies of arsenate-exchange capacity of strongly basic anion exchange resins on various factors formulated.

- Ion exchange column can be regenerated almost completely as 97% of the arsenic could be removed from the column.

Further work involved optimization of the regeneration processes to reduce waste generation. The same statistical analysis approach was used. The As(V) removal efficiencies are higher than the maximum 95% rate according to the USEPA for ion exchange as a BAT (best available technology) (USAEPA, 2003).

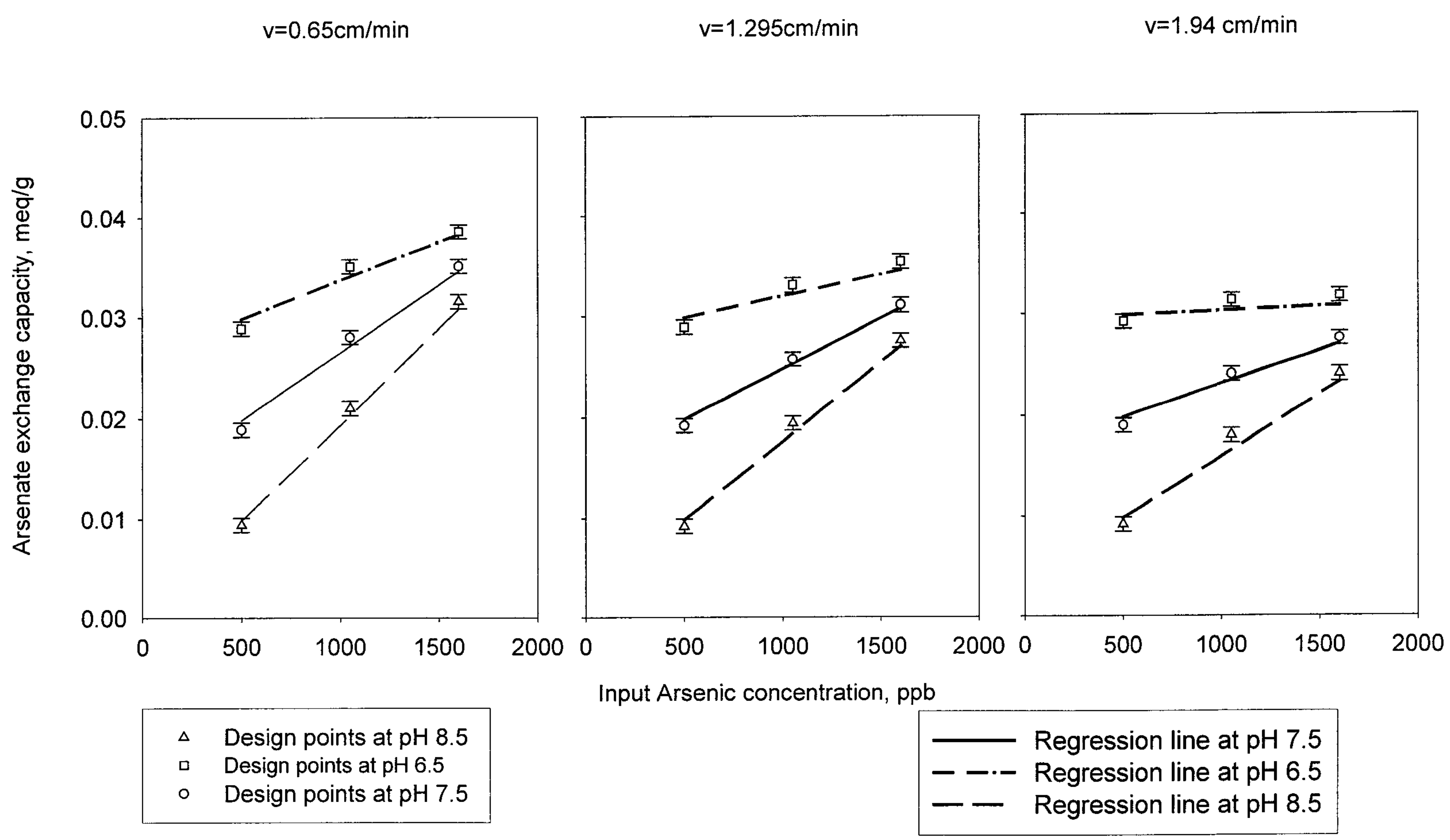


Figure 4.1-4 Dependence of arsenate-exchange capacity (Purolite A-300) on influent arsenate concentration and pH at v=0.65cm/min, v=1.295cm/min and v=1.94 cm/min

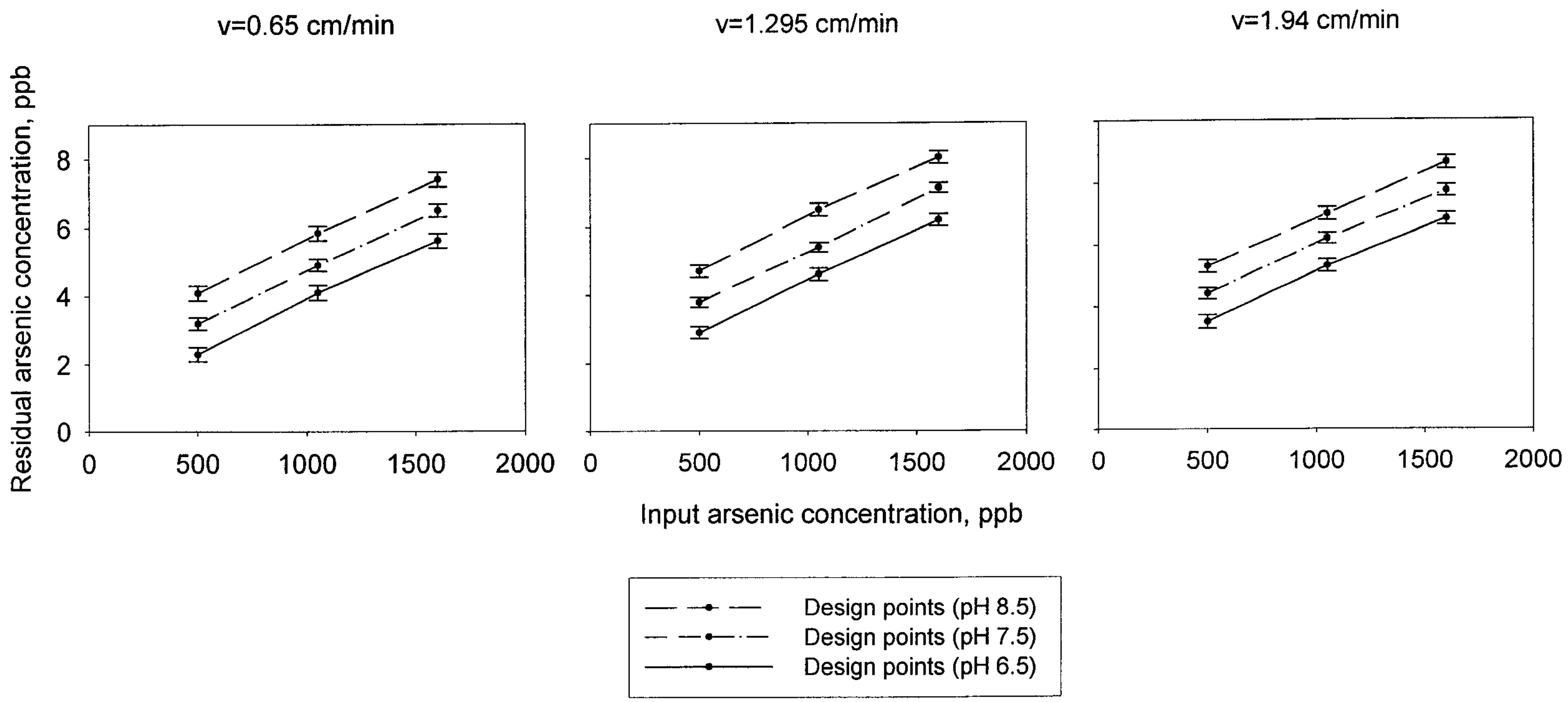


Figure 4.1-5 Dependence of residual arsenic concentration on influent arsenic concentration and pH at v=0.65cm/min, v=1.295cm/min and v=1.94 cm/min .

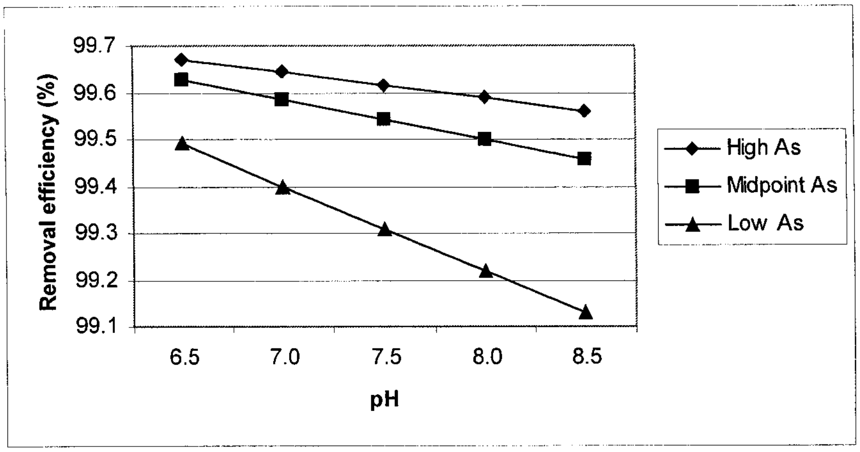


Figure 4.1-6 Effect of pH on As removal efficiency

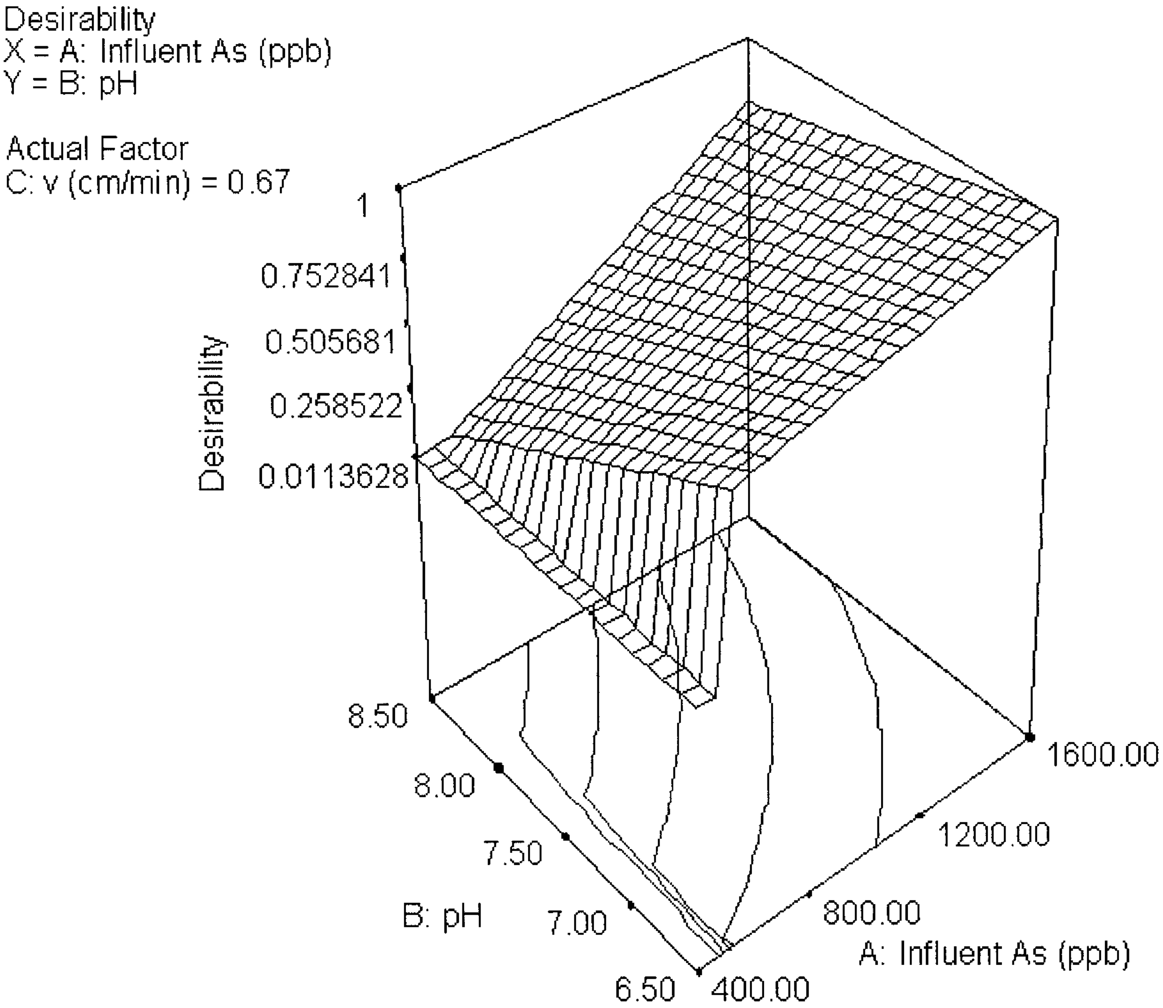


Figure 4.1-7 3D graph of the optimization of arsenic removal from groundwater by gel-type SBA in chloride form

4.2 Investigation of the peculiarities of groundwater treatment by softening Process

4.2.1 Objectives and scope

The use of groundwater contaminated with high levels of both arsenic and DOM concentration, when preparing potable water, can be justified both technically and hygienically. The presence of significant quantities of DOM in the composition of influent water, when aiming at the removal of arsenic by various technologies, leads to the following negative results. Anionic exchange media are easily contaminated or poisoned by organic compounds. The contamination, or poisoning, of anionic-exchange media by organic compounds is shown by reductions in ion exchange capacity, and increases in the amount of reagent needed for regeneration and subsequent volumes of wash water. High molecular weight organic compounds block the pores of gel-type anion exchange media, inhibiting the sorption and regeneration processes.

Some scientists consider distillation the most reliable technology to remove arsenic (Mc Nully et. al., 1986). However, the presence of significant quantities of DOM in the composition of influent water is capable of leading to the following negative results. The concentration of DOM over certain permanganate values of 150 mg O_2/L causes foaming during steam generation, reduction in capacity, and the swelling of boiler water because of which the discharge of boiler water into the steam is not excluded. In the case of boiler water discharges into steam, hydraulic shocks in the steam line are likely, and welded joints may be destroyed.

The most appropriate sorbent to remove arsenic along with DOM is macroporous anion exchange media, since when using this, it is not required to modernize the ion exchange technique in service removing arsenic. It is possible to use the existing equipment while adding or replacing the traditionally used gel-type media. The use of ion exchange for arsenic removal is widely adopted world wide. However, the occurrence of dissolved organic species is relatively new and requires at least some change in the conventional arsenic removal technology. The use of macroporous media is the most appropriate because, in this case, new units do not need to be installed. Switching from the use of gel-type resin to macroporous resin does not require new filter vessels. The columns remain the same, only the resin changes. However, an additional column of the same type may be required in specific cases. This has been described in Chapter 5 in more detail.

According to the investigations conducted earlier, macro-porous media have a higher capacity in terms of DOM, and better kinetics when activated in the chloride form (Abdullaev et. al., 1992). Proceeding with the stated above information, the objectives of this investigation were:

- To develop a mathematical model that will allow the optimum operating parameters to be determined by calculation for the removal of As in the presence of DOM onto macro-porous ion exchange media in chloride form.

- To determine optimal conditions for regeneration of the media.

Scope of the investigation

The scope of this research included:

- Chromatographic separation and identification of the organic content of influent water contaminated with As and DOM
- Selection of the principal factors that significantly affect the ion exchange capacity and residual concentrations of arsenic in the presence of DOM
- Running preliminary experiments in order to determine and justify the intervals and levels of various concentration factors as well as hydrodynamic factors.
- Determination of optimal conditions for regeneration of exhausted ion exchange media
- Determination of the dependences of ion exchange capacity and residual concentrations
- Statistical analysis of the experimental results, while formulating desirable regression equations.

4.2.2 Batch experiments

The experimental results of the adsorption of arsenate onto anion exchange resins (gel-type versus macroporous) in the presence of dissolved organic species in raw water show that gel-type strongly basic ion exchange resins have a slightly higher total anion exchange capacity but less capacity in terms of arsenate as well as DOM. Total ion exchange capacity of Purolite A-300 is shown in Table 4.2-1.

Table 4.2-1 Exchange capacity evaluation of chloride-form Purolite A-300

Sorption Capacity of Media for Species *i*	**Experimental Results** (meq/kg resin)	**Manufacturer's Capacity** (meq/kg resin)
$S_{arsenate}$	15.4	Not available
$S_{sulfate}$	436.6	Not available
$S_{phosphate}$	116.2	Not available
$S_{nitrite}$	121.4	Not available
$S_{nitrate}$	142.8	Not available
ΣS_i	832.4	3500

Macroporous anion exchange resins showed better performance in terms of arsenic removal. However, the gel-type Purolite A-300 showed a higher total ion exchange capacity than macroporous strongly basic and weakly basic resins. Gel-type resins have a higher total exchange capacity than macroporous ones. The exchange capacity evaluation of chloride form Amberlite 910 is given in Table 4.2-2.

Table 4.2-2 Exchange capacity evaluation of chloride-form Amberlite 910

Sorption Capacity of Media for Species *i*	**Experimental Results** (meq/kg resin)	**Manufaturer's Capacity** (meq/kg resin)
$S_{arsenate}$	300	Not available
$S_{sulfate}$	330	Not available
$S_{phosphate}$	50	Not available
$S_{nitrite}$	65	Not available
$S_{nitrate}$	80	Not available
ΣS_i	825	1300

The macroporous weakly basic hydroxyl form of the resin demonstrated higher arsenic removal than the gel-type strongly basic chloride form resin but lower than the macroporous chloride form of SBR. The exchange capacity evaluation of weakly basic macroporous resin Amberlite IRA 96 is presented in Table 4.2-3.

Table 4.2-3 Exchange capacity evaluation of OH-form Amberlite 96

Sorption Capacity of Media for Species *i*	**Experimental Results** (meq/kg resin)	**Manufaturer's Capacity** (meq/kg resin)
$S_{arsenate}$	240	Not available
$S_{sulfate}$	280	Not available
$S_{phosphate}$	85	Not available
$S_{nitrite}$	95	Not available

$S_{nitrate}$	100	Not available
ΣS_i	800	1400

4.2.3 Determination of the optimum conditions for regeneration

The expediency to use a mixed solution of NaCl and NaOH for regeneration at 35-40^0 C and a velocity of 4-5 m/h was established by preliminary trials. The main trials were conducted by implementing the design and analysis of experiments. A response surface experiment was implemented.

The independent factors considered were as follows: A – amount of NaCl salt, kg/tonne; B -brine concentration, %; C – salt to alkali ratio. Amount of arsenate desorbed from 1 kg of the resin was considered the target function Y. Preliminary tests determined the levels and intervals of the factors: concentration range of brine C_s = 5-10%, the ratio of the concentration of salt to that of alkali, $C_{s/a}$ =2-10 and the range of salt consumption, G_s =100-300 kg/tonne. Factor levels, their physical values and responses are given in Tables 3.2-8 and 3.2-9. ANOVA (Tables 4.2-4 through 4.2-9) indicates that A, C, AB, BC, ABC are significant model terms since values of "Prob>F" less than 0.05. In this case, B and AC terms are not significant since their "Prob>F" values are greater than 0.1.

Final equation in terms of coded factors:

$$Y = 228.72+81.56*A+16.28*C+9.92*A*B+26.00*B*C+8.12*A*B*C \quad (4.2\text{-}1)$$

Final equation in terms of actual factors:

$$Y = 146.48 + 0.88 * Gs - 14.07 * Cs - 3.20 * Cs/a - 9.08E\text{-}003 * Gs * Cs - 0.06 * Gs * Cs/a + 0.97 * Cs * Cs/a + 8.12E\text{-}003 * Gs * Cs * Cs/a \quad (4.2\text{-}2)$$

As the statistical analysis revealed, the NaCl consumption for regeneration influences the specific quantity of arsenate desorbed from the exhausted resin the most. With an increase in NaCl consumption, the Y value increases. In the selected range of concentrations, factor B has no influence on Y. Therefore, it does not appear in the regression equation. However, that the selected interval of its values was chosen correctly (from the point of view of achieving the optimal values of Y) is shown by the results of preliminary tests and a quite high value of the double interaction coefficient BC. The positive sign of this double interaction effect shows that increasing B and C simultaneously can achieve an increase in Y. The influence of B on the degree of desorption of arsenate in the presence of DOM is also shown by its presence in all double and triple interaction effects. The third, in terms of the extent of impact on Y, is the coefficient of C. The dependence between Y and C is proportional with an increase in the percent ratio of salt to alkali in the regeneration solution. The specific quantity of arsenate desorbed from the resin increases.

More detailed conclusions can be drawn from the graphical interpretation (Figures 4.2-1 to 4.2-3) of this equation (4.2-2) that describes the dependence of the desorption of $HAsO_4^{2-}$ on G_s, $C_{s/a}$ and C_s at constant values of one of the factors at zero level. As can be seen from Figure 4.2-1(a), a constant increase in the desorption of $HAsO_4^{2-}$ with an increase in G_s was observed. Besides, the higher the percent ratio of salt to alkali in the regeneration solution, the higher the degree of desorption of arsenate. The maximum effect was achieved at a ratio $C_{s/a}$ equal to 10. It is because by increasing the pH of the brine, some organic materials such as tannins become more soluble (Keller et. al., 2005). The bead will also swell, allowing better elution of such compounds from the resin (Keller et. al., 2005).

Figure 4.2-1(b) shows the same dependence of the amount of $HAsO_4^{2-}$ on G_s, but at a fixed average value of $C_{s/a}$ equal to 6. The impact of the concentration of salt on the desorption of $HAsO_4^{2-}$ at various regenerant consumptions varies. At a relatively lower consumption of regenerant, 100 kg/tonne, the maximum effect of arsenate removal is related to the use of the minimum brine concentration – 5 %. In the interval of higher consumption of salt, 200-300 kg/tonne, stronger solutions show the best regeneration capabilities. Here, the maximum removal of arsenate is related to the highest concentration – 10%. The results obtained can be explained as follows. At a lower consumption of salt at high concentration (reduced volume), the resulting volume of regeneration solution does not provide the required contact time with the exhausted resin. Considering the presence of DOM and lower intradiffusion kinetics of organic ions (Malakhkov et. al., 1988), these very circumstances lead to the fact that a diluted regeneration solution appears to be more effective for the desorption of arsenate as well as DOM at lower consumptions of NaCl. When the volume of regeneration solution provides the required contact time with the media, the regeneration efficiency of strong solutions for arsenate increases. The regeneration efficiency at a brine concentration C_s equal to 10% and a maximum NaCl consumption G_s equal to 300 kg/tonne is the highest.

Figure 4.2-2 shows the dependence of the desorption of $HAsO_4^{2-}$ on the concentration of NaCl solution (C_s). The gently sloping nature of the lines, constant G_s (Figure 4.2-2 (a)), shows the slight influence of the concentration of NaCl on $HAsO_4^{2-}$ at a fixed ratio of the concentration of NaCl to that of NaOH. A tendency to divergence of the lines is observed at the higher concentrations of salt. Besides, in the interval G_s =100-200 kg/tonne the passage of the lines indicates a decrease in the efficiency of desorption of arsenate for stronger brines, which can be explained by small volumes of regeneration solution, and therefore inadequate contact time with the media. In the area of higher consumption of NaCl, a proportional dependence of $HAsO_4^{2-}$ desorbed on C_s was observed. Attention can be drawn to an abrupt increase in the efficiency of regeneration when increasing the consumption G_s: from 100 to 300 kg/tonne.

Figure 4.2-2 (b) shows the same dependence of $HAsO_4^{2-}$ desorbed on C_s, but at a fixed average value of G_s equal to 200 kg/tonne. As the influence of the concentration of brine on $HAsO_4^{2-}$ occurs to a greater extent, the passage of lines $C_{s/a}$ has a greater slope than that at a constant G_s as shown in Figure 4.2-2. After the value of C_s reaches 6.2%, the weight of $HAsO_4^{2-}$ increases when passing over from the lower border of $C_{s/a}$ values to the higher (for the same C_s value). The largest quantity of arsenate desorbed was achieved at $C_{s/a}$ equal to 10 (at the maximum brine concentration C_s equal to 10%).

Figure 4.2-3 shows the dependence of $HAsO_4^{2-}$ on the concentration ratio of NaCl to NaOH in the regeneration solution ($C_{s/a}$). As can be seen from Figure 4.2-3 (a), at a fixed brine concentration at its average value of 7.5%, a steady increase in $HAsO_4^{2-}$ is marked with an increase in $C_{s/a}$ values in the entire interval investigated. The greatest extent of arsenate removal is characteristic for the upper borders of the G_s and $C_{s/a}$ values.

Figure 4.2-3 (b) shows the same dependence of $HAsO_4^{2-}$ on $C_{s/a}$ but at a fixed averaged value of G_s equal to 200 kg/tonne. Unlike Figure 4.2-3 (a), this dependence has both a proportional (lines C_s equal to 7.5 and 10%) and an inversely proportional character (C_s equal to 5 %).

At a sufficiently high NaCl consumption, G_s=200 kg/tonne, for C_s equal to 5%, an increase in the ratio of NaCl concentration to that of NaOH leads to a decrease in $HAsO_4^{2-}$. In the area of lower ratios of NaCl to NaOH concentration, the value of desorbed $HAsO_4^{2-}$ appears to be greater for smaller values of NaCl concentration. In this case, the regenerating power of the solution increases with an increase in alkali concentration. On the contrary, in stronger NaCl solutions, the alkali concentration must not exceed 1%. Thus, the characteristics of the regeneration process are an increase in the extent of arsenate desorption with an increase in NaCl concentration at the upper border of the ratio of NaCl to

NaOH concentration and a reverse dependence at the lower border of the ratio of these reagents.

3D surface plots of the desirability function for each optimum were used to explore the function in the factor space. Figure 4.2-4, shows a 3 D view of desirability.

Table 4.2-4 Analysis of Variance table for the optimum regeneration of macroporous anion exchange media

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	134313.2	5	26862.63	47140.23	< 0.0001	significant
A-Gs(kg/tonne)	119723.6	1	119723.6	210098.4	< 0.0001	
C-Cs/a	4769.389	1	4769.389	8369.624	< 0.0001	
AB	1180.083	1	1180.083	2070.884	< 0.0001	
BC	8112	1	8112	14235.45	< 0.0001	
ABC	528.125	1	528.125	926.787	< 0.0001	
Residual	14.81597	26	0.569845			
Lack of Fit	13.98264	21	0.66584	3.99504	0.0651	not significant
Pure Error	0.833333	5	0.166667			
Cor Total	134328	31				

Table 4.2-5 Summary of Adequacy test for the optimum regeneration of macroporous anion exchange media

Std. Dev.	0.754881		R-Squared	0.99989
Mean	228.7188		Adj R-Squared	0.999868
C.V. %	0.330048		Pred R-Squared	0.999807
PRESS	25.92995		Adeq Precision	818.3607

Table 4.2-6 Main and Interaction factors for the optimum regeneration of macroporous anion exchange media

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	228.7188	1	0.133445	228.4444	228.9931	
A-Gs(kg/tonne)	81.55556	1	0.177927	81.18982	81.92129	1
C-Cs/a	16.27778	1	0.177927	15.91204	16.64351	1
AB	9.916667	1	0.217915	9.468735	10.3646	1
BC	26	1	0.217915	25.55207	26.44793	1
ABC	8.125	1	0.266891	7.576398	8.673602	1

Table 4.2-7 Upper and lower constraints on salt consumption, brine concentration and the ratio of brine concentration to alkali concentration in order to optimize the amount of arsenate desorbed from 1 kg of resin.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Gs (kg/tonne)	is in range	100	300	1	1	3
Cs(%)	is in range	5	10	1	1	3
Cs/a	is in range	2	10	1	1	3

Arsenate desorbed (meq/kg)	maximize	102	370	1	1	3

Table 4.2-8 Solutions to optimize the specific quantity of arsenates desorbed from the exhausted media

Number	Gs(kg/tonne)	Cs(%)	Cs/a	Arsenate desorbed (meq/kg)	Desirability	
1	299.61	10.00	9.99	370.067	1.00	Selected
2	299.81	9.98	10.00	370.02	1.00	
3	299.99	10.00	9.96	370.022	1.00	
4	300.00	9.95	10.00	369.762	1.00	
5	298.41	10.00	10.00	369.005	1.00	
6	300.00	9.93	9.93	368.49	0.99	
7	300.00	10.00	9.68	366.557	0.99	
8	300.00	9.76	10.00	366.294	0.99	
9	300.00	9.68	10.00	364.946	0.98	
10	300.00	5.10	2.00	317.193	0.80	

Note: underlined values indicate the optimum combination of factors to achieve the desired maximum regeneration efficiency.

Table 4.2-9 Starting points to determine the best maximum value of the quantity of arsenates desorbed from one kg of the media subjected to the constraints

Gs(kg/tonne)	Cs(%)	Cs/a
123.62	9.68	9.68
137.38	9.55	3.10
290.28	7.32	3.83
105.50	9.19	8.56
107.86	5.81	2.97
249.88	6.89	5.03

287.98	7.00	6.82
238.50	7.43	9.62
178.50	9.52	4.69
152.72	9.68	7.38

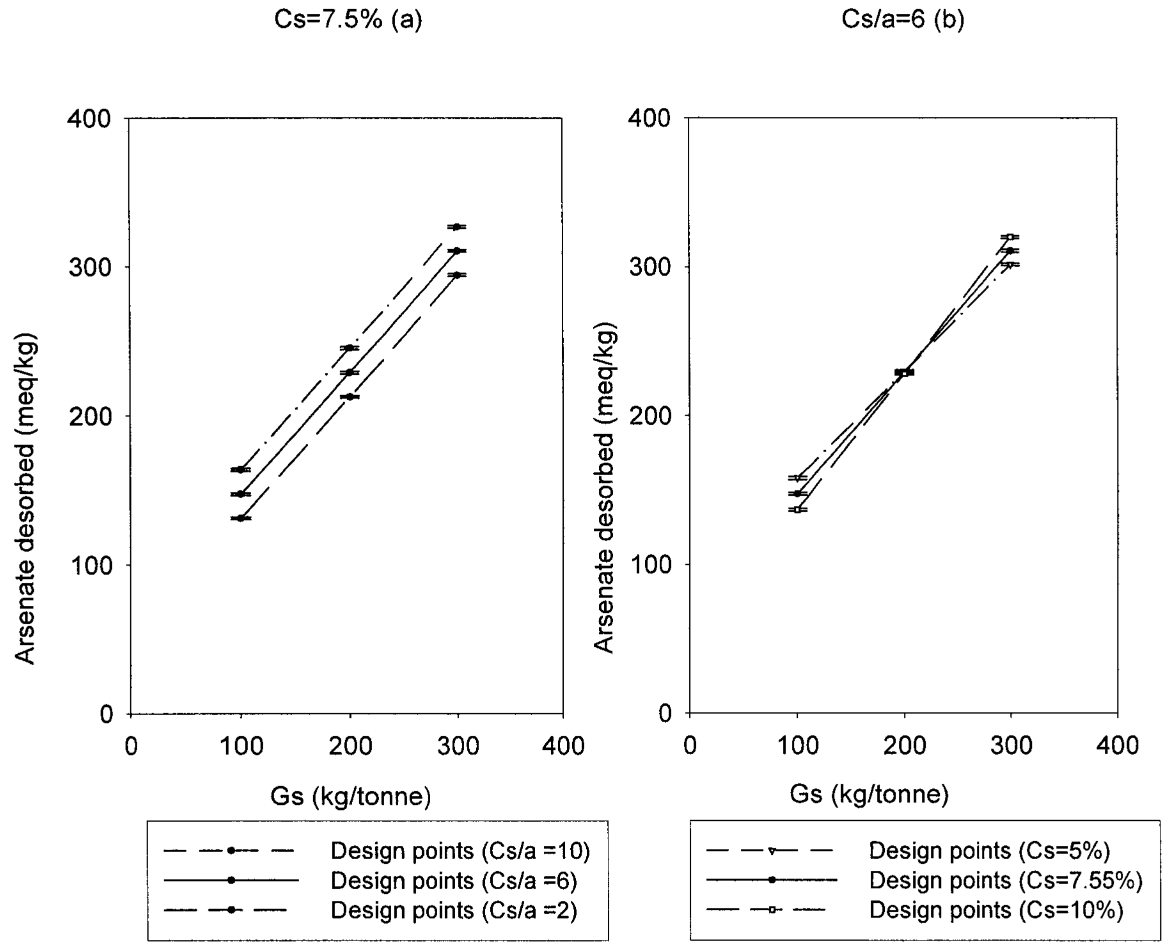


Figure 4.2-1 Dependence of a specific quantity of arsenate desorbed from 1 kg of resin on a brine consumption at a fixed average brine concentration of 7.5%(a) and at a fixed average ratio of salt to alkali concentration of 6(b).

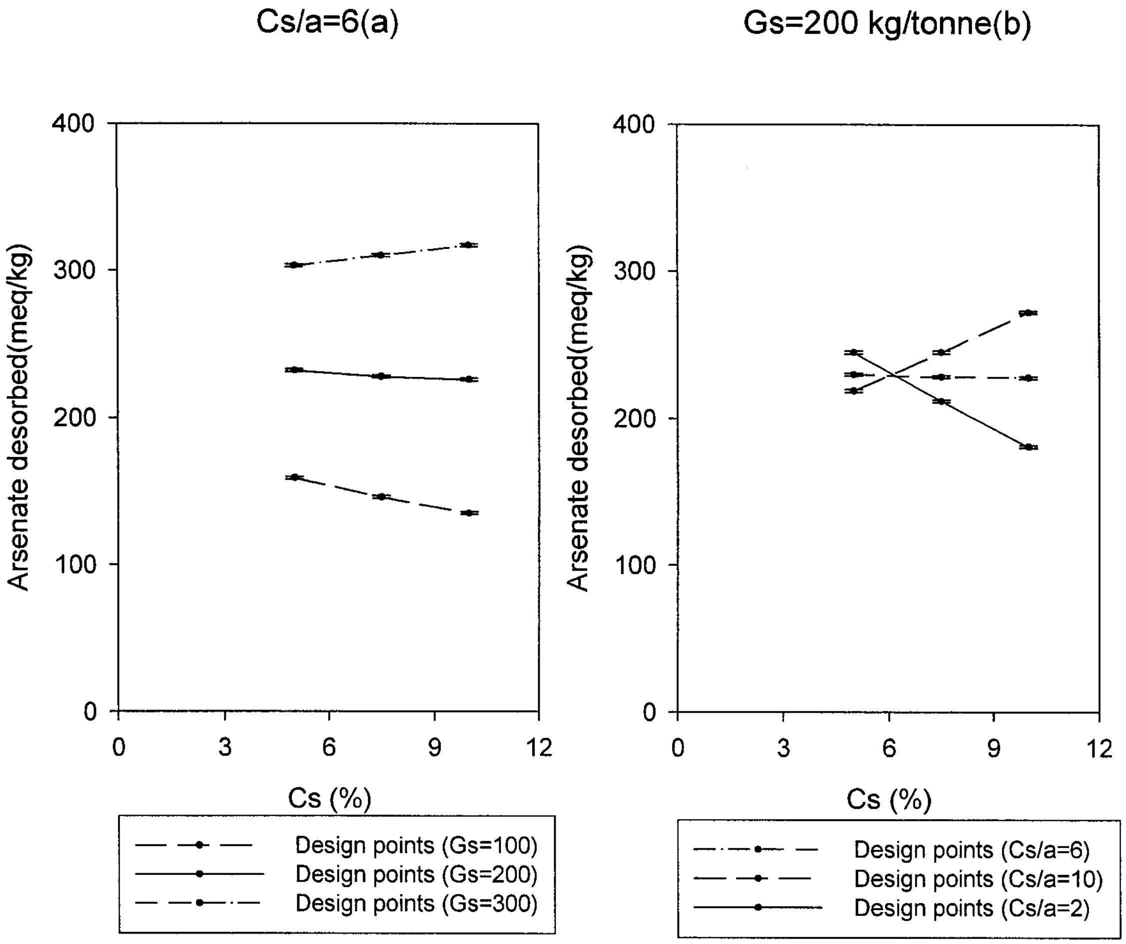


Figure 4.2-2 Dependence of specific quantity of arsenate, desorbed from 1 kg of resin, on brine concentration at a fixed average ratio of salt to alkali concentration of 6 (a) and at a fixed average salt consumption of 200 kg/tonne (b).

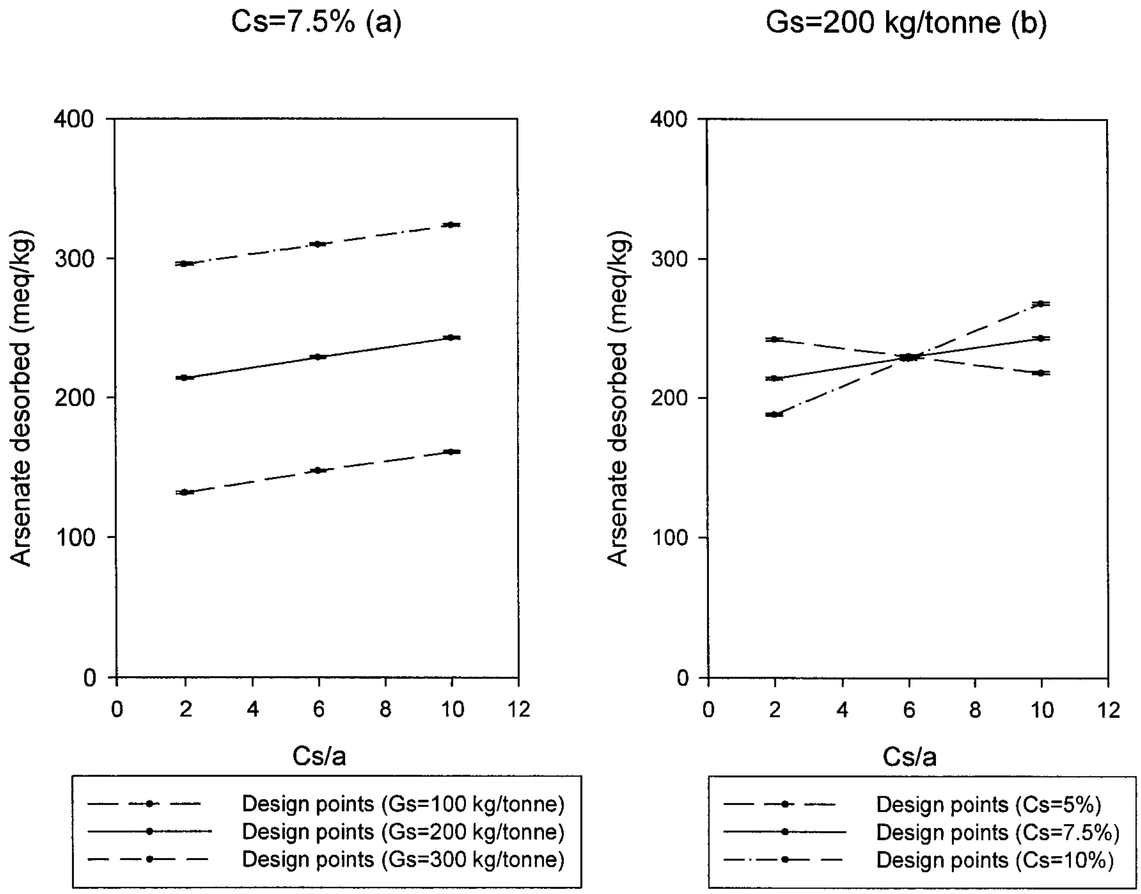


Figure 4.2-3 Dependence of specific quantity of arsenate, desorbed from 1 kg of resin, on the ratio of salt to alkali concentration at a fixed average brine concentration of 7.5 (a) and at a fixed average salt consumption of 200 kg/tonne (b).

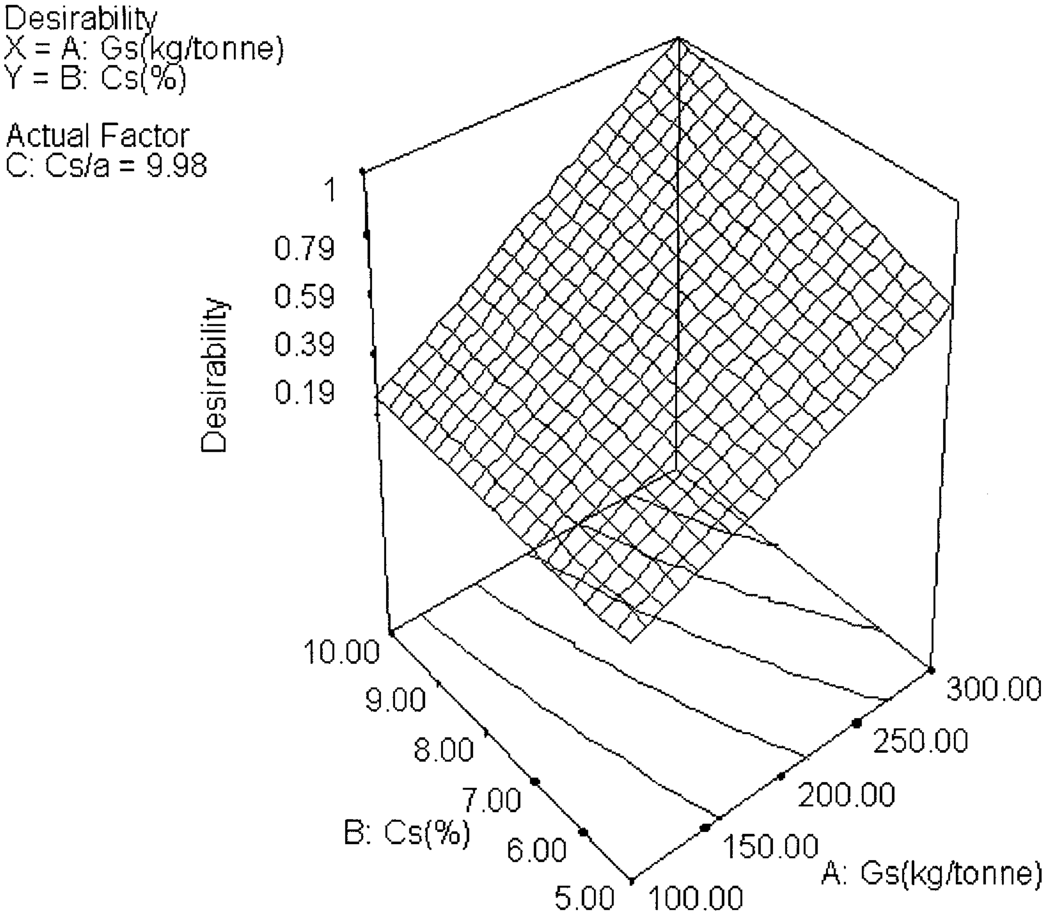


Figure 4.2-4 Optimization graph of the regeneration of exhausted resin (Amberlite 910).

4.2.4 Study of the sorption of arsenate and DOM onto Cl-form macroporous anion exchange media

Anionic exchange media are easily contaminated or poisoned by organic compounds. The contamination, or poisoning, of anionic-exchange media by organic compounds is shown by reductions in ion exchange capacity, and increases in the amount of reagent needed for regeneration and subsequent volumes of wash water. High molecular weight organic compounds (100 to 20,000 g/mole) block the pores of gel-type anion exchange media, inhibiting the sorption and regeneration processes. The removal of organic materials is best achieved by the use of macro porous or isoporous anionic-exchange media. The large pores or channels make macroporous media less susceptible than gel-type media to poisoning by organic compounds. Cationic exchange media are characteristically more stable than their anionic counterparts; the main factors that make the anion exchange action less stable in the treatment of municipal wastes can be the presence of nitrite and nitrate in water. Nitrous acid will be present in water entering an anion exchange unit following cation exchange. Effluent from cation exchange units is usually acidic [83]. The more hydrogen ions are replaced from the hydrogen form of the cation exchange resin, the more acidic the effluent is. Typical pH value ranges from 2.4 to 3.2. The primary and secondary amino groups of weakly basic anion exchange media react with nitrous acid:

$$R'\text{-}NH_2+HNO_2 \leftrightarrows R'\text{-}OH+N_2+H_2O;$$

and,

$R'=NH+HNO_2 \leftrightarrows R'=N-N=O+H_2O$; In consequence the primary amino group (NH_2) degrades with the evolution of free nitrogen but the secondary group (NH) is blocked by the nitroso group.

Anion exchange media with tertiary and quarternary ammmonium groups do not react with nitrous acid and take up nitrite ion, like some other anions of weak acids. It follows that anionic exchange media, containing primary and secondary amino groups should not be used for the treatment of waters, which have nitrite and nitrate ions.

Macroporous and isoporous anion exchange media are widely used for the removal of organic compounds in the process of potable water treatment. The application of these anionic media has led to improved plant life and output quality (Bidnaya et. al., 1986).

In the previous cycle of investigations, optimum conditions for regeneration of macroporous anion exchange media, exhausted by arsenate and DOM, were determined: NaCl consumption of 300 kg/tonne, concentration of NaCl solution of 10%, ratio of NaCl concentration to that of NaOH in the regenerant of 10, velocity of passing the regeneration solution of 4 m/h, and a temperature of 40^0C. In this section, the dependence of arsenate-exchange capacity of macroporous anion exchange media and residual concentration of arsenic in the filtrate on three concentration and hydrodynamic factors was studied. The Cl-form anion exchange media, exhausted by arsenate and DOM was regenerated in the established optimum regime.

Based on the above, a macroporous resin MTO-Amberlite IRA-910 was used for this study. Treated water from the Montreal Municipal Wastewater treatment plant, with added arsenic, served as the influent water. Independent factors considered were as follows: A – DOM concentration, mgO_2/L; B - pH values of water being treated; C – linear velocity of filtration, m/h. Arsenate-exchange capacity was considered to be the target function Y_1 and residual arsenate concentration as Y_2.

Preliminary tests determined the levels and intervals of the factors. The concentration range of DOM 3.6-11.2 ppm is typical of groundwater in Bangladesh, where high levels of arsenic are found (Jonsson et. al., 2005). The pH range of 7 to 10.4 was chosen because of the use of various coagulants in the pretreatment stage. The velocity range of 10 to 30 m/h (EBCT range of 2-6 min) is typical for most ion exchange filters (Wang et. al., 2000). Factor levels, their physical values and responses are given in Table 3.2-10. The influent water was subjected to chromatographic separation as described in Chapter 3. The results of the fractionation of influent and effluent water are given in Table 4.2-7.

Table 4.2-10 Results of the fractionation process for organic compounds in municipal wastewaters using ion exchange processing techniques

Anion exchange filter	Concentration of DOM, mgO_2/L		Content of the main groups, %		
	PV	COD	Acidic	Basic	Neutral
Initial	5.1-16	20-45	70	9	21
Filtrate Amberlite IRA-910	2-6.4	7.8-20	20	24	56

As can be seen from Table 4.2-7, the bulk of DOM (70%) belongs to the acidic group. Table 4.2-7 also shows that a macroporous strongly basic anion exchange resin can remove this group of DOM efficiently. Effluent DOM was from 7.8 to 20 mg/L as COD. The acidic group was only 20%. This is expected in comparison to what is in the literature [87]. Similar results can be expected in the groundwater of both the US superfund sites and Bangladesh.

In order to derive a regression equation, a response surface experiment was conducted. Based on the design layout, the regression equation with linear, double, and triple interactions was considered. All the coefficients of this equation were calculated by the least squares method.

ANOVA for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in alkaline medium is shown as follows. Analysis of variance is given in table 4.2-11. Summary of adequacy test is given in Table 4.2-12. Coefficient estimates are given in Table 4.2-13.

Table 4.2-11 Analysis of variance table [Terms added sequentially (first to last)] for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in alkaline medium

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	5647.39	5.00	1129.48	648.40	< 0.0001	significant
A	1820.06	1.00	1820.06	1044.84	< 0.0001	
B	3042.00	1.00	3042.00	1746.31	< 0.0001	
C	544.50	1.00	544.50	312.58	< 0.0001	
AB	126.75	1.00	126.75	72.76	< 0.0001	
AC	114.08	1.00	114.08	65.49	< 0.0001	
Residual	45.29	26.00	1.74			
Lack of Fit	39.42	21.00	1.88	1.60	0.3182	not significant
Pure Error	5.88	5.00	1.18			
Cor Total	5692.68	31.00				

The Model F-value of 648.40 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The "Lack of Fit F-value" of 1.60 implies the Lack of Fit is not significant relative to the pure error. There is a 31.82% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.2-12 Summary of adequacy test for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in alkaline medium

Std. Dev.	1.32		R-Squared	0.99
Mean	57.95		Adj R-Squared	0.99
C.V.	2.28		Pred R-Squared	0.99
PRESS	72.50		Adeq Precision	99.93

The "Pred R-Squared" of 0.9873 is in reasonable agreement with the "Adj R-Squared" of 0.9905. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 99.931 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.2-13 Main and interaction factors for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in alkaline medium

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	57.95	1.00	0.23	57.47	58.43	
A-Cdom (mg/L)	-10.06	1.00	0.31	-10.70	-9.42	1.00
B-pH	-13.00	1.00	0.31	-13.64	-12.36	1.00
C-v (m/h)	-5.50	1.00	0.31	-6.14	-4.86	1.00
AB	-3.25	1.00	0.38	-4.03	-2.47	1.00
AC	3.08	1.00	0.38	2.30	3.87	1.00

Table 4.2-14 Diagnostics case statistics for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in alkaline medium

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	87.00	86.34	0.66	0.36	0.63	0.04	0.62	20
2	75.00	76.45	-1.45	0.14	-1.19	0.04	-1.20	19
3	65.00	66.56	-1.56	0.36	-1.49	0.21	-1.52	13
4	78.00	76.59	1.41	0.23	1.21	0.07	1.22	3
5	62.00	63.45	-1.45	0.09	-1.15	0.02	-1.16	6
6	52.00	50.31	1.69	0.23	1.45	0.10	1.48	24
7	66.00	66.84	-0.84	0.36	-0.80	0.06	-0.79	4
8	49.50	50.45	-0.95	0.14	-0.78	0.02	-0.77	21
9	34.00	34.06	-0.06	0.36	-0.06	0.00	-0.06	1
10	78.00	77.76	0.24	0.23	0.21	0.00	0.20	25
11	73.00	70.95	2.05	0.09	1.62	0.04	1.68	26
12	65.00	64.15	0.85	0.23	0.73	0.03	0.73	22
13	69.00	68.01	0.99	0.09	0.79	0.01	0.78	7
14	57.00	57.95	-0.95	0.03	-0.73	0.00	-0.73	27
15	49.00	47.90	1.10	0.09	0.87	0.01	0.87	8
16	59.00	58.26	0.74	0.23	0.64	0.02	0.63	16

17	46.00	44.95	1.05	0.09	0.83	0.01	0.82	28
18	34.00	31.65	2.35	0.23	2.03	0.20	2.16	23
19	68.00	69.18	-1.18	0.36	-1.12	0.12	-1.12	31
20	65.00	65.45	-0.45	0.14	-0.37	0.00	-0.36	2
21	62.00	61.73	0.27	0.36	0.26	0.01	0.25	5
22	60.00	59.43	0.57	0.23	0.49	0.01	0.49	18
23	53.00	52.45	0.55	0.09	0.43	0.00	0.43	10
24	46.00	45.48	0.52	0.23	0.45	0.01	0.44	9
25	50.00	49.68	0.32	0.36	0.31	0.01	0.30	32
26	38.50	39.45	-0.95	0.14	-0.78	0.02	-0.77	12
27	27.00	29.23	-2.23	0.36	-2.12	0.43	-2.29	14
28	57.00	57.95	-0.95	0.03	-0.73	0.00	-0.73	17
29	58.00	57.95	0.05	0.03	0.04	0.00	0.04	29
30	59.00	57.95	1.05	0.03	0.81	0.00	0.80	15
31	56.00	57.95	-1.95	0.03	-1.50	0.01	-1.54	30
32	56.50	57.95	-1.45	0.03	-1.12	0.01	-1.12	11

As a result of a complete statistical analysis, including the elimination of insignificant coefficients by Student's criterion and adequacy test by Fisher's criterion, the following regression equation was derived.

Final equation in terms of coded factors :

$$\textbf{Arsenate capacity} = 57.95 - 10.06*A - 13.00*B - 5.50*C - 3.25*A*B + 3.08*A*C \quad (4.2\text{-}3)$$

Final equation in terms of actual factors:-

$$\textbf{Arsenate capacity} = 134.68 + 0.10*C_{DOM} - 3.92*pH - 1.15*v - 0.50*C_{DOM}*pH + 0.08*C_{DOM}*v \quad (4.2\text{-}4)$$

Statistical analysis of this equation revealed that pH values have the largest impact on Y_1. With an increase in the pH value, the arsenate-exchange capacity decreases. The second, in terms of the extent of impact on arsenate-exchange capacity, is the initial DOM concentration. The dependence between Y_1 and A is inversely proportional: with an increase in the initial DOM concentration, the arsenate-exchange capacity of the resin decreases. The negative sign of the linear coefficient at C indicates that, with an increase in the velocity of filtration, arsenate-exchange capacity decreases. The negative sign of the double interaction coefficients AB shows that an increase in Y_1 is achieved by a simultaneous decrease in the values of the factors A and B. This means that the effect of factor A depends on the effect of factor B. A decrease in either A or B alone will not provide as effective an exchange capacity as would a simultaneous decrease of both A and B.

Graphical interpretation of this equation is made in Figure 4.2-5. The figure shows the dependence of arsenate-exchange capacity of Amberlite-A910 on initial DOM concentration in the water and pH values at a fixed average filtration velocity of 20 m/h.

As can be seen from Figure 4.2-5, larger values of arsenate-exchange capacity are achieved on the lower limit of pH range, i.e. in weakly basic and neutral medium. This is obviously due to the counterion effect since the regeneration solution contained alkali as well as NaCl salt. SBA resins when regenerated with the addition of some caustic to the brine are very susceptible to hardness fouling. This may also hide ion exchange sites and reduce resin capacity at higher pH values. Particularly pH has a strong impact in the area of higher DOM concentration. Because at increased pH values the solubility of some organic species such as tannins increases thus increasing the sorption of DOM and consequently leaving less available sites for arsenate.

Likewise a regression equation was obtained that depicts the dependence of residual arsenate concentration (Y_2) on the same factors (Table 3.2-10).

ANOVA for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in alkaline medium

Response: Residual arsenic concentration

ANOVA for Response Surface Linear Model

Table 4.2-15 Analysis of variance table [Terms added sequentially (first to last)] for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in alkaline medium

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	156.71	3.00	52.24	485.85	< 0.0001	significant
A	95.68	1.00	95.68	889.93	< 0.0001	
B	42.01	1.00	42.01	390.77	< 0.0001	
C	19.01	1.00	19.01	176.85	< 0.0001	
Residual	3.01	28.00	0.11			
Lack of Fit	1.80	23.00	0.08	0.32	0.9717	not significant
Pure Error	1.21	5.00	0.24			
Cor Total	159.72	31.00				

The Model F-value of 485.85 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The "Lack of Fit F-value" of 0.32 implies the Lack of Fit is not significant relative to the pure error. There is a 97.17% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.2-16 Summary of Adequacy Test for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in alkaline medium

Std. Dev.	0.33		R-Squared	0.98
Mean	8.91		Adj R-Squared	0.98
C.V.	3.68		Pred R-Squared	0.98
PRESS	3.57		Adeq Precision	83.86

The "Pred R-Squared" of 0.9776 is in reasonable agreement with the "Adj R-Squared" of 0.9791.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 83.864 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.2-17 Main and interaction factors for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in alkaline medium

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	8.91	1.00	0.06	8.79	9.02	
A-C_{DOM} (mg/L)	2.31	1.00	0.08	2.15	2.46	1.00
B-pH	1.53	1.00	0.08	1.37	1.69	1.00
C-v (m/h)	1.03	1.00	0.08	0.87	1.19	1.00

Table 4.2-18 Diagnostics case statistics for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in alkaline medium

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	4.00	4.05	-0.05	0.20	-0.15	0.00	-0.15	20
2	6.50	6.35	0.15	0.14	0.49	0.01	0.48	19
3	8.50	8.66	-0.16	0.20	-0.53	0.02	-0.53	13
4	6.00	5.57	0.43	0.14	1.41	0.08	1.43	3
5	8.00	7.88	0.12	0.09	0.39	0.00	0.38	6
6	10.00	10.18	-0.18	0.14	-0.61	0.02	-0.60	24
7	7.00	7.10	-0.10	0.20	-0.34	0.01	-0.34	4
8	9.50	9.41	0.09	0.14	0.31	0.00	0.30	21
9	12.00	11.71	0.29	0.20	0.98	0.06	0.98	1
10	5.00	5.07	-0.07	0.14	-0.24	0.00	-0.24	25
11	7.50	7.38	0.12	0.09	0.39	0.00	0.38	26
12	10.00	9.68	0.32	0.14	1.04	0.04	1.04	22
13	7.00	6.60	0.40	0.09	1.27	0.04	1.29	7
14	9.00	8.91	0.09	0.03	0.29	0.00	0.29	27
15	11.00	11.21	-0.21	0.09	-0.68	0.01	-0.67	8

16	8.00	8.13	-0.13	0.14	-0.42	0.01	-0.42	16
17	10.50	10.43	0.07	0.09	0.21	0.00	0.21	28
18	13.00	12.74	0.26	0.14	0.86	0.03	0.85	23
19	6.00	6.10	-0.10	0.20	-0.34	0.01	-0.34	31
20	8.50	8.41	0.09	0.14	0.31	0.00	0.30	2
21	11.00	10.71	0.29	0.20	0.98	0.06	0.98	5
22	8.00	7.63	0.37	0.14	1.22	0.06	1.23	18
23	10.00	9.93	0.07	0.09	0.21	0.00	0.21	10
24	12.00	12.24	-0.24	0.14	-0.79	0.03	-0.78	9
25	9.00	9.16	-0.16	0.20	-0.53	0.02	-0.53	32
26	11.50	11.46	0.04	0.14	0.13	0.00	0.12	12
27	14.00	13.77	0.23	0.20	0.79	0.04	0.79	14
28	9.00	8.91	0.09	0.03	0.29	0.00	0.29	17
29	8.00	8.91	-0.91	0.03	-2.81	0.06	-3.25	29
30	8.50	8.91	-0.41	0.03	-1.26	0.01	-1.27	15
31	9.00	8.91	0.09	0.03	0.29	0.00	0.29	30
32	8.00	8.91	-0.91	0.03	-2.81	0.06	-3.25	11

Table 4.2-19 Upper and lower constraints on the concentration of DOM, pH and filtration velocity in order to optimize arsenate exchange capacity and effluent arsenic concentration in alkaline medium

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
C_{DOM} (mg/L)	is in range	3.6	11.2	1	1	3
pH	is in range	7.0	10.4	1	1	3
v (m/h)	is in range	10.0	30.0	1	1	3
Arsenate capacity (meq/kg)	maximize	27.0	87.0	1	1	3

Table 4.2-20 Solutions to optimize the arsenate exchange capacity and effluent As concentration in alkaline medium

Number	C_{DOM} (mg/L)	pH	v (m/h)	Arsenate capacity (meq/kg)	Desirability	
1	3.60	7.00	10.00	86.33	0.99	Selected
2	3.60	7.00	10.15	86.21	0.99	
3	3.70	7.00	10.00	86.05	0.98	
4	3.60	7.18	10.00	85.31	0.97	
5	3.60	7.58	10.00	83.01	0.93	
6	3.60	7.00	15.70	81.45	0.91	
7	6.00	7.00	10.00	80.08	0.88	

Table 4.2-21 Starting points set to determine the best maximum value of the arsenate exchange capacity and minimum value of effluent arsenic concentration subjected to the constraints in alkaline medium

C_{DOM} (mg/L)	pH	v (m/h)
9.03	7.44	12.14
7.56	9.37	10.96
7.05	7.29	19.35
7.63	7.37	17.58
4.43	7.37	22.19
10.33	8.41	14.31
9.54	7.94	17.73
5.52	9.13	18.07
6.73	9.57	29.63
10.72	8.55	18.02

Residual As concentration $=8.91+2.31*A+1.53*B+1.03*C$ (4.2-5)

Unlike Equation 4.2-3, in Equation 4.2-5, the dependence of y_2, on factors B and C, shows a direct proportional character. With an increase in pH value and filtration velocity, the residual concentration of arsenic, in the treated water, increases. Influent DOM concentration has the largest impact on Y_2. This can probably be explained by some DOM that sorbed arsenic on it and by passed the resin. The higher is the concentration of DOM in the influent water, the more are the chances that some DOM would sorb arsenic on it.

Final equation in terms of actual factors:

Residual As concentration $=-5.45+0.60*C_{DOM}+0.89*pH+0.10*v$ (4.2-6)

Graphical interpretation of this equation is made in Figure 4.2-6. It shows the dependence of residual arsenate concentration in the filtrate on initial DOM concentration in water and pH values at fixed filtration velocities of 10 m/h, 20 m/h and 30 m/h. As can be seen from this figure, the lowest values of residual arsenate concentration are achieved at the lower limits of the intervals of all three factors. As the pH value increased, the SBA resins lost strong base sites based on de-crosslinking, swelling, and partial solubility of the resin and functional groups and some even converted to weak base sites (Schreiber, 2001). This resulted in reduced total capacity and/or reduced strong base sites. At increased pH values, a higher arsenate breakthrough is thus explained by the loss of strong base sites.

Material balances were conducted to see how much arsenate was desorbed from the resin in the regeneration stage. The results are given in Table 4.2-8.

Table 4.2-22 Sorption and desorption of arsenate from the ion exchange column (Amberlite 910)

Item	Value
Water treated, L	160
Water treated, BV	800
Influent Concentration, ppb	1600
Amount of arsenic in raw water, mg	256
Residual concentration in the filtrate, ppb	4
Quantity of arsenic in the treated water, mg	0.64
Quantity of arsenic sorbed on the resin, mg	255.36
Concentration of arsenic in the spent regeneration solution including wash water, ppm	75.8
Quantity of arsenic desorbed, mg	242.6
Total volume of brine and wash water, L	3.2
As(V) removal by regeneration, %	95

Summarizing the results of the investigations carried out in this section, the following conclusions can be drawn:

- Macro-porous anion exchange media in alkaline medium sorbs arsenate effectively as well as it selectively sorbs the acidic group of DOM.

- The sorption mechanism is anionic exchange for both arsenate ions and DOM since the acidic group of DOM as well as arsenate at increased pH values is dissociated and easily soluble. It does show that molecular sorption could not take place since DOM and arsenates are not in neutral forms at the pH range 7-10.4. Material balances of the contaminants sorbed and desorbed further lead to the conclusion that complexation and/or precipitation are unlikely and insignificant.
- Increasing the pH from 7 to 10.4 decreases the sorption capability of the resin, which can be explained by the presence of the counter ion effect (OH^- ion) because of the presence of NaOH in the regeneration solution
- Polynomial dependencies of arsenate-exchange capacity of strongly basic anion exchange resin on influent DOM, pH, and filtration velocity have been established.

Ion exchange column regeneration allowed up to 95% of the arsenic as well as DOM removal from the column. This indicates the reversible nature of sorption. Tables 4.2-8 to 4.2-10 and Figure 4.2-7 show the optimization data and plots. Maximum arsenate exchange capacity of 262.7 meq/kg can be achieved at a DOM concentration of 3.6 mg/L as PV, pH 7 and at a linear velocity of filtration 10 m/h.

Table 4.2-23 Upper and lower constraints on the concentration of DOM, pH and filtration velocity

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
C_{DOM} (mg/L)	is in range	3.60	11.20	1.00	1.00	3.00
pH	is in range	7.00	10.40	1.00	1.00	3.00
v (m/h)	is in range	10.00	30.00	1.00	1.00	3.00
Arsenate capacity (meq/kg)	maximize	27.00	87.00	1.00	1.00	3.00

Note: Factor importance is the specified importance value for this factor in relation to the other factors and responses. The default is +++ (three pluses). If it is more important to achieve one factor or response than another, a higher weight can be given to the more important factor or response.

Table 4.2-24 Optimization of the arsenate exchange capacity and effluent arsenic concentration

Number	C_{DOM} (mg/L)	pH	v (m/h)	Calculated arsenate capacity (meq/kg)	Desirability	
1	3.6	7.00	10.00	86.3	0.99	Selected
2	3.6	7.00	10.15	86.2	0.99	
3	3.7	7.00	10.00	86.0	0.98	
4	3.6	7.18	10.00	85.3	0.97	
5	3.6	7.58	10.00	83.0	0.93	
6	3.6	7.00	15.70	81.4	0.91	
7	6.0	7.00	10.00	80.0	0.88	

Table 4.2-25 Starting points set to determine the best maximum value of the arsenate exchange capacity subjected to the constraints

C_{DOM} (mg/L)	pH	v (m/h)
9.03	7.44	12.14
7.56	9.37	10.96
7.05	7.29	19.35
7.63	7.37	17.58
4.43	7.37	22.19
10.33	8.41	14.31
9.54	7.94	17.73
5.52	9.13	18.07
6.73	9.57	29.63
10.72	8.55	18.02

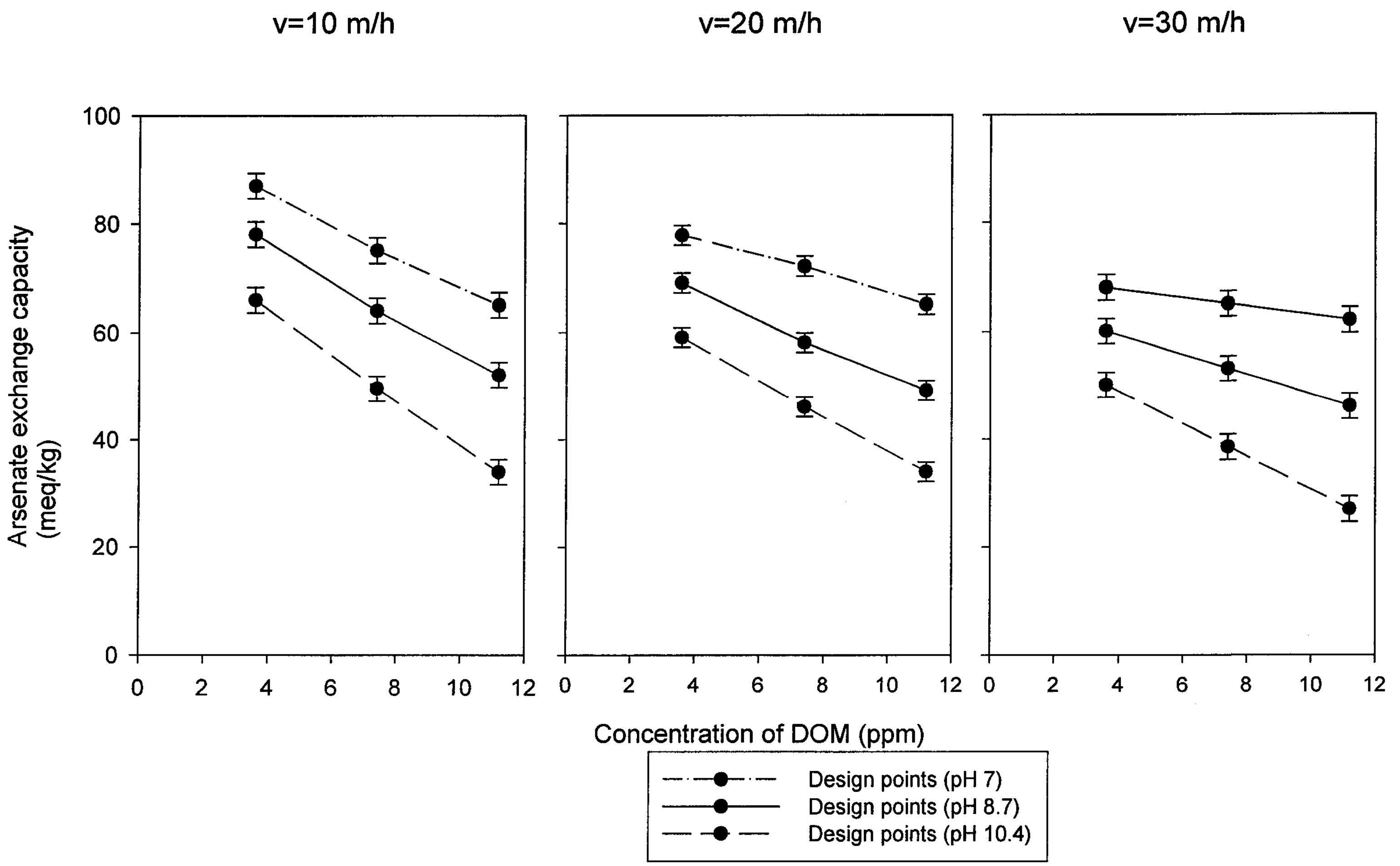


Figure 4.2-5 Dependence of arsenate exchange capacity on initial concentration of DOM and pH at a fixed filtration velocity of 10 m/h, 20 m/h and 30 m/h.

In addition to what was explained before, this is a logical conclusion that if the sorption capability of the resin is decreased with an increase in the pH of the solution (water), the effluent quality will be deteriorated. It means the less arsenic sorbed, the more arsenic would be in the effluent. This can be seen in the following figure. Low pH values are good for sorption but bad for desorption.

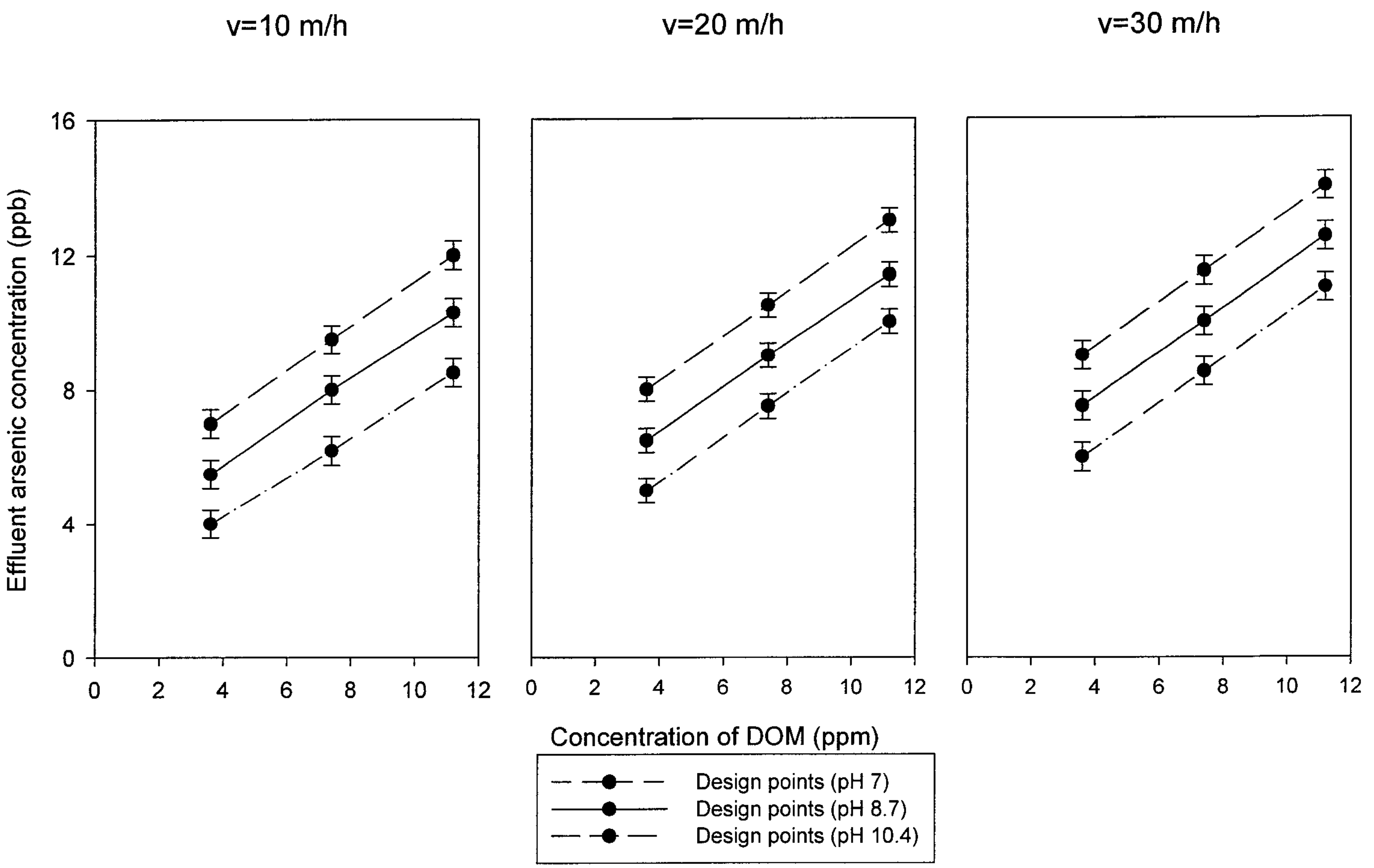


Figure 4.2-6 Dependence of residual arsenic concentration on initial concentration of DOM and pH at a fixed filtration velocity of 10 m/h, 20 m/h and 30 m/h

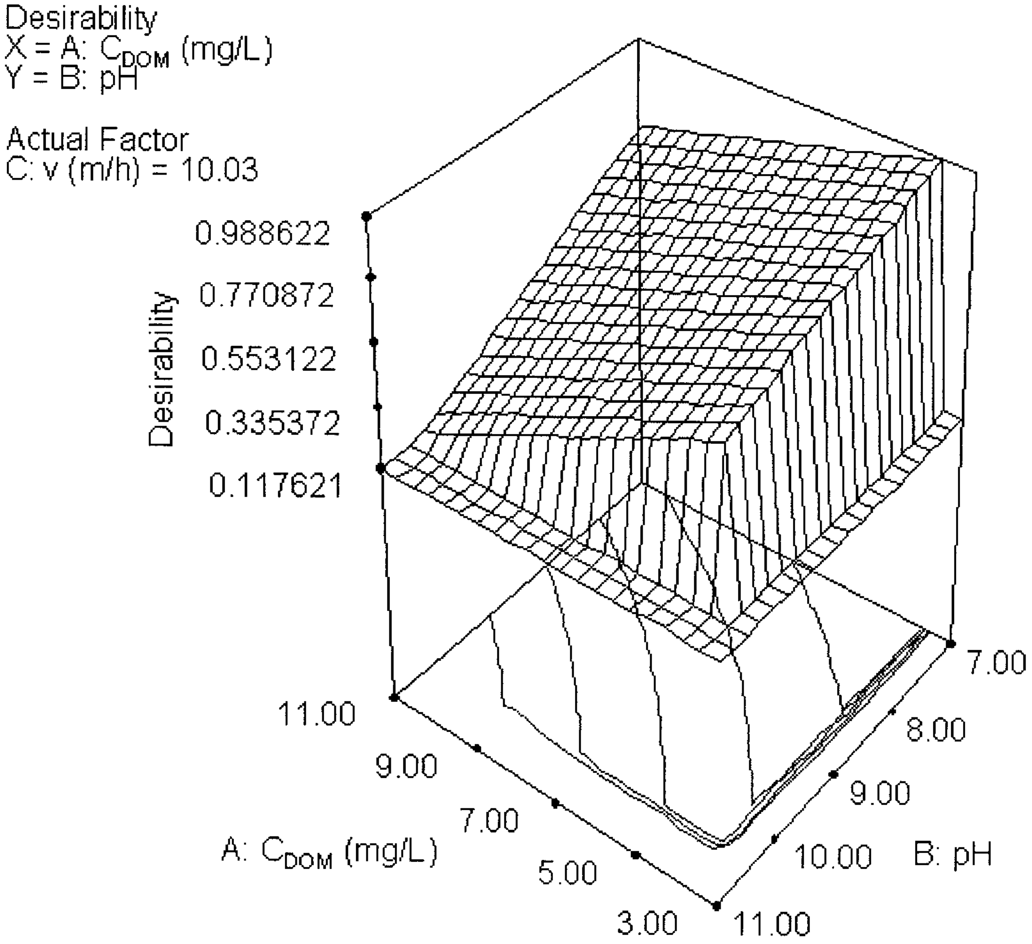


Figure 4.2-7 3D graph of the optimization of arsenic removal from groundwater contaminated also with DOM by anion exchange in chloride form

4.3 Investigation of treatment technology to remove arsenate, DOM, and other components from contaminated groundwater

4.3.1 Investigation of the patterns of sorption and desorption by chemical treatment

The efficiency of using ion exchange treatment for surface water is limited by the concentration of the anions of strong acids (Cl^-, SO_4^{2-}) less than 5 meq/L (Rutsch et. al., 1999). This limitation orients as well in the conditions of using the ion exchange process for groundwater contaminated with DOM, which has, as a rule, higher mineralization.

The ion exchange process can be applied to the treatment of groundwater contaminated with arsenate and DOM when:

- The degree of mineralization of the groundwater is relatively low, i.e. the total anionic content (Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, PO_4^{2-}) is less than 5 meq/L;
- The groundwater is diluted with other waters which have low mineral contents, e.g. surface run-off or river water, so that the total anionic concentration is less than or equal to 5 meq/L;
- COD is less than 30 to 40 mgO_2/L to permit a high-level of pretreatment with respect to dissolved organic compounds;
- Following pretreatment, when the water stream contains no surfactants, oxidants, bacterial pollutants, heavy metal cations or

other impurities, which can poison the ion exchange media.

Along with dissolved organic substances the influent water contained ammoniacal compounds, nitrites, nitrates, phosphates and other contaminants. Considering that organic substances are the most dangerous for ion exchange media, macro-porous ion exchange resins were used. However, macro-porous ion exchange media have to provide efficient arsenic removal at the same level as gel type resins.

In this section, investigations involved the study of the operating parameters of macro-porous ion exchange media in the scheme of two-stage treatment of groundwater contaminated with arsenic and DOM. The investigation was carried out to establish the nature of the sorption of organic matter (reversible and irreversible) by hydrogen- and hydroxyl-ion exchange media used in two-stage treatment, comparison of the sorption regimes of organic and mineral impurities, and the solution in this respect of the practical problems of determining the limit of duration of exchange cycles and the need to include an adsorption unit in the process sequence.

The investigation was carried out on a fixed unit incorporating dynamic columns with Amberlite –200 c (hydrogen ion form) exchange resin in both stages, and the anionic-exchange media Amberlite IRA 96 and MTO-Amberlite IRA-910 (hydroxyl ion form) in stages I and II, respectively.

Domestic waste water from the Montreal municipal treatment works was coagulated with lime, diluted with natural water from the Saint Lawrence river, As(V) was added, after which the concentration of organic matter in the treated water (with respect to COD) was within the recommended limits (18-22 mg/L) and the total anionic content was 5 meq/L. The composition of the clarified and diluted water delivered for ion exchange is shown in Table 4.3-1. The raw water contained silicate as well as other contaminants. Silicate causes no harmful effects to humans, but large amounts can cause scaling in pipes that impacts water flow, and it can interfere with iron and manganese removal. The initial concentration of organic matter is an average of those observed over all the cycles (H-form filters for the 1st and 2nd stages, 6 cycles each; OH-form filters, 140 and 600 cycles for the 1st and 2nd stages respectively) and averaged compositions are also shown for both exchange stages.

Table 4.3-1 Composition of water following each stage of a multi-stage treatment process.

Determinand	Stage I		Stage II	
	H-form resin	OH-form resin	H-form resin	OH-form resin
Acidity, meq/L	-	4.8-4.9	-	0.05-0.15
Alkalinity, meq/L	0.1-0.2/2.3-2.4	-	0.0/0.7-0.8	-
Hardness, meq/L	2.2-2.3	0.003-0.004	0.003-0.004	0
Sodium, meq/L	4.7-4.3	0.1-0.2	0.4-0.5	0.01-0.015
Ammonium, mg/L	17.0-17.5	1.0-1.2	1.0-1.2	0.4-0.5
Arsenate, mg/L	1.4-1.6	1.4-1.6	0.001-0.01	0.001-0.01
Chloride, mg/L	85.0	85.0	1.0-4.0	1.0-2.0
Sulfate, mg/L	30-40	30-40	0.2-0.5	0.2-0.5
Silicate, mg/L	8.0-9.0	8.0-9.0	8.0-9.0	8.0-9.0
Phosphate, mg/L	2.0-2.1	2.0-2.1	1.2-1.4	1.4-1.6
Nitrite, mg/L	0.16-0.20	0.16-0.20	0.02-0.03	0.02-0.03
Nitrate, mg/L	0.7-0.8	0.7-0.8	0.07-0.08	0.07-0.08
TOC, mg/L	5.7-6.1	4.4-4.6	1.2-1.4	1.0-1.2
PV (permanganate value), mgO_2/L	6.0-6.5	4.8-5.1	1.3-1.5	1.1-1.2
COD, mgO_2/L	18-22	15-17	5.5-6.0	4.4-4.9

Along with the mineral composition including arsenate, dissolved organic substances of domestic wastewater of the city of Montreal that served the influent water in this investigation were also studied. The organic materials were separated by chromatographic fractionation using cellulose based ion exchange media. This technique makes it possible to extract the dissolved organic substances and classify them as acidic, basic, or neutral. In the chromatographic separation of the organic content into acidic, basic and neutral groups, diethylaminoethylcellulose (DEAE) and carboxylmethylcellulose (CM) were used. Results of the fractionation are shown in Table 4.3-2. Analysis of DOM was conducted by various methods.

Table 4.3-2 Content of organic species by groups before treatment

Determinand	Content of organic species by groups, %		
	Acidic	Basic	Neutral
PV 6.0-6.5 mgO_2/L	74-78	3.7-6.0	15.9-18.1
COD 18-22 mgO_2/L	75-77	4.5-4.8	15.7-17.8
TOC 5.7-8.1 mgO_2/L	78-80	3.5-4.5	16.0-16.2

Note: COD – chemical oxygen demand

TOC – total organic carbon

The effluent characteristics for the hydrogen-form exchange resin, and its regeneration, in stage I and stage II, are presented in Figures 4.3-1 and 4.3-2.

The adsorption of hardness and sodium cations is similar to that observed when using a gel-type resin. The residual content of ammonia in stage I is 1 mg/L. The breakthrough of ammonia corresponds to a reduction in acidity. Ammonia (NH_3) is a basic gas and reacts with acids to form ammonium (NH_4^+). Ammonia gas reacts with sulphuric acid to form ammonium sulphate $(NH_4)_2SO_4$ and with nitric acid to form NH_4NO_3. These reactions neutralise the acids to reduce the acidity. The operating regime of stage II is characterized by the removal of residual concentrations of ammonium ions together with the sodium ions.

Unlike the gel-type cation exchange resin when using municipal wastewater, the Amberlite 200c filter cycle in stage I is characterized by stable adsorption of organic substances (DOM as COD reduced from 22 mgO_2/L to 17 mgO_2/L) and NH_4^+ (reduced from 17.5 mg/L to 1.2 mg/L) throughout the cycle. For organic substances, a high degree of sorption is characteristic of both in the 1st and 2nd stages of H-resin in comparison with the content of the basic group of DOM (Abdullaev et. al., 1992). Consequently, together with the basic group, the H-resin partially sorbs acidic and neutral groups of DOM as well (Table 4.3-3).

As can be seen from Table 4.3-3, the degree of sorption of DOM in the H-resin filters (21-23%) significantly exceeds the fraction of basic group (3.7-6.0%), which, is obviously, explained by the sorption of acidic group compounds as well. The H-filters are cation exchange columns. The fraction of the basic group of the DOM is also cationic. This is why the H-filters were expected to sorb only the basic fraction of DOM. Besides, the dominant quantity of organic compounds is removed in the 1st stage, the 2nd stage practically does not participate in the removal of DOM (only 6-7% of the initial quantity). It is because the first stage H-resin removes DOM well enough (reduces concentration from 21-23% to 6-7 %), leaving only a small quantity of DOM for stage two.

Table 4.3-3 Sorption onto macro-porous ion exchange media in the scheme of two-stage treatment

Determinand	Stage I		Stage II	
	H-resin	OH-resin	H-resin	OH-resin
Degree of sorption of DOM, % of concentration entering each filter	21-23	75-80	22-27	54-56
Degree of sorption of DOM, % of initial concentration entering H-filter, stage I	21-23	62-66	6-7	7-8
Organic-exchange capacity as PV, mgO_2/L	80-90	460-480	200-240	180-220
Total ion exchange capacity, meq/kg	450-520	700-800	90-100	110-130
Arsenate Exchange capacity, meq/kg	-	200-240	-	-

The pattern of the sorption of DOM by H-resin, in both stages, is characterized by stable in-depth sorption over the cycles (see Table 4.3-1). The residual content of DOM, in the filtrate, begins to increase only at the moment of exhaustion of H-resin filter in stage I by Na^+ and NH_4^+, but in stage II by Na^+. A relatively low degree of desorption of DOM (Figures 4.3-1 and 4.3-2) is shown, in the regeneration process (21-23% - for stage I and 10-12% for stage II of the absorbed quantity), which tends to rise with an increase in the number of cycles run. Obviously, the inadequate degree of desorption of DOM can be explained by the high absorption capability of macro-porous cation exchange resin, especially characteristic for the initial period of its operation. These circumstances did not affect the ion exchange capacity of the cation exchange resin. Arsenate is an anion and therefore was not sorbed onto the cation exchange media.

Effluent characteristics of sorption and regeneration of anion exchange filters in stages I and II are shown in Figures 4.3-3 and 4.3-4. Patterns of sorption of Cl^- and SO_4^{2-} in the first and SiO_3^{2-} and HCO_3^- in the 2nd stages are similar to those observed when using the gel-type anion exchange resins. Arsenate, nitrite and nitrate were sorbed sufficiently well during the main part of the cycle in stage I. Breakthrough concentrations of arsenate (0.01-0.1 mg/L) decreased in stage II up to 0.001-0.01 mg/L. Breakthrough concentrations of nitrite and nitrate (total 0.1-0.15 mg/L) also decreased in stage II up to 10-15 µg/L.

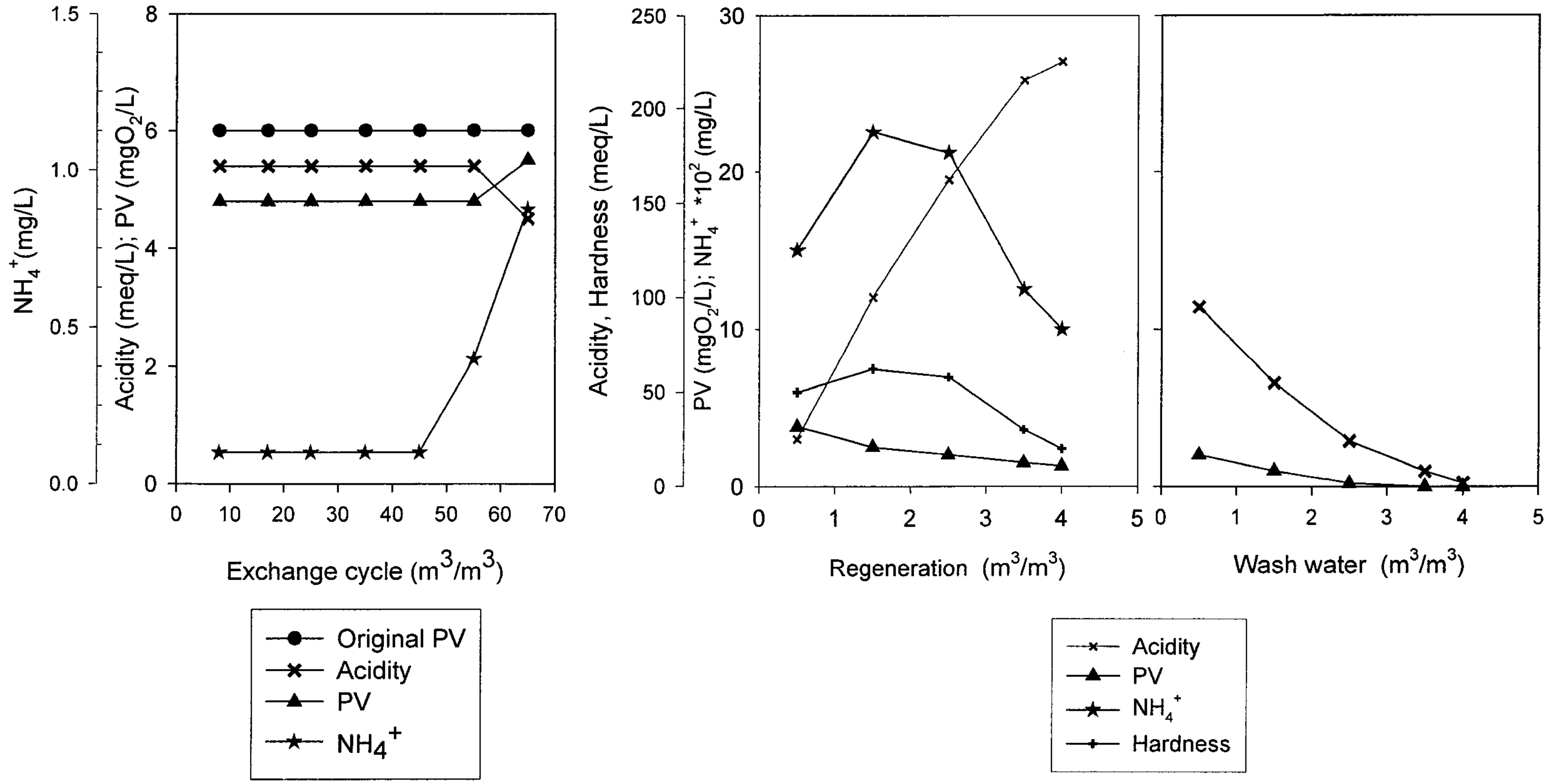


Figure 4.3-1 Effluent characteristics of the H-form cation exchange, stage 1, loaded with Amberlite 200c

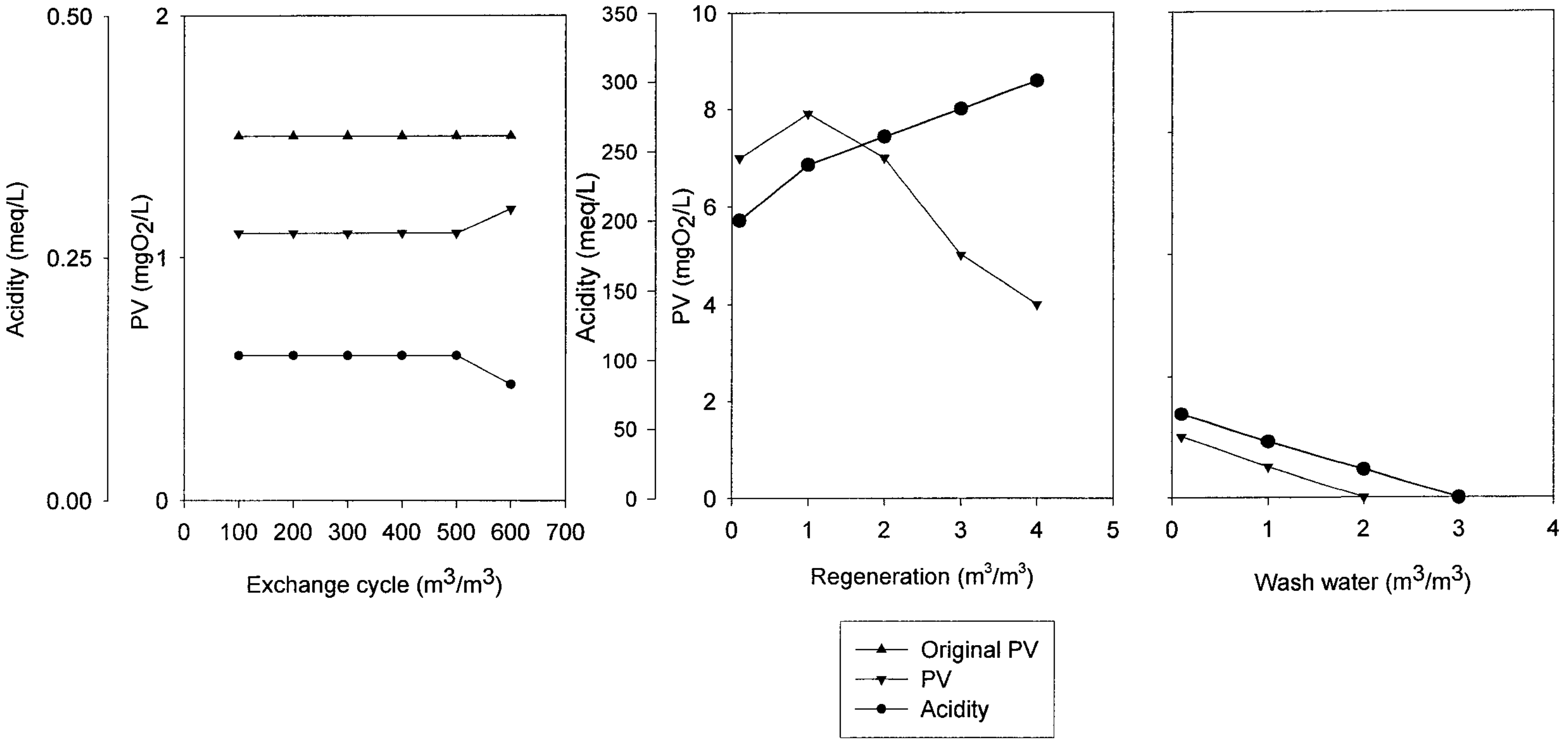


Figure 4.3-2 Effluent characteristics of the H-form cation exchange, stage 2, loaded with Amberlite 200c

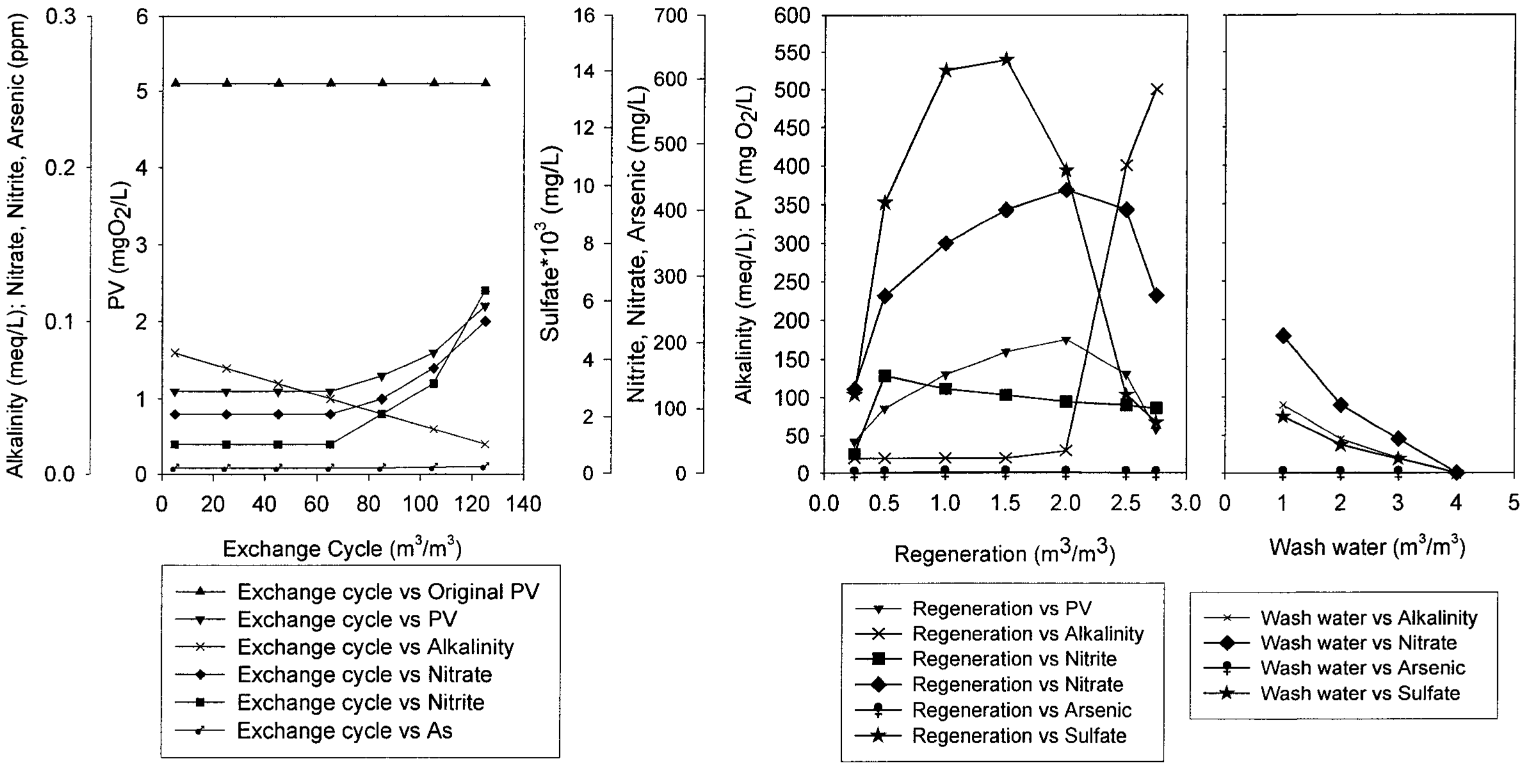


Figure 4.3-3 Effluent characteristics of the exchange cycle of the OH-form anion exchange resin, Amberlite IRA 96, stage one

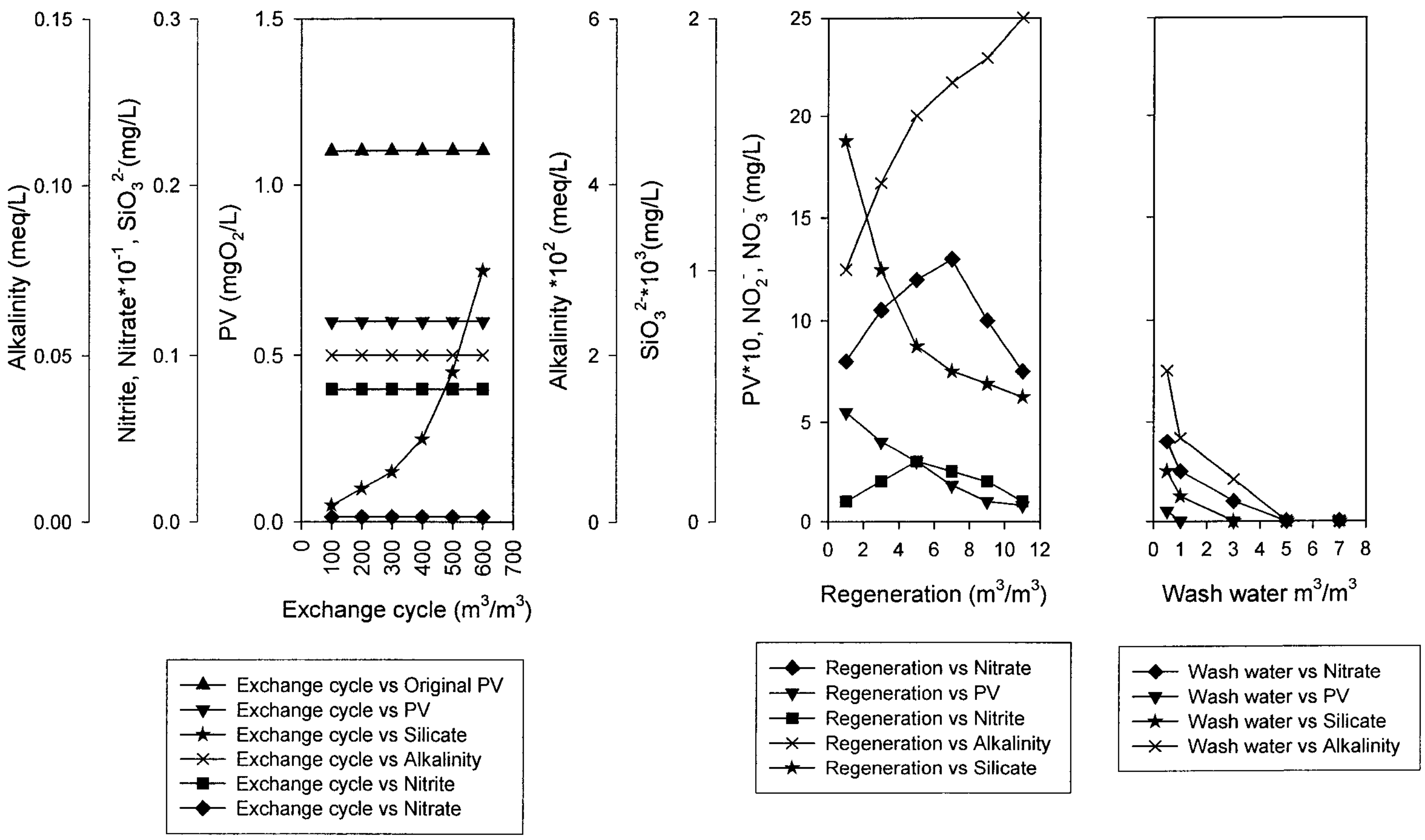


Figure 4.3-4 Effluent characteristics of the exchange cycle of the OH-form anion exchange resin Amberlite-910, stage two.

As can be seen from Table 4.3-3, the degree of sorption of DOM onto the anion exchange media is somewhat lower than the content of acidic group, which confirms its partial sorption onto the H-resin in stage I. The majority of the DOM, that is sorbed onto the anion exchange media, was removed in stage I, as compared to stage II where only 7-8% of the initial quantity was removed. The pattern of sorption of DOM in stage I is characterized by relative stability during the sorption of anions (Cl^-, SO_4^{2-}, $HAsO_4^{2-}$) Breakthrough of arsenates are accompanied by the growth of oxygen demand of the filtrate which indicates the breaktrough of organic matter as well. In stage II, sorption of the residual content of DOM is not related to the exchange of anions, i.e. strongly basic anion exchange media are capable of sorbing DOM also after exhaustion by SiO_3^{2-}. The degree of desorption of DOM was 60% of the sorbed quantity onto the weakly basic anion exchange medium (stage I) and 75-83% of that on strongly basic medium (stage II). The organo-exchange capacity and ion exchange capacity of all macro-porous ion exchange media used in this research are shown in Table 4.3-3.

Analysis of the operating parameters of macro-porous ion exchange media leads to the following conclusions. The relatively lower concentrations of DOM after the 1st stage (as a result of only 6-8% of initial quantity of DOM sorbed onto the media in stage II) causes doubt about the expediency of using macro-porous anion exchange media in stage II considering the relatively low ion exchange capacity. In this case, low concentrations of DOM (1 mgO_2/L as PV) excluded “poisoning” of the anion exchange media in stage II. Efficient sorption of breakthrough concentrations of DOM onto strongly basic gel-type anion exchange medium Purolite A-300 provides the required degree of final treatment of not only mineral but also organic impurities, which corresponds even to the criteria of ultra pure water. Ultra pure water required for boiler feed must not have a concentration of DOM over 2 mg/L as PV.

4.3.2 Efficiency of the sorption of arsenate together with organic impurities by OH-anion exchange

Technological feasibility of using macro-porous ion exchange media for chemical treatment was shown in the previous section. Patterns of the sorption of DOM and arsenate by stages of chemical treatment loaded with macro-porous cation exchange and anion exchange media were also studied. As these investigations showed, the majority of DOM removal (62-66% of the initial quantity) was provided in the first stage of the anion exchange filters. Efficient sorption of DOM in this stage excludes the necessity of using macro-porous ion exchange media in the 2nd stage of treatment (removal of arsenate and other anions).

Considering the role of weakly basic anion exchange media, a more detailed investigation of the pattern of sorption on the anion exchange medium Amberlite IRA-96 was conducted. For example, does the anion exchange medium become exhausted by organic and mineral (including arsenate) impurities at the same time at various concentration ratios? In other words, what is the influence of the ratio $C_{DOM}/\Sigma A$ (anions), as well as that of the ratio SO_4^{2-}/Cl^- on the exchange or sorption capacity at a constant concentration $\Sigma A(Cl^- + SO_4^{2-}) = 5$ meq/L?

To solve this problem, a response surface experiment was implemented. The independent factors considered were as follows: A – DOM concentration, mgO_2/L, $C_{DOM}=3\text{-}7$ mgO_2/L as PV (which corresponded to 9-21 mgO_2/L as COD); B – specific consumption of NaOH on regeneration $G_{NaOH}=40\text{-}60$ kg/tonne; C –

ratio of concentrations of the anions Cl^- and SO_4^{2-} ranging from 1 to 3.

The ranges chosen for DOM and the ratio SO_4^{2-}/Cl^- corresponded to possible modification of the composition of the pretreated domestic wastewater. The range for the consumption of NaOH corresponded to practically applicable regeneration of weakly basic anion exchange media.

Arsenate-exchange capacity, meq/kg was considered to be the target function Y. The planning matrix of the investigation carried out is shown in the methodology section. These values are indeed higher than those (0.09 meq/g) observed in Plant A investigated by the US EPA (Wang et. al. 2000). The EPA conducted long term investigations of two ion exchange treatment plants for arsenic removal. The plants were described as Plant A and Plant C. The real names and locations of these plants were not disclosed. It should be noted that Plant A used a gel-type resin Purolite A-300.

A regression equation with linear, double, and triple interactions was considered. All of the coefficients of this equation were calculated by the least squares method.

ANOVA for the determination of arsenate exchange capacity by macroporous hydroxyl-form anion exchange resin Amberlite IRA-96

- Response: Arsenate exchange capacity
ANOVA for Response Surface Reduced 2FI Model

Table 4.3-4 Analysis of variance table [Terms added sequentially (first to last)] for the determination of arsenate exchange capacity by macroporous hydroxyl-form anion exchange resin Amberlite IRA-96

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	4794.64	5.00	958.93	1817.40	< 0.0001	significant
A	1476.06	1.00	1476.06	2797.49	< 0.0001	
B	2312.00	1.00	2312.00	4381.81	< 0.0001	
C	924.50	1.00	924.50	1752.16	< 0.0001	
AB	21.33	1.00	21.33	40.43	< 0.0001	
BC	60.75	1.00	60.75	115.14	< 0.0001	
Residual	13.72	26.00	0.53			
Lack of Fit	13.72	21.00	0.65			
Pure Error	0.00	5.00	0.00			
Cor Total	4808.36	31.00				

The Model F-value of 1817.40 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table 4.3-5 Summary of adequacy test for the determination of arsenate exchange capacity by macroporous hydroxyl-form anion exchange resin Amberlite IRA-96

Std. Dev.	0.73		R-Squared	1.00
Mean	138.09		Adj R-Squared	1.00
C.V.	0.53		Pred R-Squared	1.00
PRESS	19.65		Adeq Precision	175.22

The "Pred R-Squared" of 0.9959 is in reasonable agreement with the "Adj R-Squared" of 0.9966.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 175.215 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.3-6 Coefficient estimates of main and interaction factors for the determination of arsenate exchange capacity by macroporous hydroxyl-form anion exchange resin Amberlite IRA-96

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	138.09	1.00	0.13	137.82	138.35	
A-C_{DOM}	-9.06	1.00	0.17	-9.41	-8.70	1.00
B-NaOH	11.33	1.00	0.17	10.98	11.69	1.00
C-sufate/chloride	7.17	1.00	0.17	6.81	7.52	1.00
AB	1.33	1.00	0.21	0.90	1.76	1.00
BC	-2.25	1.00	0.21	-2.68	-1.82	1.00

Table 4.3-7 Diagnostics case statistics for the determination of arsenate exchange capacity by macroporous hydroxyl-form anion exchange resin Amberlite IRA-96

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	127.00	127.72	-0.72	0.36	-1.25	0.15	-1.27	27
2	117.00	117.34	-0.34	0.23	-0.53	0.01	-0.52	11
3	107.00	106.95	0.05	0.36	0.09	0.00	0.09	12
4	140.00	139.97	0.03	0.14	0.04	0.00	0.04	32
5	131.00	130.92	0.08	0.09	0.12	0.00	0.11	9
6	122.00	121.86	0.14	0.14	0.20	0.00	0.20	10
7	152.00	152.22	-0.22	0.36	-0.39	0.01	-0.38	28
8	144.00	144.50	-0.50	0.23	-0.79	0.03	-0.78	6
9	136.00	136.78	-0.78	0.36	-1.35	0.17	-1.37	8
10	136.88	137.14	-0.27	0.23	-0.42	0.01	-0.41	4
11	126.13	126.75	-0.63	0.09	-0.90	0.01	-0.90	29
12	115.38	116.36	-0.99	0.23	-1.55	0.12	-1.59	17
13	147.00	147.14	-0.14	0.09	-0.20	0.00	-0.20	16
14	139.00	138.09	0.91	0.03	1.28	0.01	1.30	13
15	131.00	129.03	1.97	0.09	2.84	0.13	3.35	23

16	156.88	157.14	-0.27	0.23	-0.42	0.01	-0.41	26
17	149.13	149.42	-0.29	0.09	-0.42	0.00	-0.42	2
18	141.38	141.70	-0.32	0.23	-0.50	0.01	-0.50	5
19	147.00	146.56	0.44	0.36	0.76	0.06	0.76	22
20	136.00	136.17	-0.17	0.23	-0.26	0.00	-0.26	20
21	125.00	125.78	-0.78	0.36	-1.35	0.17	-1.37	19
22	154.00	154.31	-0.31	0.14	-0.46	0.01	-0.45	25
23	145.00	145.25	-0.25	0.09	-0.36	0.00	-0.36	24
24	136.00	136.20	-0.20	0.14	-0.29	0.00	-0.29	1
25	162.00	162.06	-0.06	0.36	-0.10	0.00	-0.10	3
26	154.00	154.34	-0.34	0.23	-0.53	0.01	-0.52	31
27	146.00	146.61	-0.61	0.36	-1.06	0.11	-1.06	14
28	139.00	138.09	0.91	0.03	1.28	0.01	1.30	18
29	139.00	138.09	0.91	0.03	1.28	0.01	1.30	21
30	139.00	138.09	0.91	0.03	1.28	0.01	1.30	7
31	139.00	138.09	0.91	0.03	1.28	0.01	1.30	15
32	139.00	138.09	0.91	0.03	1.28	0.01	1.30	30

Table 4.3-8 Upper and lower constraints on the concentration of DOM, pH and filtration velocity in order to optimize arsenate exchange capacity by macroporous hydroxyl-form anion exchange resin Amberlite IRA-96 and effluent arsenic concentration

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
C_{DOM}	is in range	3	7	1	1	3
NaOH	is in range	40	60	1	1	3
sufate/chloride	is in range	1	3	1	1	3
Response 1	maximize	107	162	1	1	3

Table 4.3-9 Solutions to optimize the arsenate exchange capacity of macroporous hydroxyl form resin and effluent As concentration

Number	C_{DOM}	NaOH	sufate/chloride	Response 1	Desirability	
1	3.01	59.99	3	162.001	1.00	Selected
2	3.02	59.83	3	161.844	1.00	
3	3.32	60.00	3	160.803	0.98	
4	3.00	56.32	3	159.209	0.95	
5	4.27	60.00	1	147.319	0.73	

5 Solutions found

Table 4.3-10 Starting points set to determine the best maximum value of the arsenate exchange capacity of macroporous hydroxyl-form resin and minimum value of effluent arsenic concentration subjected to the constraints

C_{DOM}	NaOH	sufate/chloride
3.58	57.53	2.59
5.35	47.62	2.07
6.35	41.17	1.50
6.48	53.11	1.35
3.21	49.21	2.12
4.51	56.09	2.40
5.31	49.89	2.75
4.89	50.78	1.08
3.61	46.51	2.42
6.99	56.73	2.33

As a result of a complete statistical analysis, including the elimination of insignificant coefficients by Student's criterion and adequacy test by Fisher's criterion, the following regression equation was derived.

Final equation in terms of coded factors:

$$Y = 138.09 - 9.06*A + 11.33*B + 7.17*C + 1.33*A*B - 2.25*B*C \qquad (4.3\text{-}1)$$

Statistical analysis of this equation revealed that the specific quantity of NaOH on regeneration has the largest impact on the arsenate-exchange capacity of anion exchange media (OH-form). With an increase in the specific quantity of

NaOH, the arsenate-exchange capacity increases. The second, in terms of the extent of impact on arsenate-exchange capacity, is the initial DOM concentration. The dependence between Y and A (C_{DOM}) is inversely proportional. With an increase in the initial DOM concentration, the arsenate-exchange capacity of the resin decreases. The positive sign of the linear coefficient at C shows that, with an increase in the sulfate to chloride ratio, the arsenate-exchange capacity increases. The peculiarity of the sorption of DOM by macro-porous anion exchange media is that its exhaustion by arsenate, no matter how much the initial DOM concentration was, occurred at the same time as the breakthrough of the latter in the filtrate, i.e. the exhaustion of the exchange capacity also limits the sorption of DOM.

Final equation in terms of actual factors:

$$Y = 83.89 - 7.86 * C_{DOM} + 1.25 * G_{NaOH} + 18.41667 * \text{sufate/chloride} + 0.06 * C_{DOM} * G_{NaOH} - 0.22 * G_{NaOH} * \text{sufate/chloride} \qquad (4.3\text{-}2)$$

Graphical interpretation of this equation is shown in Figure 4.3-5. As can be seen from this figure, larger values of arsenate-exchange capacity are achieved at the lower limit of the DOM range and the upper one of the intervals of NaOH consumption for regeneration and the ratio of sulfate to chloride concentrations.

As a whole, the investigation conducted showed that macro-porous anion exchange media are characterized by an acceptable arsenate-exchange capacity (based on the centerpoint arsenate exchange capacity of 142.5 meq/kg) while simultaneously providing efficient sorption of DOM. Figure 4.3-6 shows the optimization plot of the arsenate exchange capacity by weakly basic macroporous anion exchange medium Amberlite IRA 96.

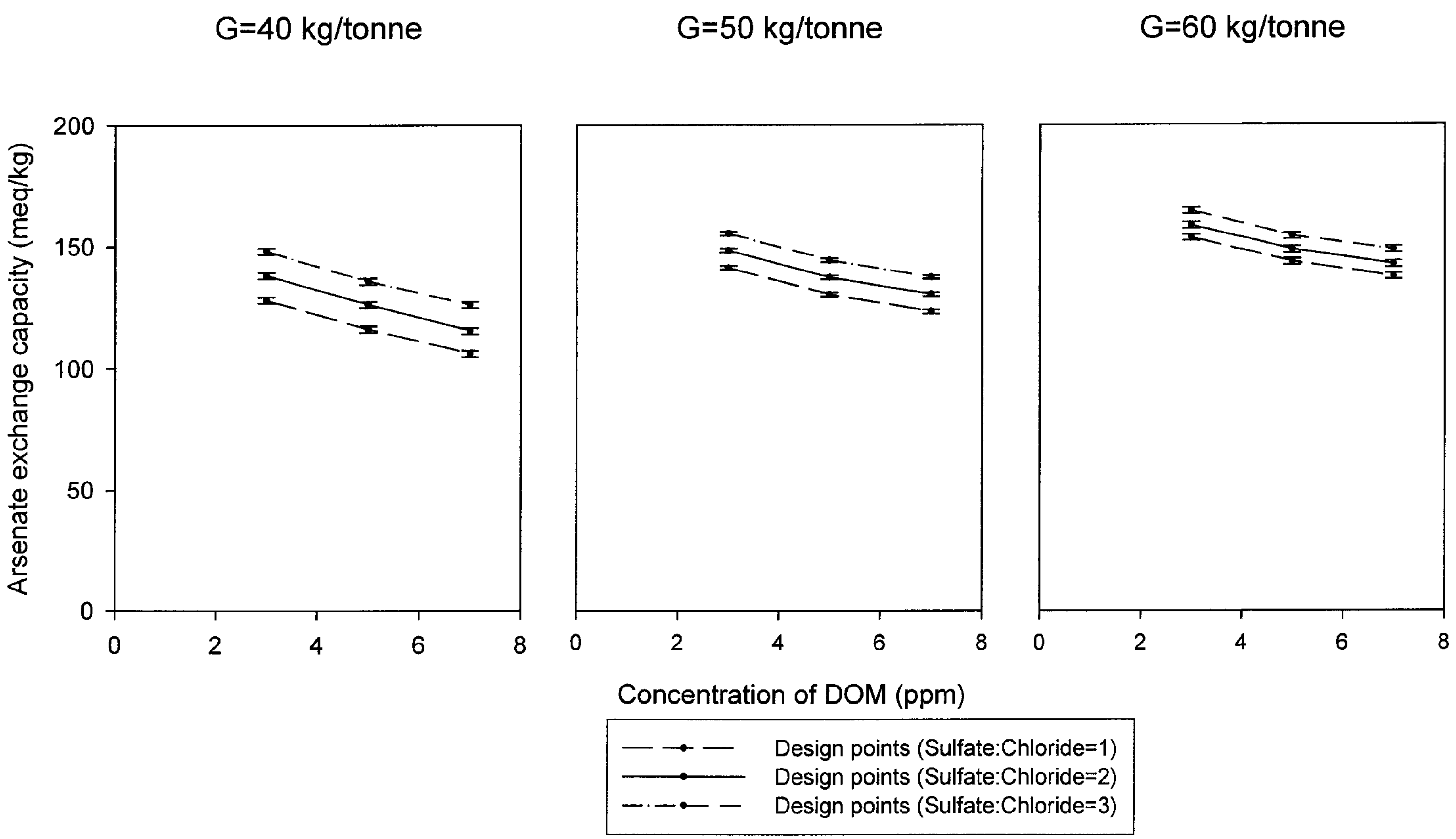


Figure 4.3-5 C_{DOM}- $C_{sulfate/chloride}$ interaction graph of arsenate exchange capacity at a fixed G_{NAOH} value of 40 kg/tonne, 50 kg/tonne and 60 kg/tonne

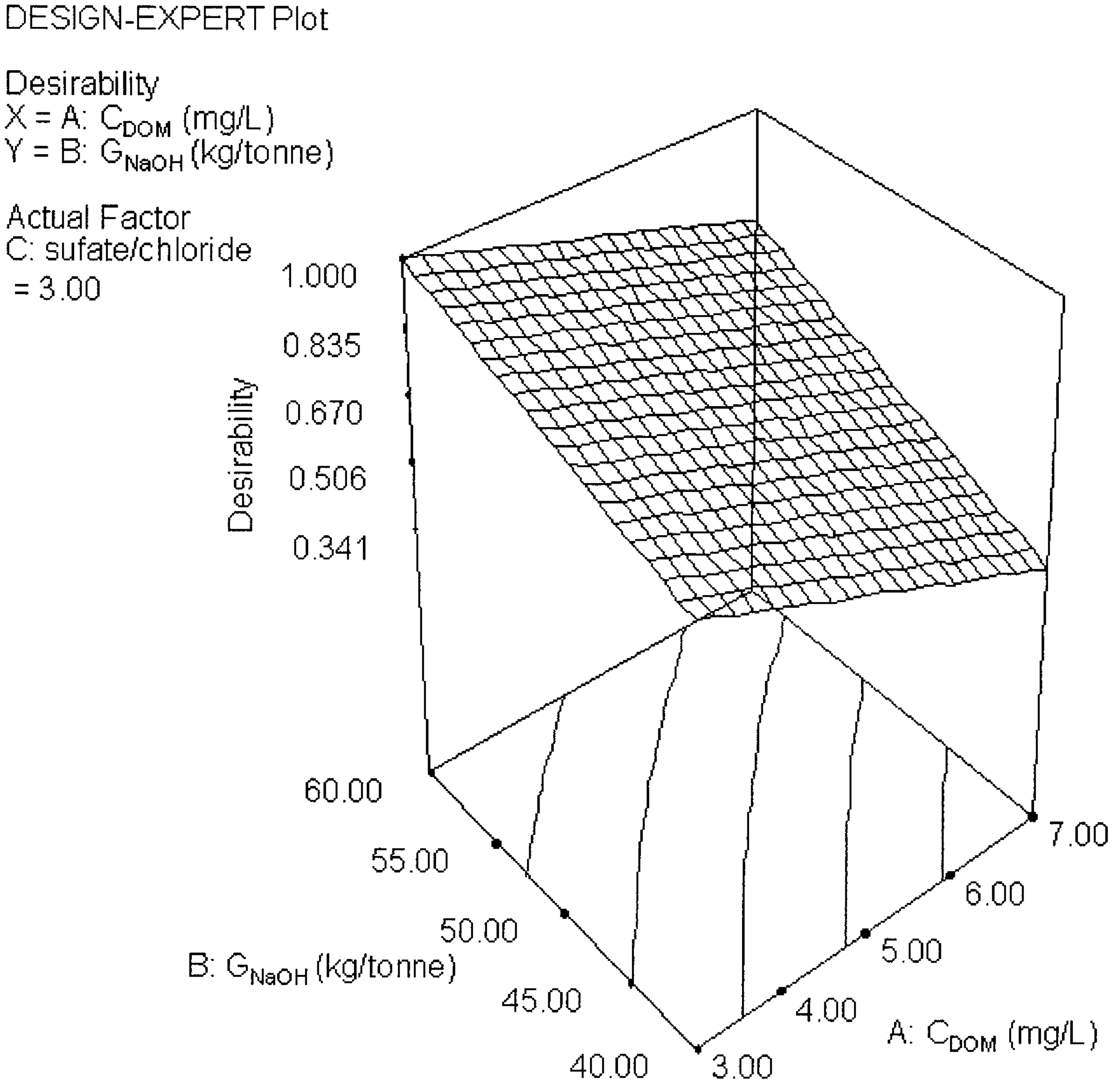


Figure 4.3-6 3D plot of the optimization of arsenate exchange capacity

4.4 Sorption of arsenate and DOM onto the Cl-form Macro-porous Anion exchange Media

The dependence of the arsenate-exchange capacity of macroporous anion exchange media and residual concentration of arsenic in the filtrate on three concentrations and hydrodynamic factors were studied. The Cl-form anion exchange media, exhausted by arsenate and DOM were regenerated in the established optimum regime (which is NaCl consumption of 300 kg/tonne, concentration of NaCl solution of 10%, ratio of NaCl concentration to that of NaOH in regenerant of 10, velocity of passing the regeneration solution 4 m/h, temperature 50°C). This investigation differs from that conducted earlier (section 4.2.4) by a different pH range of 2 to 7 (factor B). Besides, the concentrations of DOM in water being treated were also changed to the range of 3 to 7 mg/L. The decrease in the initial concentration of DOM was a result of diluting the municipal wastewater before delivery to the treatment system. Factor C remained unchanged.

Independent factors considered were as follows: A – DOM concentration, mgO_2/L; B - pH values of water being treated; C – linear velocity of filtration, m/h. Arsenate-exchange capacity was considered to be the target function Y_1 and residual arsenate concentration as Y_2. The planning matrix of the investigation carried out is shown in Table 3.2-13.

ANOVA for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in acidic medium

.

Response: Arsenate exchange capacity

ANOVA for Response Surface Reduced 2FI Model

Table 4.4-1 Analysis of variance table [Terms added sequentially (first to last)] for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in acidic medium

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	21077.47	4.00	5269.37	206431.64	< 0.0001	significant
A	10057.25	1.00	10057.25	394000.71	< 0.0001	
B	4572.07	1.00	4572.07	179114.46	< 0.0001	
C	4702.10	1.00	4702.10	184208.64	< 0.0001	
AC	1746.05	1.00	1746.05	68402.76	< 0.0001	
Residual	0.69	27.00	0.03			
Lack of Fit	0.24	22.00	0.01	0.12	0.9998	not significant
Pure Error	0.45	5.00	0.09			
Cor Total	21078.16	31.00				

The Model F-value of 206431.64 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The "Lack of Fit F-value" of 0.12 implies the Lack of Fit is not significant relative to the pure error. There is a 99.98% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.4-2 Summary of adequacy test for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in acidic medium

Std. Dev.	0.16		R-Squared	1.00
Mean	228.75		Adj R-Squared	1.00
C.V.	0.07		Pred R-Squared	1.00
PRESS	0.76		Adeq Precision	1765.13

The "Pred R-Squared" of 1.0000 is in reasonable agreement with the "Adj R-Squared" of 1.0000.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 1765.133 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.4-3 Coefficient estimates of main and interaction factors for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in acidic medium

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	228.75	1	0.03	228.69	228.80	
A-Input DOM	-23.64	1	0.04	-23.71	-23.56	1
B-pH	-15.94	1	0.04	-16.01	-15.86	1
C-v	-16.16	1	0.04	-16.24	-16.09	1
AC	12.06	1	0.05	11.97	12.16	1

Table 4.4-4 Diagnostics case statistics for the determination of arsenate exchange capacity by macroporous chloride-form anion exchange resin in acidic medium

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	296.59	296.55	0.04	0.28	0.31	0.01	0.30	16
2	260.89	260.85	0.04	0.14	0.28	0.00	0.28	18
3	225.19	225.15	0.04	0.28	0.31	0.01	0.30	20
4	280.65	280.61	0.04	0.23	0.30	0.01	0.29	19
5	244.95	244.91	0.04	0.09	0.27	0.00	0.27	3
6	209.25	209.21	0.04	0.23	0.30	0.01	0.29	32
7	264.71	264.67	0.04	0.28	0.31	0.01	0.30	5
8	229.01	228.97	0.04	0.14	0.28	0.00	0.28	26
9	193.31	193.27	0.04	0.28	0.31	0.01	0.30	21
10	268.36	268.32	0.04	0.14	0.28	0.00	0.28	31
11	244.72	244.68	0.04	0.09	0.27	0.00	0.27	22
12	221.09	221.05	0.04	0.14	0.28	0.00	0.28	7
13	252.42	252.38	0.04	0.09	0.27	0.00	0.27	9
14	228.79	228.75	0.04	0.03	0.27	0.00	0.26	15

15	205.15	205.11	0.04	0.09	0.27	0.00	0.27	11
16	236.49	236.45	0.04	0.14	0.28	0.00	0.28	29
17	212.85	212.81	0.04	0.09	0.27	0.00	0.27	23
18	189.21	189.17	0.04	0.14	0.28	0.00	0.28	12
19	240.14	240.10	0.04	0.28	0.31	0.01	0.30	13
20	228.56	228.52	0.04	0.14	0.28	0.00	0.28	2
21	216.99	216.95	0.04	0.28	0.31	0.01	0.30	25
22	224.20	224.16	0.04	0.23	0.30	0.01	0.29	24
23	212.62	212.58	0.04	0.09	0.27	0.00	0.27	30
24	201.05	201.01	0.04	0.23	0.30	0.01	0.29	28
25	208.26	208.22	0.04	0.28	0.31	0.01	0.30	14
26	196.69	196.65	0.04	0.14	0.28	0.00	0.28	8
27	185.11	185.07	0.04	0.28	0.31	0.01	0.30	6
28	228.00	228.75	-0.75	0.03	-4.74	0.14	-11.359 *	4
29	228.50	228.75	-0.25	0.03	-1.56	0.02	-1.61	27
30	228.80	228.75	0.05	0.03	0.35	0.00	0.34	17
31	228.70	228.75	-0.05	0.03	-0.29	0.00	-0.28	10
32	228.60	228.75	-0.15	0.03	-0.92	0.01	-0.92	1

Table 4.4-5 Upper and lower constraints on the concentration of DOM, pH and filtration velocity in order to optimize arsenate exchange capacity and effluent arsenic concentration in acidic medium

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Input DOM	is in range	3.00	7.00	1	1	3
pH	is in range	2.00	7.00	1	1	3
v	is in range	10.00	30.00	1	1	3
As-capacity	maximize	185.11	296.59	1	1	3

Table 4.4-6 Solutions to optimize the arsenate exchange capacity and effluent As concentration in acidic medium

Number	Input DOM	pH	v	As-capacity	Desirability	
1	3.00	2.00	10.00	296.545	1.00	Selected
2	3.02	2.00	10.00	296.181	1.00	
3	3.00	2.13	10.00	295.696	0.99	
4	3.13	2.00	10.00	294.203	0.98	
5	3.00	3.25	10.00	288.596	0.93	
6	3.00	2.00	13.92	285.473	0.90	
7	3.00	6.78	10.00	266.053	0.73	

7 Solutions found

Number of Starting Points 10

Table 4.4-7 Starting points set to determine the best maximum value of the arsenate exchange capacity and minimum value of effluent arsenic concentration subjected to the constraints in acidic medium

Input DOM	pH	v
3.67	3.28	24.53
4.21	4.78	20.68
6.29	4.20	13.83
4.86	4.82	19.96
5.22	5.30	19.12
4.70	6.31	25.49
3.39	3.15	13.66
6.21	4.14	26.87
7.00	6.99	11.60
5.70	5.19	14.26

In order to derive a regression equation, a response surface experiment was conducted. Based on the matrix (Table 3.2-13) a regression model with linear, double, and triple interactions was considered. All the coefficients of this equation were calculated by the least squares method. As a result of a complete statistical analysis, including the elimination of insignificant coefficients by Student's criterion and adequacy test by Fisher's criterion (see Appendix A.6), the following regression equation was derived. The predictive model is listed in both actual and coded terms. The coded equation is useful for identifying the relative significance of the factors by comparing the factor coefficients. This comparison cannot be made with the actual equation because the coefficients are scaled to accommodate the units of each factor. The equations give identical predictions.

The final equation in terms of the coded factors is:

$$\text{As-capacity} = 228.75 - 23.64 * A - 15.94 * B - 16.16 * C + 12.06 * A * C \quad (4.4\text{-}1)$$

Statistical analysis of this equation revealed that initial concentrations of DOM (A) have the largest impact on Y_1. With an increase in the influent DOM concentration, the arsenate-exchange capacity decreases. In terms of the extent of impact on arsenate-exchange capacity, pH (B) and filtration velocity (C) are almost equal. The dependence between Y_1 and these factors is inversely proportional: with an increase in pH and filtration velocity, the arsenate-exchange capacity of the resin decreases.

Comparing the patterns established earlier (section 4.2.4) for operating conditions at increased pH values (7 to 10.4), the following can be stated: higher arsenate-exchange capacity is achieved in acidic medium. This can probably be explained by the strong dependency of the degree of ionization of weakly basic resins on pH. Weak base resins exhibit minimum exchange capacity above a pH of 7.0. Besides, the equality of significance of factors B and C shows the increased influence of filtration velocity on the sorption capacity by DOM (in alkaline medium $b_2>b_3$).

Considering that the predominant portion of DOM is acidic with carboxyl and phenol-hydroxyl groups it can be assumed that the latter are weakly dissociated in acidic medium. Because of this, the sorption mechanism for DOM is chiefly of molecular nature. Since undissociated molecules are not charged, the sorption of dissolved organic species must take place principally due to physical (van der Waals') forces. The same applies to arsenic since the ionic form of arsenate dominates at pH>3 (Wang et. al., 2000). Molecular sorption is characterized by weak kinetics and it strongly depends on the filtration velocity (Malakhkov et. al., 1988). This is the reason why the growth of the linear coefficient at C was observed.

The final equation in terms of the actual factors is:

$$\text{As-capacity} = 409.16 - 23.88 \cdot C_{DOM} - 6.37 \cdot pH - 4.63 \cdot v + 0.60 \cdot C_{DOM} \cdot v \qquad (4.4\text{-}2)$$

Graphical interpretation of this equation is shown in Figure 4.4-1. This figure shows the dependence of arsenate-exchange capacity on initial DOM concentration in water, pH values and filtration velocities. Larger values of arsenate-exchange capacity are achieved at the lower limit of the pH range, i.e. acidic medium. Particularly pH has a strong impact in the area of higher DOM concentration (the distance between lines appears to be the largest at v=30m/h, the pH is constant), for which the lowest value of capacity was noted. With an increase in initial DOM concentration, the arsenate-exchange capacity decreases. As pH changes, surface charge also changes in the following way:

⇒At low pH, surface sites are protonated: and the surface will be *cationic*, or positively charged.

⇒At high pH, the surface hydroxyls lose their protons: and the surface is anionic.

Only chemicals that tend to ionize are significantly affected by pH. The only influence on neutral molecules would be the change in the character of the surface. At low pH, humic materials as well as arsenic species are nearly neutral and more hydrophobic (Schwarzenbach et. al., 1993). The degree of dissociation of a weak base resin is strongly influenced by the solution pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0.

Likewise a regression equation was obtained that depicts the dependence of residual arsenate concentration (y_2) on the same factors (Table 3.2-13

ANOVA for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in acidic medium

Response: Residual arsenic concentration

ANOVA for Response Surface Reduced 2FI Model

Table 4.4-8 Analysis of variance table [Terms added sequentially (first to last)] for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in acidic medium

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	82.41	5.00	16.48	2129.42	< 0.0001	significant
A	49.17	1.00	49.17	6352.42	< 0.0001	
B	10.05	1.00	10.05	1298.40	< 0.0001	
C	20.91	1.00	20.91	2701.27	< 0.0001	
AB	1.08	1.00	1.08	139.53	< 0.0001	
AC	1.20	1.00	1.20	155.46	< 0.0001	
Residual	0.20	26.00	0.01			
Lack of Fit	0.11	21.00	0.01	0.30	0.9760	not significant
Pure Error	0.09	5.00	0.02			
Cor Total	82.61	31.00				

The Model F-value of 2129.42 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

The "Lack of Fit F-value" of 0.30 implies the Lack of Fit is not significant relative to the pure error. There is a 97.60% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.4-9 Summary of adequacy test for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in acidic medium

Std. Dev.	0.09		R-Squared	1.00
Mean	8.12		Adj R-Squared	1.00
C.V.	1.08		Pred R-Squared	1.00
PRESS	0.28		Adeq Precision	182.58

The "Pred R-Squared" of 0.9967 is in reasonable agreement with the "Adj R-Squared" of 0.9971.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 182.579 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.4-10 Coefficient estimates of main and interaction factors for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in acidic medium

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	8.12	1	0.02	8.09	8.15	
A-Input DOM	1.65	1	0.02	1.61	1.70	1
B-pH	0.75	1	0.02	0.70	0.79	1
C-v	1.08	1	0.02	1.04	1.12	1
AB	0.30	1	0.03	0.25	0.35	1
AC	-0.32	1	0.03	-0.37	-0.26	1

Table 4.4-11 Diagnostics case statistics for the determination of residual arsenic concentration by macroporous chloride-form anion exchange resin in acidic medium

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	4.70	4.62	0.08	0.36	1.08	0.11	1.08	16
2	6.30	6.29	0.01	0.14	0.08	0.00	0.08	18
3	8.00	7.96	0.04	0.36	0.52	0.03	0.52	20
4	5.00	5.07	-0.07	0.23	-0.92	0.04	-0.92	19
5	7.00	7.04	-0.04	0.09	-0.49	0.00	-0.48	3
6	9.00	9.01	-0.01	0.23	-0.13	0.00	-0.13	32
7	5.50	5.52	-0.02	0.36	-0.27	0.01	-0.26	5
8	7.80	7.79	0.01	0.14	0.14	0.00	0.14	26
9	10.00	10.06	-0.06	0.36	-0.82	0.06	-0.82	21
10	6.00	6.02	-0.02	0.23	-0.24	0.00	-0.24	31
11	7.50	7.37	0.13	0.09	1.53	0.04	1.57	22
12	8.70	8.72	-0.02	0.23	-0.31	0.00	-0.31	7
13	6.50	6.47	0.03	0.09	0.40	0.00	0.40	9
14	8.00	8.12	-0.12	0.03	-1.37	0.01	-1.40	15
15	9.75	9.77	-0.02	0.09	-0.26	0.00	-0.25	11

16	7.00	6.91	0.09	0.23	1.12	0.06	1.13	29
17	8.85	8.87	-0.02	0.09	-0.19	0.00	-0.19	23
18	11.00	10.82	0.18	0.23	2.34	0.27	2.58	12
19	7.40	7.41	-0.01	0.36	-0.19	0.00	-0.18	13
20	8.40	8.45	-0.05	0.14	-0.61	0.01	-0.60	2
21	9.50	9.49	0.01	0.36	0.21	0.00	0.20	25
22	7.90	7.86	0.04	0.23	0.51	0.01	0.50	24
23	9.10	9.20	-0.10	0.09	-1.15	0.02	-1.16	30
24	10.60	10.53	0.07	0.23	0.87	0.04	0.87	28
25	8.30	8.31	-0.01	0.36	-0.11	0.00	-0.11	14
26	10.00	9.94	0.06	0.14	0.69	0.01	0.68	8
27	11.50	11.58	-0.08	0.36	-1.14	0.12	-1.15	6
28	8.00	8.12	-0.12	0.03	-1.37	0.01	-1.40	4
29	8.20	8.12	0.08	0.03	0.94	0.00	0.94	27
30	8.00	8.12	-0.12	0.03	-1.37	0.01	-1.40	17
31	8.30	8.12	0.18	0.03	2.09	0.02	2.25	10
32	8.00	8.12	-0.12	0.03	-1.37	0.01	-1.40	1

Final equation in terms of coded factors:

Effluent As =8.12+1.65*A+0.75* B+1.08 * C+0.30 * A * B-0.32* A * C (4.4-3)

To compare this equation with Equation 4.2-5 for operating conditions in alkaline medium, it can be noted that the general pattern is preserved. The residual concentration increases with an increase in all of the factors. However, there is a difference –an increase in the influence of factor C in comparison with factor B ($b_3 > b_2$) on the response function. Thus, the factor filtration velocity in acidic medium becomes the 2nd in terms of the extent of influence on effluent quality. This also indicates the molecular nature of the sorption of arsenate by Cl-form macro-porous media in acidic medium. As the literature review indicates, sorbent surfaces in aqueous systems adsorb water molecules via strong electrostatic interactions called *hydrogen bonds*, where the proton on water associates with the surface oxygen at the sorbent surface (Karickhoff et. al., 1979). For a solute to chemisorb at the resin surface, the sorbing molecule must displace one of these strongly bound waters, a difficult, and energy-intensive interaction. For this reason, the K_{sorp} (sorption constant) would be expected to be low for neutral organic compounds, and higher for polar compounds that can compete for charged sites.

Final equation in terms of actual factors:

$$\textbf{Effluent As} = 0.25+0.87 * C_{DOM} - 1.11E\text{-}003 * pH + 0.18 * v + 0.06 * C_{DOM} * pH - 0.015 * C_{DOM} * v \qquad (4.4\text{-}4)$$

Graphical interpretation of this equation is shown in Figure 4.4-2. It shows the dependence of residual arsenate concentration in the filtrate on initial DOM concentration in water and pH values at velocities of 10 m/h, 20 m/h and 30 m/h. The lowest values of residual arsenate concentration were achieved on the lower limit of the intervals of all three factors. The influence of pH on effluent quality is particularly noticeable in the area of higher initial concentrations of DOM. Changes in pH dramatically affect organic acids and bases by changing solubility (Schwarzenbach et. al., 1993). Cations resulting from the protonation of an organic base, for example, may more strongly sorb to the resin than the neutral species. As the solubility of a hydrophobic compound decreases, the adsorption coefficient increases, probably from entropy driven interaction with the surface. This probably explains why at the higher influent concentrations of DOM, pH has the most influence.

Summarizing the results of the investigations carried out in this section the following conclusions can be drawn. Macro-porous anion exchange media in acidic medium sorbs arsenate effectively as well as it sorbs all groups of DOM. The sorption mechanism of DOM is molecular, since the acidic group of DOM as well as arsenate at low pH values is weakly dissociated and insoluble in water.

Increasing the filtration velocity from 10 to 30 decreases the sorption capability of the resin (by 2.3%), which is characteristic of the molecular mechanism of sorption. Polynomial dependencies of arsenate-sorption capacity of strongly basic and weakly basic resins on the presence of dissolved organic species, pH and filtration velocity have been established. The ion exchange column can be regenerated almost completely as over 95% of the arsenic as well as the DOM could be removed from the column. This indicates the reversible nature of sorption. Resin life is expected to be 1893- 7,571 m^3 or 5 to 9 years (based on an upflow backwash flowrate of 19 L/min) when properly handled, stored, maintained and regenerated (Schreiber, 2001). An addition to the filter loaded with macroporous anion exchange resin e.g. Amberlite IRA 910 after H-filter stage one, in the process sequence (units loaded with gel-type resins) solves the problem of preventing the poisoning of the gel-type resins. The strongly basic macroporous resin sorbs the organic matter, thus guarding against the entrance of DOM in the other gel-type resin columns.

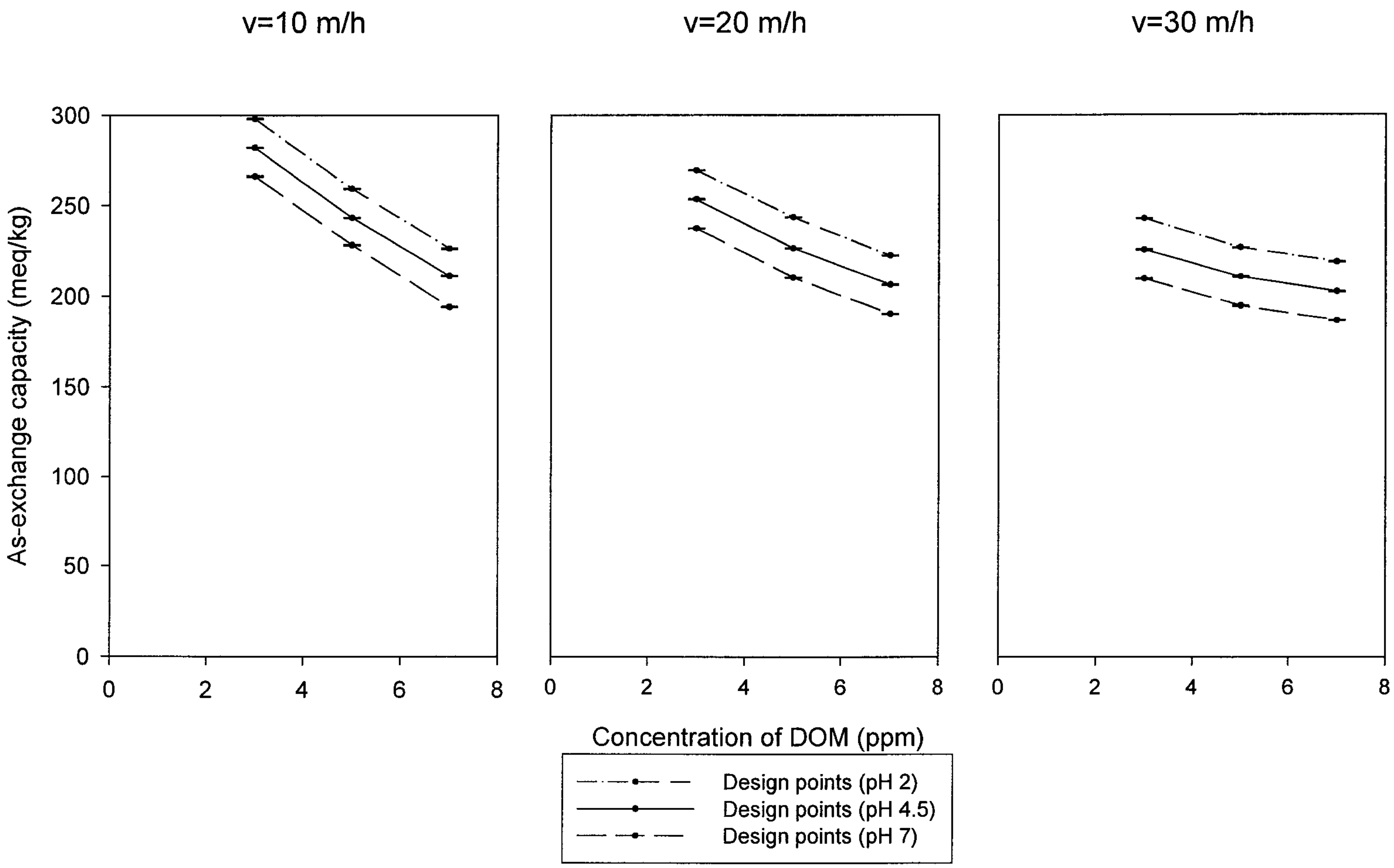


Figure 4.4-1 C_{DOM}-pH interaction at a fixed filtration velocity of 10 m/h, 20 m/h and 30 m/h

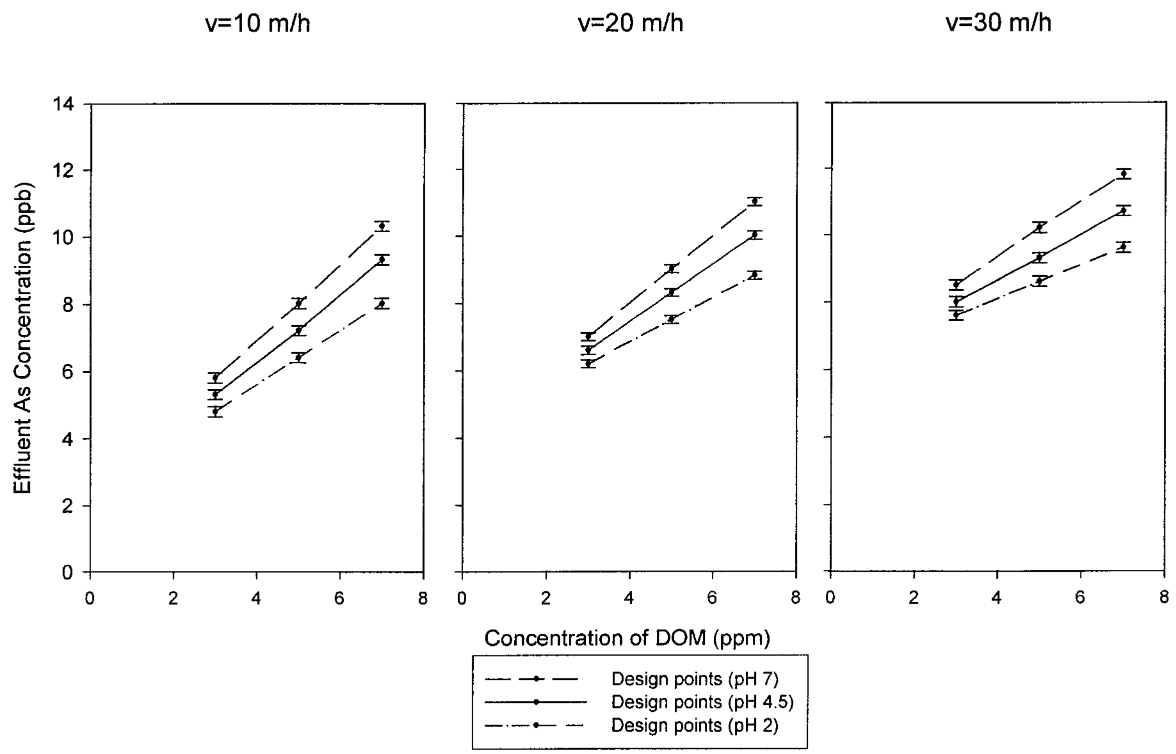


Figure 4.4-2 C_{DOM}-pH interaction on residual arsenic concentration at a fixed filtration velocity of 10 m/h, 20 m/h and 30 m/h

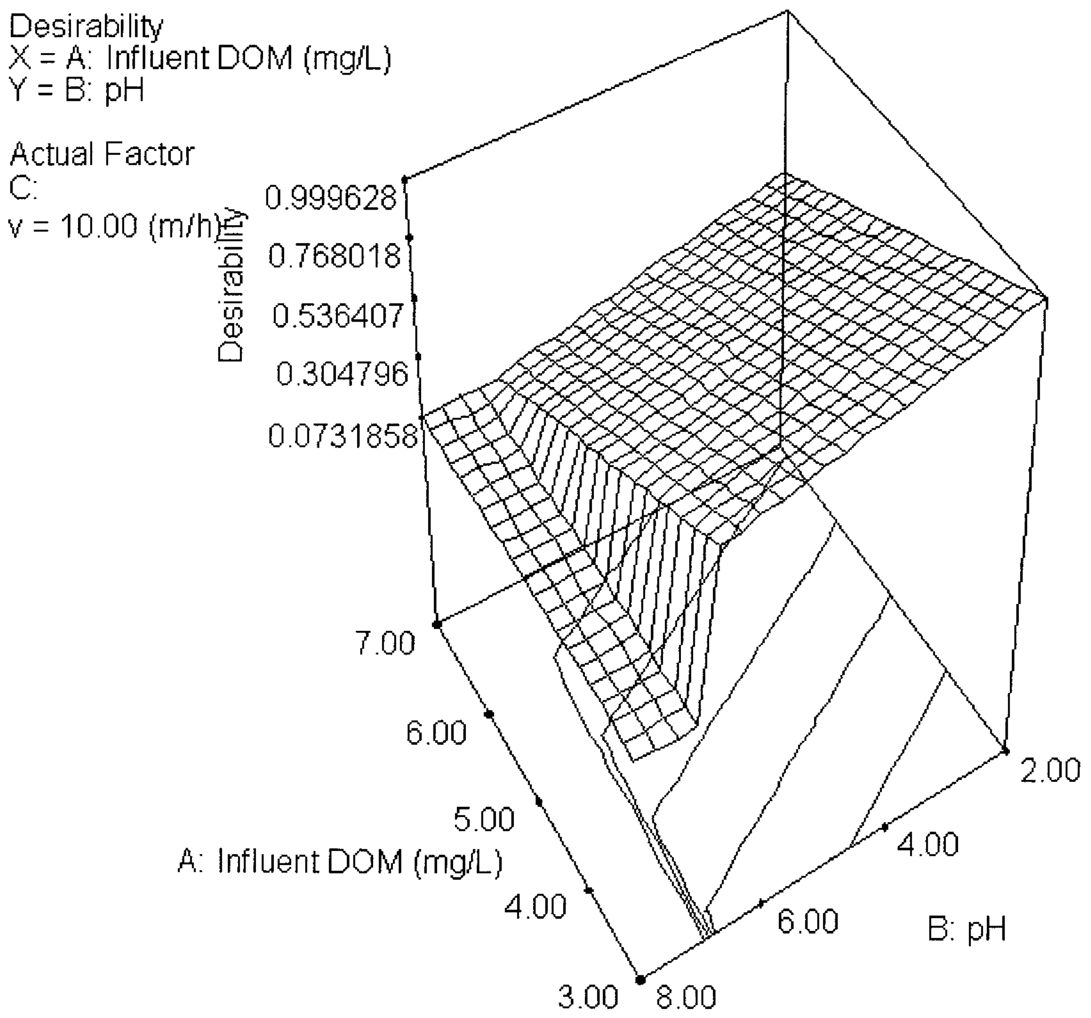


Figure 4.4-3 Optimization plot of minimum residual arsenic concentration.

4.5 Summary of results

Alkaline effluent is characteristic of a Na-cationic softener. A Na-cationic softener would remove neither arsenates nor DOM. If such a softener encounters arsenates and DOM in water to be treated, the filter becomes useless for the production of potable water. In such a case, a macroporous strongly basic anion exchange media in the chloride form has to be added after the Na-form filter. Dissolved organic species play a significant negative role in arsenic removal. The predominance of acidic groups of DOM in influent water was also shown. Thus, the removal of acidic species of organic substances is an essential prerequisite for efficient arsenic removal. As the investigations showed and as can be seen in Table 4.5-1, a macroporous SBA resin in chloride form in an alkaline medium can remove acidic groups of DOM from 62 to 66%. The sorption mechanism is anionic. However, at a high pH level (10.4), the arsenate exchange capacity decreases (arsenic at pH 10 becomes insoluble in water, arsenate fraction decreases and arsenite fraction increases), and the effluent arsenic concentration increases. Addition of a macroporous SBA resin in the process sequence removes acidic DOM and arsenates efficiently.

Likewise, an acidic effluent is characteristic of a H-cationic softener. A H-cationic softener would remove neither arsenates nor DOM. Gel-type anion exchange filters added after the H-cationic exchange filters in a two-stage treatment system would remove organic free arsenates quite efficiently. However, the occurrence of DOM in the water being treated would poison the gel-type SBA, which is a problem.

Table 4.5-1 Summary of the results from investigations carried out

Resin type				pH	DOM removal	Arsenate exchange capacity	Effluent As	Mechanism
					(%)	(meq/kg)	(ppb)	
SBA	Macroporous	Cl-form	Amberlite 910	2.0	56	298.6	4.8	Molecular sorption
			Amberlite 910	7.0	92 (acidic species only)	86.2	4.0	Anionic exchange
			Amberlite 910	10.4	72 (acidic species only)	69.5	6.8	Anionic exchange
	Gel	No DOM	Purolite A-300	6.5	-	40.0	2.4	Anionic exchange
			Purolite A-300	8.5	-	30.0	8.3	Anionic exchange
		DOM present	Purolite A-300	6.7	17	15.4	10.0	Anionic exchange
WBA	Macroporous	OH-form	Amberlite IRA-96	2.0	80	161.0	4.6	Molecular sorption

As was discussed and shown earlier, macroporous SBA sorbs various groups of DOM in an acidic medium. As the investigations showed, a macroporous SBA resin in the chloride form in an acidic medium can remove various groups of DOM and arsenates considerably. The removal mechanism is largely molecular sorption. Addition of a macroporous SBA resin after a H-cationic filter (stage one) in a two-stage process sequence protects the gel-type anionic exchange resin from being poisoned by DOM.

It is important to select the right resin for the effective treatment of water. When to use which ion exchange resin while treating water of certain composition is the first question that would arise in a decision-making. Figure 4.5-1 shows the schematic of when to use what resin to remove As in the presence of how much of DOM and other inorganic ion concentrations.

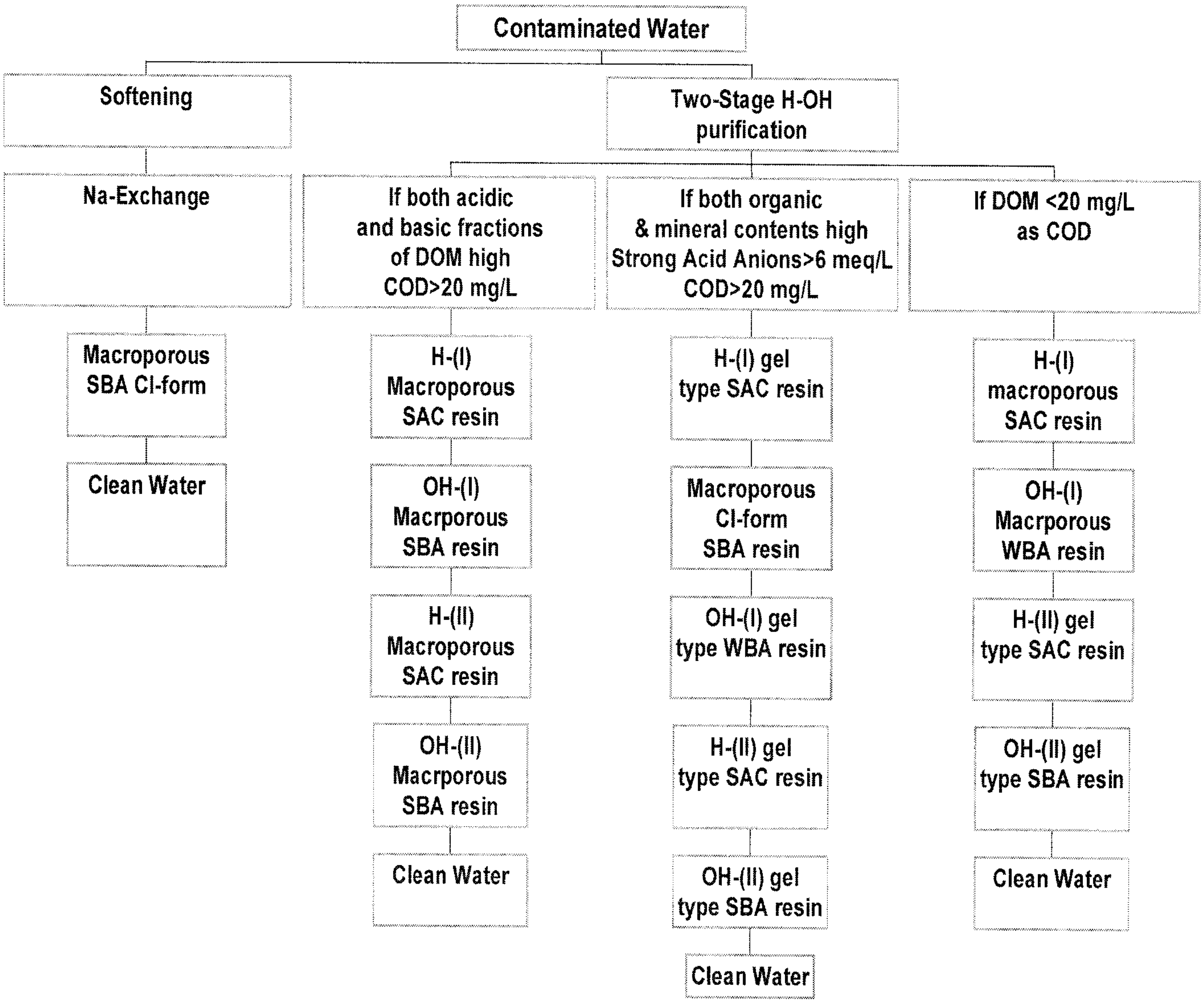


Figure 4.5-1 Schematic of the use of macroporous ion exchange resin depending on the water composition

As can be seen from Figure 4.5-1, this is an important guide for people encountering differing water to treat in terms of the composition of water. If some one has a simple softening unit with added chloride anion exchange filter and if he finds some organic materials in the water he needs to use macroporous strongly basic anion exchange resin instead of gel-type one. If someone has a two-stage deionization unit, he finds COD greater than 20 mg/L, and both the organics of acidic group and basic group are high he needs to use macroporous resins in both stages. This may happen in case there are some industrial sources of organic contamination.

5. TECHNICAL, ECONOMIC, AND ENVIRONMENTAL INDICES OF THE PROPOSED SCHEMES

5.1 Description of the proposed schemes of arsenic removal and softening

The following schemes of ion exchange treatment are proposed based on the results obtained through the investigations. These are ion exchange processes designed to remove arsenic from contaminated groundwater containing dissolved organic matter for a flow rate of 0.5 m^3/h for 1500 people. Until recently, it was believed that groundwater did not contain DOM. The knowledge of arsenic contamination alone prompted the addition of anion exchange filters to the traditional softeners. The existence or occurrence of DOM in groundwater was still ignored. It is now that the scientific community found high levels of DOM in groundwater, especially where arsenic levels are also high. DOM concentrations as high as 5 mg/L as TOC, which is approximately equivalent to 15 mg/L as COD in Bangladeshi groundwater are now well documented (Jonsson et. al., 2004). As can be seen in Figure 2.5-3, DOM concentrations range from 3 to 5 mg/L as TOC or 9 to 15 mg/L as COD.

As it is well known, the preparation of potable water from such sources requires a two-stage treatment system (Rutsch et. al., 1999). For the scheme mentioned, several variants of the process have been devised as follows.

1. Loading H-cationic and OH-anionic filters, in both stages, with macroporous ion exchange media (Figure 5.1-1).

2. Loading H-cationic and OH-anionic filters, in stage one only, with macroporous ion exchange media (Figure 5.1-2).
3. Adding a chloride-form filter with macroporous anion exchange resin in the process sequence prior to.the filters which are loaded with gel-type resins (Figure 5.1-3).

The feasibility of each of the proposed variants is based on the following conditions. The use of the first variant is justified when groundwater containing increased concentration of dissolved organic substances (over 20 mgO_2/L as COD) of acidic as well as of basic nature. In this case, a single stage of macroporous ion exchange media will not provide the required sorption of DOM so as to prevent the organic fouling of gel-type resins in stage two. Besides, a breakthrough of DOM also in stage two cannot be excluded, which may result in a violation of the drinking water standard (US EPA) with respect to electro-conductivity (i.e. over 450 μS/cm). The operating regime and parameters for turning off the filters in different stages remain the same, in the proposed scheme, as those when operating with gel-type resins.

However, there are some peculiarities regarding this ion exchange process. The concentration of the DOM increases as acidity reduces, i.e. Na^+ breaks through in the 1st stage H-filters. The 1st stage of OH-filters sorbs strong acid anions as well as arsenates, nitrites, nitrates and organic substances. The breakthrough of arsenates, nitrites and nitrates takes place somewhat earlier than the resin exhaustion with respect to chloride ions, but the concentration of DOM increases as the chloride ions increases in the filtrate. Macroporous anion exchange media becomes exhausted with respect to strong acid anions almost at the same time as they do with respect to organic substances.

H-cationic filters, in the 2nd stage, sorbs only a small amount of DOM remaining after the 1st stage of treatment. The presence of DOM does not change the efficiency and nature of the sorption of sodium ions. The use of the macroporous media in this stage can be justified when using groundwater highly contaminated with industrial wastes containing increased levels of DOM (basic group). Textile, leather processing, ferrous and non-ferrous metal refining, and chemicals, petrochemicals, oil-refining, and pulp and paper are the main industries of concern.

OH-filters in the 2nd stage provide significant sorption of residual arsenates and DOM after the 1st stage. In this case, the exhaustion, with respect to strong acid anions including arsenates, of strongly basic macroporous anionic exchange resin does not take place at the same time when it gets exhausted with respect to DOM. Using macroporous media in this stage can be justified when using groundwater highly contaminated with the acidic groups of DOM.

Application of the 2nd variant is being recommended when treating waters with a relatively lower concentration of arsenic and DOM (below 20 mgO_2/L as COD). In this case, a single stage macroporous anion exchange resin reduces the concentration of DOM to 3 to 4 mgO_2/L, which satisfies the normal operating conditions of gel-type media for efficient arsenic removal.

Loading only the first stage anionic filter with macroporous media is recommended for waters that contain mostly acidic DOM (from 60 to 70% and higher). As investigations showed that the H-form gel-type cation exchange media are quite stable even when using waters that contain DOM up to 30 mgO_2/L as COD.

Implementation of these two variants is being recommended when constructing new treatment units. At the design stage, the operating characteristics of the macroporous ion exchange media can be considered. The exchange capacity of macroporous media differs from that of the gel-type media. Macroporous media usually have lower total exchange capacity than that of gel-type ones (about 37% lower) (Sarvacel, 2004). It is also important to take the waste treatment and disposal units into account regarding the design of treatment units.

Implementation of the third variant is recommended for existing treatment units that are designed to remove arsenic using the gel-type media from groundwater with no DOM. Since the presence of DOM in ground water is a new issue, most arsenic removal plants did not consider the concentrations of DOM at all. To transfer the existing units to macroporous media may require reconstruction and addition of filters to satisfy the design capacity due to the lower exchange capacity of macroporous media.

Another factor that justifies the usefulness of the third variant is the combination of higher DOM concentration (over 20 mgO_2/L) and increased concentrations of strong acid anions including arsenates (over 6 to 7 meq/L, which is about 600 mg/L). For the above mentioned conditions of increased ionic loads on the 1st stage filters, it is more beneficial to use gel-type media that have higher capacities than macroporous ones.

Besides, macroporous media in OH-form have lower capacities with respect to arsenates when treating relatively high concentrations of DOM. In these conditions, it is useful to add an independent filter in the process sequence using a chloride form macroporous anion exchange resin. Strongly basic anion exchange resin Amberlite 910 in chloride form has a higher capacity with respect to arsenic and DOM than in OH-form. It also has a higher capacity compared to that of the weakly basic anion exchange media IRA 96.

For water softeners operating on water contaminated with arsenic and DOM, a Na-Cl-ionization scheme is being recommended (Figure 5.1-4). Unlike schemes designed for removal of arsenic from cleaner groundwater, the chloride filter should be loaded with macroporous anionic exchange media. In this case simultaneous water desulfatization is provided as well.

To provide better conditions for the sorption of DOM pretreatment by coagulation with aluminum or ferrous sulfate with lime should be considered. Dosing with lime promotes more complete oxidation of bivalent iron to form slightly soluble ferric hydroxide, as well as the precipitation of calcium carbonate and magnesium hydroxide. In this case, liming should be conducted in the carbonate regime, since Mg is necessary in spent solution to settle DOM. Besides it is absolutely necessary to neutralize the clarified alkaline water by acidification (pH 7.15) in order to create optimal conditions for the sorption of NH_4^+ by cation exchange (if it is required) and DOM by the macroporous anion exchange media.

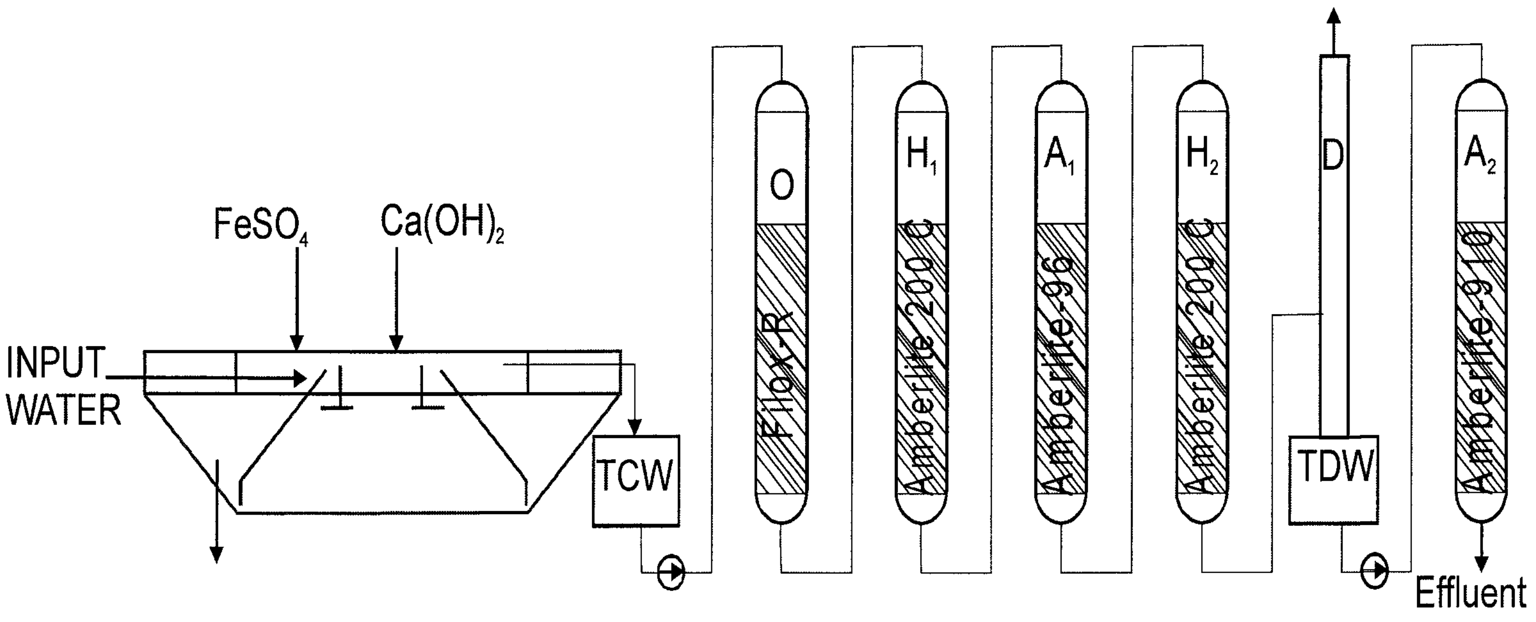


Figure 5.1-1 Schematic diagram of treatment with macroporous ion exchange media loaded in both stages. O represents the oxidizing column; H_1 and H_2 are hydrogen cation exchange columns in stage one and two resepectively; A_1 and A_2 are hydroxide anion exchange columns in stage one and two resepectively; TCW, D and TDW are tank for clarified water, decarbonizer and tank for decarbonized water.

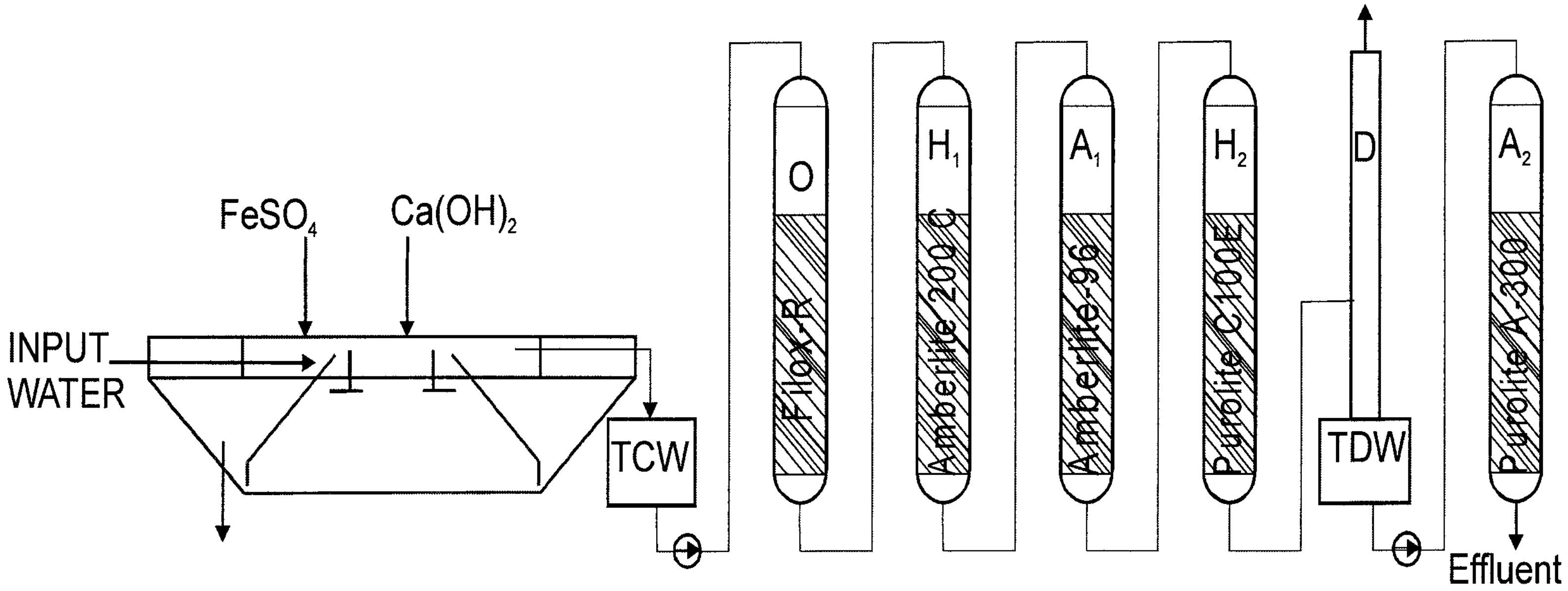


Figure 5.1-2 Schematic diagram of treatment with macroporous ion exchange media loaded in stage one

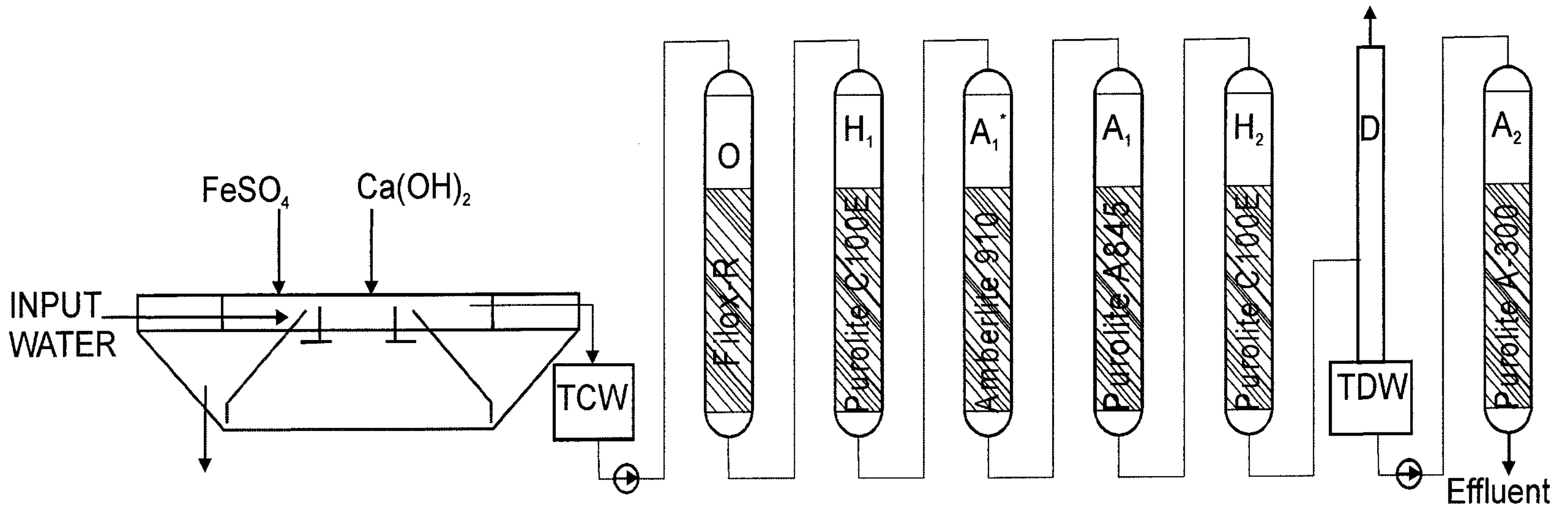


Figure 5.1-3 Schematic diagram of treatment with gel-type ion exchange media loaded in both stages and additional Cl-filter with macroporous anion exchange resin

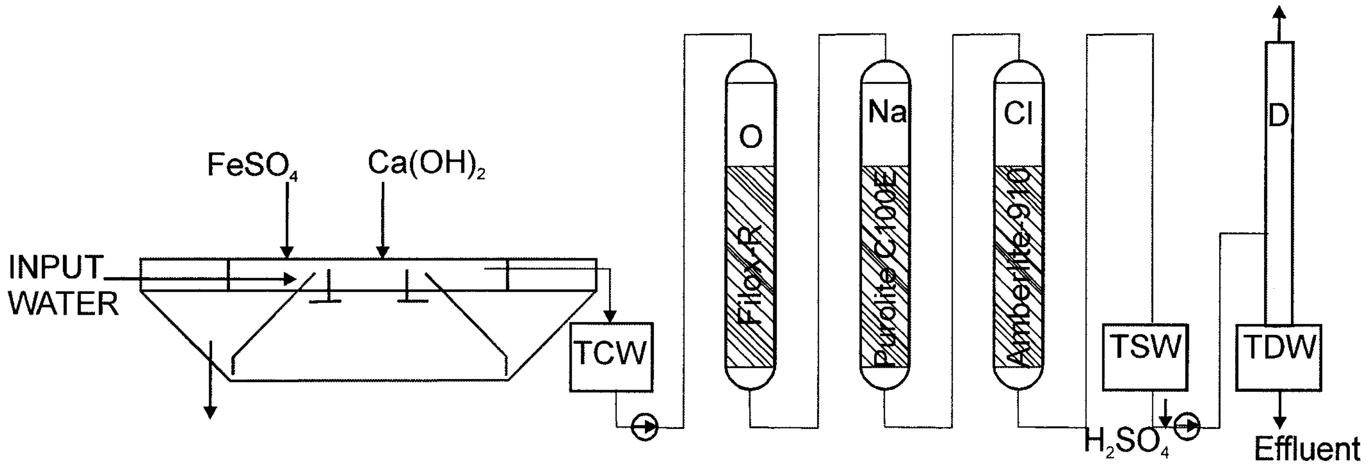


Figure 5.1-4 Schematic diagram of Na-Cl ion exchange process for softening and arsenic removal

5.2 Waste handling

Although the pre-oxidation medium Filox-R does not create any concern in terms of hazardous waste disposal, both the ion exchange resin and spent regeneration solution (from the ion exchange column) do. Filox-R is a naturally occurring ore, which serves as a catalytic filter media. It normally requires only backwashing, but the use of oxidizers such as chlorine or potassium permanganate enhances its action. Filox-R is solid manganese dioxide. This media catalytically oxidizes As(III) to As(V) using dissolved oxygen in the water. It does not have safety and regulatory issues (USAEPA, 2003).

There are three types of waste: backwash water from pre-filters, spent regenerant, and spent media. The two most probable methods for disposal of backwash water from pre-filters are indirect disposal through a POTW (Publicly Owned Treatment Works) or by settling the solids, recycling the supernatant, and sending the solid sludge to a landfill (not a hazardous waste landfill). Regarding the brine used in IX regeneration, there are two waste disposal options. Spent brine that contains less than 5.0 mg/L of arsenic (EPA, 2003) can either be disposed of via indirect discharge to Publicly Owned Treatment Works or treated onsite.

When indirect discharge is not an option, the system must deal with the waste on-site. The most common approach for treating brine waste (containing less than 5.0 mg/L of arsenic) is chemical precipitation with iron-based salts and subsequent solids thickening. Thickening can be conducted using a settling basin, or for more rapid results, mechanical dewatering equipment. The brine decant can then be sent to an evaporation pond (USA EPA, 2003).

Spent brine used in the regeneration of arsenic-laden resin may be classified as hazardous. Therefore, manipulating the chemical form of the waste on-site constitutes treatment of a hazardous waste, which has extensive permit requirements and cost implications. As a result, when the brine waste stream contains over 5.0 mg/L of arsenic, indirect discharge to a POTW (Publicly Owned Treatment Works) is considered the only viable option for small utilities. It is because out of the two options, treating high concentration arsenic laden sludge on site is considered expensive. When this option is unavailable, on-site regeneration of arsenic-laden resin should not be performed. Rather, the resin should be disposed of at a municipal solid waste landfill and replaced with fresh resin (EPA, 2003).

The appropriate disposal method for spent resin is dependent on the results of the TCLP (Toxicity Characteristic Leaching Procedure). The TCLP is for solid phase leachability for the spent resins using acetate at pH 5. Solid waste streams are subject to the Toxicity Characteristic Leaching Procedure (TCLP). This test is used to simulate the potential for leaching in a landfill setting. The TCLP leachate (liquid from solid wastes) must be lower than the TC value (5.0 mg/L) in order for the waste to be classified as non-hazardous (USA EPA, 2003).

Complete detoxification of arsenic laden sludge can be achieved by producing scorodite. Traditionally scorodite is produced by the precipitation from arsenic-rich solutions in pressurized vessels at a temperature between 150 and 200^{0}C. Recent research has made this even easier, at ambient pressure. Droppert D J (2001) describes the precipitation-production of crystalline scorodite ($FeAsO_4.2H_2O$) from arsenic-rich sulphate-based metallurgical solutions at ambient pressure (95° C). Arsenic is precipitated by means of a controlled precipitation technique in which the supersaturation of the solution is carefully controlled. By controlling the supersaturation in the presence of seed material, the formation of amorphous ferric arsenate is prevented. Scorodite is known to be the most stable As(V) compound and is therefore preferred as a host mineral for arsenic immobilization.

For all schemes of water treatment units discussed earlier in section 5.1, the spent regeneration solutions will contain desorbed organic substances in addition to arsenic. The presence of dissolved organic substances in the spent regeneration solutions will complicate matters, and in a number of cases will inhibit their utilization according to traditional waste treatment and disposal techniques. For this reason, the following schematic diagrams of the utilization of spent regeneration solutions from water softener and treatment units that were modified in relation to the presence of desorbed organic substances.

Figure 5.2-1 shows the schematic diagram of the utilization of spent regeneration solutions from Na-Cl ionization softener unit equipped with a macroporous anion exchange media chloride filter. The Na-filter operates in the softening regime while the Cl-filter is in the regime of the sorption of arsenate ions and DOM. In actual conditions, the Cl-filter becomes exhausted with respect to DOM and arsenate ions at the same time.

The sodium-cationic exchange media was activated with a 15% NaCl solution and the chloride anionic exchange media with a 10% to 15% NaCl solution in a mixture with 1% to 1.5% NaOH solution respectively. Spent solutions from sodium and chloride filters contained NaCl as well as Ca^{2+}, Mg^{2+} and SO_4^{2-}, DOM, OH^- respectively. The concentrated part of the spent solutions from sodium and chloride filters was collected and supplied to the clarifier.

If magnesium chloride, which is one of the rapid-acting coagulants, is used as the coagulant, it is preferably used in an amount of about 0.3 to 0.8% (Ko et. al., 1987). Considering that arsenic and dissolved organic substances mainly sorb on to the settling flocs of $Mg(OH)_2$, the $MgCl_2$ was dosed into the clarifier when the Mg^{2+} concentration in the clarifier appeared to be inadequate.

As a result, the crystallization and precipitation of $Mg(OH)_2$, $CaSO_4$ and $CaCO_3$ took place in the clarifier. Adding NaCl up to the initial concentration, after Ca and Mg compounds are removed, restored the softened solution. This was then divided into two volumes. One of them was assigned for regeneration of Na-cationic filter. Therefore, in order to prevent carbonation of the cationic exchange media, the residual concentration of alkalinity in the recovered regeneration solution was neutralized by acidification. The 2nd volume was assigned for the regeneration of chloride-form anion exchange media. Therefore, adding NaOH alkali to the initial concentration of 1% to 1.5% restored the regeneration solution.

The proposed technology enabled 96% removal of arsenic and 80% DOM to be achieved. The residual concentration of arsenic and DOM in the recovered regeneration solution did not inhibit the regeneration of Na-Cl-filters. Figure 5.2-2 shows the schematic diagram of the utilization of spent regeneration solution from the chemical treatment unit with macroporous ion exchange media. Spent regeneration solutions from H-cationic and OH-anionic filters were collected in a clarifier. The solutions contained Ca^{2+}, Mg^{2+}, Na^{+}, $HAsO_4^{2-}$, Cl^{-}, SO_4^{2-}, CO_3^{2-}, SiO_3^{2-}, OH^{-} as well as desorbed DOM. The spent regeneration solutions were collected in a clarifier and treated with $Ca(OH)_2$ and Mg_2SO_4. This resulted in the crystallization of $CaSO_4$ and $Mg(OH)_2$. The crystallization was possible not only because of the mutual reactions among spent regeneration solutions but also due to reagent treatment. The latter provided production of developed surfaces of $Mg(OH)_2$ flocs. The dose was chosen on the basis of specific sorption capacity of $Mg(OH)_2$ with respect to DOM i.e. 3 mg of oxidizability for 1 mg of precipitate.

The extent of DOM removal in the clarifier was 60% to 70% and arsenic was over 93%. The residual concentrations of DOM and arsenic did not seem to inhibit the softening of the spent regeneration solutions by the Na-cationic filter of the wastewater treatment unit, concentrating in the vapor diffusion apparatus, and recycling the concentrate (NaCl) for regeneration of the Na-cationic filters of both initial water treatment and spent regeneration solution treatment units.

Figure 5.2-3 shows the schematic diagram of the utilization of spent regeneration solutions from the additional filter with macroporous media. The spent regeneration solution containing NaCl, NaOH, arsenate, sulfate and DOM was collected in a clarifier. The reagent treatment was conducted in two stages. In stage 1, the spent regeneration solution was treated with ferric chloride in the quantity equivalent to the quantity of hydroxyl ions. Arsenic will be sorbed onto the flocs of crystallizing ferric hydroxide. The arsenic removal efficiency was found to be about 95%. The residual concentration of arsenic did not seem to be a concern in terms of regeneration efficiency. After having the precipitate separated, the solution was treated with $Ca(OH)_2$. In this stage, the sulfate ions were removed and the initial hydroxyl ions recovered (pH range of 10.5 to 11.0). The recuperated solution was found to contain chloride and hydroxyl ions identical to the initial concentration. The reactions are as follows:

$FeCl_3 + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ + 3Cl^-$

$3H^+ + 3HCO_3^- \leftrightarrow 3H_2CO_3$

$Ca(OH)_2 + H_2CO_3 \leftrightarrow CaCO_3 + 2H_2O$

$Ca(OH)_2 + Ca(HCO_3)_2 \leftrightarrow 2CaCO_3 + 2H_2O$

$2Ca(OH)_2 + 2SO_4^{2-} \leftrightarrow 2CaSO_4 + 4OH^-$

$2Ca(OH)_2 + 4SO_4^{2-} + 4H_2O \leftrightarrow 2Ca(HSO_4)_2 + 8OH^-$

The precipitates from all the proposed schemes were collected in a pressure vessel, heated and then subjected to the EPA recommended TCLP test. As can be seen from Table 5.2-1, the arsenic concentration was well below the regulatory limit (which is 5 mg/L).

Table 5.2-1 TCLP result summary for arsenic

Test method	EPA Method 1311
TCLP maximum allowable concentration for arsenic (mg/L)	5.00
Number of samples	8
Mean result (mg/L)	1.50
Standard deviation	0.29
95% confidence limit (mg/L)	1.44 -1.55
TCLP Result	Passed

The bulk of the liquid waste was reused as discussed earlier and the collected sludge was relatively small for treatment by a small pressure vessel and subsequent crystallization of the sludge.

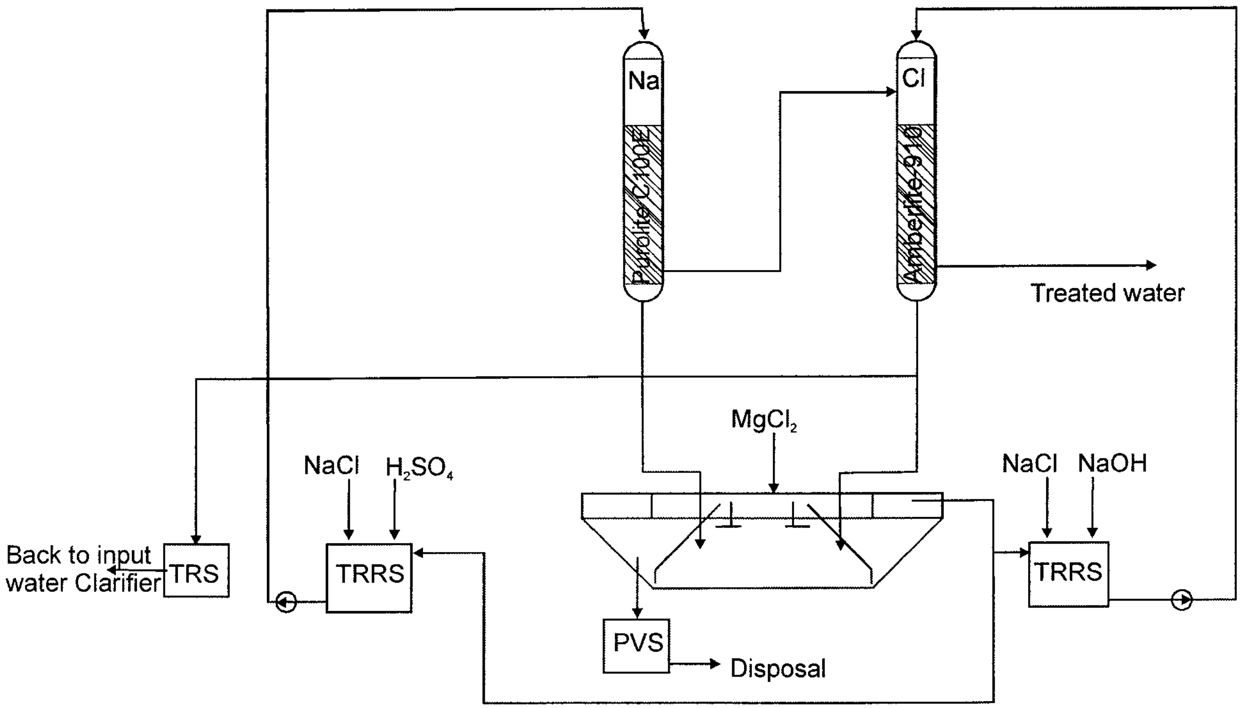


Figure 5.2-1 Schematic diagram of the utilization of spent regeneration solutions from water softeners with macroporous chloride form anion exchange media. TRRS represents the tank for recovered regeneration solution; PVS is a pressure vessel for sludge treatment.

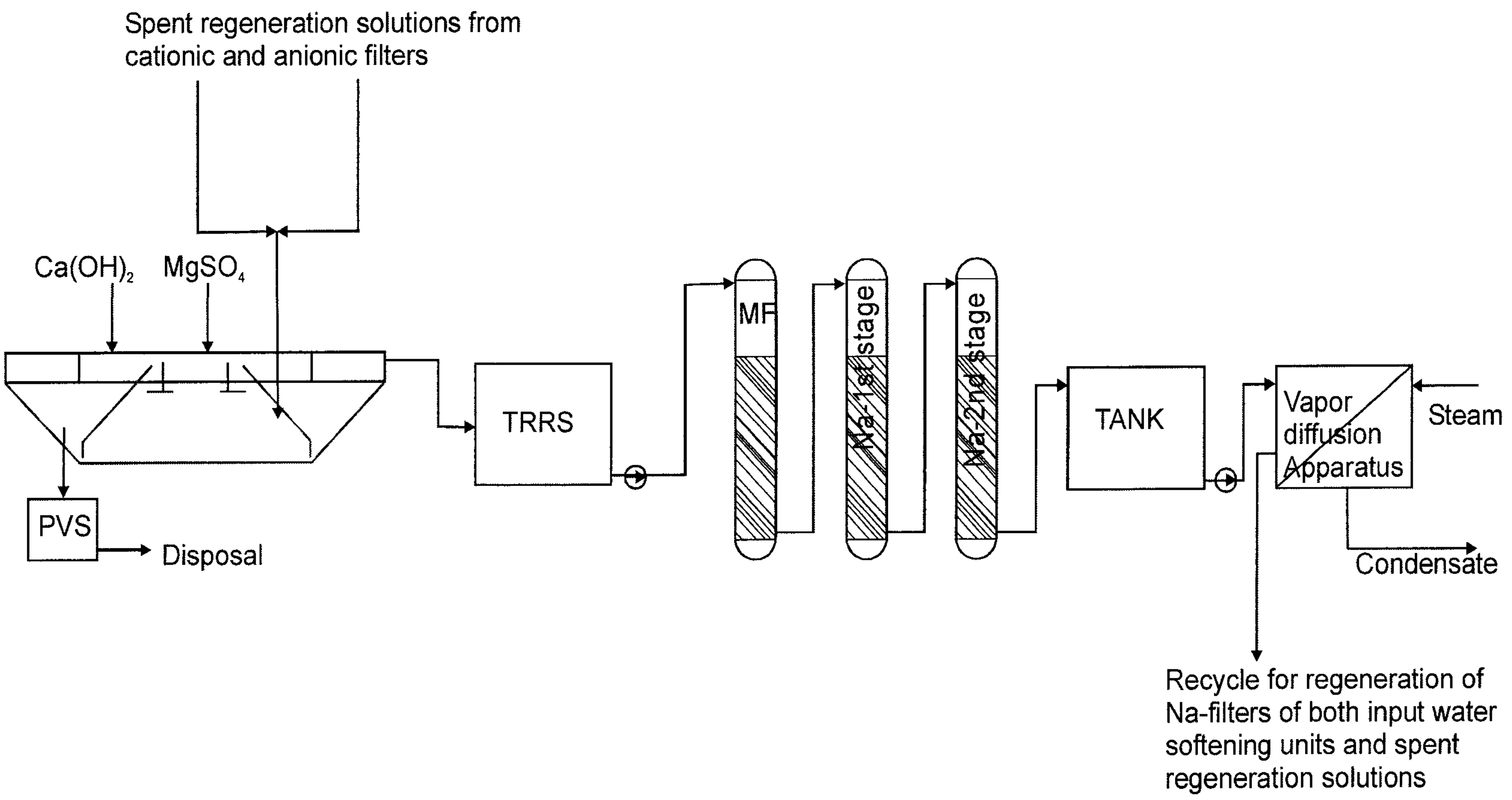


Figure 5.2-2 Schematic diagram of the utilization of spent regeneration solutions from chemical treatment units with macroporous media

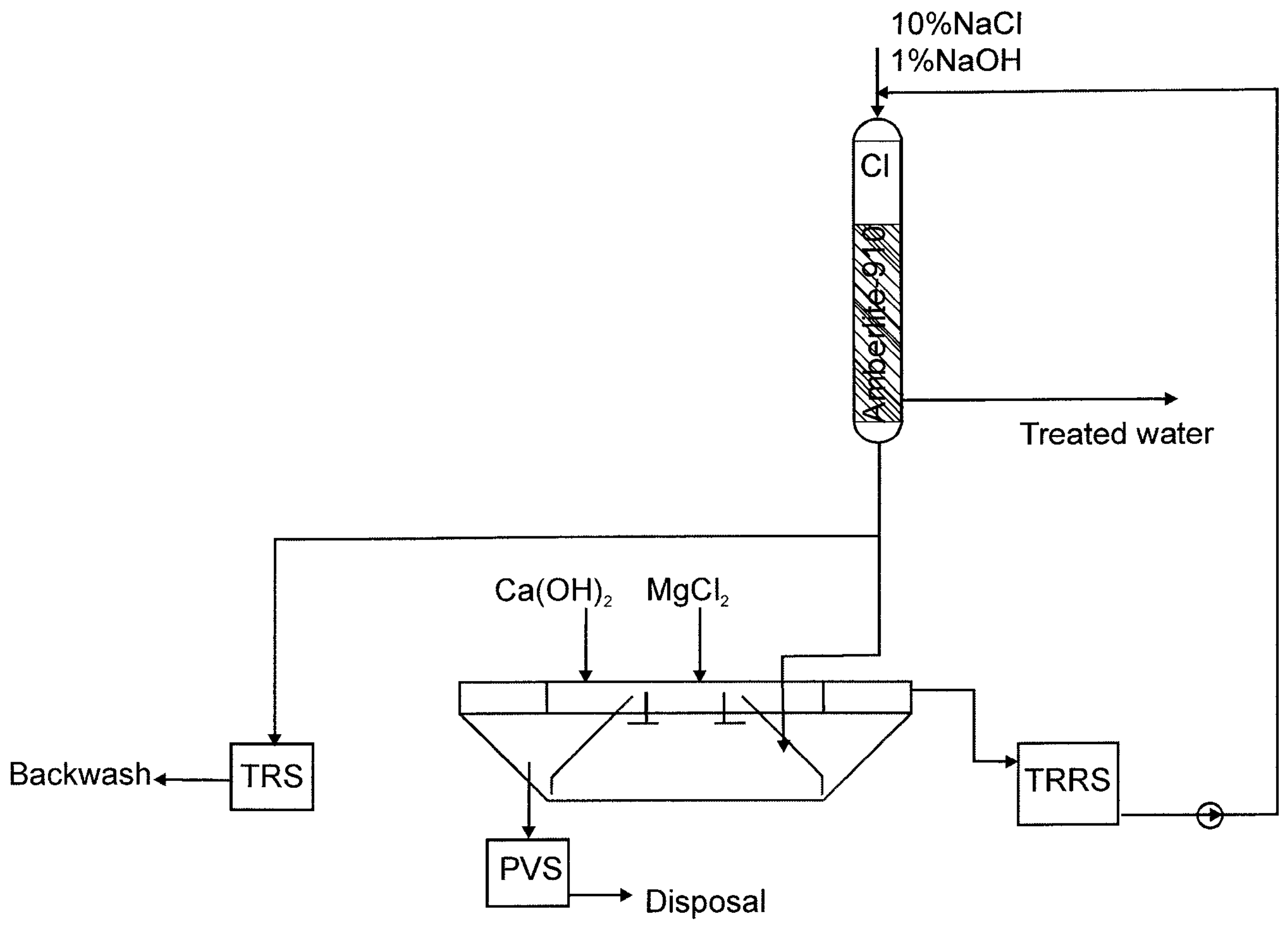


Figure 5.2-3 Schematic diagram of the utilization of spent regeneration solutions from the additional filter with macroporous media

5.3 Technical, economic, and environmental efficiency of using macro-porous ion exchange media

Environmental pollution does great economic damage. Recently, much attention has been paid worldwide to the development of processes that produce as little waste as possible. When a zero or low discharge water system is designed it is important to make a realistic estimate of its economic efficiency, taking into account the reduced environmental damage. Methodology for the calculation of economic efficiency in this section was developed by Abdullaev et al. (1992). Detailed calculation of the cost analysis of the use of ion exchange is presented in Appendix A.1. Annual arsenic treatment costs in the US (Gerald, 2000) and those estimated in this section for use in Bangladesh are given in Table 5.3-1. The calculation was based on a flow rate of 0.5 m^3/h for 1500 people. Figures 5.3-1 and 5.3-2 show ion exchange capital costs and annual operation and maintenance costs.

Table 5.3-1 Annual arsenic treatment cost in the US and Bangladesh

Item	**Country**	
	U.S.A. (US $)	**Bangladesh (US $)**
Treatment Capital Costs	29,332	1,947
Treatment O&M Costs	8,924	50
Waste Disposal Capital Costs	3,955	383
Waste Disposal O&M Costs	412	21
Annual Costs	1 2,478	636

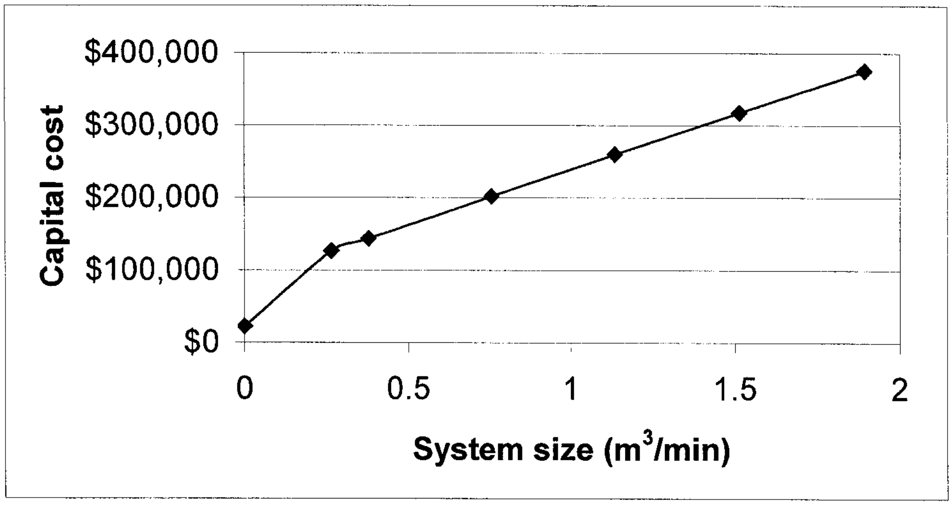


Figure 5.3-1 Ion exchange capital costs (EPA, 2000)

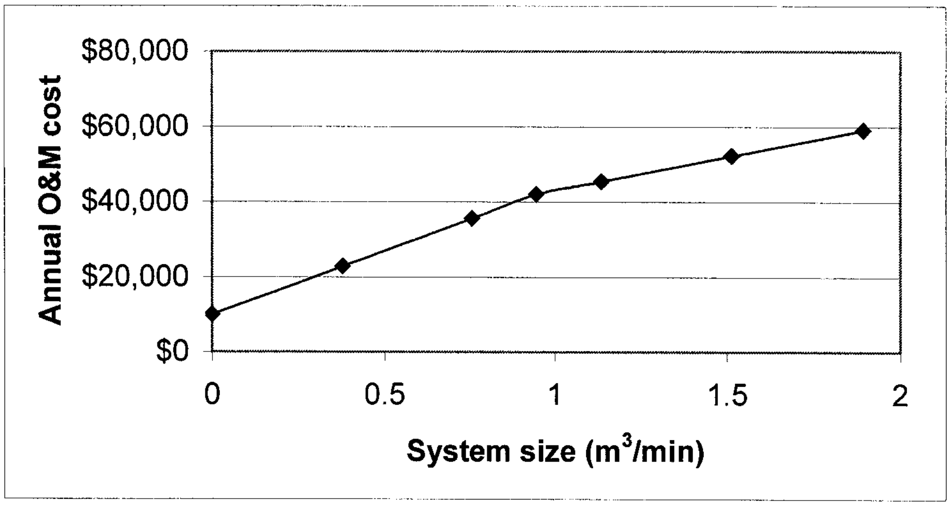


Figure 5.3-2 Ion exchange annual O&M costs (EPA,2000)

As can be seen from Table 5.3-1, both capital costs and operating & maintenance costs vary significantly. This is primarily due to the low cost of materials, equipment, chemicals and labor in Bangladesh. This indicates that expensive technologies such as ion exchange can be implemented in poor countries such as Bangladesh.

Economic efficiency is not the cost analysis alone but the difference between the overall benefit and the total cost. Such benefits come from lower mortality, morbidity, risk reduction, substitution of surface water with groundwater etc. Detailed calculation of economic efficiency is given in Appendix A.1. The economic efficiency amounted to about $9,400 Cdn per year for 1500 people. This figure is quite reasonable. Well-documented calculations of this kind by others are scarce.

6. CONCLUDING REMARKS

As stated in the introduction, this research work does not attempt to cover the complex of geological, economic and legal problems connected with the remediation of arsenic from groundwater. The investigation was limited to the problems of the ion exchange technology when removing arsenic from groundwater in the presence of DOM. There has been no discussion of the origin and mechanism underlying the arsenic problem or the development of waste-free techniques for the preparation of drinking water from arsenic contaminated groundwater. In other words this research work did not focus on any waste-free techniques. Many of these problems have not yet been solved, although they are under study by others; some are still some way from being solved even now, and some will only be solved in the far-distant future.

Despite all of the above, the main problems of removing arsenic from groundwater by ion exchange have been taken into consideration in the research. The coexistence of arsenic and DOM is not a region specific issue. This is a general case where nonanthropogenic arsenic is detected in its dissolved form in the groundwater. Therefore, this research work is applicable anywhere in the world. Various case studies of the Bangladeshi groundwater served to be the most pronounced examples of the coexistence of arsenic and DOM. The planning of the experiments has been worked out sufficiently well to enable a start to be made on the study of the peculiarities of arsenic removal by ion exchange in the presence of DOM. The application of the results in Bangladesh is an added contribution to the theoretical development carried out in the research work.

6.1 Scientific novelties

- Conception of the sorption of a high concentration of arsenic, in the presence of dissolved organic substances, by macroporous ion exchange media has been worked out both theoretically (regression models) and experimentally.
- The necessity of removing DOM has been technically substantiated when removing arsenic by softeners in a Na-Cl-ionization scheme with the Cl-filter loaded with macroporous anionic exchange media. The dynamics of arsenic removal by anion exchange media in alkaline medium has been studied implementing DOE (design of experiments) and analysis while deriving polynomial dependences, which inter-relate the factors that impact the arsenate exchange capacity and effluent arsenic concentration.
- The possibility of removing acidic group of DOM selectively and thus enhancing arsenic removal efficiency has been established by chromatographic separation and identification of DOM in water being investigated. The anionic mechanism of sorption, in alkaline medium, with respect to arsenates and their competitor DOM has been established. Optimum conditions for regeneration of macroporous

anion exchange media have been determined: NaCl consumption being 300 kg/tonne, concentration of NaCl solution being 10% and the ratio of percentile concentration of NaCl to that of NaOH being 10.

- Sorption of arsenates in the presence of DOM onto macroporous anion exchange media in two-stage treatment processes has been studied. Several variants of the treatment units have been worked out depending on the level of mineralization and concentration of DOM in water being treated, and also considering the condition for implementation of the process (existing or design-stage treatment units): 1) loading H-cationic and OH-anionic exchange filters of both stages with macroporous ion exchange media; 2) loading only the first stage filters with macroporous ion exchange media; 3) adding a separate filter with macroporous anion exchange medium in the process sequence that has operated on gel-type resins.
- From 60% to 66% of arsenic can be removed in the first stage of two-stage treatment unit. Empirical dependence has been formulated of the arsenate exchange capacity of weakly basic anion exchange media on influent DOM, NaOH consumption and the ratio of sulfate to chloride.
- A mathematical model has been built that characterizes the dependence of arsenate exchange capacity and effluent arsenic concentration on the consumption of regeneration solution, influent

DOM and filtration velocity in acidic medium. In acidic medium, DOM of various groups sorbed efficiently and the basic mechanism was molecular sorption. The factors that influence the exchange capacity and effluent water quality have been optimized.

- Waste handling techniques for softeners as well as treatment units have been proposed. A reagent based technology for the treatment of spent regeneration solutions by $Ca(OH)_2$ and $MgCl_2$ (or $MgSO_4$) has been worked out.

6.2 Practical values

- The use of the results of the investigations carried out are not limited to any geographical location such as Bangladesh but are applicable worldwide.
- The practicality of this research work is not only the potential implementation of arsenic removal by macroporous ion exchange media in a rural village (Nakol, Magura) in Bangladesh but also at some industrial areas. As part of this research work, 12 tubewells were tested in this area. Groundwater analysis showed a dissolved total arsenic concentration over 300 ppb and that of DOM in the range of 9 to 21 mg/L as COD. Onsite batch tests showed satisfactory arsenic removal (below 10 ppb of effluent arsenic). Installation of one such unit is ongoing. The reliability of the proposed regression equations will be tested by the performance of this full-scale

treatment unit in the near future. Some thermal power stations in Bangladesh might also benefit in their use of surface water, which is highly contaminated with dissolved organic matter.

- The practicality of the treatment schemes with respect to whether villagers would be able to make use of them is counted on the fact that there is at least one high school in each village of Bangladesh. A high school chemistry teacher has a university degree. Besides, the unit operators are not expected to understand the mechanisms underlying the treatment techniques. No doubt, the villagers would be able to do the kind of robotic jobs required for this purpose. It is noteworthy that ion exchange is the easiest to handle technique of all of the established technologies. Ion exchange reduces effectively the effluent arsenic concentrations well below the Bangladeshi standard (50 ppb). A 10 ppb effluent level while maintaining the minimum costs involved would only be welcome.

6.3 Recommendations for future work

- The use of contaminated groundwater, in preference to its simulation in a lab, is recommended to carry out investigations such as the determination of a coagulation regime. The use of trilinear diagrams is recommended in the investigation procedures, which would allow the effects of different factors to be studied, revealing the optimum ranges of arsenic reduction and, making apparent the relative efficiency of the various reagents and the necessary dosing ratios.

- Conduct full-scale studies to check whether the regression equations are statistically significant thus promoting them to the status of 'theory'. Although lab-scale or semi-scale studies provide regression equations that are an essential start and the bulk part to get to real theories, such equations are often considered to be empirical generalization. The practicality of these regression models should be further validated at implementation stages. The regression equations have their limitations such as the number of factors and levels. The increasing of factors and their levels can be recommended if time and money permit to do so.
- Investigate the potential for the use of the regression models in industries including but not limited to metallurgical, textile, leather, oil refining and thermal power stations. Thermal power stations are probably the most water-consuming industries. They use surface water, which is not only highly polluted with dissolved organic matter but also with arsenic.
- Analogous regression models need to be built for mixed resins. Composition-property diagrams are widely used in chemical technology research when studying the efficiency of processes depending only on component ratios.
- An easy to use guide of arsenic removal should be produced.

7. BIBLIOGRAPHY

1. Abdullaev K M, Malakhkov I A, Dyachov V I, Sirotkina I S, Poletaev L N. 1980. “Chromatographic separation of DOM from municipal wastewaters subjected to Na-cationization.” *Chemistry and water technology* 2(1): 53-56. (Material in Russian).
2. Abdullaev K.M., I.A.Malakhov, 1992. *Urban Waste Waters*. Chichester, West Sussex: Ellis Horwood.
3. Abrams J M. 1982. “Organic fouling of ion exchange resins”. In *Water and Wastewater. Physicochem. Meth.*, Amsterdam, pp. 213-224.
4. Aerni H R, Kobler B, Rutishauser B V, Wettstein F E, Fischer R, Giger W, Hungerbuhler A, Marazuela M D, Peter A, Schonenberger R, Vogeli A C, Suter M J, Eggen R I. 2004. “Combined biological and chemical assessment of estrogenic activities in wastewater treatment plant effluents.” *Anal. Bioanal. Chem.* 378(3): 688 – 696.
5. Ahnazarova S L, Kafarov V V. 1978. *Optimization of experiments in chemistry and chemical technology.* Moscow, U.S.S.R.: Vishaya Shkola.
6. Aiken G R, McKnight D M, Thorn K A, and Thurman E. M. 1992. “Isolation of hydrophilic organic acids from water using nonionic macroporous resins.” *Org. Geochem.* 18(4): 567–573.
7. Alain G. 1988. “Polymer supports with high accessibility.” *Pure & Appl. Chem.* 60(3): 365-376.

8. Alimova A T., Korenman Y. I., Taldikina S N. 1981. "Study of the sorption of nitro and alkyl phenols by microporous ion exchange media." *Journal of Colloidal Chemistry* 43(3): 455-463. (Material in Russian)

9. Alimova A. T. , Korenman, Y. I. 1989. "Sorption of phenol by macroporous anion exchange media AB-17-2P." *Journal of Colloidal Chemistry* 41(3): 563-565. (Material in Russian)

10. Alken Murray Corp. 2003. *Interpreting Water Analysis Test Results*, New Hyde Park, N.Y. : Alken Murray Corp.

11. Altshuler G.N., Staroverova V. I., 1989. "Thermodynamics of the exchange of organic ions and the sorption of nicotinic acid on macroporous anion exchange media." *Journal of Physical Chemistry* 53(4): 1000-1002. (Material in Russian).

12. American Society for Testing and Materials. 1984. *Standard Methods of Test for Acidity or Alkalinity of Water.* Philadelphia: American Society for Testing and Materials

13. Ashirov A. 1983. *Ion exchange treatment of wastewaters, solutions and gases.* Moscow: Chemistry (Material in Russian).

14. Ayten S and Azmi T. 2004. "Immobilization of Lipases on Different Carriers and Their Use in Synthesis of Pentyl Isovalerates." *Taylor & Francis* 34(2): 169 - 178.

15. Azanova V. V. and Hradil J. 1999. "Sorption properties of macroporous

and hypercrosslinked copolymers." *React. Funct. Polym.* 41(4): 163-175.

16. Babichenko, S., Poryvkina L., Frank de Vos, and Hans Hoevenaar, 1999 *Diagnosis of organic compounds in water quality monitoring*. Moscow.
17. Banerjee D.M, McArthur, J.M., Hudson-Edward K.A., Mishra R., Purohit R., Ravenscroft P., Cronin A., Howarth R.J., Chatterjee A., Talukder T., Lowry D., Houghton S., Chadha D.K. 2004. "Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications." *Applied Geochemistry* 19: 1255–1293.
18. Bidnaya D.S., Ignatov U.I., 1986. "Influence of solutions on the sorption of aromatic amines." *Theory and practice of sorption processes* 18(3): 106-109 (Material in Russian).
19. Bodo S, Joachim W. (2003), *Experiments in Environmental Economics – a Survey.* FEMM Working Paper Series, 03010. Magdeburg.
20. Boullemant A, Vigneault B, Fortin C and Campbell P. 2004. "Uptake of Neutral Metal Complexes by a Green Alga: Influence of pH and Humic Substances." *Australian Journal of Chemistry* 57(10) 931–936
21. Bullock J. 2002. *Nitroxy Radical Catalyzed Oxidation of Carbohydrates.* Colorado: National Renewable Energy Laboratory Golden.
22. Calmon C. 1986. "Recent developments in water treatment by ion exchange." *Reach. Polym.* 4(2): 131-146.

23. Carlyle R. M. 1982. “Use of synthetic adsorbents in chemical processes.” *Effl. Wat. Treat. J.* 22: 55-59.

24. Carniel A, Bianco C, Zanin N., 1998. “Determination of organic compounds in water: correlation between the Kuebel method (permanganate oxidizability) and TOC (total organic carbon).” (in Italian). *Boll Chim Igien* 49:223–226.

25. Clapp, C. E., Hayes M. H., and Swift. R. S., 1993. *Isolation, fractionation, functionalities, and concepts of structure of soil organic macromolecules*. Organic Substances in Soil and Water. Cambridge: Royal Society of Chemistry.

26. Clifford, D. A., Ghurye, A.G., Tripp, A.R. 1998. “Arsenic Ion exchange Process with Reuse of Spent Brine.” In *Water Research*. Denver: American Water Works Assoc.

27. Clifford, D.A., 1998. “Treatment Options for Removing Arsenic From Drinking Water in Small Communities.” In *Arsenic Pollution of Groundwater: Causes, Effects, Remedies*. Dhaka: Dhaka Community Hospital.

28. Clifford, D.A., 1999. “Arsenic Removal Options: Activated Alumina Adsorption, Anion Exchange, and Iron Coagulation-Microfiltration.” In *Arsenic Technical Work*. Washington, D. C.: American Water Works Assoc.

29. Clifford, D.A., 1986. "Synthesis of Dual Mechanism Ion Exchange/Redox Resins and Ion Exchange/Coordinating Resins with Applications to Metal Ion Separations." In *Metals Speciation and Recovery*. Chicago, IL: International symposium.

30. Cornel, P. and Sontheimer H. 1986. "Sorption of dissolved organics from aqueous solution by polystyrene resins. Resin characterization and sorption equilibrium." *Chem. Eng. Sci.* 41: 1791-1800.

31. Dal, V.V. 1974. "Humic impurities of natural waters and their removal by ion exchange resins." *Water supply and sewerage* 4: 25-27 (Material in Russian).

32. Daniels S. L., Lloyd L. Kempe, Thomas J. Billy, and Alfred M. Beeton, 1965. *Detection And Measurement Of Organic Lampricide Residues.* Michigan: U.S. Bureau of Commercial Fisheries.

33. Davidov, A.T. Rudneva S.I. Ignatov U.I. 1987. "Study of the sorption rate of aromatic amines from acidic solvents." *Chemistry and chemical technology* 20(6): 940-942 (Material in Russian).

34. Don B and T. Neil Davis.1997. "Arsenate and Phosphates – Chemical Look-alikes." *Alaska Science Forum* 168.

35. Dore M. 1975. "Adsorption des amines aromatiques sur les echangeurs anioniques. " *Bull. Chim. Soc.* 9(10): 2339-2344.

36. DOW Corp. *DOWEX G-26 (H) Cation Exchange Resin*. 2002. Midland, Michigan: DOW corp.

37. Droppert D.J. and Demopoulos G.P., 2001. "Ambient pressure production of crystalline scorodite from arsenic-rich metallurgical effluent solutions." *Canadian Mining and Metallurgical Bulletin* .94(1051): 116-122.

38. EPA. Office of Water. 2003. *Arsenic Treatment Technology Handbook.* Cincinnati, OH: U.S. EPA.

39. EPA. Office of Water. 2000. *Technologies And Costs For Removal Of Arsenic From Drinking Water.* Washington D.C: U.S. EPA.

40. Ergojhin, E. E. 1979. *High permeable ion exchange media.* Alma Ata: Science (Material in Russian).

41. Exploring the Environment™ (ETE). 2003. Glossary: Alkalinity. Wheeling Jesuit University.

42. Ficklin W.H., 1983. "Separation of Arsenic (III) and Arsenic (V) in Groundwaters by Ion Exchange." *Talanta* 30(5): 371-373.

43. Frimmel, F. H., Assenmacher M., Sorensen M., Abbt-Braun G. and Grabe G.,1999. "Removal of hydrophilic pollutants from water with organic adsorption polymers." *Chem. Eng. Proc.* 38: 601-610.

44. Gerald, D. S. 2000. *Arsenic in Drinking Water Rule Economic Analysis.* Washington D.C: U.S. EPA.

45. Ghurye, A.G., Clifford, D. A., Tripp, A.R. 1998. "Arsenic Removal by Ion Exchange with and Without Brine Reuse." In *Inorganic Contaminants.* San Antonio, TX: American Water Works Assoc.

46. Gjessing, E. 1970. “Ultra filtration of Aquatic humus.” *Environmental Science and technology* 4(5): 437-438.

47. Gray, P.A., Bonin T.A., Ahmed M.F. 2004. “Dhaka’s waterways: Save the Buriganga River Program.” In *Water Quality Research.* Burlington: Canada Center for Inland waters.

48. Gromoglacov, A., Kopilov A., Subbotina N, Mamet V. Pilshikov A. 1977. *Water Preparation. Processes and Apparatus.* Moscow: Vishaya Shkola (Material in Russian).

49. Gusler, G. M., Browne T. E. and Cohen Y. 1993. “Sorption of organics from aqueous solution onto polymeric resins.” *Ind. Eng. Chem. Res.* 32: 2727-2735.

50. Hand, D. W., Ali A. N., Bulloch J. L., DeBraske M. L., Crittenden J. C. and Hokanson D. R.1999. “Adsorption equilibrium modeling of space station wastewaters.” *J. Environ. Eng.* 125: 540-547.

51. Hartmeier, W. 1992. “Bioprocesses with integrated product removal.” In: *Downstream Processing in Biotechnology.* New Delhi: Tata McGraw-Hill.

52. Heitzsch, O., Stephan H., Gloe K., Muhl P. and Hellmig R. 1994. “Removal of ethoxylated aliphatic amines from zinc containing effluents by adsorption on macroporous resins.” *Chem. Eng. Technol.* 17: 30-33.

53. Hering, J., Pen-Yuan C., Wilkie J A. 1997. “Arsenic Removal from Drinking Water During Coagulation.” *Journal of Environmental Engineering* 123(8): 800-807

54. Hinkelmann,.K, Kempthorne.O. 1994. *Design and Analysis of Experiments*. New York :John Wiley & Sons Inc.

55. Homer, V. J. 1996. “Aggregation patterns from humics of different chemical compositions.” In *Abstracts of Invited Papers*. of the 7th IHSS International Meeting. St. Paul, MN.

56. Homer, V. J. 1998. “Fractal probes of humic aggregation: Scattering techniques for fractal dimension determinations.” pp. 75–112. In *Fractals in Soil Science*. Washington, D.C: CRC Press.

57. Homer, V. J., J. F. McCarthy, and Z.-H. Chen. 1992. *Fractal dimension: A probe of humic aggregation properties*. Minneapolis: Clay Minerals Society

58. HPLC Columns & Bulk Resins. “Hamilton PRP-X400 Columns for the Analysis of Glyphosate in Drinking and Source Water.” 2004. Hamilton: HPLC Columns & Bulk Resins.

59. Huang M. and Schnitzer M. 2002. “Interactions of Soil Minerals with Natural Organics and Microbes.” *Soil Sci. Soc. Am. Spec.* Publ. 17, Madison, Wisconsin.

60. Huizhong Ma, Herbert E. A and Yujun Y. 2000. *Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent.* In: *Doctoral thesis*, Department of Civil and Environmental Engineering, University of Delaware, Newark, USA.

61. Ian R. B., Brusotti G., Masato M. and Ley S.V. 2002. Synthesis of nornicotine, nicotine and other functionalised derivatives using

solid-supported reagents and scavengers. *Journal of the Chemical Society, Perkin Transactions 1*(2): 143 - 154

62. International Farakka Committee. 2003. *National documentation on the problems of arsenic and Farakka*. New York: International Farakka Committee Inc., U.S.A.

63. Johnston R., Heijnen H., 2004. *Safe Water Technology for Arsenic Removal.* Dhaka, Bangladesh: UNICEF and WHO Environmental Health.

64. Jonsson, L., Lundell L. *2004. "Targeting safe aquifers in regions with arsenic-rich groundwater in Bangladesh. Case study in Matlab Upazila." Uppsala: Swedish University of Agricultural Sciences, SLU External Relations.*

65. Kang. M., Kawasaki.M., 2000. "Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes." In *Membranes in Drinking and Industrial Water Production.* Italy: L'Aquila.

66. Kang, XX, Oka K., 1989. "Acid-base fractionation of lipophilic components in human urine and their high-performance liquid chromatography equipped with multichannel ultraviolet detector: an application to xanthine derivatives." *Yakugaku Zasshi* 109(4):274-279.

67. Karickhoff, S.W., Brown, D.S., and Scott, T.A., 1979. "Sorption of hydrophobic pollutants on natural sediments." *Water Res.* 13: 241-248.

68. Kehew, A.E. 2001. *Applied Chemical Hydrogeology.* New Jersey: Prentice-Hall.

69. Keller, Michael C. 2005. "Basic Ion Exchange for Residential Water Treatment." *WC&P* 47(11): 17-21.

70. Khanna, P.K., Ludwig B. and Raison R.J. 1996. "Comparing modelled and observed effects of ash additions on chemistry of a highly acid soil." *Australian Journal of Soil Research* 34(6): 999 - 1013.

71. KIM and KIM, 1998. "Effects of nitrogenous components of urine on sperm motility: an in vitro study." *International journal of andrology* 21(1):29.

72. Kinniburgh DG, Smedley PL. 2001. *Groundwater studies of arsenic contamination in Bangladesh*. U.K: British Geological Survey.

73. Ko (Nara, JP); Matsumura; Yasushi (Nara, JP);Sengoku; Koji (Nara, JP);Nagatome; Yoshiaki (Nara, JP), 1987. *Process for preparing tofu charged into a container*. United States Patent 4678677.

74. KÖgel-Knabner, I., W. Zech, and P. G. Hatcher. 1988. "Chemical composition of the organic matter in forest soils: The humus layer." *Z. Pflanzenernähr. Bodenkd.* 151:331–340.

75. Korenman, Y. I. Alimova A T., Taldikina S N., Nurtdinova L D. 1989. "Extraction of small quantities of nitrophenols from water by macroporous ion exchange media." *Journal of Analytical chemistry* 34(12): 2425-2427 (Material in Russian).

76. Kotz, J. & Treichel P., 1999. *Chemistry & chemical reactivity.* Fourth edition. New York: Harcourt Brace.

77. Kuckuk R. and Burba P. 2000. "Analytical fractionation of aquatic humic substances by metal affinity chromatography on iron(III)-coated cellulose." *J Anal Chem.* 368(7): 689-696.

78. LaMOTTE COMPANY. 2001. *1200 Colorimeter, Sulfate.* Chestertown, Maryland: LaMOTTE COMPANY

79. LaMOTTE COMPANY. 2003. *1200 Colorimeter, Phosphate.* Chestertown, Maryland: LaMOTTE COMPANY.

80. Leenheer, J.A., 1996. "Isolation, and characterization of hydrophilic constituents of dissolved organic matter in water." In *Natural Organic Matter Workshop.* France: Poitiers.

81. Levchenko, T M, Savchina L A. 1982. "Sorption of DOM by ion exchange media." *Chemistry and water technology* 4(6): 494-507. (Material in Russian).

82. Lide, D., 1992. *CRC Handbook of Chemistry and Physics.* Boca Raton, FL: CRC Press.

83. Loraine A. Huchler, 2002. MarTech Systems, Inc., Lawrenceville, NJ. "Non-chemical Water Treatment Systems: Histories, Principles and Literature Review" *IWC* 02(46).

84. Maity N., Payne G. F. and Chipchosky J. L. 1991. "Adsorptive separations based on the differences in solute-sorbent hydrogen-bonding strengths." *Ind. Eng. Chem. Res.* 30: 2456-2463.

85. Malakhov, I.A. Poletaev L.N. Yakobishbili I. S, Amirkhanova I.A. 1987. "Study of the sorption of DOM from city wastewaters." *Theory and practice of sorption processes* 19: 63-66. (Material in Russian).

86. Malakhkov, I.A. Abdullaev K.M., Poletaev L.N. Sobol A.S. 1988. *Water treatment at thermal power stations using municipal wastewaters.* Moscow: Energoatomizdat (Material in Russian).

87. Malakhov I A, Poletaev L N, Saiduzzaman A K. 1992. "Study of the desalination of tertiary treated municipal wastewater by macroporous ion exchange media." *Journal of chemistry and water technology* 14 (12): 919-924 (Material in Russian).

88. Manza, I. A., Golubchenko I. T. and Bezuglaya A. K 1983. "Gas-liquid chromatographic determination of products from alkylation of phenol by 1-decene." *Springer Verlag* 19(8).

89. Marchand, E. 1995. *A Comparison of the Effectiveness of Reverse Osmosis and Ion Exchange Technologies on the Removal of the Bromide Ion.* Washington, D.C: US EPA.

90. Marcus M, Ajaya D. 2003. *The Fluid Mosaic – Water Governance in the Context of Variability, Uncertainty and Change.* Boulder, Colorado: Institute of Development Studies.

91. Martin, J. P., and K. Haider, 1986. Influence of mineral colloids on turnover rates of soil organic carbon. IN P. M. Huang and M. Schnitzer (eds.), Interactions of Soil Minerals with Natural Organics and

Microbes. *Soil Sci. Soc. Am. Spec. Publ.* 17: 283-304. Madison, Wisconsin.

92. Matthew, J. DeMarco, Arup K. SenGupta, John E. 2003. "Greenleaf Arsenic removal using a polymeric/inorganic hybrid sorbent." *Water Research* 37 (2003): 164–176.
93. McArthur, J.M., Ravenscroft P., Safiullah S., 2004. "Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh." *Water Resources Research* 37(1): 109-117.
94. McCarthy J. F., Homer, V. J., and Z.-H. Chen. 1992. "The effect of concentration and pH on the size and aggregate structure of humic acid." In *Organic Substances In Soil and Water.* Lancaster University, UK.
95. McDowell, W. H., and T. Wood. 1984. "Soil processes control dissolved organic carbon concentrations in stream water." *Soil Sci.* 137:23-32.
96. Mc. Nully, Eumann M., Bevan C.A. 1986. "Anion exchange resin-kinetic testing – an indispensable diagnostic tool for condensate polisher troubleshooting." *International water conference:* 332-339. Pittsburg, Pa.
97. Mc. William J.D., 1978. "Protecting demineralizers from organic fouling." *Chemical Engineering* 85(12): 80-84.
98. Michael, G. 1993. "The reversible removal of naturally occurring organics using sodium chloride ion exchange resins." Watertech.
99. Michael, M. Reddy, and George A. 1998. "Speciation and fractionation modeling studies -- dissolved organic carbon (doc)-mercury

interaction." *Journal of Analytical Chemistry* Publisher: Springer-Verlag Heidelberg ISSN: 0937-0633

100. Miller, D., Bashir-Uddin S., Mahmoud A., Gani D. and Allemann R. 2004. "Removal of the phosphate group in mechanism-based inhibitors of inositol monophosphatase leads to unusual inhibitory activity." *Organic & Biomolecular Chemistry* 2(5): 671 – 688.

101. Moldes, A.B., Alonso J.L., Parajó J.C. 2001. "Resin Selection and Single-Step Production and Recovery of Lactic Acid from Pretreated Wood." *Applied Biochemistry and Biotechnology* 95(2): 69-81.

102. Montgomery, D C. 1996. *Design and Analysis of Experiments.* New York : John Wiley and Sons.

103. National Guidelines and Standards Office. 2005. *National Pollutant Release Inventory Guidance Manual for the Wastewater Sector, Substances Used or Formed During the Wastewater Treatment Process.* Ottawa: Environment Canada

104. Nicholadze, G.I. 1987. *Treatment technology of natural waters.* Moscow: Vishaya Shkola (Material in Russian).

105. Odegard, N., Koottater S. 1982. "Removal of Humic Substances from Natural Waters by Reverse Osmosis." *Water Res.* 11(5): 613-620.

106. Osterberg, R. and K. Mortensen. 1992. "Fractal dimension of humic acids." *Eur. Biophys. J.* 21:163–167.

107. Osterberg, R., L. Szajdak, and K. Mortensen. 1994. “Temperature-dependent restructuring of fractal humic acids: A proton-dependent process.” *Environ. International* 20:77–80.

108. Pan, B., Chen J., Zhang Q. and Wang Y. 1999. “Treatment and resource reuse of industrial wastewater from production process of phenyl acetic acid.” *J. React. Polym.* 8: 82-89.

109. Pashkov, L V., Lustgarten B.I. Grigoreva V.A., 1972. “Ion exchange materials in water preparation.” In *Water preparation, water regime and chemical control in steam powered plants.* Moscow: Energy (Material in Russian).

110. Pauling, L. 1970. *General Chemistry.* Mineola, NY: Dover Publications.

111. Pavlovich, M L., Skorokhod O R. 1985. “Influence of the nature of mixed water-organic solvents on the molecular sorption of fatty acids by sulfo-cationic exchange media КУ-2x8.” *Vesti ByloRussian university* 2(2): 16-19 (Material in Russian).

112. Payne, G. F. 1990. “Selective adsorption of solutes based on hydrogen bonding.” *Sep. Sci. Technol.* 25:1117-1129.

113. Perdue, E. M. 1982. “Analytical constraints on the structural features of humic substances.” *Geochim. Cosmochim. Acta.* 48:1435–1442.

114. Philippov, N. A. Yavshits G D, Reisfeld V O. 1986. “Sorption of oxygen containing liquids by sulfocation exchange media.” *Journal Applied chemistry* 49(11): 2250-2553 (Material in Russian).

115. Pochhali L., Adhikary S K, Rao K C. 1977. “Molecular adsorption and ion exchange of weak organic electrolytes on ion exchange resin.” *J. Indian Chem. Soc.* 54(9): 889-893.

116. Popov, V.V., Joffe A.Z., Maksimov V.A. Bulan V.A. 1977. “The use of anion exchange to remove organic substances from natural waters.” *Chemical fibers* 1: 72-73 (Material in Russian).

117. Puget, P., C. Chenu, and J. Balesdent, 1995. “Total and young organic matter distributions in aggregates of silty cultivated soils.” *Eur. J. Soil Sci.* 46:449-459.

118. Purolite. 1999. *Organic Fouling Of Anion Ion Exchange Resins.* Purolite technical bulletin.

119. Pushnyak A.N. Sayad Mustafa. 1989. *Ligand sorption of ethanolamines on cation exchange media KU2 and KB4 P-2.* Kishenev (Material in Russian).

120. Reynolds T.D., Richards P.A. 1996. *Unit operations and processes in environmental engineering.* Boston: PWS.

121. Rice, J. A. and J. S. Lin, 1994. Fractal dimensions of humic materials In Proceedings of the 6th IHSS International Meeting.

122. Rice, J. A., and J. S. Lin, 1992. Fractal nature of humic materials. Abstract The A.S.C. Meeting, San Francisco.

123. Rice, J. A., and J. S. Lin, 1993. “Fractal nature of humic materials.”

Env. Sci. and Tech. 27:413–414.

124. Robins, R.G. 1985. The Aqueous Chemistry of Arsenic In Relation to Hydrometallurgical Processes, Impurtity Control and Disposal, In: Proceedings of CIM Metallurgical Society, 15th Annual Hydrometallurgical Meeting:1-1 to 1-26.

125. Rojstaczer M. and Mohammed R I. 2004. "Surface water not always the answer to Bangladesh arsenic pollution problem" *Science Blog.*

126. Rutsch, M., Geipel, G., Brendler, V., Bernhard, G., Nitsche, H. 1999. "Interaction of uranium(VI) with arsenate(V) in aqueous solution studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS)." *Radiochim. Acta* 86: 135-141.

127. Saalfield S., Quicksall A., Renshaw C E. and Bostick B C. 2005. Reductive mechanisms of arsenic mobilization from contaminated sediments. Goldschmidt Conference Abstracts "Speciation of Metals and Metalloids".

128. Salt S.C., 1973. "Water treatment by ion exchange" *Effluent and water treatment journal* 13(12): 768-773.

129. Sannolo, N, Vajro P., Caporale C., Acampora A., Malorni A. 1981. "Extraction of fecal lipids and identification of hydroxystearic acid by gas chromatography-mass spectrometry (GC/MS)." *Boll Soc Ital Biol Sper.* 57(1): 118-24.

130. Schreiber, G. 2001. "Ion Exchange Resin Life" *Puronews* 1(5).

131. Schwarzenbach, R P, Gschwend P M, Imoden D M. 1993. *Environmental Organic Chemistry.* New York: Wiley and Sons.

132. Schweitzer, H. A. 1979. *Handbook of Separation techniques for Chemical Engineers.* New York, NY: McGraw Hill.

133. Sedlak, D. L., Rula A. Deeb, Elisabeth L. Hawley, William A. Mitch, Timothy D. Durbin, Sam Mowbray, Steve Carr. 2005. "Sources and Fate of Nitrosodimethylamine and its Precursors in Municipal Wastewater Treatment Plants." *Water Environment Research* 77(1).

134. Selemenov, V.F., Putilina M.M., Voitovich V.V. 1982. "Interaction between macroporous anion exchange media and the solutions of tartaric acid. Theory and practice of sorption processes." 7:5-9 (Material in Russian).

135. Senesi, N., Lorusso G. F., Miano T. M., Maggipinto C., Rizzi F., and Capozzi V., 1994. "The fractal dimension of humic substances as a function of pH by turbidity measurements." In *Abstracts of Invited and Volunteered Papers of the 6th IHSS International Meeting.*

136. SERVACEL 2004. *Cellulose Ion Exchangers – Overview.* Heidelberg: SERVACEL® bulletin.

137. Simpson, E. J., Koros W. J. and Schechter R. S. 1996a. "An emerging class of volatile organic compound sorbents: Friedel-Crafts modified polystyrenes. 1. Synthesis, characterization, and performance in aqueous-

and vapor-phase applications." Ind. Eng. Chem. Res. 35: 1195-1205.

138. Simpson, E. J., Koros W. J. and Schechter R. S., 1996b. An emerging class of volatile organic compound sorbents: Friedel-Crafts modified polystyrenes. 2. Performance comparison with commercially-available sorbents and isotherm ananlysis." *Ind. Eng. Chem. Res.* 35: 4635-4645.

139. Sirotkina I S, 1977. "Systematic schemes for the analysis of organic substances in natural waters." In *Problems in analytical chemistry and methods of analyses of natural and wastewaters*: 196-203. (Material in Russian).

140. Starobinets, G L, Zimina I F, Lapko V N. 1986. "Nonionic sorption of chlorides of primary aliphatic amines." *Chemical sciences* 2: 23-27. (Material in Russian).

141. Tilsli, G.M. 1975. "Clean up of fouled ion exchange resin bed." *Effluent and water treatment journal* 15(11): 560-563.

142. Tisdall, J. M., 1996. "Formation of soil aggregates and accumulation of soil organic matter." *Soil sci.*: 57-96.

143. Tisdall, J. M., and Oades J. M. 1982. "Organic matter and water stable aggregates in soils." *J. Soil Sci.* 33:141-163.

144. Tripp, A.R., Clifford, D.A., and Ghurye, A.G. 1998. "Development of a Novel Anion Exchange Process for Arsenic Removal from Water." In *Arsenic Exposure and Health Effects*. San Diego, Ca.: Society of Environmental Geochemistry and Health.

145. Tsitovich, I.K. Kuzmenko E L. 1988. "Dependence of anion exchange and nonionic sorption of mono-carbonic acids by strongly basic anion exchange media on the concentrations of their ionic and molecular forms." *Journal of physical chemistry* 52(2): 436-438 (Material in Russian).

146. Tsyurupa, M. P., Davankov V. A. and Rogoshin S. V. 1974. "Macronet isoporous ion exchange resins." *J. Polym. Sci.* 47: 189-195.

147. UNEP (United Nations Environment Programme). 2004 *Analytical Methods for Environmental Water Quality.* Global Environment Monitoring System (GEMS)/Water Programme.

148. USDHHS (U.S. Department Of Health And Human Services), 2005. *Toxicological Profile for Arsenic.* Unpublished report. Public Health Service Agency for Toxic Substances and Disease Registry.

149. USA EPA. Office of Water. 2003. *Arsenic Treatment Technology Evaluation Handbook for Small Systems.* U.S. EPA.

150. US EPA, 2003. *National Priorities List, Construction Complete.* Midvale, Utah: U.S. EPA.

151. United States Environmental Protection Agency, Arsenic Treatment Technology Design Manual for Small Systems, 2002. Unpublished report. EPA, 600-X-XX-XXX.

152. United States EPA. Office of water. *2003. Guidance Document:* Arsenic Treatment for Small Water Systems. U S EPA.

153. Wang, L, Chen A, Fields. K. 2000. “Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants". Washington, D.C: EPA.

154. Water TH. 2001. *Latest Developed Iron-removing Filter media, “Filox-R”.* Bangkok: Water TH.

155. Weber, W. J., Jr. and van Vliet B. M. 1981a. “Synthetic adsorbents and activated carbons for water treatment: overview and experimental comparisons.” *J. Am. Wat. Works Assoc.* 73: 420-426.

156. Welch, A A., Michael S. L, and Hughes, J L. 1988. “Arsenic in Groundwater of the Western United States.” *Groundwater* 26(3): 333-347.

157. Wilson, M. A., Vassallo A. M., Perdue E. M., and Reuter J. H. 1987. “A compositional and solid state nuclear magnetic resonance study of humic and fulvic acid fractions of soil organic matter.” *Anal. Chem.* 59:551–558.

158. Winchester, E., McMullin M. 2003. Arsenic Removal from Drinking Water. St.John's, NL: Newfoundland and Labrador Environmental Industry Association.

159. Yamasaki, M F. 2004. “Efficient phenols removal of wastewater from phenolic resin plants using crosslinked cyclodextrin particles.” In *the16th International Congress Of Chemical And Process Engineering.* Prague, Czech Republic

160. Zhang Q., Wang Y., Li X. and Chen J. 1997. “Treatment of wastewater

from nitrobenzene and nitrochlorobenzene production by resin adsorption process." *Hua Gong Huan Bao.* 17: 323-326

8. APPENDIX

Appendix A.1 Technical, Economic, and Environmental Efficiency of Using Macro-porous Ion Exchange Media when treating Groundwater With High Concentrations of Arsenic and DOM in the Potable Water Supply

The reduction in damage is the difference between the possible damage, D_{pos}, caused by continuous discharge of pollutants deep into the groundwater while taking no measure at all, and D_a, the actual damage that is done to the economy as a result of the discharge of the remaining pollutants after treatment and over some period of time.

$$D_{pr} = D_{pos} - D_a$$

The damage to water resources can be taken as being the cost of the complex measures needed to compensate for pollution of the water source. Any change in water quality in a natural reservoir due to both naturally occurring contamination (arsenic and DOM), and human activity (mainly domestic waste discharge), and which results in an increase in the cost of use of the water, causes economic damage. The damage arising from deterioration in natural water quality is defined by the related increase in cost. Such cost impacts are seen not only in extended water treatment units, but also in reduced productivity in agriculture and forestry. Additional costs also occur in the areas of the social services, including sanitary, medical, cultural, and welfare facilities.

The economic damage caused by individual housing and communal services is determined by working out the total losses arising from the discharge of wastewaters in the village under consideration. The damage, D, is calculated on the basis of the increased costs of water treatment:

$$D = \sum_{i=1}^{n} (C_i + E_n K_i)$$

where C_i is the current net cost of water treatment; E_n is a coefficient of compensation; K_i is the capital investment required for water treatment; n is the number of different stages of water treatment required.

Part of the cost of ownership comprises the basic costs, such as capital investment, staff costs, amortization and maintenance; the balance is made up of the day-to-day running expenses. The cost of ownership can be determined from:

$$E_{sp} = \frac{E_n K + C_i}{Q_c} + \frac{c_{sp} T}{k_{ir}}$$

where E_{sp} is the specific cost of ownership, expressed in relation to the treatment of 1 m^3/hr of water; C_i is the current cost, and depends on the calculated capacity of the treatment unit and the water quality over the design period; c_{sp} is the current specific cost of treatment of 1 m^3/hr taken as an average value over the full annual cycle; T is the number of hours during which the treatment unit operates in a year; Q_c is the estimated water consumption, m^3/hr; and, k_{ir} is a coefficient expressing the irregularity of hourly water consumption in a year, and is equal to the ratio of maximum to average hourly consumption over a year.

It is also important to determine the damage resulting from increasing concentrations of different contaminants in the water resource:

$$D_p = P_{Ic} - P_{IIc}$$

where p is the pollution type – e.g. arsenic, iron, BOD, COD, surfactants, phosphate, ammonia, dissolved solids, etc.; and, P_{Ic} and P_{Iic} are the corresponding additional net costs of treating water containing this or that pollutant, as compared to uncontaminated water.

The Economic Efficiency of Using Ion Exchange when treating Groundwater With High Concentrations of Iron, Arsenic and DOM in the Potable Water Supply.

Various technological schemes developed for various regions in Bangladesh are presented in previous sections. The worst-case scenario is the presence of arsenic, iron and DOM in groundwater. The economic efficiency of treating such water by ion exchange is worked out in this section.

The overall economic efficiency of using treated highly contaminated groundwater in drinkable water supply will be constituted of the following savings:

$E=D_{pr} + E_{nfw} - C_{tp}$

Where, D_{pr} is the estimated savings in reduced damage, E_{nfw} is the saving due to the use of treated underground water for drinking and cooking purposes instead of using natural fresh water; C_{tp} is the cost of treatment process.

Financial evaluation of the reduction in damage arising from discharges of various contaminants into the groundwater can be determined using the following formula:

$D_{pr} = \gamma.\sigma.M$

Where

γ - a constant, numerical value of which equals 148415.1 BDT/Tonne

This constant reflects reduction in human mortality and morbidity risks.

σ_k – dimensionless constant, having different values for different water sources.

M – effective mass of annual discharge in the water source

M can be determined using the following formula:

$$M = \sum_{i=1}^{N} A_i x m_i$$

where i – number of discharged contaminant;

N – total number of discharged contaminants;

A_i – index of relative toxicity of i-th contaminant in the groundwater;

m_i – total mass of i^{th} contaminant, arising from annual discharge, Tonne/Yr;

If contaminated waters of j^{th} type are discharged only from the resource under consideration and concentration of i^{th} contaminant C_{ij} (g/m^3) in the contaminated water of j^{th} type is relatively constant during the year, the mass of annual entrance of i^{th} contaminant with the contaminated water of j^{th} type m_{ij} (Tonne/year) can be approximately determined using the following formula:

$$m_{ij} = c_{ij} \, . \, v_j$$

$$A_i = \frac{1}{MCL_{p/xi}}$$

where $MCL_{p/xi}$ is maximum concentration limit of i^{th} contaminant in the water source, used for drinking purposes g/m^3.

In this section economic efficiency of using highly contaminated groundwater is being worked out. Preparation of potable water will be carried out by chemical treatment with a capacity of 0.5 m^3/h. Groundwater contaminated with arsenic, iron and DOM will be supplied to the treatment units.

The composition of the characteristic ingredients of some groundwaters in Bangladesh is presented in Table A-8-1. The data presented in this section was collected from fieldwork studies in Bangladesh.

Table A-8-1 Composition of Bangladeshi groundwater

Ingredient	Original groundwater (ppm)	Pretreated groundwater (ppm)
BOD_{20}	15	5
COD	36	12
PV	12	4
Arsenic (III)	10	10
Ammonia	8	6
Iron	0.17	0.08
Surfactant	1.2	0.8

Below is presented the estimated savings in reduced damage (0.5 m^3/hr) calculated using aforementioned formulae.

Results are presented in Table A-8-2..

Since the groundwater source is used for drinking purposes, $\sigma_k=1.3$. Taking this into account, the reduction in damage will constitute:

D_{pr} =148415.1 x 1.3 x 2.2752192=438979.95 BDT/yr. (from here on, the estimated results are given in the prices of 2004)

Table A.8-2 Estimated annual discharge of contaminants into groundwater in Bangladesh

Contaminants	Concentration C_i, g/m^3	Annual volume of groundwater used for drinking purposes, V, m^3/yr	Mass of annual discharge into groundwater, m_i, Tonne/yr	$MCL_{p/xi}$, g/m^3	A_i, Tonne/yr	$M_i=m_i \times A_i$, Tonne/yr
BOD_{20}	15	4362	0.06543	3	0.33	0.0215919
Arsenic (III)	1	4362	0.004362	0.01	100	0.4362
Ammonia	8	4362	0.034896	0.05	20	0.69792
Iron	5	4362	0.02181	0.3	3.33	0.0726273
Surfactant	12	4362	0.052344	0.05	20	1.04688
Total: $\sum_{i=1}^{5} M_i = 2.2752192$						

Note: The concentrations given in this table are based on the following volumetric assumptions: kitchen use 3.13; drinking 4.83 (in units of liters per head per day). Population has been assumed to be 1500 people.

Table A.8-3 Operating parameters of Cl-anion exchange filter loaded with macro-porous anion exchange media

Parameters	**Value**	**Unit of measurement**
Filter diameter	0.254	meter
Volume of resin	0.04	m^3
Specific consumption of NaCl on regeneration	300	kg/ m^3
Specific consumption of NaOH on regeneration	30	kg/ m^3
Volume of spent regeneration solution	0.12	m^3
Concentration of DOM in spent regeneration solution	290	gO_2/m^3
Concentration of arsenic in spent regeneration solution	19.33	g/m^3
Specific consumption of wash water	7.5	m^3
Duration of exchange cycle	4	weeks
Duration of regeneration	70	minute
Annual frequency of regeneration	12	

Table A.8-4 Cost of equipment in ion exchange treatment unit (data acquired from market inquiries in Bangladesh)

Item	Name of equipment	Characteristics	Quantity	Cost, BDT	
				Unit	Total
1	Filter Vessel	Volume 0.07 m^3	2	787	1574
2	Pressure tank	1 m^3	2	5839	11678
3	NaCl+NaOH solution tank	20 L	1	117	117
4	$KMnO_4$ tank	20 L	1	117	117
5	Tank platform	1 storey	1	3100	3100
6	Storage tank	1 m^3	1	5839	5839
7	Flow meter		3	1000	3000
ΣTotal cost=25425					

Table A.8-5 Cost of equipment in spent regeneration solution treatment and waste handling unit (data acquired from market inquiries in Bangladesh)

Item	Name of equipment	Characteristics	Quantity	Cost, BDT	
				Unit	Total
1	Sedimentation tank	Volume 0.12 m^3	2	700	1400
2	Recovered spent regeneration solution tank	0.15 m^3	2	876	1752
3	Wash water tank	0.3 m^3	2	1869	3738
4	Pressure vessel	7 L	1	900	900
Σ Total cost=7790 BDT					

Economic efficiency [2] of substituting natural fresh water with treated groundwater can be determined using the following formula:

$E_{nfw} = Ex_{nfw} - Ex_{cgw}$

Where Ex_{nfw} is the expenses on natural fresh water, BDT/yr and E_{cgw} is expenses on contaminated groundwater (pretreatment and disinfection) BDT/yr.

$Ex_{nfw} = Q_{nfw} \times C_{nfw}$

Where Q_{nfw} is the volume of natural fresh water to be used for drinking purposes, m^3/yr.

C_{nfw} is the cost of natural fresh water, BDT/m^3 (C_{nfw}=12 BDT/m^3).

$E_{cgw} = Q_{cgw} \times C_{gw}$

where Q_{cgw} is the volume of groundwater to be used for drinking purposes, m^3/yr.

C_{gw} is the cost of groundwater, BDT/m^3 (C_{gw}=6.8 BDT/m^3).

Finally: $E_{nfw} = Q_{nfw} \times (C_{nfw} - C_{gw})$ =4362 (12-6.8) BDT/yr = 22682.4 BDT/yr.

Expenditure on ion exchange treatment of groundwater contaminated with arsenic, DOM, and iron, can be determined by the following formula.

$EX_{IX} = E_n \times K_{IX} + C_{OIX}$

where K_{IX} is the capital investment required for water treatment;

E_n is a coefficient of compensation; C_{OIX} is the annual operating cost of the sorption treatment of arsenic and DOM, BDT/yr.

Capital investment includes the following components: capital investment on filtration vessels K_F, their installation K_M and anticorrosion coating $K_{CTG;}$ capital investment on automation and technological control K_{AUT}, on building and construction K_{CONS} and ion exchange and oxidizing material $K_{IX/OX}$. In addition, total capital investment includes cost of onsite treatment equipment K_{LTE}, assigned for removal of arsenic and DOM while recovering spent regeneration solutions.

$$K = K_F + K_M + K_{CTG} + K_{AUT} + K_{CONS} + K_{IX/OX} + K_{LTE}$$

All components of the capital investment except for K_{AUT} , K_{CONS} , $K_{IX/OX}$ and K_{LTE} can be determined through expenditure on filtration vessels by means of introducing corresponding coefficients. Thus the formula to estimate K is transformed as follows:

$$K = n(3.7 \times P_F + 1574) + K_{equip}^{Cl} + K_{IX/OX} + K_{LTE}$$

Where n is the number of filtration tanks and 1574 BDT is total expenses on construction and automation.

The total cost of 0.04 m^3 of macro-porous ion exchange resin and that of solid-phase oxidizing media equals 15000 BDT.

Considering the small design capacity of the unit, Q=0.5 m^3/hr, two identical filtration tanks are chosen each having 1.37 m by length and 0.254 m diameter (one to be used as ion exchange tank and the other as oxidizing filter). The capacity of one ion exchange filter would be:

$C=A \times v = 0.05 \times 10 = 0.5\ m^3/hr$

Where A is the surface area of ion exchange vessel, m^2; and v is the linear velocity of filtration, m/hr. Number of ion exchange filters was limited to one because of small frequency of regeneration (once every 4 weeks), duration of regeneration (70 minutes). The oxidizing filter would be backwashed every 3 days with treated water from the storage tank. The backwash would last for 15 to 20 minutes at a flow rate of 41.6 L/min.

The cost of the two filtration vessels amounts to 1574 BDT, and the cost of loaded materials (IX resin and manganese dioxide based oxidizing media) is 15000 BDT. The total equipment required for ion exchange treatment, the specifications and quantities are given in Table A-8-4. The total cost of additional equipment required for this unit excluding filter vessels amounts to 20851 BDT. The expenditure on the installation of equipment in ion exchange treatment unit is 40% of the cost of the equipment and amounts to:

$0.4 \times 20851 = 8340.4$ BDT

The cost of pipes and their installation was taken to be 35% of the total cost (based on the Public Works Department (**PWD**) Bangladesh recommendations) of equipment and its installation.

0.35 (20851+ 8340.4)=10216.99 BDT

Expenditure on building and construction was taken to be 30% (**PWD** recommendations) of total expenditure.

0.3(20851+ 8340.4+10216.99)=11822.52 BDT

Thus additional cost required for ion exchange treatment unit amounts to:

K^{Cl}_{equip}=20851+ 8340.4+10216.99+11822.52 +3000 (flow meters)

=51230.9+3000=54230.9 BDT

The last component of additional capital investment is K_{LTE}, which is related to expenditure on unit for treatment of spent regeneration solutions and waste handling. According to the technology developed for recovering spent regeneration solutions and detoxifying arsenic laden sludge for safe onsite disposal, the treatment equipment includes sedimentation tank, tanks and pressure vessel. The cost of the mentioned equipment, its characteristics and quantity is given in Table A-8-5.

The expenditure on the installation of equipment in local treatment unit is 40% (**PWD** recommendations) of the cost of the equipment and amounts to:

0.4 x 7790= 3116 BDT

The cost of the pipes and their installation was taken to be 35% of the total cost of equipment and its installation.

0.35 (7790+ 3116)=3817.1 BDT

Expenditure on building and construction was taken to be 30% of total expenditure.

0.3(7790+ 3116+3817.1)=4416.93 BDTd

Thus the total capital investment on the local treatment unit K_{LTE} amounts to: 7790+ 3116+3817.1 +4416.93 =19140.03 BDT

All additional capital investment costs on the whole treatment facility amount to:

K= 2(3.7 x 787 + 1574) + 54230.9 + 15000 + 19140.03=8971.8+ 54230.9 + 15000 + 19140.03 =97343 BDT

The annual operating cost can be determined using the following formula:

$O = O^{CI} + O^{LTU}$

Where O^{CI} is the annual operating cost of ion exchange treatment unit; O^{LTU} is annual operating cost of local (onsite) treatment unit.

The formula can be expanded showing all its components as follows:

$$O = O_a^{Cl} + O_a^{LTU} + O_R^{Cl} + O_R^{LTU} + O_F^{Cl} + O_{RR}^{Cl} + O_{RR}^{LTU} + O_{oth}^{Cl} + O_{oth}^{LTU}$$

where O_a^{Cl} and O_a^{LTU} are amortization costs; O_R^{Cl} and O_R^{LTU} are costs of reagents; O_F^{Cl} is cost of resin to fill up; O_{RR}^{Cl} and O_{RR}^{LTU} are routine repair costs; O_{oth}^{Cl} and O_{oth}^{LTU} are other costs.

Amortization costs are proportional to the capital investment:

O_a^{Cl} =0.08(K_{IX} - K_{LTE})=0.08(97342.74-19140.03)=6256.217 BDT/yr.

O_a^{LTU} =0.08(K_{LTE})=0.08(19140.03)=1531.2 BDT/yr.

The Cl-anion exchange filter would be activated only with a mixture of NaCl and NaOH. Afterwards Cl^- and OH^- ions would be refilled while treating spent regeneration solution with $MgCl_2$ and $Ca(OH)_2$ (section 5.2). Consumption of NaCl and NaOH by a single time regeneration of Cl-anion exchange filter would amount to:

Q_{NaCl} = G_{NaCl} x V x n = 300 x 0.04 x 1 = 12 kg/yr.

$Q_{NaOH} = G_{NaOH} \times V \times n = 30 \times 0.04 \times 1 = 1.2$ kg/yr.

Specific consumption of salt (G_{NaCl}) and alkali (G_{NaOH}) as well as Bed Volume of the ion exchange filter is taken from Table A-8-3.

At a cost of 12 BDT/ kg NaCl and 140 BDT/kg NaOH, the annual operating cost for regeneration of ion exchange filter would amount to 12 x 12 + 1.2 x 140 = 144+168=312 BDT/yr.

In addition, lime would be used for coagulation of raw water. At a lime dose rate of 50 mg-CaO/L, yearly consumption would be 218.1 kg/yr while treating 4362 m^3 of raw water. This would cost 2181 BDT/yr.

Thus O_R^{Cl} =312+2181=2493 BDT/yr.

The initial regeneration solution contains 250 g-equiv/m^3 of OH-ions. Approximately one fifth of OH-ions would sorb onto the anion exchange resin while passing regeneration solution through the filter. Consequently the spent regeneration solution will contain 200 eq/m^3 of OH-ions. An amount of $MgCl_2$ equivalent to this quantity would be dosed into the spent regeneration solution in order to remove DOM and arsenic and to recharge Cl^- ions. Thus yearly consumption of $MgCl_2$ would be:

$Q_{MgCl2} = G_{MgCl2} \times V_{s.r.s} \times n \times N = 200 \times 0.12 \times 1 \times 12 = 288$ g-eq/yr.

The volume of spent regeneration solution from a single filter ($V_{s.r.s}$) and annual frequency of regeneration (N) is taken from Table A-8-3.

Annual consumption of 100% $MgCl_2$ would thus amount to (288 g-eq/yr)x47.7 = 13.74 kg/yr. Annual consumption of 45% commercial $MgCl_2$ would amount to 13.74 x (100/45) = 30.53 kg/yr. At a cost of 25 BDT/kg $MgCl_2$, the annual cost of $MgCl_2$ will equal (30.53 kg/yr) x (25 BDT/kg $MgCl_2$) = 763.25 BDT/yr.

After separating the $Mg(OH)_2$ sediment, $Ca(OH)_2$ will be introduced into the clarified water aiming at raising the concentration of OH^- ions up to their initial concentration of 250 g-eq/m^3 and getting the SO_4^{2-} settled as Ca_2SO_4.

Yearly consumption of $Ca(OH)_2$ would be:

$Q_{Ca(OH)2} = G_{Ca(OH)2} \times V_{s.r.s} \times n \times N = 250 \times 0.12 \times 1 \times 12 = 360$ g-eq/yr.

The volume of spent regeneration solution from a single filter ($V_{s.r.s}$) and the annual frequency of regeneration (N) is taken from Table A-8-3.

Annual consumption of 100% $Ca(OH)_2$ would thus amount to (360 g-eq/yr)x 28 = 10.08 kg/yr. Annual consumption of 50% commercial $Ca(OH)_2$ would amount to 10.08 x (100/50) = 20.16 kg/yr. At a cost of 15 BDT/kg $Ca(OH)_2$, annual cost of $Ca(OH)_2$ will equal (20.16 kg/yr) x (15 BDT/kg $Ca(OH)_2$) = 302.4 BDT/yr.

Thus O_R^{LTU} =763.25+302.4 = 1065 BDT/yr.

Annual filling up of IX resin and oxidizing material will cost 10% of $K_{IX/OX}$ i.e. O_F^{Cl} =0.1 x 15000 = 1500 BDT/yr.

Annual cost of routine repairs was taken to be 20% of amortization (**PWD** recommendations):

O_{RR}^{Cl} =0.2 x 6256.2 = 1251.24 BDT/yr

O_{RR}^{LTU} =0.2 x 1531.2 = 306.24 BDT/yr

Other costs were determined using the following formula:

O_{oth}^{Cl} =0.3($O_a^{Cl}+O_{RR}^{Cl}$)=0.3(6256.217 +1251.24)=2252.23 BDT/yr

O_{oth}^{LTU} =0.3($O_a^{LTU}+O_{RR}^{LTU}$)=0.3(1531.2 +306.24)=551.23 BDT/yr

Thus the annual operating cost of ion exchange treatment will amount to:

O =6256.217+1531.2+2493+1065+1500+1251.24+306.24+2252.23+551.23

=17206 BDT/yr

Thus the effective expenditure on the IX treatment was calculated as follows:

$EX_{IX} = E_n \times K_{IX} + C_{OIX} = 0.15\ (97343) + 17206 = 31807$ BDT

Finally the economic efficiency of using ion exchange when treating groundwater with high concentrations (14 mg/L) of iron, arsenic and DOM:

$E = D_{pr} + E_{nfw} - C_{tp} = 438979.95 + 22682.4 - 31807 = 429{,}855.35$ BDT/yr

429,855.35 BDT = 9,397.3342 Cdn

Bangladeshi Taka = Canadian Dollars

1 BDT = 0.0218616 Cdn $

1 Cdn $ = 45.7423 BDT

Year 2004