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Effect of Surfactants on the Sorption and Transport of Cu(II) in a Sandy Soil: Batch, Column Experiments and Modeling

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Abstract

Effect of Surfactants on the Sorption and Transport of Cu(II) in a Sandy Soil: Batch, Column Experiments and Modeling

Qiao Li

Recently, surfactants have shown some potential for remediation of heavy metal contaminated soil, although research in this area has been limited. Batch and column studies were conducted to investigate the sorption processes and transport behavior of Cu(II) in a sandy soil in the presence of surfactants. SDS (sodium dodecyl sulfate) and Triton X-100 were chosen as representatives of an anionic surfactant and a nonionic surfactant, respectively. Results showed that the anionic surfactant (SDS) significantly decreased the retention of Cu(II) in the sandy soil and was more effective in removal of Cu(II) than the nonionic surfactant (Triton X-100) in the both batch and column experiments. Further, both SDS and Triton X-100 appeared more effective in removing Cu(II) under increasing acidic conditions.

Description of the sorption process and transport of heavy metals is necessary for identifying the fate of heavy metals in soils. The batch-generated sorption isotherms were found to be quantitatively higher than those calculated in columns. The sorption processes of Cu(II) in the soil column showed a strong nonequilibrium. Both a first-order kinetic model and a two-region model were not capable of describing the entire experimental breakthrough curve (BTC) in most instances.

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b	dimensionless constant
C	solute concentration in solution
C_{tot}	total concentration
C^{im}	concentration in the immobile water
C^{m}	concentration in the mobile water
D	dispersion coefficient
D^{m}	dispersion coefficient in the mobile region
$erfc()$	complementary error function
f	fraction of a dynamic or easily accessible region
k_1	first-order decay rate coefficient
k_b	backward reaction rate coefficient
K_d	linear distribution coefficient
k_f	forward reaction rate coefficient
K_f	distribution coefficient
L	length of soil column
Pe	column Peclet number
P_v	pore volume
Q	average flux of water through columns
R	retardation factor
R^2	coefficient of determination

S amount of solute retained by the soil

S_m maximum sorption capacity

S^m amount of solutes sorbed in the dynamic region

S^{im} amount of solutes sorbed in the stagnant region

S_{max} total sites in the soil

S^m_{max} total sites in the dynamic region

S^{im}_{max} total sites in the stagnant region

t time

t_0 average time

$t(c)$ retention time

v pore-water velocity

v^m average pore-water velocity in the mobile region

x length of the domain

θ^m mobile water fraction

θ^{im} immobile water fraction

Φ^m vacant or unfilled sites within the dynamic region

Φ^{im} vacant or unfilled sites within the stagnant region

α mass transfer coefficient

ρ bulk density of the porous medium

β constant

θ volumetric water content

λ hydraulic dispersivity

CHAPTER ONE

Introduction

1.1 Background

Chemical releases into the subsurface are pervasive environmental problems. There are currently many sites that contain soils contaminated with heavy metals, such as Superfund sites in the United States. Cleanup of heavy metal-contaminated soil is one of the most common problems at hazardous waste sites throughout the world. Metal containing waste materials include municipal solid wastes, industrial by-products, sewage sludge, dredged material, wastes from mining and smelting operations, filter residues from waste water treatment and atmospheric emission control, ashes and slags from burning of coal, oil, and from incineration of municipal refuse and sewage sludge (Merian, 1991). Lead, chromium, copper, zinc, arsenic, and cadmium are the most often encountered metals. Leachate and run-off from soils contaminated with heavy metals potentially degrade groundwater and surface water quality.

Heavy metals are toxic to human beings and animals and pose a threat to groundwater supplies if they are not disposed of properly. Unlike organic contaminants that can be destroyed by biodegradation, chemical oxidation, or incineration, metal contaminants can remain on site and threaten environmental quality for a long time or until they are removed. Remediation of heavy metal contaminated soils represents a formidable challenge.

Recent efforts using chemical chelators within aqueous solutions have shown much promise for washing or flushing of heavy metals from contaminated soils (Peters, 1999). Numerous studies on the chelating extraction of heavy metals from contaminated soils have been conducted (Peters, 1999 and Hong et al., 1999). Additionally, surfactants have shown some potential for remediation of heavy metal contaminated soil although research in this area has been limited.

The sorption of heavy metals onto soil particles affects the movement and fate of heavy metals in soil. Therefore, accurate description of the retention or sorption process of heavy metals is important.

1.2 Objectives

The overall objectives of this study are outlined below:

1) Determination of the mechanism of surfactant enhanced extraction of heavy metal from contaminated soils by investigating the adsorption of Cu(II) on a sandy soil (artificial) in the presence of surfactants. Anionic (sodium dodecyl sulfate, SDS) and nonionic (Triton X-100) surfactants were used in this study. A complexing agent, Ethylenediaminetetraacetic acid (EDTA) was also used in this study to compare to the surfactants.
2) Investigation of the effect of surfactant flushing on the adsorption and desorption of Cu(II) in a soil column by comparing with those results obtained in batch experiments.

3) Examination of the relationship between the batch-generated sorption isotherms and those calculated in columns.

4) Modeling the transport of Cu(II) in the soil columns by choosing appropriate sorption models.

CHAPTER TWO

Literature Review

2.1 Introduction to soil washing/flushing technology

Heavy metals may be present in soils either adsorbed onto the various components of the soil or as separate metal compounds. Metal contamination is generally found on the finer soil particles since these have a higher surface area per unit volume, and thus are favored for adsorption-type phenomena. In addition, the fine soil fraction usually contains the natural organic component of soil, which could serve as a sink for organic contaminants. Peters et al. (1992) have stated that metals are often preferentially bound to clays and humic materials. There are two basic strategies that have been adopted for the remediation of heavy metal-contaminated soils, technologies that leave the metal in the soil, and technologies that remove the heavy metals from the soil (Rampley et al., 1998). Technologies such as solidification/stabilization and vitrification immobilize contaminants, thereby minimizing their migration. Techniques such as soil washing and *in situ* soil flushing transfer the contaminants to a liquid phase by desorption and solubilization (Reed et al., 1996). Soil washing can be a physical and/or chemical process that results in the separation, segregation, and volume reduction of hazardous materials and/or the chemical transformation of contaminants to nonhazardous materials (Semer and Reddy, 1996). Generally, *in situ* flushing technologies are more economical and are safer than *ex situ* technologies because excavation is not required. Factors affecting heavy metal retention by soils include: pH, soil type and horizon, cation exchange capacity

CEC, natural organic matter, age of contamination, and the presence of other inorganic contaminants (Reed et al., 1996).

Pickering (1986) identified four ways in which metals are mobilized in soils: (1) changes in the acidity; (2) changes in solution ionic strength; (3) changes in the REDOX potential; and (4) formation of complexes. In practice, acid washing and chelator soil washing are the two most prevalent removal methods (Rampley et al., 1998). A chelant is a ligand that contains two or more electron-donor groups so that more than one bond is formed between the metal ion and the ligand (Cline et al., 1995). The most common chelating agent studied in the literature is EDTA (Reed et al., 1996).

Recently, surfactants have shown some potential for environmental remediation of heavy metals from soil though research in this area has been limited. It is possible that surfactant adsorption may displace adsorbed metals, thereby mobilizing them.

Contaminants sorbed to soil particles are separated from soil in an aqueous-based soil washing system. The wash or flush water may be augmented with a basic leaching agent, acids, surfactants, pH adjustments, or chelating agents to help remove organics and heavy metals (Peters, 1999). Factors affecting soil washing/soil flushing processes include clay content, complex waste mixtures, high humic content, metals concentrations, mineralogy, particle size distribution/soil texture, separation coefficient, and wash solution. Some previous studies involving chelant and surfactant extraction for removal of heavy metals from soils are described below.

2.2 Chelant method

The ability of chelating agents to form stable metal complexes and thus mobilize the heavy metals from contaminated soil makes chelating agents promising extractive agents for the treatment of soils polluted with heavy metals. Chelating extraction can offer permanent removal of heavy metals from the contaminated soil. EDTA, the most common chelant, can readily form soluble complexes with metal ions, reducing the quantity of metals retained by soil particles and thereby increasing heavy-metal mobility (Cline et al., 1995).

The use of chelating extraction of heavy metals from contaminated soils has recently attracted a great deal of research interest. Ellis et al. (1986) performed the sequential treatment of soil contaminated with cadmium, chromium, copper, lead, and nickel, using EDTA, hydroxylamine hydrochloride, and citrate buffer. The results of the three-agent sequential extraction showed that, compared to bulk untreated soil, this extraction removed nearly 100% of the lead and cadmium, 73% of the copper, 52% of the chromium, and 23% of the nickel. Elliot et al. (1989) performed a series of batch experiments to evaluate extractive decontamination of Pb-polluted soil using EDTA. Results from their study indicated that increasing EDTA concentration resulted in greater Pb release. Recovery of Pb was generally greatest under acidic conditions and decreased modestly as the pH increased. Peters and Shem (1992) observed that extraction of lead with EDTA was rapid, reaching equilibrium within a contact time of 1.0 hour; extraction of lead with NTA (nitrilotriacetic acid) was slower requiring a contact time of approximately 3.0 hours to reach equilibrium. Reed et al. (1996) investigated the removal

of Pb(II) from a synthetically contaminated sandy loam soil using 0.1N HCl, 0.01M EDTA, and 1.0M calcium chloride ($CaCl_2$) in a continuous flow mode. Pb removal efficiencies were 85%, 100%, and 78% for HCl, EDTA, and $CaCl_2$, respectively. Hong et al. (1999) studied the extraction, recovery, and biostability of EDTA for remediation of Pb-contaminated soil. Their study showed that EDTA was able to extract Pb completely from the tested soil, and that it remained amenable to recovery by the addition of cationic and anionic precipitants in the alkaline pH range. It was also relatively biostable even under conditions very favorable toward biodegradation. Previous studies involving chelant extraction of heavy metals from contaminated soils can be found in Peters (1999).

2.3 Surfactant method

Because of the limitations of pump-and-treat technology, attention is now focused on the feasibility of surfactant use to increase its efficiency (West et al., 1992). Surfactants have been studied widely for use in soil washing and enhanced oil recovery. Surfactants are particularly attractive for this process because many of them have low toxicity and favorable biodegradability, and can thus be more environmental friendly than many organic-solvent based systems (Deshpande et al., 1999). Recently, surfactants have shown some potential for environmental remediation of heavy metals from soil. Surfactant enhanced remediation of organic contaminants is fairly well understood; However, the role of surfactants in remediation of subsurface metal contamination is less well understood (Nivas et al., 1996). The definition of surfactant, the mechanisms of surfactant enhanced remediation of organic contaminants, and some previous studies

related to surfactant enhanced remediation of heavy metal contaminants are described below.

2.3.1 Definition of Surfactants

Comprehensive overview of surfactants and subsurface remediation is found in West and Harwell (1992), Wison and Clarke (1994), Cheah et al. (1998), and Desphande et al. (1999). The word surfactant is a contraction of the descriptive phrase surface-active agent. Surfactants are surface active because they concentrate at interfacial regions: air-water, oil-water, and solid-liquid interfaces, for example. The surface activity of surfactants derives from their amphiphilic structure, meaning that their molecules contain one soluble and one insoluble moiety. In aqueous systems, a surfactant has a polar or

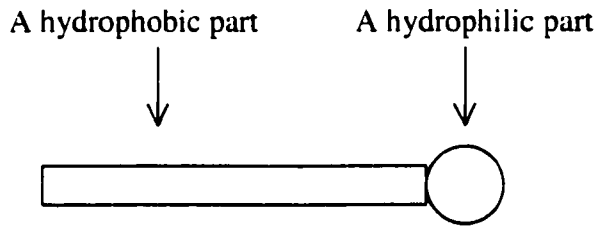

Figure 2.1 Basic structure of a surfactant.

ionic hydrophilic moiety (water liking) and a nonpolar hydrophobic moiety (water hating), referred to as the head and tail groups, respectively. A surfactant molecule can be represented as in Figure 2.1. Hydrophobic portions (tails) are usually hydrocarbon chains typically containing 12 or more carbon atoms. Hydrophilic portions (heads) are usually

ionic ($-COO^-$, $-SO_4^-$, $-N(CH_3)_3^+$, for example) or polar (oxyethylene chains, $-NH_2$, etc.). One of the most common surfactants, sodium dodecyl sulfate, is a good example of this structure. The dodecyl chain has a very low water solubility whereas the sulfate group has a very high water solubility. In surfactant solutions, the surfactants tend to concentrate at the air/water interface, where the hydrophilic heads can be hydrated in the water while the hydrophobic tails do not disrupt the hydrogen-bond structure of the water by being immersed in the aqueous phase. By concentrating at the air/water interface of the solution, the surfactant species are able to reduce the free energy of the system, thereby increase its stability.

Surfactants are classified according to the nature of the hydrophilic portion of the molecule. The head group may carry a negative charge (anionic, e.g. sodium dodecylsulfate), a positive charge (cationic, e.g. Emcol CC-9), both negative and positive charge (zwitterionic, e.g. B-N-alkyl aminopropionic acid), or no charge (nonionic, e.g. Triton X-100). Differences in the chemistry of surfactants due to the nature of the hydrophobic tails (degree of branching, carbon number, aromaticity) are usually less pronounced than those due to the nature of the hydrophilic head group.

A phenomenon unique to surfactants is the self-assembly of molecules into dynamic clusters called micelles (see Figure 2.2). Micelle formation occurs above a critical concentration of surfactant monomers, referred to as the critical micelle concentration (CMC), which is different for every surfactant (Rose, 1989). CMCs typically range between 0.1 and 10 mM. The CMC is a function of the structure of the surfactant, the

temperature of the surfactant solution, the concentration of added electrolytes, and the concentration of solubilizates (Harwell, 1992). In a micelle, the individual monomers are oriented with their hydrophilic moieties in contact with the aqueous phase and their hydrophobic moieties tucked into the interior of the aggregate. The average number of surfactant molecules in a micelle is called the aggregation number.

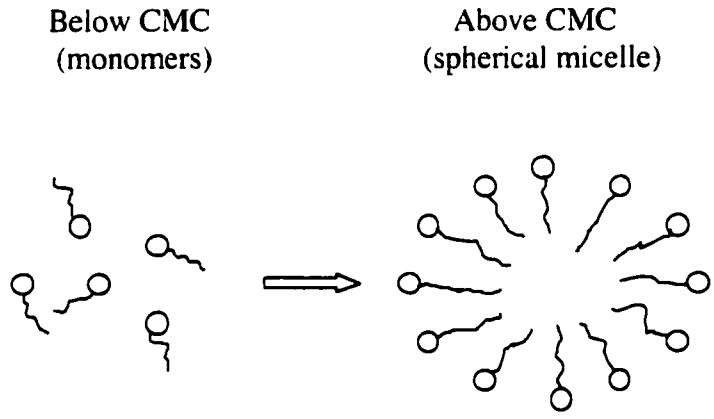

Figure 2.2 Example of surfactant micellization

2.3.2 Surfactant enhanced organic contaminated soils

Surfactants show significant potential for application in enhancing the remediation of contaminated soil and groundwater. Surfactants enhance organic contaminant recovery in soil washing/flushing through two very different mechanisms. First, surfactants reduce the oil-water interfacial tension and the capillary forces that trap the residual organic. As a result, the residual oil saturation in the presence of surfactant is appreciably lower, and more oil is mobilized than with simple water floods alone. Secondly, surfactants are capable of forming dynamic aggregates known as micelles. Above the CMC, the

hydrophobic end of the surfactant molecule will cluster together inside the micelle structure with the hydrophilic end exposed to the aqueous phase on the exterior. Consequently, the interior of a micelle constitutes a compatible environment for hydrophobic organic molecules; the process of incorporation of these molecules into a micelle is known as solubilization.

Below the CMC, surfactants exist in the monomeric state, and no enhancement of organic solubility is generally observed (Hiemenz, 1986). However, the aqueous solubility of certain highly hydrophoblic organic compounds can be enhanced by certain surfactants even below the CMC (Kile et al., 1989), a process similar to the partitioning of highly insoluble organic compounds to the organic carbon fraction of dissolved organic macronmolecules (Chiou et al., 1987).

The effectiveness of a surfactant in enhancing the removal of a subsurface contaminant can be expected to be a function not only of the surfactant's interaction with the contaminants, but also of the surfactant's interaction with the aquifer media at the conditions in the aquifer (Harwell, 1992). Harwell points out that the types of surfactant behavior such as precipitation, liquid crystal formation, formation of a coacervate phase, partitioning into trapped residual phases, or adsorption onto the aquifer's solid surfaces could be anticipated as potentially reducing the surfactant's ability to remove the contaminant.

Numerous studies of the use of surfactants for the remediation of organic-contaminated soils can be found in the literature (Abdual and Gibson, 1991; Brownawell et al., 1991; Boyd et al., 1991).

2.3.3 Surfactant enhanced remediation of metal contaminated soils

Surfactants have shown some potential for environmental remediation of heavy metals from soil, though research in this area has been limited. It is possible that surfactant adsorption may displace metals, thus mobilizing them. If the surfactant adsorption is intended to serve as a barrier for organic contaminant migration, then the mobilization of the metals may be a negative effect. However, if remediation of the metals contaminated material is an objective, then the mobilization of the metals is a positive effect (Sabatini et al., 1992).

The possible mechanisms for the extraction of heavy metals by surfactants are ion exchange, precipitation-dissolution, and counterion binding (Rosen, 1979). The first mechanism for enhanced heavy metal removal from soil surface is ion exchange: a negatively charged ion adsorbed onto subsurface is replaced by negatively charged surfactant ions from solution. Since micelles are not directly involved in ion exchange (monomers are), exchangeable ions will increase below the CMC and remain relatively constant above the CMC (Nivas, et al., 1996). A second mechanism for enhanced heavy metal removal from soil surface is counterion binding. For ionic micelles, the interfacial region between the aqueous solution and the micelle contains the ionic head groups, the Stern layer of the electrical double layer pertaining to these groups, more than one half of

the counterions associated with the micelle, and water. Navis et al. (1996) suspected that precipitating cations (e.g. Ca^{2+}, Ba^{2+}) would be attracted to the surfactant micelles. He depicted that counterion binding could be a mechanism for surfactant micelles to promote dissolution of precipitated heavy metals when the concentration of surfactant exceeds the CMC, thereby enhancing the removal of chromium from soil. The third mechanism, it is also possible that the surfactants precipitate with the cations of the insoluble mineral phased by heavy metals and then could enhance dissolution of the heavy metals ions. Anionic surfactants can also interact with a negatively charged surface. They associate with multivalent surface cations or are precipitate. Siffert et al. (1992) interpreted the adsorption of anionic surfactants like dodecylsulfate, dodecylbenzenesulfate and dodecylbenzenesulfonate at minerals qualitatively as precipitation at the mineral surface. Ilic et al. (1996) found that on Ni- and Cu-montmorillonite, dodecylsulfate (DS-) forms ion pairs with the cations on the soil surface. In all cases, DS- is not bound above the CMC, but metal ions are mobilized from the surface, either by solubilization of the precipitates or by formation of mixed micelles. For Ca- and Pb- montmorillonite, DS- is precipitated as $Me(DS)_2$. Also, when CMC is exceeded, the precipitates are solubilized in the micelles of the bulk solution.

Some previous studies related to surfactant enhanced remediation of heavy metal contaminants are described below.

Okada (1988) investigated the possible use of surfactants in ion chromatography to exclude inorganic anions and cations, a method know as micellar exclusion

chromatography. Some surfactants were used in the mobile phase to investigate the effect of the cationic species on the retention behavior of the solute anions. He found that the addition of complexing agents affected the partition of metal cations to the stationary phase. The retention of metal cations in anionic surfactant micelles was successfully modeled by treating it as a simple ion-exchange process.

Hessling et al. (1989) investigated the soil washing techniques for remediation of lead-contaminated soils at battery recycling facilities. Three wash solutions were studied for their efficacy in removing lead from these soils: (1) tap water alone at pH 7, (2) tap water plus anionic surfactant in a 0.5% solution, and (3) tap water plus 3:1 molar ratio of EDTA to toxic metals at pH 7–8. Tap water alone did not appreciably dissolve the lead in the soil. Surfactants and chelating agents such as EDTA offer good potential as soil washing additives for enhancing the removal of lead from soils.

The U.S. EPA conducted a series of laboratory bench-scale soil washing studies using water, EDTA, or a surfactant to treat soils from metal recycling sites (PEI Associates, 1989 and Royer et al., 1992). Soil washing did not remove significant quantities of lead from any of the soil fractions. The lead was not concentrated in any particular soil fraction, but rather was distributed among the fractions. EDTA was more effective in removing lead than either the surfactant or water washes.

Simmons et al. (1992) performed ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) experiments for metal ion separation by utilizing an amphiphilic ligand,

solubilized in micelles, to selectively complex a target metal ion in a mixture of metal cations. The characteristic of anionic surfactants complexing and associating with metal cations has been applied to enhance the removal of metal ions.

Nivas et al. (1996) identified the optimal surfactant systems for remediating chromate-contaminated subsurface environments by comparing the removal of chromium (VI) by deionized (DI) water, and water containing surfactant with and without complexing agents and evaluating the surfactant losses in batch and column tests. Results of the batch studies demonstrated that surfactants, when used alone, were able to enhance the extraction of chromate 2.0-2.5 times greater than water. In the presence of a complexing agent the system was able to enhance the chromate elution by 9.3-12.0 times greater than water alone (or 3.7-5.7 times greater than surfactant without the complexing agent). Results of their studies demonstrated that the surfactant system containing Dowfax 8390 (anionic surfactant) and diphenyl carbazide (a complexing agent) was most effective in remediation of the chromium contaminated soil.

Huang et al. (1997) tested four surfactants for naphthalene solubilization capacity, surfactant sorption to soil, and treatability for a sandy soil artificially contaminated with lead and naphthalene. In their study, only Dowfax C10 (anionic) and Triton X-100 (nonionic) were used for the desorption of lead (Pb) from Minoa soil. The addition of the anionic surfactant showed an enhancement for Pb desorption across a wide pH range, with increased amounts of Pb desorbed with increased surfactant concentration. For Triton X-100, there was no enhancement of Pb desorption for concentrations up to 50

mM. At low pH, the nonionic surfactant actually inhibited the desorption of sorbed Pb. They concluded it is likely that Pb reacts with the head group of the anionic surfactant enhancing Pb desorption in an analogous manner to that of a soluble complexing ligand.

Doong et al. (1998) investigated the addition of surfactant to remediate cadmium-contaminated soils. Anionic (sodium dodecyl surfate, SDS), nonionic (Triton X-100, TX100) and cationic (cetyltrimethylammonium bromide, CTAB) surfactants were chosen to elucidate the extraction efficiency of surfactant. EDTA and diphenylthiocarbazone (DPC) were also added to enhance the extraction efficiencies of surfactant. Moreover, the pH effect was examined to determine the optimal surfactant system. They found that the addition of anionic and nonionic surfactants can enhance desorption rates of cadmium, lead and zinc but the addition of cationic surfactant decreased the desorption efficiency of heavy metals. The desorption efficiency was found to increase linearly with the increasing surfactant concentration below the CMC and remained relatively constant above the CMC. Moreover, they found the addition of EDTA can significantly enhance the desorption efficiency of heavy metals. Cationic surfactant was shown to be a more effective surfactant than anionic and nonionic surfactants in extracting heavy metals under acidic environment. However, the addition of DPC lowered the heavy metal removal by 2 to 4 times. Also, increasing pH value can decrease the extraction capabilities of nonionic and anionic surfactant. The authors concluded that surfactants combined with complexing agents could effectively be used as chemical amendments to flush cadmium-contaminated soil by proper selection of the type and concentration of surfactant and complexing agent at different pH values.

Mulligan et al. (1999) evaluated the feasibility of using a biodegradable surfactant, surfactin, to remove heavy metals from a contaminated soil and sediments by sequential batch washes. Results showed that after one and five batch washings of the soil, 25 and 70% of the copper, 6 and 25% of the zinc, and 5 and 15% of the cadmium could be removed by 0.1% surfactin with 1% NaOH, respectively. From the sediment, 15% of the copper and 6% of the zinc could be removed after a single washing with 0.25% surfactin/1% NaOH. Mulligan et al. (1999) further studied the biosurfactant enhanced removal of heavy metals from oil-contaminated soil by using two other biosurfactants, a rhamnolipid and a sopborolipid. Highest levels of zinc removal were obtained using 12% rhamnolipid (19.5% of the zinc) and 4% sopborolipid /0.7% HCl (15.8% of the zinc). Highest copper removal rates were achieved (greater than 25%) with 12% rhamnolipid or with 2% rhamnolipid /1% NaOH. A series of five batch washes removed 100% of the zinc by using 4% sopborolipid/0.7% HCl. In their conclusion, the authors point to the feasibility of removing the metals with the anionic biosurfactants tested even though the exchangeable metal fractions were very low.

Peters (1999) stated that cationic surfactants could be used to modify soil surfaces to promote displacement of metal cations from the solid to the liquid phase. Surfactants can cause the transfer of the soil-bound metal to the liquid phase through ion exchange processes. Desorption and mobilization processes of previously adsorbed metal cations on negatively charged soil surfaces can be applied to in situ soil remediation. He illustrated it by citing the following studies.

Beveridge et al. (1983) investigated the effect of a range of commercially available, water soluble surfactants on the uptake of Cu, Zn, Cd and Pb ions by three types of clay (Kaolinite, illite, and a montmorillonite) over the pH range 3-10. Results from batch equilibrium tests on clay suspensions indicated that the presence of surfactants of different types influenced metal ion uptake by clays to differing degrees. The adsorption of lead, cadmium, copper, and zinc was significantly reduced in the presence of small amounts of cationic surfactant, particularly with montmorillonite clays. One of the more promising aspects of the study involved the very low solution concentration (0.005% by weight) required to cause desorption.

Kornecki et al. (1998) investigated the feasibility of using cationic surfactants to desorb lead (Pb) from contaminated soil using a two-phase test program. For nearly all the surfactants tested, increasing the surfactant solution concentration resulted in decreased pH and increased Pb desorption. Deionized water alone desorbed only 1% of the lead. Lead desorption using a 0.025M surfactant solution was pH dependent. As the pH decreased, desorption of Pb increased. The researchers also compared the Pb extraction efficiency to that using EDTA. EDTA desorbed 94% to 97% of the lead and was not influenced by either solution pH or soil type.

CHAPTER THREE

Sorption and Transport Models

3.1 Introduction

Description of sorption processes of chemicals from a fluid phase onto a solid matrix plays a fundamental role in most disciplines of environmental science. In soil science and subsurface hydrology, this type of information is essential to estimate the mobility of pollutants such as heavy metals, radionuclides, and organic compounds in soils, groundwater aquifers, and fractured rocks (Burgisser et al., 1993). Understanding the mathematical models that include retention and release reactions of heavy metals with the soil matrix and the transport behavior of heavy metals is necessary for identifying the fate of heavy metals in soils. To achieve this goal, retention and release reactions associated with heavy metals in soil are need to be quantified. Retention and release reactions in the soils include precipitation-dissolution, ion exchange, and adsorption-desorption reactions (Amacher et al., 1986). The factors that influence retention and release are soil properties including texture, bulk density, pH, organic matter content, and the type and amount of clay minerals (Selim et al., 1996). Heavy-metal retention has been found to generally increase with increases in soil pH, cation-exchange capacity (CEC), organic matter content, clay content, and the metal oxide content of a soil (Cline et al., 1995). Adsorption is the process whereby a solute binds to the surface of soil particles to form solute-surface site complexes. Ion exchange is the process whereby charged solutes replace ions on soil particles. Adsorption and ion exchange are related in that an ionic solute species may form a surface complex and may replace another ionic solute species

already on the surface binding site. Selim et al. (1996) have stated that the term "retention" or the commonly used term "sorption" should be used when the mechanism of solute removal from solution is unknown, and the term "adsorption" should be used only to describe the formation of solute-surface site complexes. However, the term "adsorption" has often been used to include all processes mentioned above in most experiments. In this study, "adsorption" is understood to include all these processes.

Two terms commonly used in discussing sorption theory are sorbate and sorbent. The sorbate is the contaminant that adheres to the sorbent, or sorbing material. In reference to metal-contaminated soil, the sorbate will usually be a heavy metal, and the sorbent will be the soil.

3.2 Sorption models

Sorption or retention process is determined experimentally by measuring how much of a solute can be sorbed by a particular soil. If the sorption process is rapid compared with the flow velocity, the solute will reach an equilibrium condition with the sorbed phase. This process can be described by an equilibrium sorption isotherm. If the sorption process is slow compared with the flow velocity, the solute may not come to the equilibrium condition with the sorbed phase, and a kinetic sorption model will be needed to describe the process. Both equilibrium and kinetic sorption models have been popularly used to describe the sorption or exchange process. Equilibrium and kinetic models are discussed in this section.

3.2.1 Equilibrium sorption models

Models for characterizing the equilibrium distributions of solute among the phases and interfaces of environmental systems typically relate the amount of solute, S, sorbed per unit of sorbing phase or interface to the amount of solute, C, retained in the solvent phase. An expression of this type evaluated at a fixed system temperature constitutes a retention or sorption "isotherm". Linear, Freundlich, and Langmuir equations are perhaps the most commonly used isotherms to describe equilibrium reactions.

3.2.1.1 Freundlich isotherm

The Freundlich equation is frequently used to describe the sorption reactive solute onto the soil matrix. The Freundlich equation is given by

$$S = K_f C^b \tag{3-1}$$

where S is the amount of solute retained by the soil, in μg/g or mg/kg; C is the solute concentration in solution in mg/l or μg/ml ; K_f is the distribution coefficient in l/kg or ml/g ; and the parameter b is dimensionless and typically has a value of $b < 1$. A typical Freundlich isotherm is shown in Figure 3.1(a). The distribution coefficient describes the partitioning of a solute species between solid and liquid phases over the concentration range of interest and is analogous to the equilibrium constant for a chemical reaction. For $b = 1$, the Freundlich equation is often referred to as the linear retention equation:

$$S = K_d C \tag{3-2}$$

where K_d is the linear distribution coefficient (l/kg or ml/g), which is commonly referred to in the literature. The linear sorption isotherm is shown in Figure 3.2. Note that K_d is

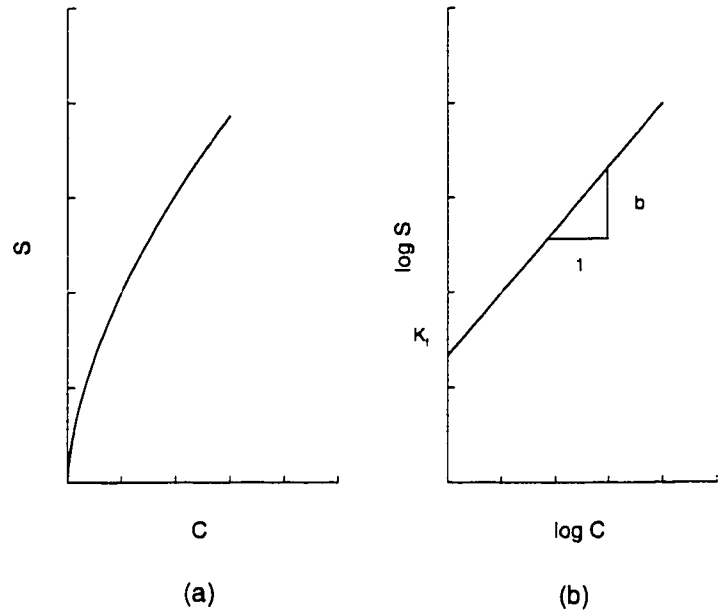

Figure 3.1 (a) Freundlich retention isotherm plotted in terms of S versus C.

(b) Freundlich retention isotherm plotted in terms of log S versus log C.

equal to the slope of the linear sorption isotherm. Although the Freundlich equation has been rigorously derived, the goodness-of-fit of the Freundlich equation to solute sorption data does not provide definitive information about the actual process involved, since the equation is capable of describing a wide variety of data. Often, complex sorption processes can at least in part be described by relatively simple models such as the Freundlich equation. Therefore, the Freundlich parameter K_f and b are best regarded as descriptive parameters in the absence of independent evidence concerning the actual retention mechanism (Selim and Amacher, 1996).

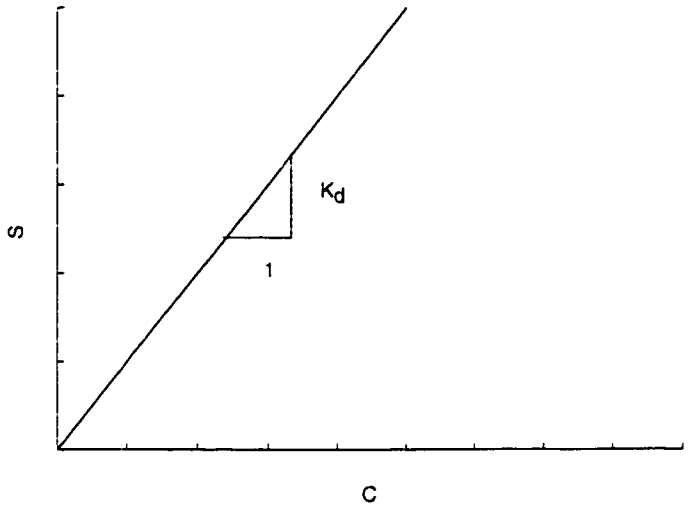

Figure 3.2 Linear retention isotherm with S versus C plotting as a straight line.

Logarithmic representation of the Freundlich equation is frequently used to represent the experimental data. So, the slope of the best-fit curve provides the nonlinear parameter b and the intercept K_f in the equation $\log(S) = K_f + b \log(C)$, when a linear representation of the data in the log form is achieved (Figure 3.1(b)).

3.2.1.2 Langmuir isotherm

The Langmuir isotherm (Figure 3.3) is the oldest and most commonly encountered in soil. The major advantage of the Langmuir equation over linear and Freundlich types is that a maximum sorption capacity is incorporated into the formulation of the model, which may be regared as a measure of the amount of available retention sites on the solid

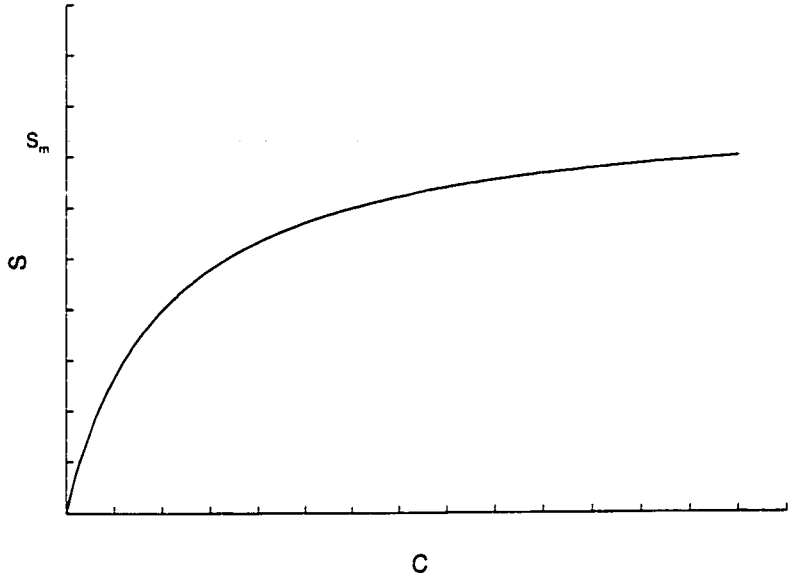

Figure 3.3 Nonlinear Langmuir retention isotherm plotted in terms of S versus C.

phase. The standard form of the Langmuir equation is

$$\frac{S}{S_m} = \frac{\beta C}{1+\beta C} \tag{3-3}$$

where β and S_m are adjustable parameters. Here β (in ml/g or l/kg) is a measure of the bond strength of the molecules on the matrix surface and S_m (in µg/g or mg/kg of soil) is the maximum sorption capacity or total amount of available sites per unit soil mass. In an attempt to classify the various shapes of sorption isotherms, it was recognized that the Langmuir isotherm is the most commonly used and is often referred to as the *L-curve isotherm.*

3.2.2 Kinetic sorption models

As described previously, all the equilibrium models assume that the rate of change in concentration due to sorption is very rapid and that the flow rate is low enough that equilibrium can be reached. If this is not the case and equilibrium is not attained, as stated earlier, a kinetic model is more appropriate. Usually, the kinetic models are linked to appropriate solute transport equations to describe the rate that solute is sorbed onto the solid surface and desorbed from the surface. The one-dimensional convective-dispersive solute transport model will be described in a later section.

3.2.2.1 The irreversible first-order kinetic sorption model

The most simple nonequilibrium condition is that the rate of sorption is a function of the concentration of the solute remaining in solution and that once sorbed onto the solid, the solute cannot be desorbed. The irreversible nonlinear first-order kinetic sorption model is given by:

$$\frac{\partial S}{\partial t} = k_1 C \tag{3-4}$$

where S is the amount of solute retained by the soil (mg/kg), C is the solute concentration in solution (mg/l), and k_1 is a first-order decay rate coefficient (l/kg·h), respectively.

3.2.2.2 The reversible nonlinear first-order kinetic sorption model

If the rate of solute sorption is related to the amount that has already been sorbed and the reaction is reversible where the forward (sorption) reaction is nonlinear, whereas the

backward (desorption) reaction is linear, then the reversible nonlinear first-order kinetic sorption model can be used. The equation for this model is:

$$\frac{\partial S}{\partial t} = k_f C^b - k_b S \tag{3-5}$$

where k_f and k_b are forward and backward reaction rate coefficients in l/kg·h and h^{-1}, respcetively. The b is a dimensionless parameter commonly less than unity and represents the order of the nonlinear reaction. For small values of k_f and k_b, the rate of sorption is rapid and should approach equilibrium in a relatively short time. In fact, at a large time ($t \rightarrow \infty$), when the rate of sorption approaches zero, the above equation yields:

$$S = \frac{k_f}{k_b} C^b = K_f C^b \tag{3-6}$$

This is commonly known as the Freundlich equation.

When forward (sorption) reaction is also linear, namely, the nonlinear parameter b is equal to 1, equation 3-5 becomes a reversible linear kinetic sorption model:

$$\frac{\partial S}{\partial t} = k_f C - k_b S \tag{3-7}$$

In a formulation similar to the nonlinear case, at long enough time ($t \rightarrow \infty$), the rate of retention approaches zero, the above equation reduces to:

$$S = \frac{k_f}{k_b} C = K_d C \tag{3-8}$$

This is similar to that for linear retention isotherms where equilibrium conditions were assumed. Therefore, for linear or Freundlich isotherms, one may regard the distribution

coefficient, K_d and K_f, as the ratio of the rate of sorption or retention (forward reaction) to the rate of desorption or release (backward reaction).

3.3 Solute transport models

The fate of heavy metals in soils depends on retention reactions and transport of the various species in the soils. Numerous studies have been carried out for the purpose of describing the potential mobility of some heavy metals in soil by using mathematical models including a description of the retention processes in the soil matrix. Three solute transport models that are used in this study will be described.

The main migration and transport processes of solutes in groundwater may include advection, diffusion, dispersion, adsorption, biodegradation, and chemical reaction (Bedient et al., 1994). Advection is the movement of contaminants along with flowing ground water at the seepage velocity in porous media. Diffusion is a molecular mass-transport process in which solutes move from areas of higher concentration to areas of lower concentration. Dispersion is a mixing process caused by velocity variations in the porous media. The general form of the partial differential equation used to describe one-dimensional, convective-dispersive transport of solute in a uniform porous medium or soil under saturated, steady water flow conditions (Freeze and Cherry, 1979) may be written as

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x} \qquad (3\text{-}9)$$

where C is the aqueous-phase concentration of solute (mg/l); S is the sorbed phase concentration (mg/kg soil); t is the time in hours(h); x is the length of the domain(cm); D

is the dispersion coefficient (cm^2/h); v is the pore-water velocity (cm/h); ρ is the bulk density of the porous medium(g/cm^3); and θ is the volumetric water content (cm^3/cm^3). This equation is valid irrespective of whether retention or sorption is an equilibrium or a kinetic process. If there is no solute retention by the soil, the above equation is reduced to:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{3-10}$$

In this case, the solute is regarded as a nonreactive tracer. The breakthrough curve (BTC) of tracer usually is used to estimate the dispersion coefficient, D.

3.3.1 A nonlinear Freundlich equilibrium transport model

The first model assumes nonlinear Freundlich equilibrium retention (Eq. 3-1), in which case, by coupling the equations 3-1 and 3-9, a nonlinear equilibrium solute transport model can be expressed as:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{3-11}$$

where $R = (1 + bC^{b-1}K_f \rho/\theta)$ is the retardation factor for the nonlinear equilibrium sorption.

3.3.2 A nonlinear, reversible first-order kinetic transport model

A second model assumes solute nonequilibrium sorption for all sorption sites. The resulting nonlinear, reversible first-order kinetic transport model is given by Eq. 3-9 with $\partial S/\partial t$ defined by the first order kinetic type (Mansell et al., 1977)

$$\rho \frac{\partial S}{\partial t} = k_f \theta C^b - k_b \rho S \tag{3-12}$$

where k_f and k_b are forward and backward reaction rate coefficient in h^{-1}, respectively.

3.3.3 A mobile-immobile or two-region transport model

Mass transfer of sorbing solutes may be affected by both chemical and physical nonequilibrium processes (Fesch et al., 1998). According to him, chemical reactions between solutes and sorbents may be slow compared to the respective physical transport processes. This chemical nonequilibrium results in early breakthrough and/or tailing of solute breakthrough curves (BTCs) in miscible displacement experiments; On the other hand, nonequilibrium may be due to solute diffusion into stagnant or immobile regions of the porous medium. Such physical nonequilibrium also gives rise to early breakthrough and / or tailing of BTCs, but affects both conservative and sorbing solutes. Numerous models have been developed to describe nonequilibrium solute transport in porous media. The most common approaches include two-site models, which refer to chemical nonequilibrium, or two-region models, which account for physical nonequilibrium. Selim et al. (1976) proposed the two-site model concept, which states that it is possible to regard type I sites as those where equilibrium is rapidly reached (i.e., in a few minutes or hours). In contrast, type II sites are highly kinetic and may require several days or months for local equilibrium to be achieved. This model was developed to describe observed batch results that showed rapid initial retention reactions followed by slower retention reactions. The model also developed to describe the excessive tailing of breakthrough curves obtained from pulse inputs in miscible displacement experiments. The conceptual approach of mobile-immobile or two-region model was proposed by van Genuchten and

Wierenga (1976) by combining advective-dispersive transport with nonlinear sorption and intra-aggregate diffusion. It assumes that the soil is aggregated under either saturated or unsaturated flow. Within soil aggregates, where micropores are dominant, diffusion is the primary process. In contrast, convection and dispersion are the dominant processes in the marco (or intra-aggregate) pore spaces that occur between large aggregates. The mobile-immobile model has been successfully used to describe heavy metal transport in soils (for a review see Selim and Amacher, 1996). A mobile-immobile or two-region model (Selim and Amacher, 1988) is described below.

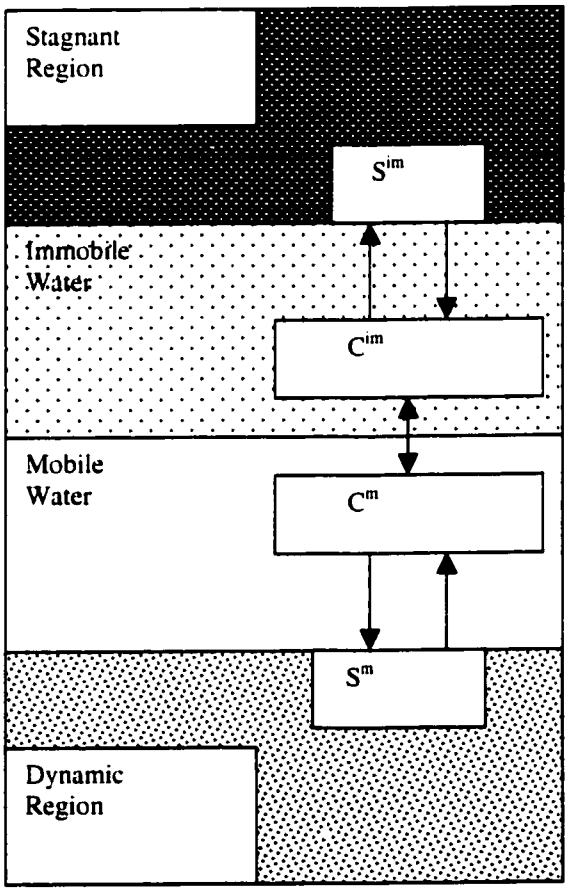

Figure 3.4 Schematic diagram of the mobile-immobile or two-region concept.

The equations for mobile-immobile model of a reactive solute through soils by incorporating the reversible and irreversible retention processes are:

$$\theta^m \frac{\partial C^m}{\partial t} + f\rho \frac{\partial S^m}{\partial t} = \theta^m D \frac{\partial^2 C^m}{\partial x^2} - v^m \theta^m \frac{\partial C^m}{\partial x} - \alpha(C^m - C^{im}) \tag{3-13}$$

and

$$\theta^{im} \frac{\partial C^{im}}{\partial t} + (1-f)\rho \frac{\partial S^{im}}{\partial t} = \alpha(C^m - C^{im}) \tag{3-14}$$

where θ^m and θ^{im} are mobile and immobile water fractions, respectively. The terms C^m and C^{im} are the concentrations in the mobile and immobile water. In addition, D^m and v^m are the hydrodynamic dispersion coefficient and the average pore-water velocity in the mobile region. It is assumed that the immobile water (θ^{im}) is located inside aggregate pores (intra-aggregate) where solute transfer occurs by diffusion only. In both equations, α is a mass transfer coefficient (h^{-1}) that governs the tranfer of solutes between the mobile- and immobile- water phases. A fraction f is a dynamic or easily accessible region and the remaining fraction is a stagnant or less accessible region (see Figure 3.4). Moreover, S^m and S^{im} are the amount of solutes sorbed in the dynamic and stagnant regions. The rates of reaction of S^m and S^{im} were considered as:

$$\partial S^m / \partial t = k_f (\theta^m / \rho) \Phi^m C^m - k_b S^m \tag{3-15}$$

and

$$\partial S^{im} / \partial t = k_f (\theta^{im} / \rho) \Phi^{im} C^{im} - k_b S^{im} \tag{3-16}$$

where Φ^m and Φ^{im} represent the vacant or unfilled sites (mg/kg soil) within the dynamic and the stagnant regions, respectively. In addition, the terms Φ^m and Φ^{im} can be expressed as :

$$\Phi^m = S^m_{max} - S^m = fS_{max} - S^m \tag{3-17}$$

and

$$\Phi^{im} = S^{im}_{max} - S^{im} = (1-f)S_{max} - S^{im} \tag{3-18}$$

where S_{max}, S^m_{max} and S^{im}_{max} are the total amount of the sites in the soil matrix, total sites in the dynamic region, and the total in the stagnant region (mg/kg), respectively. These terms are related by:

$$S_{max} = S^m_{max} + S^{im}_{max} \tag{3-19}$$

It is assumed S_{max} represents the maximum adsorption capacity of an individual soil.

3.3.4 Initial and boundary conditions

The Equations 3-9 to 3-22 were solved subject to following initial and boundary conditions

$$C = 0 \qquad t = 0, 0 \le x \le L \tag{3-20a}$$

$$S = 0 \qquad t = 0, 0 \le x \le L \tag{3-20b}$$

$$-D\frac{\partial C}{\partial x} + vC = vC_0 \qquad x = 0, 0 \le t \le t' \tag{3-21a}$$

$$-D\frac{\partial C}{\partial x} + vC = 0 \qquad x = 0, t > t' \tag{3-21b}$$

$$\frac{\partial C}{\partial x} = 0 \qquad x = L,\ t > 0 \qquad (3\text{-}22)$$

where, L is the length of soil column. Equations 3-21a and 3-21b represent the constant flux boundary conditions which allows the existence of a transition region with which concentration could disperse and vary continuously. These initial and boundary conditions also hold for the two-region model, provided C, v, and D are replaced by C^m, v^m, and D^m, respectively, and plus:

$$C^m = C'^m = 0 \qquad x = 0,\ 0 \le t \le t' \qquad (3\text{-}23)$$

$$S^m = S'^m = 0 \qquad x = 0,\ 0 \le t \le t' \qquad (3\text{-}24)$$

Numerical solutions of the above models were obtained with the finite difference method using solution schemes (Selim and Amacher, 1996) which were modified to the individual model.

3.4 Methodologies for studying retention processes

The retention or sorption equilibrium is usually characterized by the adsorption isotherm. Measurements of isotherms are commonly obtained in the laboratory by performing batch experiments. Batch experiments consist of mixing a series of samples of the adsorbent with solutions in a closed system containing the solute(s) under study for a period of time long enough to allow the attainment of adsorbate-solute equilibrium, and then separating phases. The solution is then analyzed for the solute, and the difference between the initial amount in solution and the final concentration is taken as an indirect

measurement of the amount that has been sorbed onto the solid phases. Such experiments have been used in numerous studies to date.

Although the batch experiment can be easily performed for studying sorption processes, the conditions in batch experiments are generally not representative of field conditions. In addition, many sources of errors (e.g., separation, and solid-to-solution ratio) in the batch experiments are possible (Roy, 1992). Some techniques such as flow-reactors for the determination of sorption parameters have been developed (Carski et al., 1985; Miller et al., 1989; Qualls et al., 1992; Burgisser et al., 1993). One of alternatives to the classical batch experiment which allows simple and rapid measurements of an entire, possibly nonlinear adsorption isotherm relies on column experiments (Burgisser et al., 1993). Column experiments generally consist of a small column packed with a sample of the soil through which an appropriate solvent flows. When a steady flow is reached, the solute is injected at the inlet of the column and its concentration is recorded at the outlet. The concentration vs. time curve (elution curve) contains most of information of the interactions between the solute and the soil. The method of the column experiment for determining the adsorption isotherms (Aris and Amundson, 1973; Schweich and Sardin 1981; Burglsser et al., 1993) is described below.

Eq. 3-9 is the general form of the partial differential equation used to describe one-dimensional, convective-dispersive transport of solute in a uniform porous medium or soil under saturated, steady water flow conditions. In the case of no adsorption, the total concentration of species C_{tot} is equal to the concentration in the solution C (i.e., $C_{tot} = C$).

In this case, the species is called a conservative (or ideal) tracer. For an adsorbed species, the total concentration is given by the sum of the concentration in solution C and the concentration on the sorbate, namely

$$C_{tot} = C + \frac{\rho}{\theta} S \tag{3-25}$$

In the case of rapid adsorption (local equilibrium), the concentration of adsorbed species S is a unique function of the concentration of the dissolved species C. The shape of the breakthrough curve of the linear adsorption is the same as the breakthrough of a conservative tracer. The breakthrough is just delayed in time by the retention factor $R = 1 + \frac{\rho}{\theta} K_d$. Figure 3.5 is a schematic representation of three elution curves assocated with the three possible shapes of the isotherms with a uniform and steady flow together with dispersion effects neglected. The breakthrough curve for a linear adsorption isotherm is a symmetrical elution curve which is illustrated in Figure 3.5a. Due to the linearity of the isotherms, the value of the retention factor does not depend on the concentration of the solution. In the case of a nonlinear isotherms, however, the value of the retention factor does depend on the concentration of the chemical. Nonlinear isotherms give curves which include sharp breaks, and leading and tailing partions (Figure 3.5b,c). Moreover the leading or tailing behaviour is assocated with the convexity or concavity of the isotherms. If the flow is steady and uniform, these curves can be readily interpreted. Golden (1969) proposed a very simple rule concerning the relation between the shape of the nonlinear isotherms and the shape of an elution curve due to a step injection of the solute. Suppose the isotherm is convex (see Figure 3.5b), then

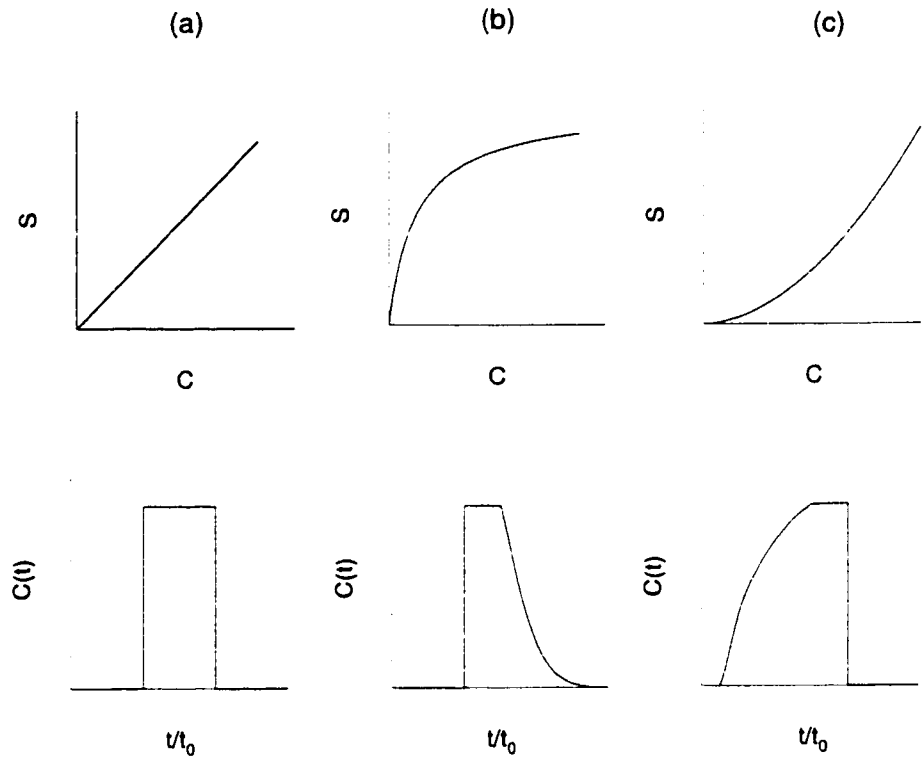

Figure 3.5 Schematic representation of the relation between the adsorption and elution curve due to a step concentration change without dispersion effects. (a) linear, (b) convex, (c) concave.

according to the Golden rule (Golden 1969; Schweich and Sardin, 1981) a step concentration increase at the column input leads to a self-sharpening front, and in the case of a step decrease, a diffuse front will be formed. This behavior is caused by the fact that the retention of solute decreases with increasing concentration in solution (Burgisser et al., 1993). In the case of the adsorption front, the retention decreases with increasing

concentration, resulting in the development of a narrow, self-sharpening front. In the case of the desorption front, the retention increases in time and leads to a broad, diffuse front. The reverse behavior is observed in the case of a concave adsorption isotherm (see Figure 3.5c).

Aris and Amundson (1973) have shown that the tailing part of the elution curve (without dispersion) is such that:

$$t(c) = t_0(1 + \frac{\rho}{\theta}\frac{\partial S}{\partial c}) \tag{3-26}$$

where an average time t_0 is defined as L/v (L is column length). The concentration at the column outlet is dependent on retention time $t(c)$ and can easily be measured ($t(c)/t_0$ is equivalent to the number of pore volumes eluted). This equation represents essentially the derivative of the adsorption isotherm. An experimental record of the retention time $t(c)$ can be integrated to obtain the adsorption isotherm (Burgisser et al., 1993).

$$S = \frac{\theta}{\rho}\int_0^c (\frac{t(c')}{t_0} - 1)dc' \tag{3-27}$$

Burgisser et al. (1993) stated that a column Peclet number, $Pe = Lv/D$, greater than 50 can be considered as sufficiently large (i.e., dispersion coefficient D is sufficiently small) for determination of isotherms.

CHAPTER FOUR

Experimental Materials and Methods

4.1 Materials

The soils used in this study are predominantly Ottawa sand mixed with a very small quantity of Bentonite. All experimental soil samples were made of 98% of Ottawa sand and 2% of bentonite by weight. Ottawa sand was obtained from Geneq Inc, Canada and bentonite was purchased from Sial Inc, Canada. Ottawa sand (size < 10 mesh) used in this study contains 0.12% organic material. The specific surface area of Ottawa sand has been reported to be 0.1 m^2/g. (Chiou et al., 1993). Bentonite is a commercial name for rocks or clay deposits composed largely of the clay mineral montmorillonite. It typically displays a very low permeability and a high cation exchange capacity (Grim, 1962). It is typically a very fine clay with surface areas in excess of 600 m^2/g (Grim, 1962).

Table 4.1. The physical and chemical properties of Ottawa sand and bentonite

soil type	particle size	pH (in water)	CEC[1] (meq/100g)	organic matter content[2] (%)
Ottawa sand	< mesh 10[3]	9.4	0	0.12%
Bentonite	< mesh 325	6.7	110.5 (pH=5.9)	3.1%

(1) H. H. Rump, and H. Krist, Laboratory manual for the examination of water, waste water and soil. 1988, VCH Publishers, pp.154.

(2) Determined at 550°C combustion.

(3) U.S. standard sieve no.10 (2mm).

Commercially available bentonite with a particle size which is less than 325 mesh size was used. It was found to have a high cation exchange capacity of 110.5 meq/100g at a pH of 5.9 in this study. The Ottawa sand and bentonite were placed in an oven at a temperature of 105°C for a minimum of 24 hours before testing. The physical and chemical properties of Ottawa sand and bentonite are shown in Table 4.1.

The surfactants, Triton X-100 and SDS (Sodium dodecyl sulfate) were obtained from SIGMA Chemical Co, U.S.A. SDS and Triton X-100 were used to represent anionic and nonionic surfactants, respectively. Because of its expected strong complexation with the soil matrix (Huang et al, 1997), the cationic surfactant was not selected. EDTA (Ethylenediamine Tetraacetic Acid) was obtained from ICN Biomedicals, Inc, U.S.A. Curpric Sulfate ($CuSO_4$) was used to make copper (Cu) solution as the contaminant. Sodium nitrate ($NaNO_3$) was used as a tracer or electrolyte solution for column experiments. Both $CuSO_4$ and $NaNO_3$ were purchased from Fisher Scientific Company, U.S.A. All the above chemicals were used as received. Several physical and chemical characteristics of surfactants (SDS and Triton X-100) are listed in Table 4.2.

Table 4.2. Characteristics of surfactants used in this study

surfactant	type	chemical formula	M.W. (g)	CMC
Triton X-100	nonionic	$C_8H_{17}C_6H_4(OC_2H_4)_{10}OH$	646.87	1.8×10^{-4} (M/l) [1]
SDS	anionic	$C_{12}H_{25}OSO_3^-Na^+$	288.4	2300(mg/l) [2]

(1) Edwards et al., 1994

(2) Doong et al., 1996

4.2 Batch experiments

All soil samples were dried at 105°C for a minimum of 24 hours before usage. There were two sets of batch experiments in this study. In the first set, four different surfactant concentrations below or above CMC were used to determine the effect of surfactant concentration on the adsorption isotherms of Cu(II) in soils. Concentration of 0, 0.2, 1.0, 4,0 CMC and 0, 0.28, 1.39, 5.56 CMC were selected for SDS and Triton X-100 respectively. The concentration of 0.01M was selected for EDTA because EDTA has been commonly investigated as a chelant to remove heavy metals from contaminated soils. The final solution pH of this set of experiments was kept as 5.5. In the second set of experiments, the final solution pH of 3.5 was investigated to check the effect of the solution pH on the sorption isotherms of Cu(II) in soils. Only 5.56 CMC Triton X-100 and 1.0 CMC and 4.0 CMC SDS were selected for the second set of batch experiments.

In all batch test experiments, 3.0 g of soil and 30 ml Cu(II) solution at various concentrations (0 to 100 mg/l) with SDS or Triton X-100 or EDTA were mixed in clean 50 ml plastic Nalgene centrifuge tubes equipped with snap-on caps. The ratio of solid to liquid was 1:10. Surfactant solutions of varying concentrations were made with surfactant stock and distilled water. Cu(II) soultions of varying concentrations were also made with $CuSO_4$ stock and distilled water. Small amounts of HNO_3 (10N) and NaOH (10N) were also added to provide the solutions with final pH values 5.5 and 3.5 respectively. The amount of HNO_3 and NaOH added were too small to affect the total concentrations of Cu(II) and surfactants in the tubes. The solution pH was measured by a pH meter (Orion Model 720A). The suspensions were then shaken on a reciprocating orbital shaker at 160

rpm for 24 hours at a room temperature of 25 ± 2°C. Phase separation was accomplished by centrifugation (IEC HN_SII Centrifuge) at 3,500 rpm for 15 minutes. The supernatants were filtered with 0.45 μm glass fiber filters (Whatman). The filtrates were acidified with HNO_3 for Cu analysis by Atomic Absorption Spectroscopy (AAS, AAnalyst 100). Sample blanks and standards were used as controls in every batch test, to ensure mass balance.

4.3 Column experiments

All column experiments were conducted at room temperature (25 ± 2°C). The experimental set-up is shown in Figure 4.1. Plastic columns (L = 34.5 cm, D = 3.65 cm) with metal end

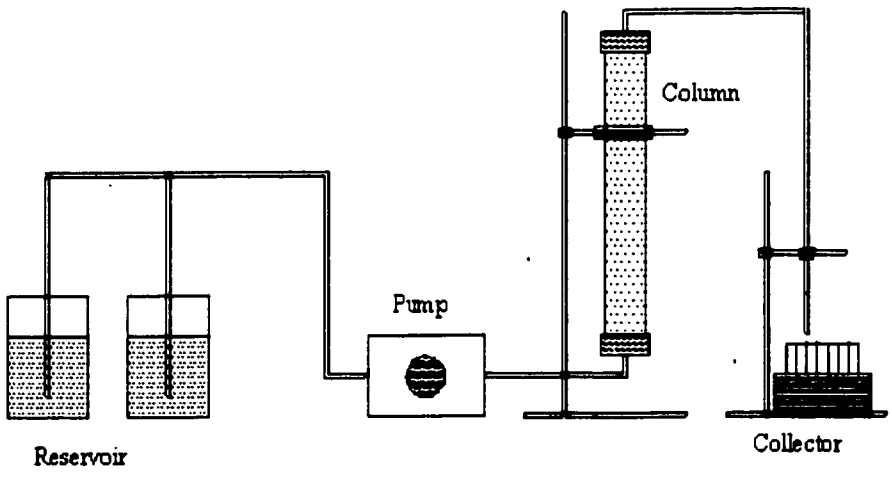

Figure 4.1 Experimental set-up for column experiments.

pieces were equipped with a pore stone and also a Whatman filter paper (0.7 μm). The purpose of having a pore stone at both ends of the column fitted with was to ensure

uniformly radial distribution at the column inlet and reduce dispersion at the outlet. A peristaltic pump was connected to the column with a two-way valve to switch the solute reservoirs without flow interruption. The columns were packed dry with 675 ± 0.5g soil, under continuous tapping against the plastic wall as the dried soil was added. The soil was placed in the column in 14 layers. The purpose of tapping the column and 14 layers of soil in the column was to pack the soil uniformly. The pore volume of the packed column was determined by the weight difference of the water-saturated column versus the dry soil column, assuming complete saturation.

Before applying a pulse of solute to the soil column, an electrolyte solution (0.01M $NaNO_3$) was pumped from bottom to top through the column until the water saturated and steady-state conditions were reached. This required approximately 15 ~ 20 pore volumes. Meanwhile, the velocities of flow were adjusted to the desired level. Pore water velocities were checked gravimetrically via the outflow. In average, pore water velocity (v) was calculated using the following formula:

$$v = \frac{QL}{P_v} \tag{4-1}$$

where Q is the average flux of water through columns, L is the column length, and P_v is the pore volume.

Various concentrations of the surfactants or distilled water with 100 mg/L Cu(II) with a solution pH of 5.5 or 3.5 were pumped through the column. All such solutions contained 0.01M $NaNO_3$ in order to prevent migration of fines by providing uniform ionic strength conditions. At first, some pore volumes of these solutions are pumped through the

column. This was followed by just background solutions (without Cu(II)) having the same pH. The column effluent was manually collected at a constant time interval and then acidified with HNO_3 for Cu analysis by AAS. The sample volumes depended on the test conditions and the frequency of observations.

For estimation of the apparent dispersion coefficient D, 0.2M $NaNO_3$ solution was used as a relatively nonreactive tracer (Burgisser et al., 1993). Before pumping a pulse of $NaNO_3$ solution to the soil column, some pore volumes of distilled water were pumped through the column. The concentrations of $NaNO_3$ at the outlet of the column were measured by a Digital Conductivity Meter (Fisher Scientific 09-328).

CHAPTER FIVE

Results and Discussions

5.1 Batch tests

5.1.1 Effect of concentration

The results of batch experiments with Cu(II) are shown in Figures 5.1-5.3. The amount of Cu(II) adsorbed expressed in milligrams of Cu(II) per gram of soil has been plotted against the equilibrium Cu(II) concentration in solution (mg/l). As stated earlier, the adsorption characteristics of Cu(II) in soil were assessed in the presence of a nonionic surfactant (Triton X-100), an anionic surfactant (SDS) and EDTA at different concentrations. Surfactant concentration is an important factor influencing the sorption of heavy metals in the soil. The sorption data in Figures 5.1-5.3 indicate that the adsorption behaviors of Cu(II) in soil in the presence of Triton X-100, SDS and EDTA are not similar at a pH of 5.5. In Figure 5.1, the data show that an increase in the concentration of Triton X-100 has an effect on the sorption of Cu(II) in soil for high concentrations above CMC. The differences in sorbed Cu(II) for the lower surfactant concentrations tested are not significant. For an initial Cu(II) concentration of 82 mg/l, after 24 hours the sorbed Cu(II) concentrations are 410, 440, 350, and 360 mg/kg in the presence of 0, 0.28, 1.39, and 5.56 CMC Triton X-100, respectively. Also for an initial Cu(II) concentration of 42 mg/l, in the presence of 0, 0.28, 1.39, and 5.56 CMC Triton X-100, the sorbed Cu(II) concentrations are 300, 280, 280, and 280 mg/kg, respectively. However, in Figure 5.2, an increase in the concentration of SDS results in a significant decrease of the sorbed Cu(II) in soil except for concentrations below CMC.

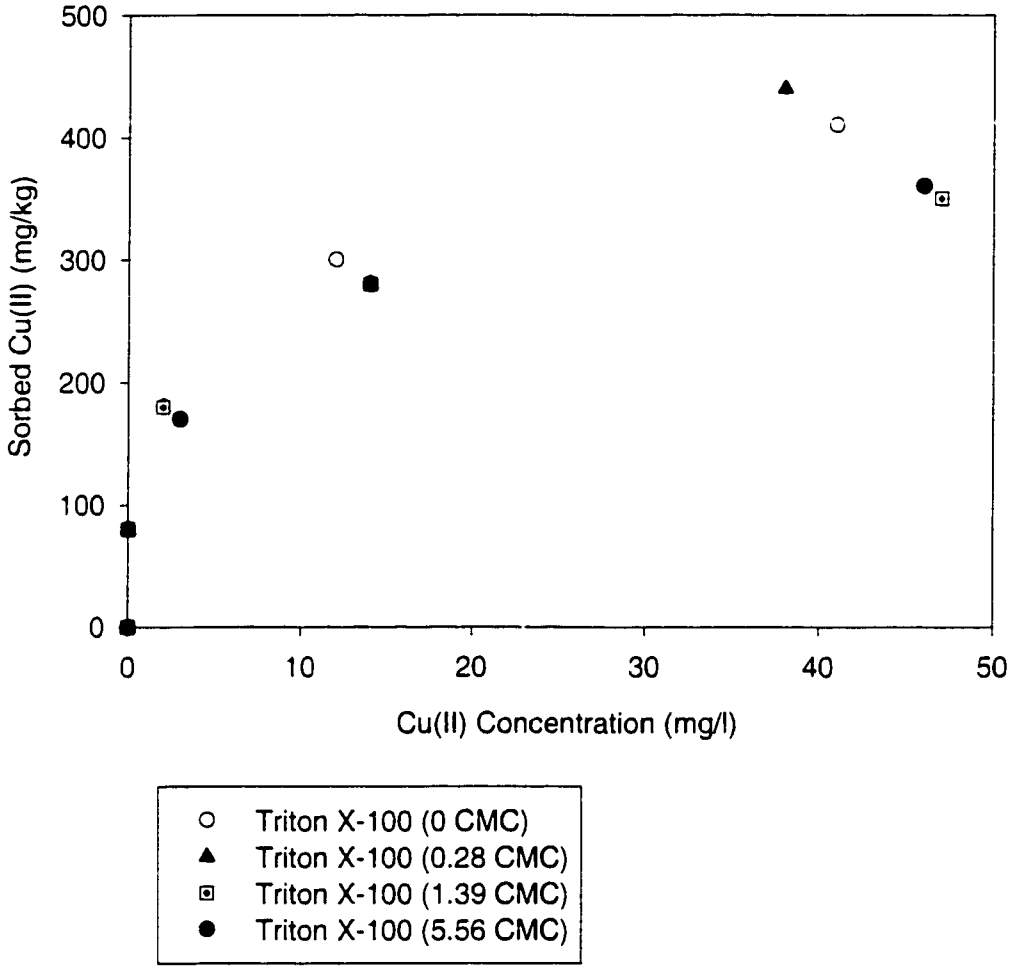

Figure 5.1 Sorption isotherms for Cu(II) after 24 hours on soil in the presence of Triton X-100 at a pH of 5.5.

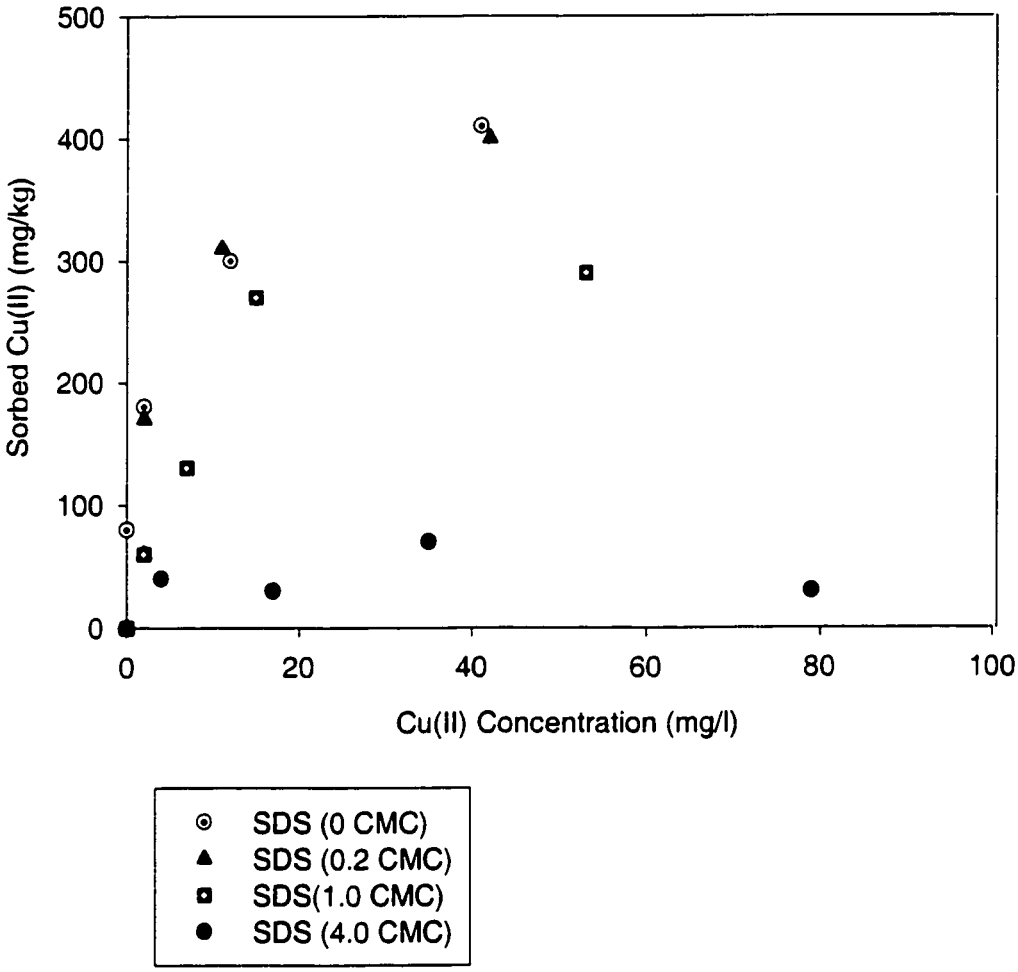

Figure 5.2 Sorption isotherms for Cu(II) after 24 hours on soil in the presence of SDS at a pH of 5.5.

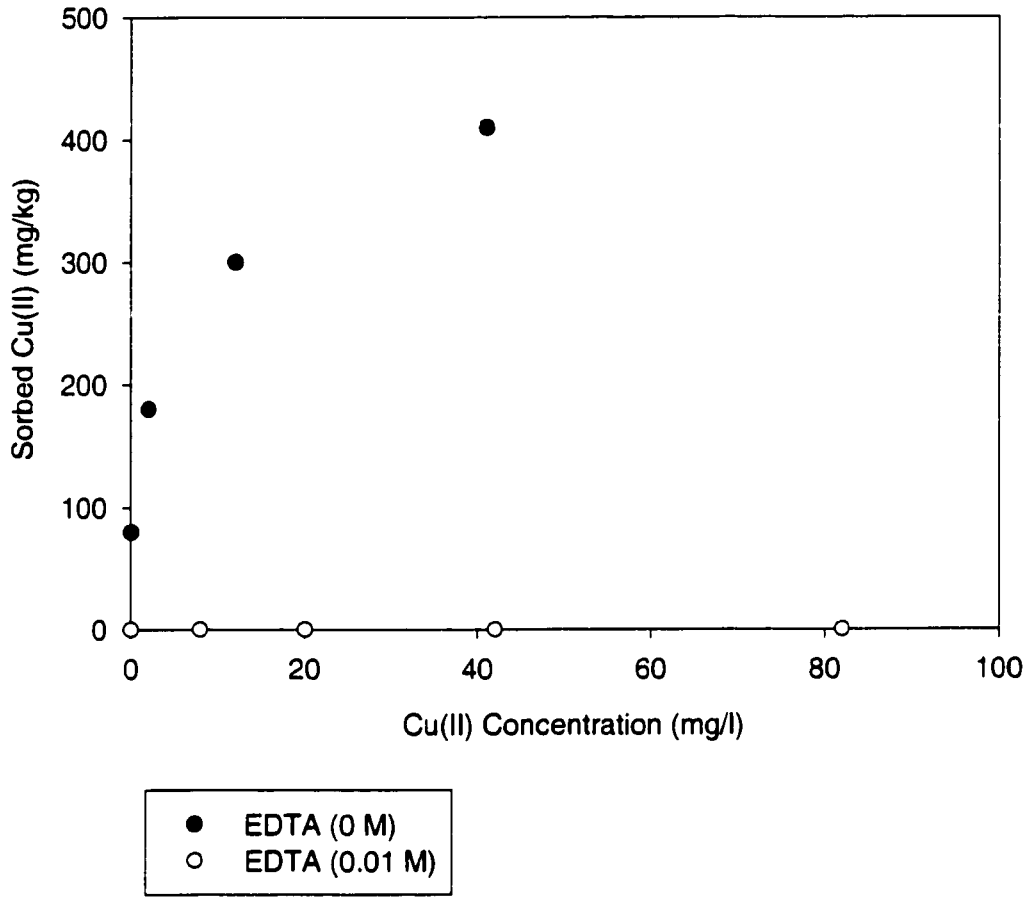

Figure 5.3 Sorption isotherms for Cu(II) after 24 hours on soil in the presence of EDTA at a pH of 5.5.

There is a significant decrease in the sorbed Cu(II) when the concentration of SDS is increased from 1.0 CMC to 4.0 CMC. The sorbed Cu(II) concentrations are 80,180, 300, and 410 mg/kg and 60, 170, 310, and 400 mg/kg for initial Cu(II) concentrations of 8, 20, 42, and 82 mg/l with distilled water alone and in the presence of 0.2 CMC SDS, respectively. However, in the presence of 1.0 CMC SDS and 4.0 CMC SDS, the sorbed Cu(II) concentrations are 60, 130, 270, 290 and 40, 30, 70, 30 mg/kg, respectively. SDS is shown to be a more effective surfactant than Triton X-100 in extracting Cu(II) from the soil. In the presence of 0.01M EDTA (Figure 5.3), the sorbed Cu(II) is 0 mg/kg. All Cu(II) is extracted from the soil by forming complexes with EDTA in the solution (Cline et al., 1995). Thus, the results in Figure 5.3 reinforce the fact that chelating agents are well suited for removing metals bound by soils.

The mechanisms of surfactant enhanced desorption of Cu(II) has been discussed in Chapter Two. Since Cu(II) is a cation, the anionic surfactant SDS would not be involved in the ion exchange with Cu(II). Figure 5.2 indicates that the effect of SDS on the sorption of Cu(II) in soil is not noticeable until surfactant concentrations exceed the CMC. In addition, greater Cu(II) removal is observed as the surfactant concentration continues to increase above the CMC. These results are consistent with a mechanism of counterion binding for the extraction of Cu(II) by SDS. It is known that adsorption of cations onto soil particles occurs predominantly on surfaces that are negatively charged, such as organic matter, clay, and metal (hydr)oxides (Temminghoff et al., 1994). Bentonite is composed largely of clay mineral montmorillonite. The cation exchange capacity (CEC) of bentonite used in this study is 110.5 meq/100g at a pH of 5.9, and cation exchange capacity of Ottawa sand is 0 meq/100g. Also, bentonite contains 3.1% of

organic matter while Ottawa sand contains only 0.12% of organic matter. So Cu(II) is predominantly adsorbed onto the surface of bentonite. It is thus likely that precipitation-dissolution may be another mechanism for SDS to displace the Cu(II) from the soil surface.

The results for Triton X-100 (Figure 5.1) show that the majority of Cu(II) removal occurs above the CMC for high concentrations of Cu(II), with little or no removal below the CMC. These results are consistent with a mechanism of micellar solubilization as reported by Siffert et al. (1992). Precipitation-dissolution is a possible mechanism for Triton X-100 to displace the Cu(II) on the soil surface. Doong et al (1996) found that more Triton X-100 was needed to reach the CMC in soil-water systems than in soil-free systems. So, they concluded that Triton X-100 can be sorbed onto soil though it is a nonionic surfactant. Ray et al. (1995) found that the nonionic surfactant Tergitol 15-S-7 has the adsorption properties on clays. In their study, montmorillonite not only sorbed the largest quantity of Tergitol 15-S-7 but also held it most strongly. It may thus be possible that Triton X-100 displace some bound Cu(II) in the experiments reported here.

5.1.2 Effect of pH

The level of pH of surfactant solutions and soil suspension is another important factor that affects sorption of Cu(II) in the presence of surfactants. Only Distilled water, 5.56 CMC Triton X-100, 1.0 CMC and 4.0 CMC SDS were selected for sorption tests at a pH of 3.5. The data are shown in Figure 5.4. In addition, the data in Table 5.1 indicate the differences in the sorbed Cu(II) at a solution pH of 3.5 to 5.5. As illustrated in Table

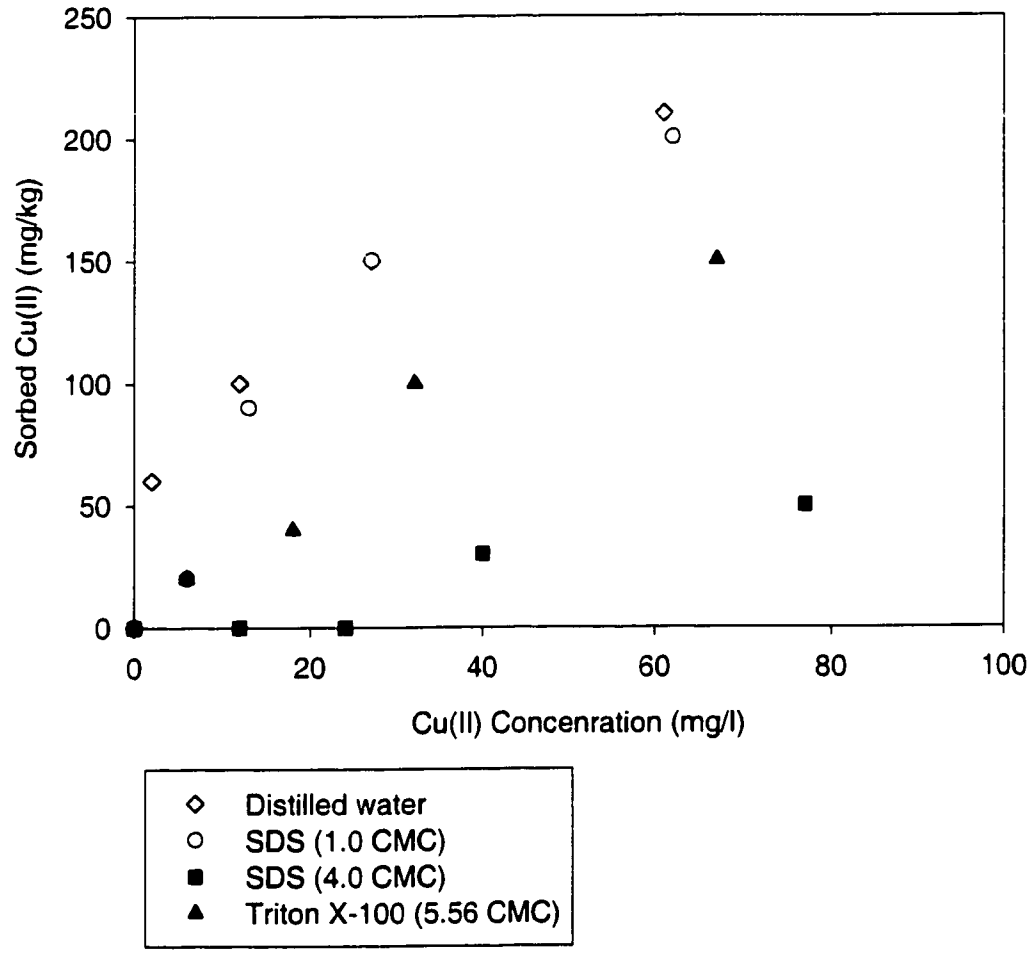

Figure 5.4 Sorption isotherms for Cu(II) after 24 hours on soil at a pH of 3.5.

5.1, in the presence of distilled water alone, only 60, 100, 150, and 210 mg/kg Cu(II) remain in the soil at a pH of 3.5 while there are 80, 180, 300, and 410 mg/kg Cu(II) remain in the soil at a pH of 5.5. As the soil pH decreases, the amount of copper desorbed from the soil increases. At a pH of 5.5, the difference in sorbed copper between Triton X-100 and distilled water is minor. But, at a pH of 3.5, the difference is very large. It is likely that Triton X-100 could displace more copper ions from soil surface under more acidic conditions. But, the differences of sorbed Cu(II) between 1.0 CMC SDS and distilled water are minor at a pH of 3.5 compared to a pH of 5.5. The 4.0 CMC SDS is shown to be the most effective surfactant concentration to extract the sorbed copper ions from the soil. At low initial concentrations essentially, all of the Cu(II) is released from the soil at the low pH. At an initial concentrations of 82 mg/l, only 50 mg/kg of Cu(II) remain in the soil in the presence of 4.0 CMC SDS compared to 210 mg/kg of Cu(II) in the presence of distilled water alone. These results show that surfactants offer a good potential for enhancing the removal of copper from the soil under more acidic condition.

Table 5.1 Effect of pH on the sorbed Cu(II) in soil, mg/kg

	Final solution pH	Initial concentration of Cu(II) (mg/l)			
		8	20	42	82
Distilled water	5.5	80	180	300	410
	3.5	60	100	150	210
5.56 CMC Triton X-100	5.5	80	170	280	360
	3.5	20	40	100	150
1.0 CMC SDS	5.5	60	130	270	290
	3.5	20	90	150	200
4.0 CMC SDS	5.5	40	30	70	30
	3.5	0	0	30	50

5.1.3 Sorption isotherms

Kinniburgh (1986) demonstrated that retention or sorption isotherms could be characterized by their behavior at low and high concentrations. There are two limiting criteria. At low concentration (c), it is

$$\lim_{c\to 0}\left(\frac{\partial S}{\partial c}\right)=\infty \qquad or \qquad \left.\frac{\partial S}{\partial c}\right|_{c=0}=\text{constant} \tag{5-1}$$

and at high concentration (c), it is

$$\lim_{c\to\infty} S(c)=\infty \qquad or \qquad \lim_{c\to\infty} S(c)=S_{max} \tag{5-2}$$

The Freundlich isotherm will approach an infinite value but the Langumir isotherm will approach a constant value at high c, usually denoted as the *sorption maximum*. The sorption maximum may be related to the specific surface area of the pure substances. Simple observation of the slope of the data often allows one to guess the isotherm that may best fit experimental results. The data in Figures 5.1-5.4 display essentially nonlinear relationship between the adsorbed Cu(II) and the equilibrium concentration within the tested conditions, where the sorptivity gradient is the highest at low Cu(II) concentration, gradually decreasing to an asymptotic value. Therefore, the mathematical representation of two of the most commonly used isotherms, the Freundlich and Langmuir isotherms, are used to fit the experimental data at pH values 3.5 and 5.5, respectively. A nonlinear regression (nonlinear least squares, NLLS) technique is used for estimating the sorption coefficient of the nonlinear Freundlich isotherms and nonlinear Langmuir isotherms, respectively. The coefficient of determination, R^2, is used as a measure of the goodness-of-fit. The selected experimental data together with fitted

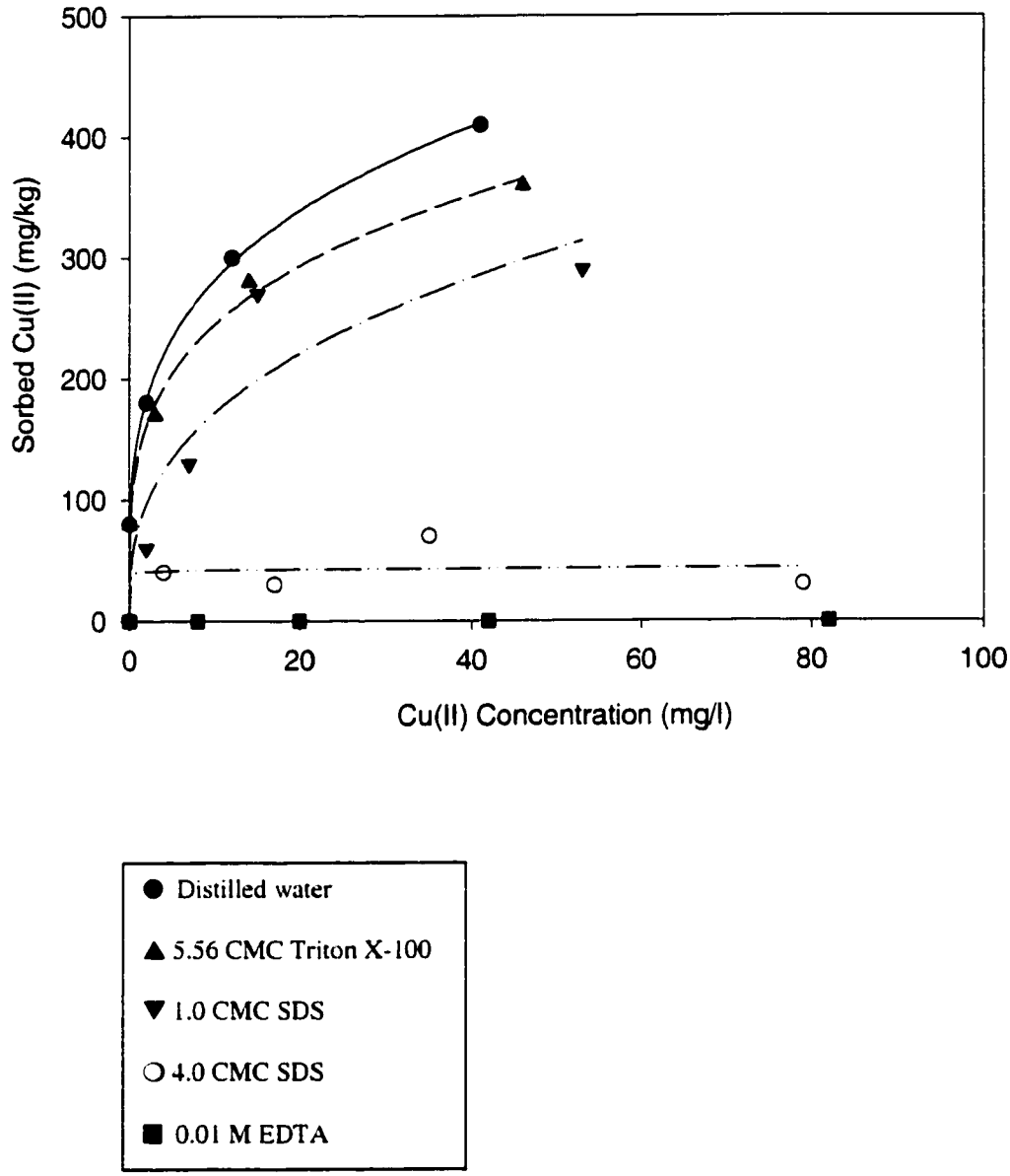

Figure 5.5 Nonlinear Freundlich sorption isotherms for Cu(II) after 24 hours on soil at a pH of 5.5, symbols are experimental data and lines are fitted isotherms.

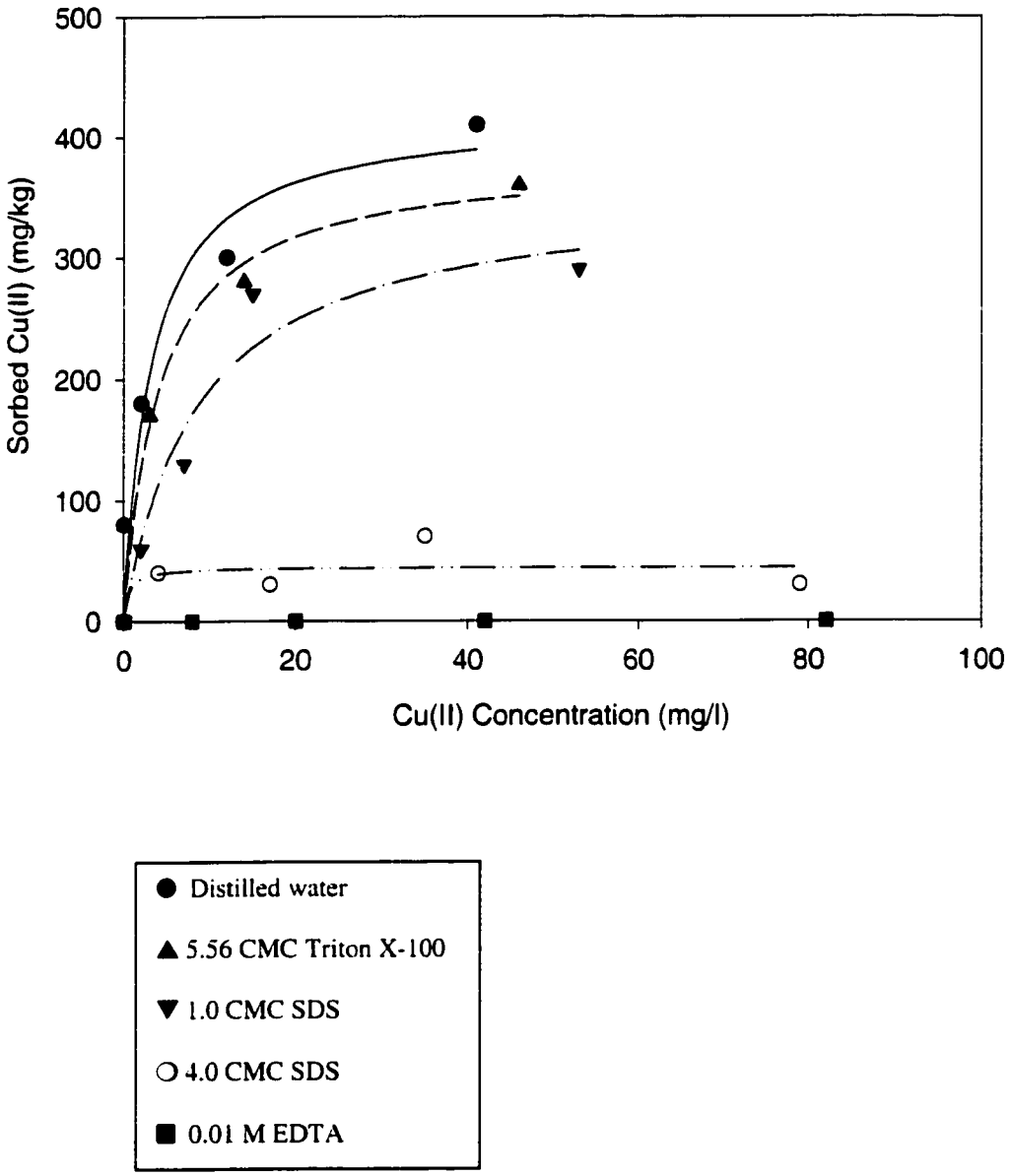

Figure 5.6 Nonlinear Langmuir sorption isotherms for Cu(II) after 24 hours on soil at a pH of 5.5, symbols are experimental data and lines are fitted isotherms.

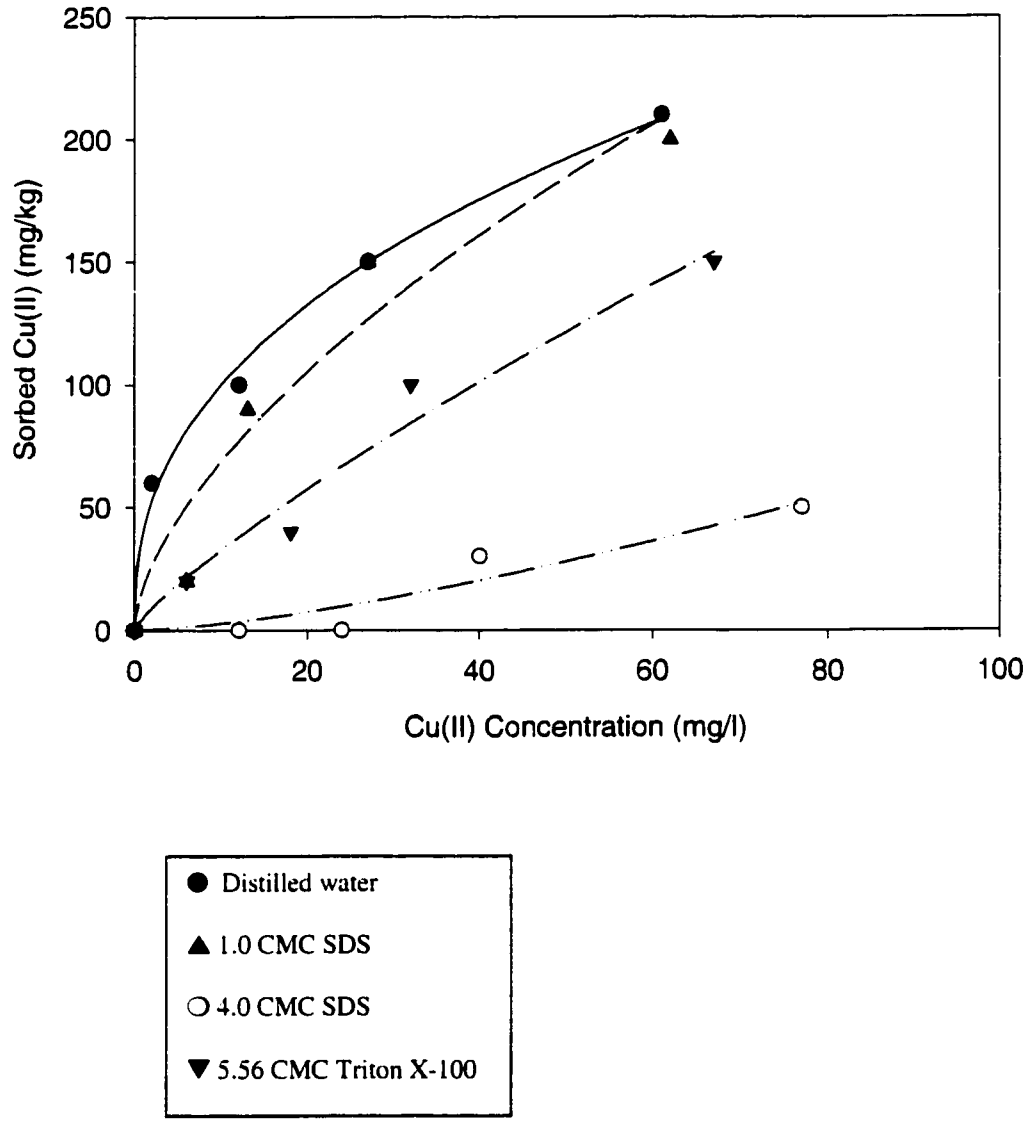

Figure 5.7 Nonlinear Freundlich sorption isotherms for Cu(II) after 24 hours on soil at a pH of 3.5, symbols are experimental data and lines are fitted isotherms.

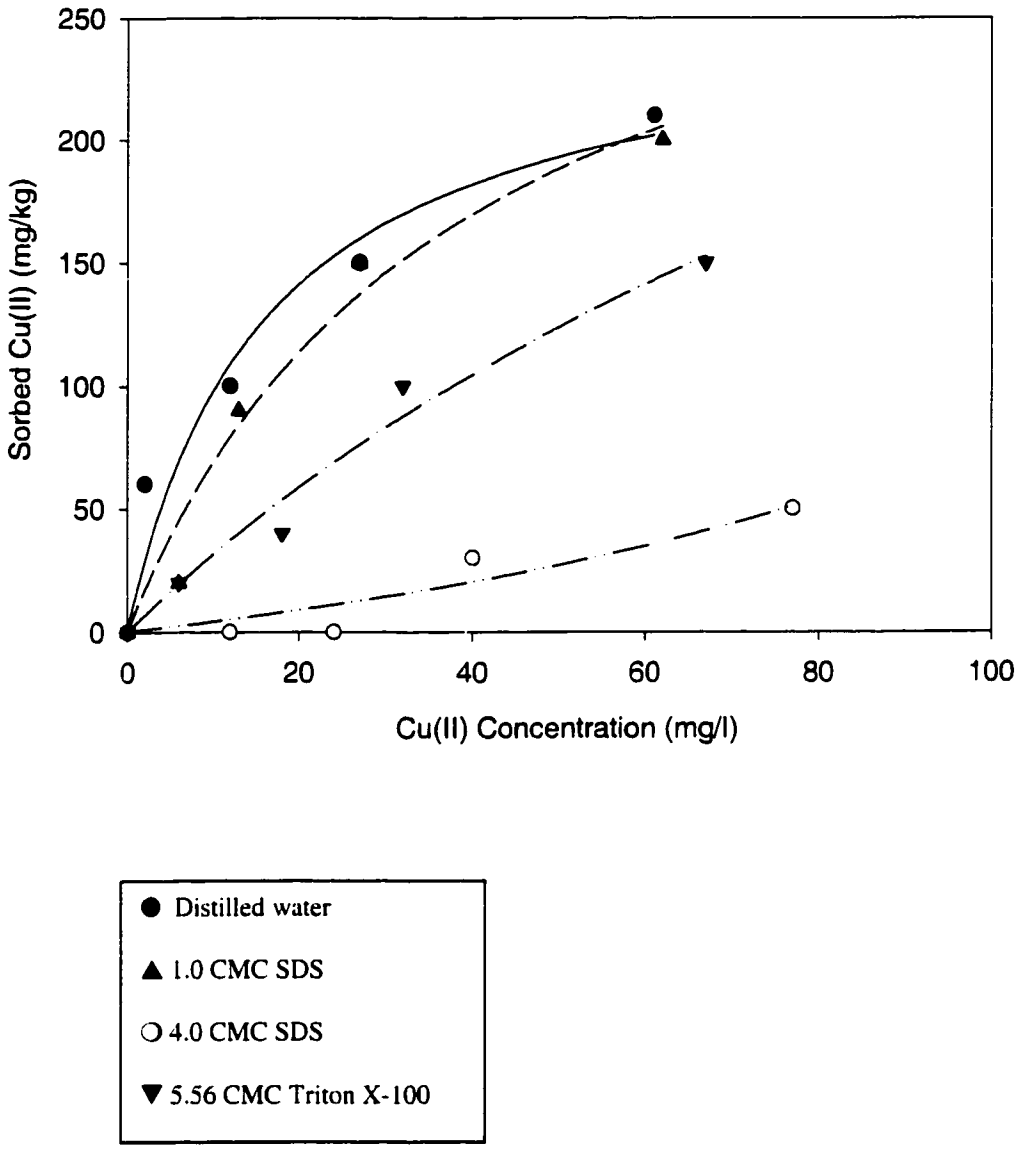

Figure 5.8 Nonlinear Langmuir sorption isotherms for Cu(II) after 24 hours on soil at a pH of 3.5, symbols are experimental data and lines are fitted isotherms.

sorption isotherms are shown in Figures 5.5-5.8. The optimized parameters for all isotherms are shown in Table 5.2.

Table 5.2 Summary of optimized isotherm parameters

Solution	Isotherm type	pH	S_m (mg/kg)	β (l/mg)	K_f (l/kg)	b	R^2
Distilled water	Freundlich	5.5	-	-	151.6	0.20	0.940
	Langmuir	5.5	419	0.320	-	-	0.925
	Freundlich	3.5	-	-	39.6	0.40	0.995
	Langmuir	3.5	255	0.062	-	-	0.952
5.56 CMC Triton X-100	Freundlich	5.5	-	-	133.6	0.26	0.921
	Langmuir	5.5	382	0.245	-	-	0.919
	Freundlich	3.5	-	-	5.0	0.81	0.972
	Langmuir	3.5	473	0.007	-	-	0.977
1.0 CMC SDS	Freundlich	5.5	-	-	74.8	0.36	0.886
	Langmuir	5.5	356	0.116	-	-	0.952
	Freundlich	3.5	-	-	16.9	0.61	0.941
	Langmuir	3.5	333	0.026	-	-	0.970
4.0 CMC SDS	Freundlich	5.5	-	-	41.1	0.02	0.574
	Langmuir	5.5	44	1.850	-	-	0.579
	Freundlich	3.5	-	-	0.1	1.45	0.902
	Langmuir	3.5	79	-0.005	-	-	0.884

As mentioned earlier, the sorption isotherms show EDTA has the greatest effect on the adsorption of Cu(II) followed by SDS and Triton X-100. Also a decrease of solution pH from 5.5 to 3.5 resulted in changes of Cu(II) sorption. For distilled water, the Freundlich sorption isotherm (Table 5.2) provided a slightly better approximation than the Langmuir sorption isotherm when the observed sorption over the entire range of Cu(II) was fitted to the model at pH of 5.5 and 3.5 (coefficient of determination, R^2, of 0.940 and 0.995 to 0.925 and 0.952), respectively. In the presence of Triton X-100, both Freundlich and Langmuir sorption isotherms provide good approximations at pH of 5.5 and 3.5 (R^2 are 0.921, 0.972 and 0.919, 0.977, respectively). In the presence of 1.0 CMC SDS (Figure

5.5), the Freundlich sorption isotherm provide a poor approximation with an over-estimation of sorption at a pH of 5.5 (R^2 is 0.886). Both the Freundlich sorption isotherm and the Langmuir sorption isotherm provide relatively poor approximations at a pH of 5.5 (R^2 are 0.574 and 0.579, respectively) in the presence of 4.0 CMC SDS, respectively. Based on Figures 5.5 through 5.8, neither isotherm equation guaranteed successful description of the measured results.

From the data in Table 5.2, a correlation between solution type and the partition coefficient (K_f) or maximum sorption capacity (S_m) can be demonstrated in this study for Freundlich sorption isotherm or Langmuir sorption isotherm, respectively. The K_f decreases form 151.6 to 133.6, 74.8, and 41.1 L/kg when the solution with distilled water alone changes to 5.56 CMC Triton X-100, 1.0 CMC SDS and 4.0 CMC SDS, respectively, at a pH of 5.5. Similarly at a pH of 3.5, the K_f decreases from 39.62 to 16.93, 5.03, and 0.10 L/kg when solution with distilled water alone changes to 1.0 CMC SDS, 5.56 CMC Triton X-100 and 4.0 CMC SDS, respectively. Similar trends are noted with the values of maximum sorption capacity. Thus, it can be concluded that surfactant enhanced removal of heavy metals from contaminated soil is feasible by proper selection of the surfactant.

5.2 Column tests

The experimental BTCs are compared to the adsorption isotherms obtained in the batch tests in Figures 5.9 to 5.15. The in situ method of calculating the adsorption isotherms from the desorption front (decreasing part) of BTCs has been described in Chapter Three.

The data points of the desorption front were interpolated by using a least-squares spline fit. The trapezoidal integration technique was employed to get the adsorption isotherms by numerically integrating the Eq. 3-27. It is necessary to extrapolate the elution curve down to zero by eye. The hydraulic dispersivity ($\lambda = D/v$) of the soil packed column is 0.373 cm (see section 5.3). The corresponding column Peclet number, $Pe = vL/D$, is 92.5. The result indicates that the flow regime in all column studies was dominated by advection which allows us to neglect dispersion effects in the determining isotherms from the BTCs (Burgisser et al., 1993). All isotherms calculated from the column breakthrough data are shown as solid lines in the Figures 5.9b through 5.15b. A summary of experimental conditions and experimental results of the column studies are shown in Table 5.3 and Table 5.4, respectively. Langmuir isotherms were fitted to the data from the column experiments in order to calculate the maximum sorption capacity (S_m) for comparison with batch experiments. These results are shown in Table 5.5. In the plots of BTCs, the abscissa t/t_0 is equivalent to the number of pore volumes eluted.

Figure 5.9a shows the breakthrough curve for Cu(II) transport in soil with the solution pH of 5.5, where the Cu(II) step input duration is $0 \leq t/t_0 \leq 16.6$ The breakthrough curve shows a sharp front (adsorption part) and a diffuse tail (desorption part) with a maximum concentration of 65 mg/l. The shape of the breakthrough curve indicates that the adsorption isotherm is likely to be nonlinear. Schweich and Sardin (1981) stated that it might be difficult to decide whether the elution curves are due to a nonlinear adsorption isotherm in a uniform and steady flow, or to a linear adsorption isotherm in a complicated flow pattern. In this study, the soil was packed homogeneously in 14 layers in every

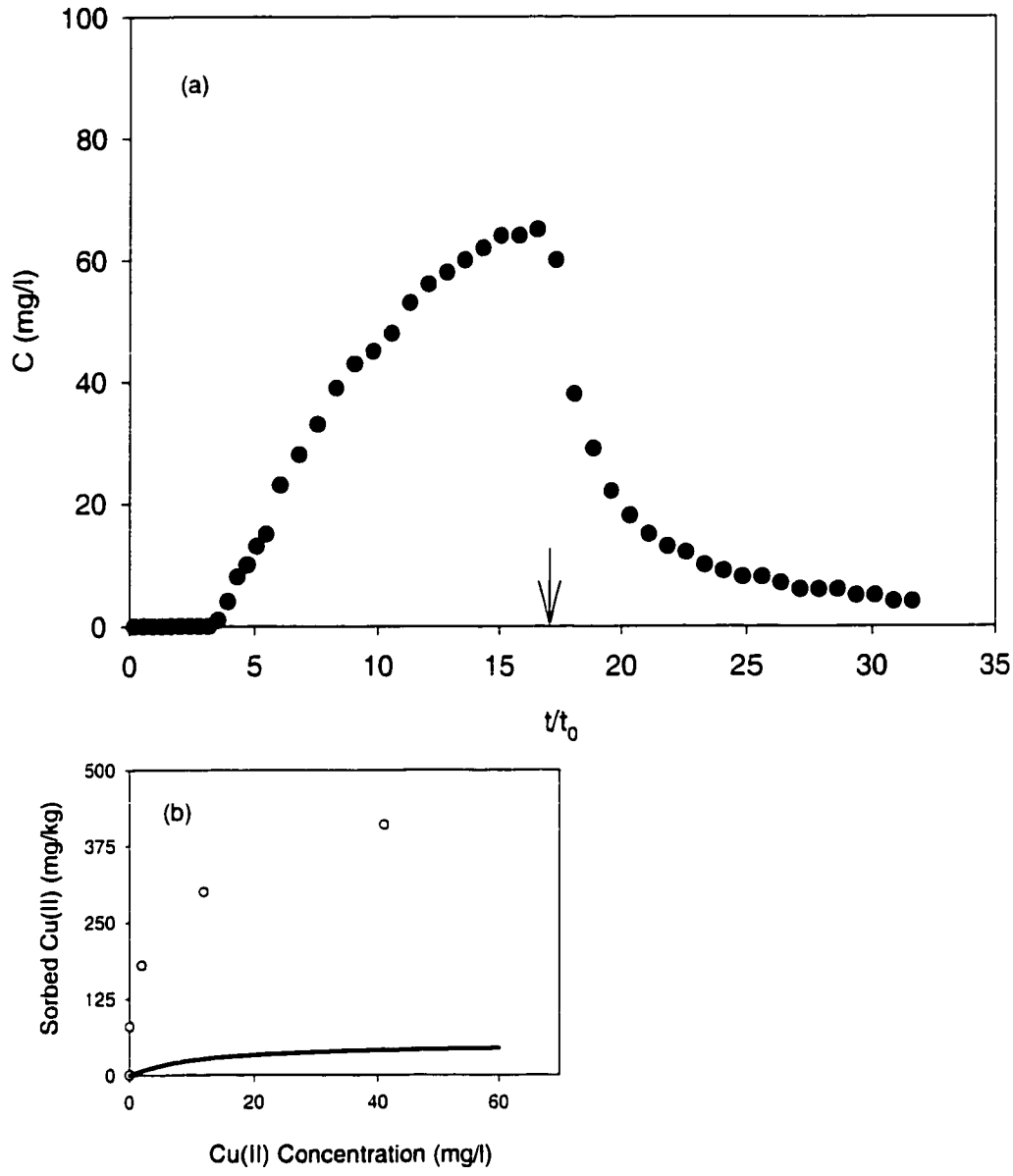

Figure 5.9 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of distilled water alone at a pH of 5.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

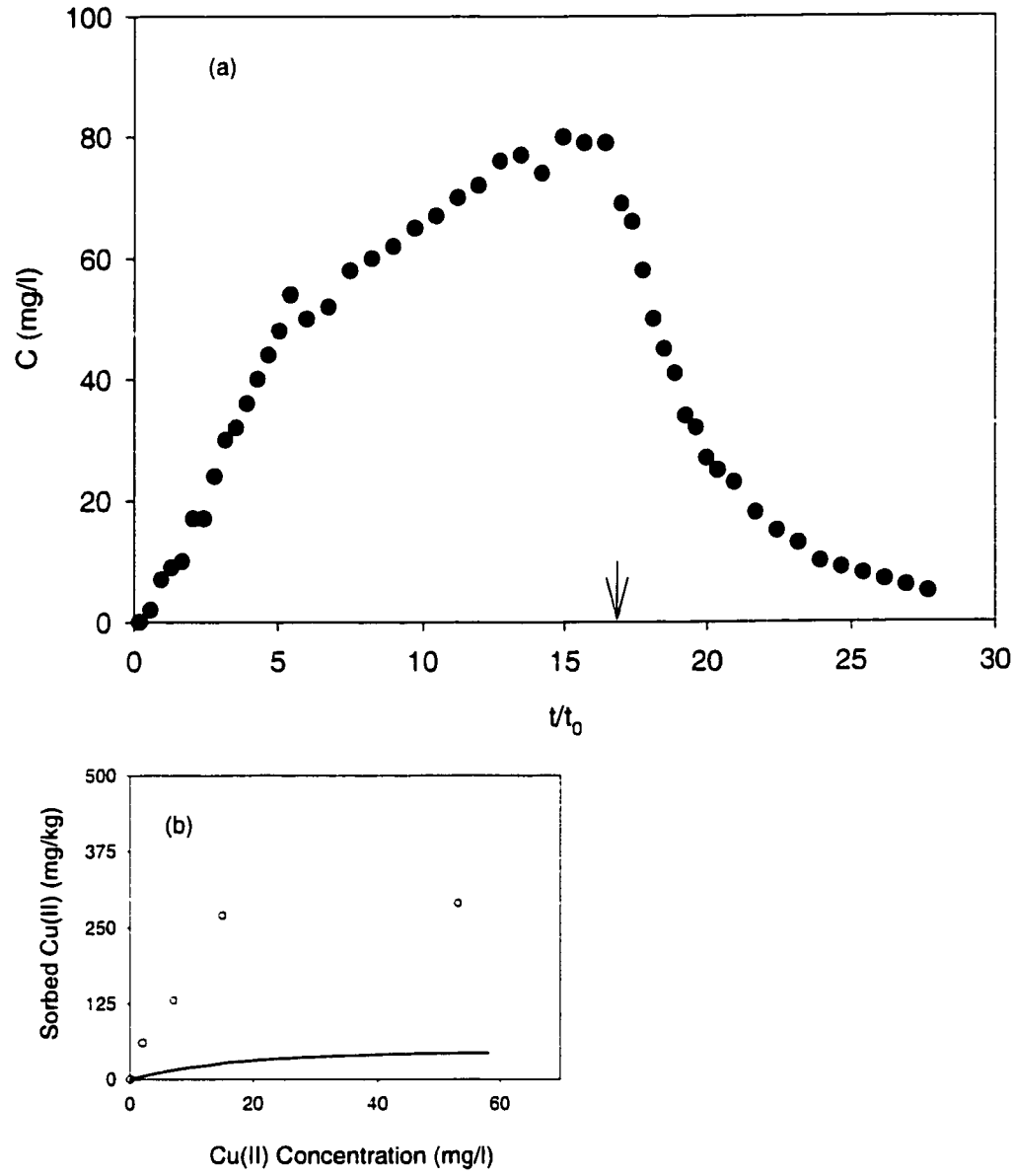

Figure 5.10 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of 1.0 CMC SDS at a pH of 5.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

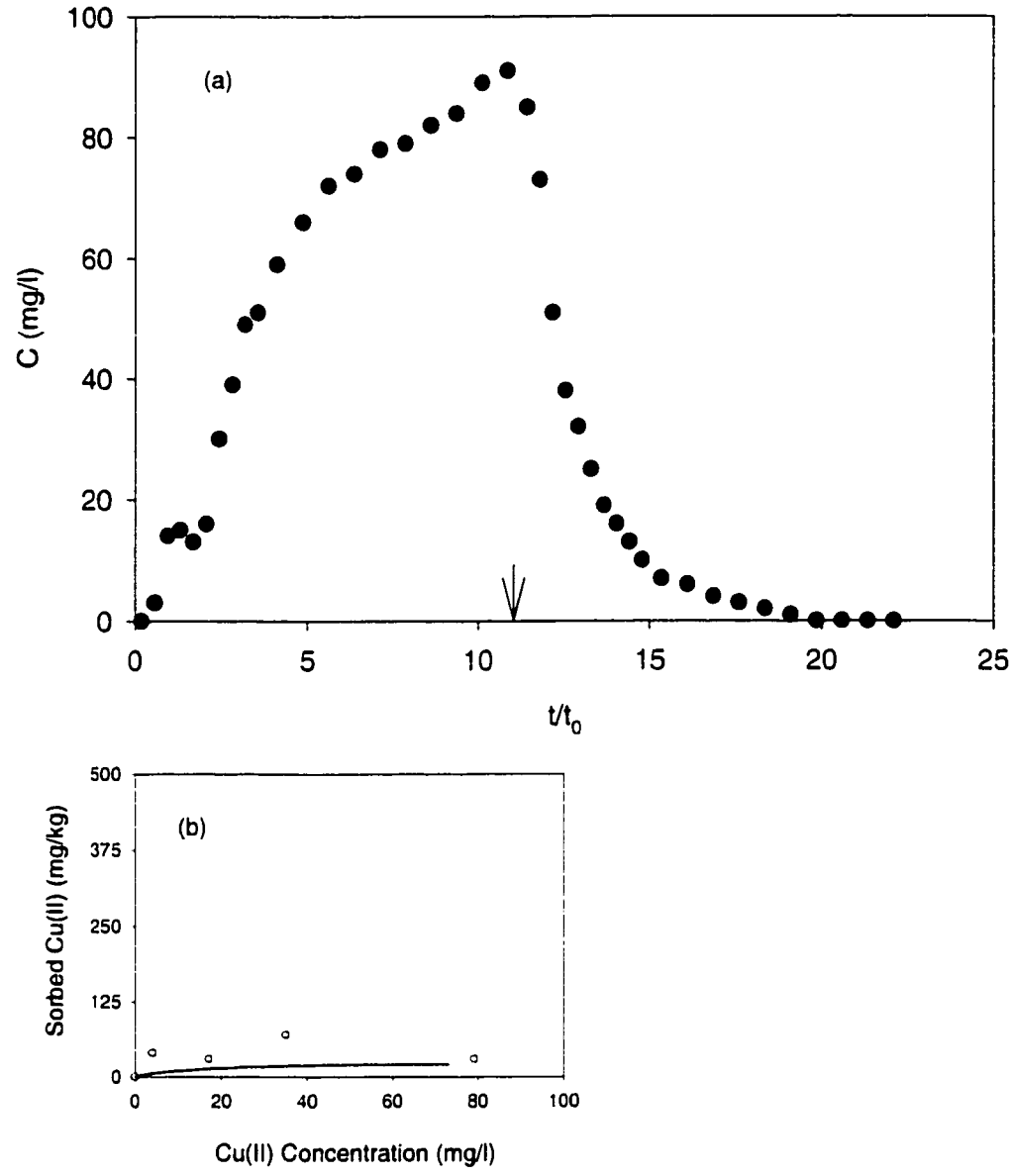

Figure 5.11 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of 4.0 CMC SDS at a pH of 5.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

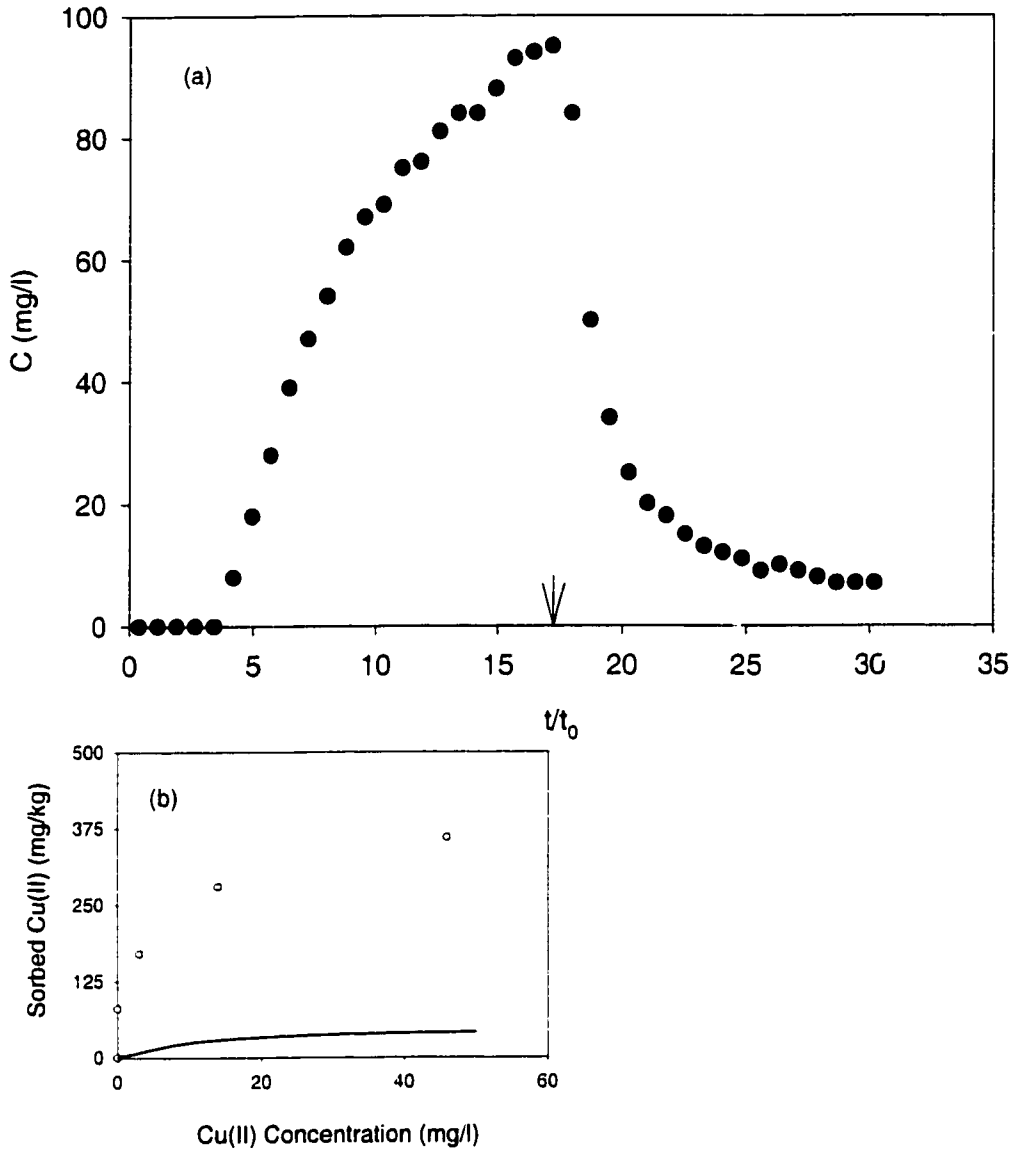

Figure 5.12 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of 5.56 CMC Triton X-100 at a pH of 5.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

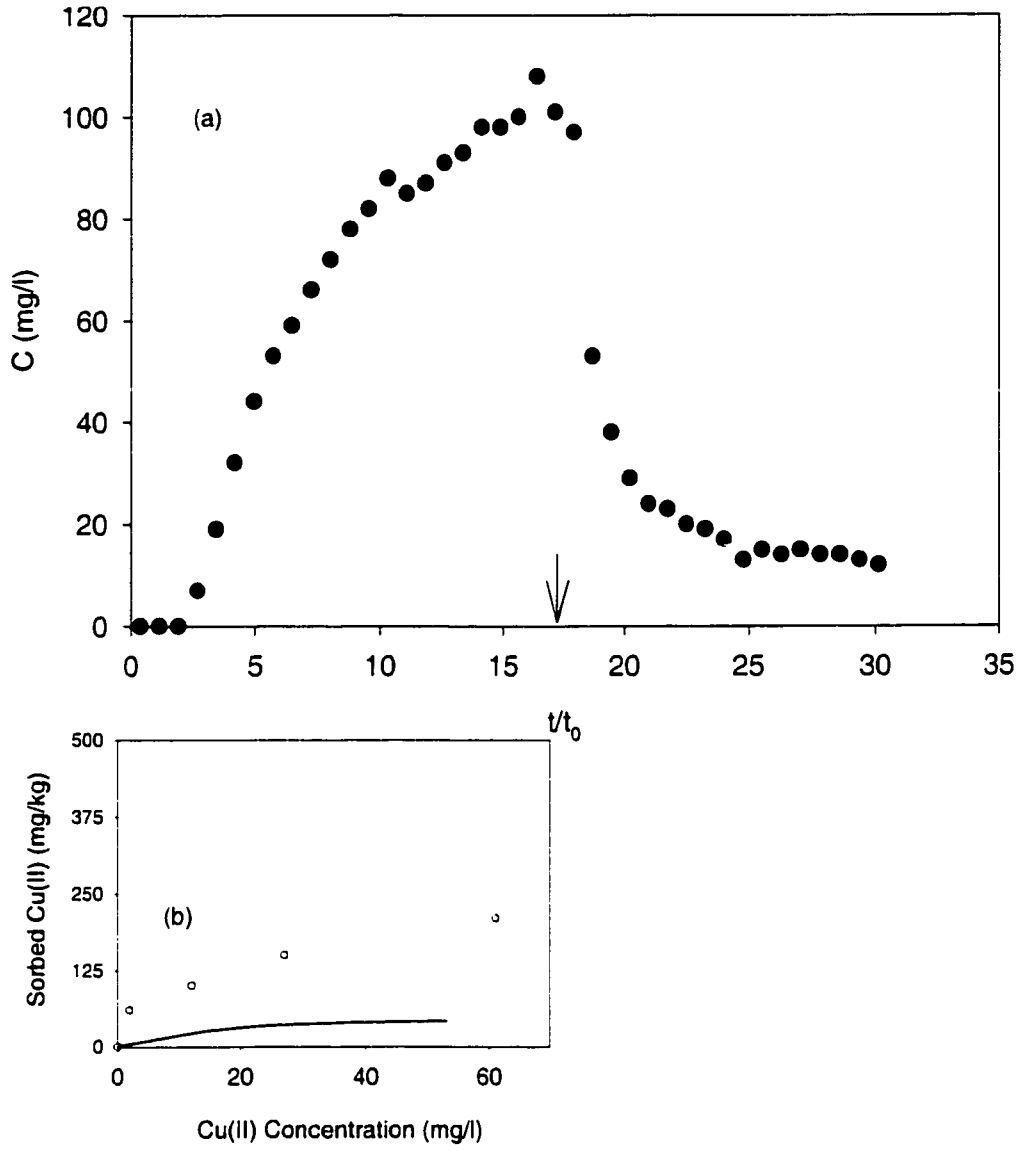

Figure 5.13 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of distilled water alone at a pH of 3.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

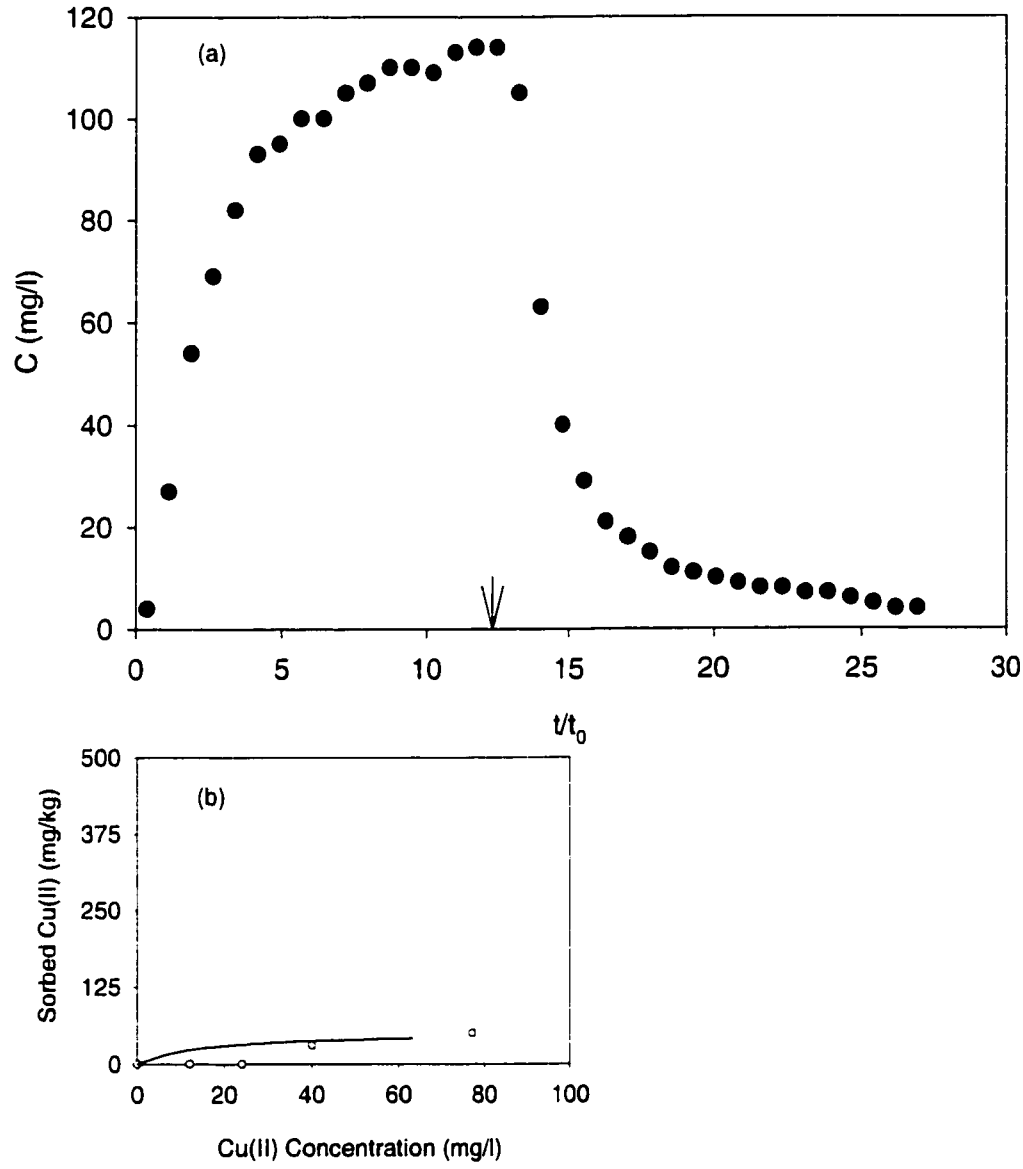

Figure 5.14 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of 4.0 CMC SDS at a pH of 3.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

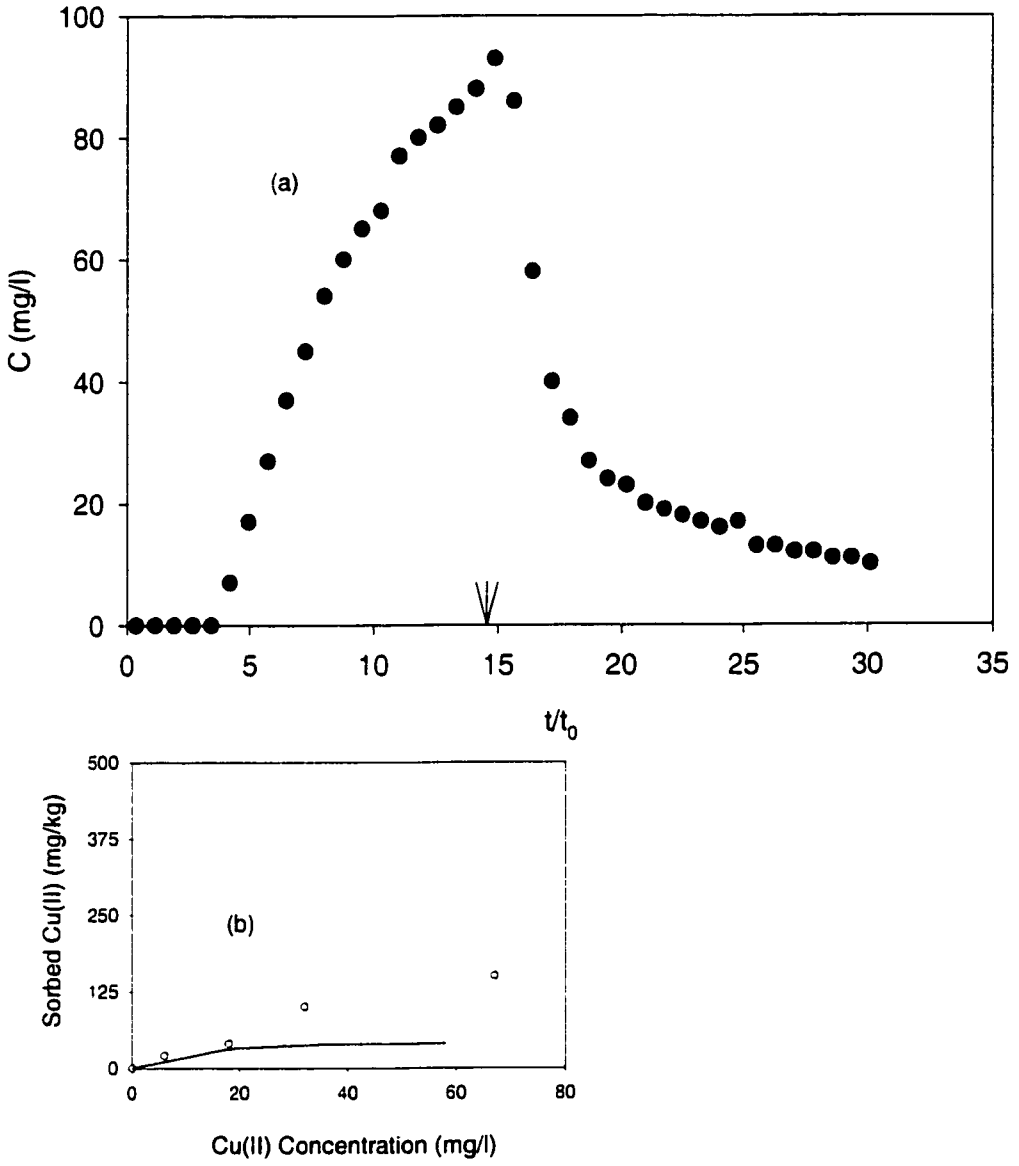

Figure 5.15 Experimental BTC (a) and adsorption data from batch experiments (b) in the presence of 5.56 CMC Triton X-100 at a pH of 3.5. The solid line in (b) is calculated from the diffuse desorption front beginning at the arrow of the BTC.

Table 5.3 Summary of experimental conditions for the column experiments

Background solution	Solution pH	C_0 (mg/l)	Pore water velocities (cm/min)	θ	Step length (t/t_0)
Distilled water	5.5	106	2.8	0.37	16.6
1.0 CMC SDS	5.5	105	2.9	0.37	16.4
4.0 CMC SDS	5.5	107	2.8	0.37	10.9
5.56 CMC TX-100	5.5	112	2.9	0.37	17.2
Distilled water	3.5	110	2.9	0.36	17.1
4.0 CMC SDS	3.5	115	2.9	0.36	12.5
5.56 CMC TX-100	3.5	98	2.8	0.37	14.9

Note: Bulk density of soil (ρ) is 1.87 g/cm^3 for all column experiments.

column and the Cu(II) solution was injected only after the soil was saturated and steady-state conditions were achieved by passing an electrolyte solution (0.01M $NaNO_3$) through the column from bottom to top for approximately 15-20 pore volumes. It can thus be assumed that the flow had reached steady and uniform conditions. The flow pattern should not affect the adsorption isotherms in this study. Since the adsorption front of the breakthrough curve exhibits substantial tailing, the adsorption does not apparently attain linearity in the concentration range considered. Thus, the trapezoidal integration technique will cause some calculation errors. Burgisser et al. (1993) have stated that this method will still give reasonably good agreement with the batch data obtained in their own study. The calculated adsorption isotherm is shown in Figure 5.9b. The nonlinearity of the calculated adsorption isotherm is in good agreement with the results of the batch experiments. The maximum sorption capacity in flow systems is almost one order of

magnitude less than those obtained in the batch experiments. This discrepancy will be discussed in a later section.

Figure 5.10a and Figure 5.11a show the breakthrough curves for Cu(II) transport in soil with the solution pH of 5.5 for a Cu(II) step input duration $0 \leq t/t_0 \leq 16.4$ and $0 \leq t/t_0 \leq 10.9$ in the presence of 1.0 CMC SDS and 4.0 CMC SDS, respectively. Although the shape of the breakthrough curves with a sharp adsorption front and a diffuse desorption tail is similar to Figure 5.9a, there are important differences. In Figure 5.9a, almost all Cu(II) is sorbed onto the soil in the first 3-4 pore volumes of flow, but in Figure 5.10a or Figure 5.11a, the concentration of Cu(II) is significantly higher in the same pore volumes. This result demonstrates that SDS has a significant effect on the retention of Cu(II) by soil. Also the retention rate is lower in the presence of 4.0 CMC SDS than in the presence of 1.0 CMC SDS. This conclusion is also evident in Table 5.4. At a pH of 5.5, when 2250 ml solution is passed through the column, only 154 mg of Cu(II) is sorbed per kilogram of soil for 1.0 CMC SDS, which is less than 223 mg of Cu(II) sorbed per kilogram of soil for distilled water. Although only 1500 ml solution is passed through the column in the presence of 4.0 CMC SDS, the sorbed Cu(II) is 65 mg per kilogram of soil when the elution curve reaches the maximum. These results agree well with the batch experiments which shown that SDS can displace the sorbed Cu(II) and then mobilize metal from the soil, and higher concentration of SDS (above CMC) can mobilize additional Cu(II) from the soil.

Figure 5.12a shows the breakthrough curve for Cu(II) transport in soil when the solution pH is 5.5 in the presence of 5.56 CMC Triton X-100. The Cu(II) step input duration is 0

Table 5.4 Summary of experimental results of the column experiments

Background solution	Solution pH	C_0 (mg/l)	Adsorption process		Desorption process	
			Volumes (ml)	Sorbed Cu(II) (mg/kg)	Volumes (ml)	Removed Cu(II) (mg/kg)
Distilled water	5.5	106	2250	223	2000	26
1.0 CMC SDS	5.5	105	2250	154	1500	33
4.0 CMC SDS	5.5	107	1500	65	1500	11
5.56 CMC TX-100	5.5	112	2300	191	1700	31
Distilled water	3.5	110	2300	138	1700	44
4.0 CMC SDS	3.5	115	1700	45	1900	35
5.56 CMC TX-100	3.5	98	2000	141	2000	53

$\leq t/t_0 \leq 17.2$. The breakthrough curve shows a sharp adsorption front and a diffuse desorption tail similar to Figure 4.9a. Only a small difference can be seen in Table 5.4 for the whole adsorption process. The 191 mg of Cu(II) sorbed per kilogram of soil for 5.56 CMC Triton X-100 is lower than 223 mg of Cu(II) sorbed per kilogram of soil for distilled water. This implies that the nonionic surfactant (Triton X-100) has some effect on the sorption of Cu(II), but that this effect is not as pronounced as the anionic surfactant (SDS). The batch experiments discussed earlier suggest that counterion binding and precipitation-dissolution are likely mechanisms for enhancing Cu(II) displacement by an anionic surfactant (SDS), but only precipitation-dissolution is likely for the nonionic surfactant (Triton X-100). Thus, the results from the column experiments reinforce the conclusions obtained in the batch experiments.

Figures 5.13a to 5.15a show the breakthrough curves for Cu(II) transport in soil with a solution pH of 3.5, in the presence of distilled water alone, 4.0 CMC SDS, and 5.56 CMC Triton X-100, respectively. In all cases, more Cu(II) is mobilized at the lower pH.

From an examination of Figures 5.9a to 5.15a, it can be concluded that the adsorption of Cu(II) is decreased in the presence of surfactants in solution at a pH of 5.5, moreover, the anionic surfactant (SDS) is more effective than the nonionic surfactant (Triton X-100). Mobilization increases with increasing concentration of SDS. The surfactants are more effective in mobilizing sorbed Cu(II) under increasing acidic conditions. All these results agree well with the batch experiments.

Table 5.5 Comparison of maximum sorption capacity (S_m) of Langmuir isotherms for batch and column experiments.

	pH	Batch experiments		Column experiments	
		S_m(mg/kg)	R^2	S_m(mg/kg)	R^2
Distilled water	5.5	419	0.925	53	0.999
	3.5	255	0.952	57	0.998
1.0 CMC SDS	5.5	356	0.952	60	0.998
4.0 CMC SDS	5.5	44	0.579	26	0.999
	3.5	79	0.884	52	0.999
5.56 CMC	5.5	382	0.919	54	0.987
Triton X-100	3.5	473	0.977	48	0.997

In Figures 5.9a through 5.15a all breakthrough curves show a sharp adsorption front and a diffuse desorption tail. This implies that whereas surfactants decrease the retention rate

of Cu(II), they do not change the nonlinear characteristic of the retention isotherms. Furthermore, Figures 5.9b through 5.15b show that the sorption capacity of soil for Cu(II) in batch experiments is considerably higher than in column experiments. The quantitative difference can be seen in Table 5.5. The maximum sorption capacities, S_m, of Langmuir isotherms in the batch experiments are about 1.5 to 10 times greater than those obtained in the column experiments.

The differences between batch-generated adsorption isotherms and these calculated in columns warrants a closer examination. The question has received considerable attention in the literature. By using both batch techniques and short column reactors, Theis et al. (1988) obtained ferricyanide sorption maxima in the flow systems that were two orders of magnitude less than those in the batch systems. They suggested that ferricyanide adsorption caused the adsorbent particles to flocculate, thereby reducing the apparent site density. Persaud and Wierenga (1982) have pointed out that the desorption of some species in flow systems will not only change the composition of the adsorbed phase but of the aqueous phase as well. This argument suggests that adsorption equilibria should, in fact, be different in batch and flow systems. Miller et al. (1989) suggested that the solid/solution ratio could affect adsorption equilibria in batch systems. Fesch et al. (1998) compared the Langmuir-Freundlich type sorption isotherms of 1,3-Dinitrobenzene (DNB) for clay-coated quartz sand as determined by both batch and column methods. The maximum sorption capacity in the batch experiment is 6 times higher than that obtained in column experiments. They explained that the higher sorption in batch experiments may be due in an increase of accessible clay surface area resulting from

disaggregation of clay clusters during shaking and/or from abrasion processes. This mechanism is considered to be likely in the experiments reported here. The soil used in this study was a mixture of Ottawa sand and Bentonite. Bentonite consists largely of the clay mineral montmorillonite. Montmorillonite is a three-layer clay mineral with alternating layers of silica-alumina-silica sheets, which are weakly bonded to each other. As a result, these sheets can separate and allow water and other chemicals in solution to enter between them. The separation of the sheets increases the net surface area of montmorillonite. This could imply that the amount of surface area of montmorillonite increases during the batch shaking processes. Such an increase in surface area is much less likely in a packed column. Other possible sources of the observed differences include a loss of clay minerals during the initial conditioning of the column, as well as limited accessibility of clay sorption sites in the column due to dense packing.

5.3 Modeling of transport

5.3.1 Estimation of D

The hydrodynamic dispersion coefficient (D) of Eq. 3-9 was estimated by trial and error from the sodium nitrate breakthrough curve (BTC) which was symmetrical in shape (Figure 5.16). In the plots of BTC, the number of pore volumes eluted is equivalent to the abscissa t/t_0. The calculated BTC was fitted to the observed data using an analytical solution of the classical convection-dispersion transport equation (Eq. 3-10) with corresponding initial and boundary conditions (Eq. 3-20 to 3-22) for a nonreactive solute reported by Parker (1984):

$$C(x,t) = C_0 A(x,t) \qquad (0 < t \le t') \qquad (5\text{-}1)$$

and

$$C(x,t) = C_0 A(x,t) - C_0 A(x,t-t') \qquad (t > t') \qquad (5\text{-}2)$$

where

$$A(x,t) = \frac{1}{2} erfc\left[\frac{x-vt}{2(Dt)^{1/2}}\right] + \left[\frac{v^2 t}{\pi D}\right]^{1/2} \exp\left[\frac{-(x-vt)^2}{4Dt}\right] - \left(\frac{1}{2} + \frac{vx}{2D} + \frac{v^2 t}{2D}\right) \exp(vx/D) erfc\left[\frac{x+vt}{2(Dt)^{1/2}}\right] \qquad (5\text{-}3)$$

where $erfc()$ is a complementary error function, and x is the domain length. The calculated hydraulic dispersivity, λ, for the soil packed column is 0.373 cm. The dispersion coefficient, D, for each column experiment was calculated using the measured pore-water velocity, v, and the optimized dispersivity value with the relationship: $D = \lambda v$ (Freeze and Cherry, 1979).

5.3.2 Nonlinear Freundlich equilibrium model

The observed and simulated BTCs are shown in Figures 5.17 to 5.23. Some optimized parameters for the different models used in Figures 5.17 to 5.23 are presented in Table 5.6. The batch-determined parameters for the nonlinear Freundlich equilibrium model will result in a much longer lagged Cu(II) elution BTC position (not shown in the figures) compared to the experimental dada. In fact, all these BTCs are asymmetrical or skewed in shape. Thus, the equilibrium model based on the assumption of instantaneous adsorption fails to describe the experimental data. The overall shape of the experimental BTCs suggest that the nonlinear Freundlich equilibrium model is inadequately to describe the Cu(II) sorption processes in the soil columns.

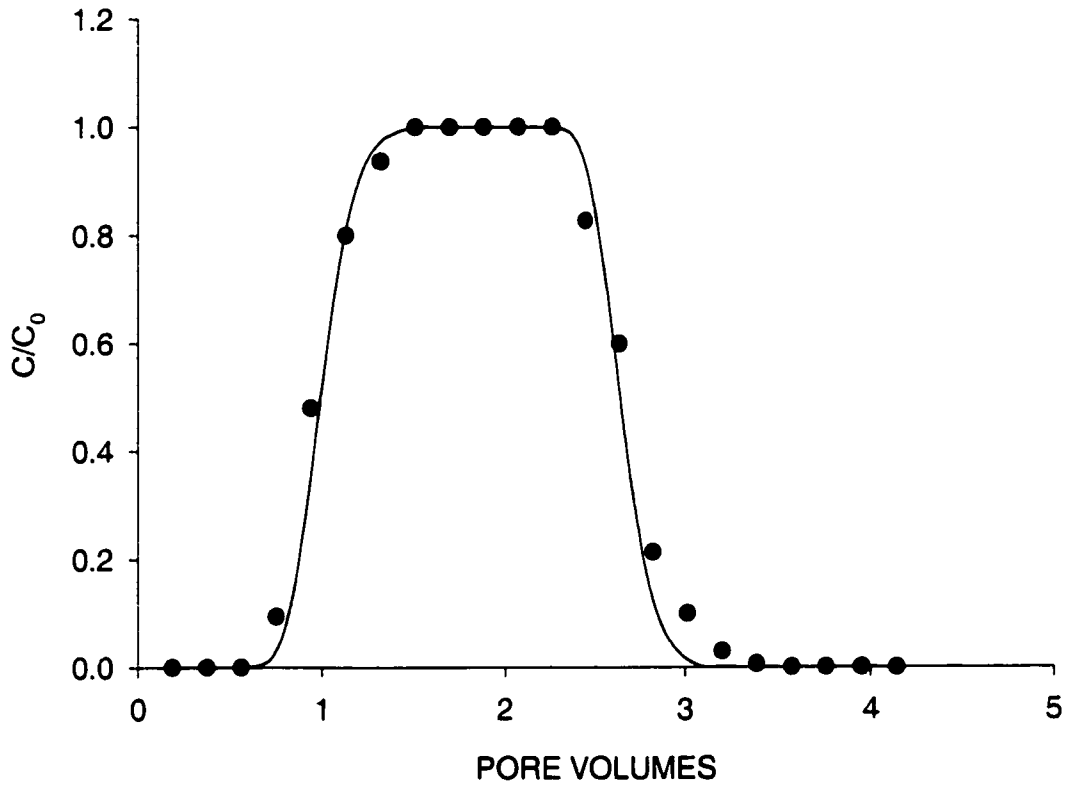

Figure 5.16 Sodium nitrate breakthrough results from soil column experiment. Solid line is model fitted BTC, and solid circles are experimental data.

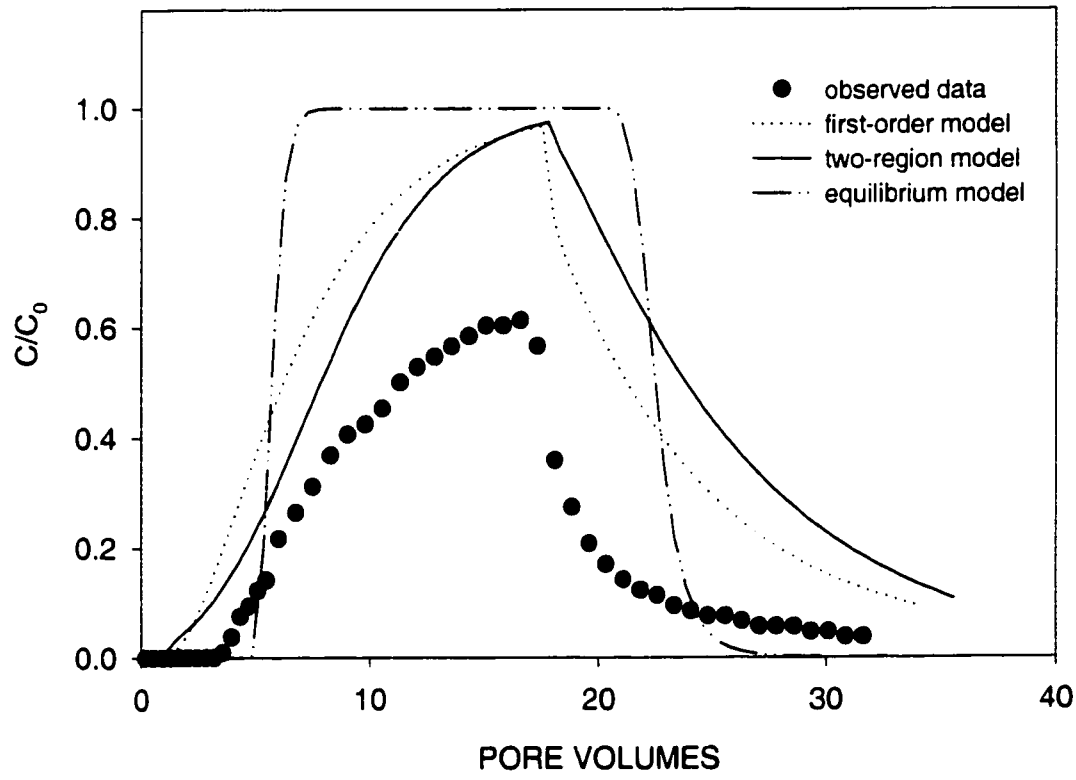

Figure 5.17 Observed and simulated BTC of Cu(II) in the presence of distilled water alone at a pH of 5.5.

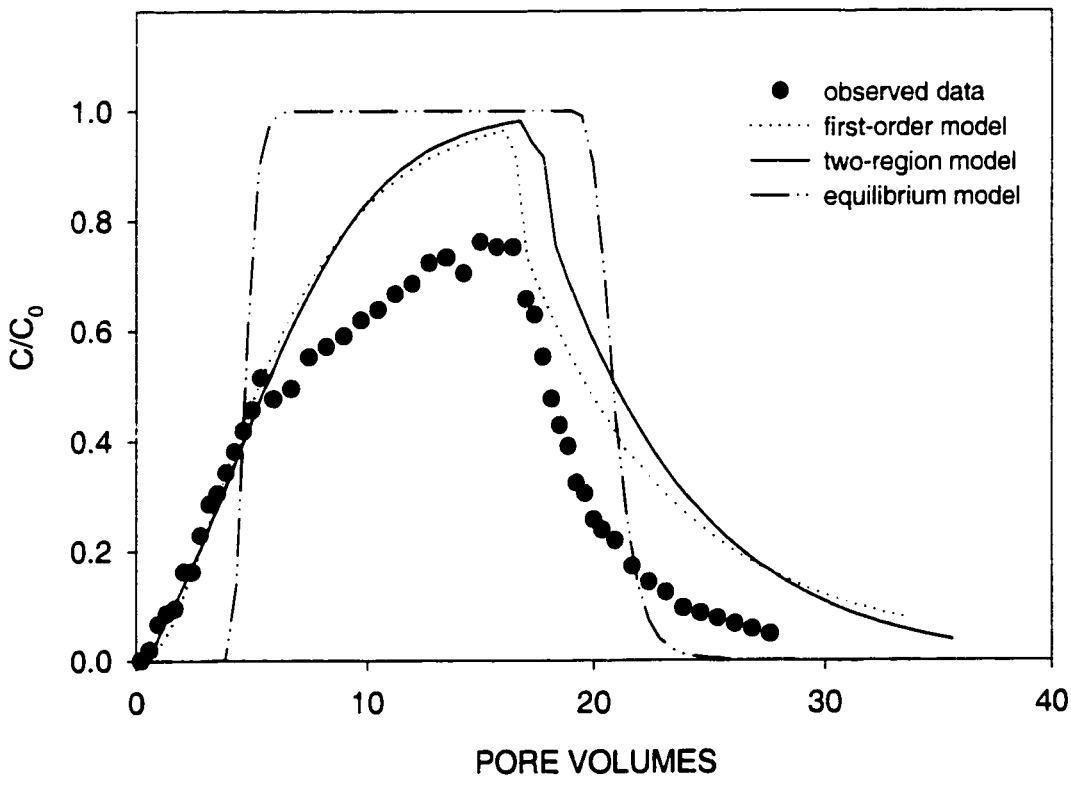

Figure 5.18 Observed and simulated BTC of Cu(II) in the presence of 1.0 CMC SDS at a pH of 5.5.

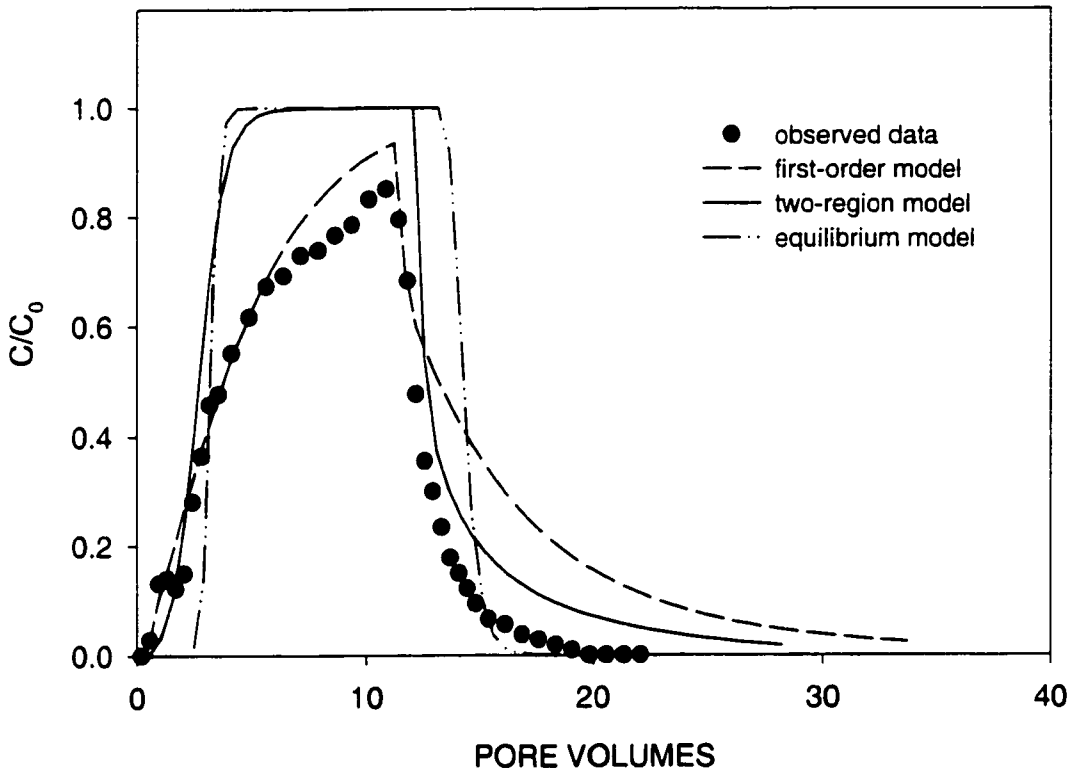

Figure 5.19 Observed and simulated BTC of Cu(II) in the presence of 4.0 CMC SDS at a pH of 5.5.

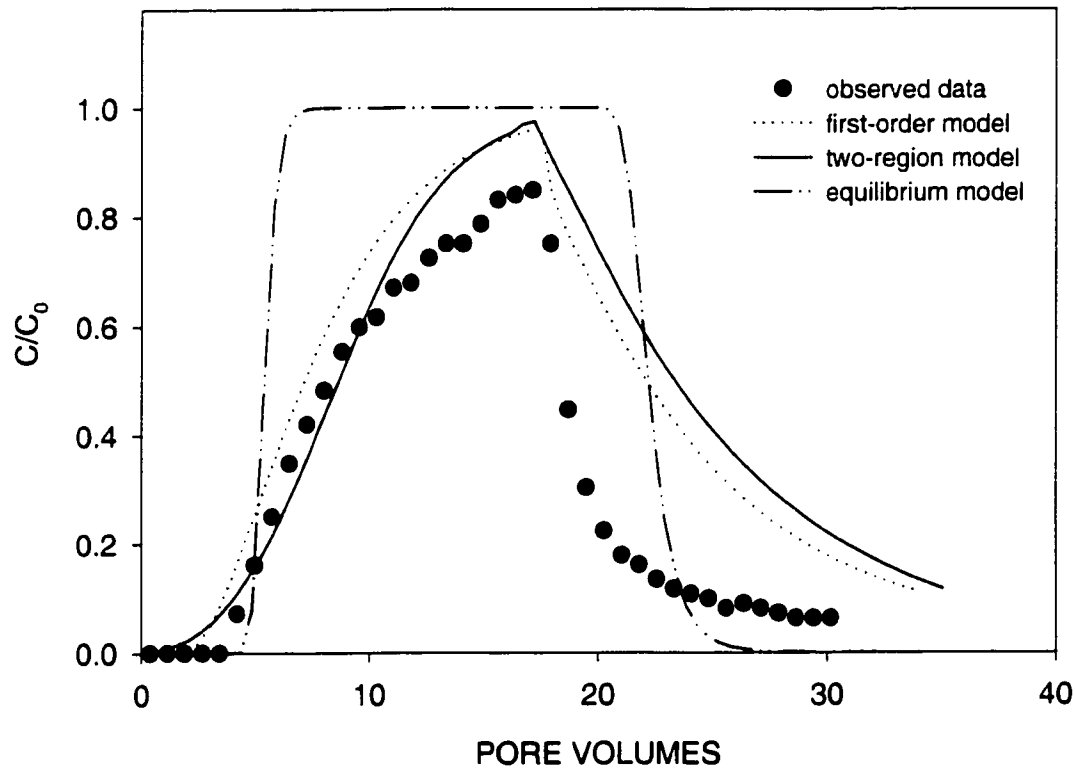

Figure 5.20 Observed and simulated BTC of Cu(II) in the presence of 5.56 CMC Triton X-100 at a pH of 5.5.

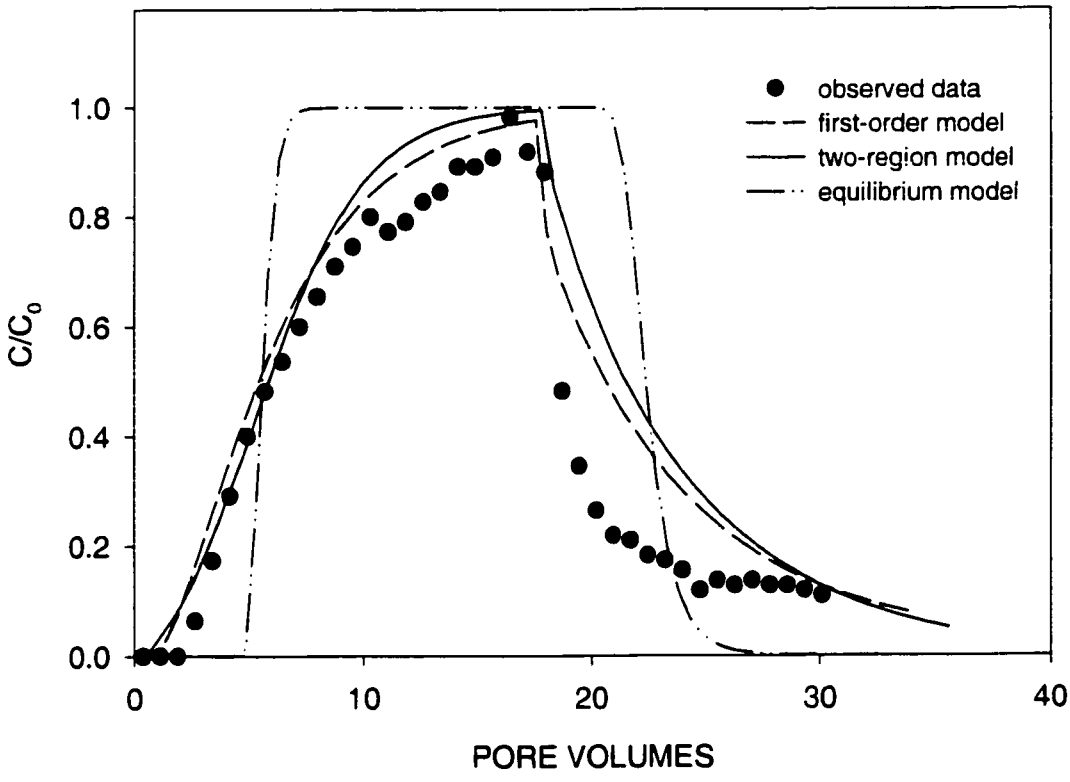

Figure 5.21 Observed and simulated BTC of Cu(II) in the presence Of distilled water alone at a pH of 3.5.

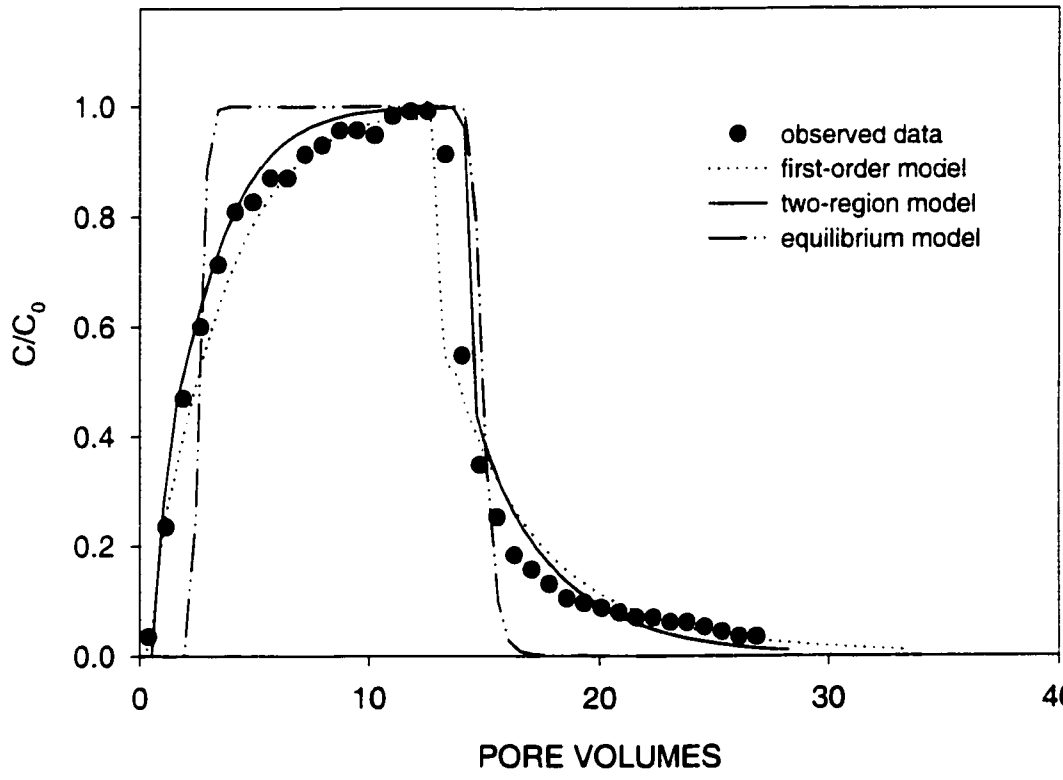

Figure 5.22 Observed and simulated BTC of Cu(II) in the presence of 4.0 CMC SDS at a pH of 3.5.

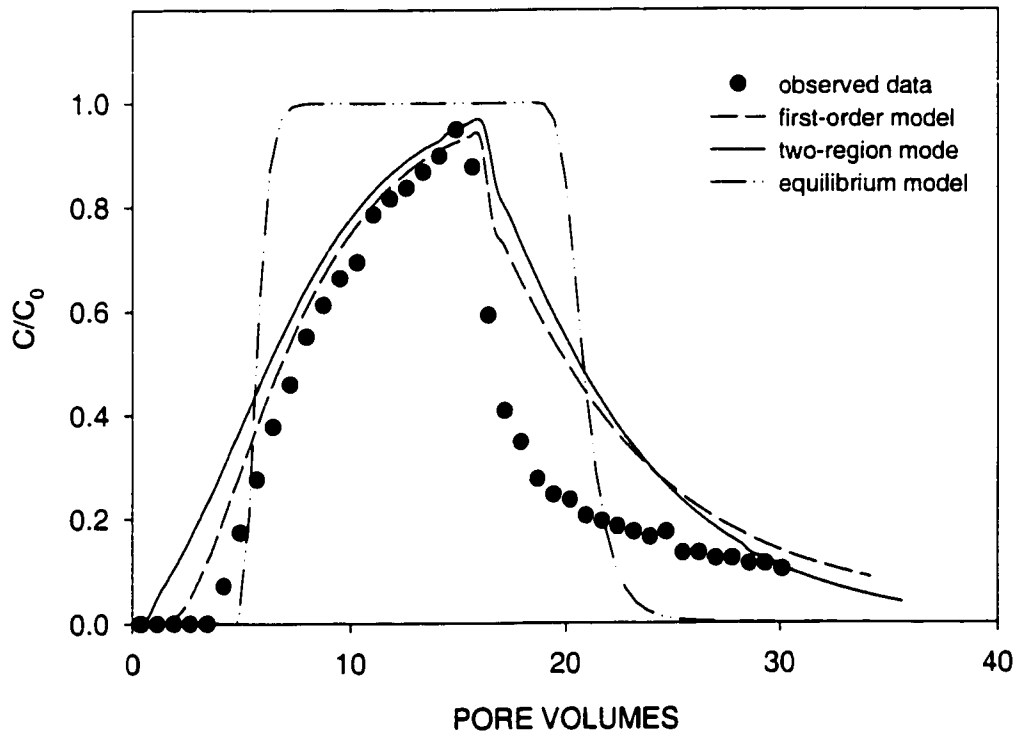

Figure 5.23 Observed and simulated BTC of Cu(II) in the presence of 5.56 CMC Triton X-100 at a pH of 3.5.

5.3.3 Nonlinear, reversible first-order kinetic model

The forward rate coefficient, k_f, the backward rate coefficient, k_b, and the order of the nonlinear reaction, b, were estimated by curve-fitting to the measured BTC data due to absence of independent measurements of these model parameters. The nonlinear, reversible first-order kinetic transport simulations generally compared poorly with the observed data except for some simulated BTCs (Figure 5.22). However, the agreement of the asymmetrical or skewed shape between simulated and observed BTCs improved markedly for all experiments when sorption nonequilibrium was introduced into the transport simulations. The effects of surfactants and pH on the elution portion of the BTC have been discussed in the previous section. Although the relationship among them can also be reflected in the model by choosing different parameters, the relationships are not as apparent as that in the modeling of sorption isotherms in the batch experiments.

Table 5.6 Some optimized parameters for the models used in Figures 5.17 - 5.23.

Figure No	First-order model			Two-region model				Equilibrium model	
	k_f (h^{-1})	k_b (h^{-1})	b	α (h^{-1})	S_m (mg/kg)	k_f (h^{-1})	k_b (h^{-1})	K_f (l/kg)	b
Figure 5.17	81.0	2.0	0.6	0.05	419	0.07	2.1	1.5	0.9
Figure 5.18	74.5	2.0	0.6	0.05	356	0.05	2.1	1.2	0.9
Figure 5.19	57.5	2.1	0.6	0.05	44	0.5	2.1	0.7	0.9
Figure 5.20	100.0	2.2	0.6	0.05	382	0.085	2.1	1.4	0.9
Figure 5.21	71.0	2.0	0.6	0.05	255	0.084	2.1	1.45	0.9
Figure 5.22	46.2	2.6	0.6	0.05	79	0.08	2.1	0.5	0.9
Figure 5.23	92.0	2.1	0.6	0.05	473	0.04	2.1	1.48	0.9

5.3.4 Two-region model

The fraction of sites f (see Eq. 3.13) is assumed to be same as the relative amount of water in the two regions, i.e., $f = \theta^m / \theta$ (Selim and Amacher, 1988). The value of 0.965 for f is estimated by using the curve-fitting of the tracer (sodium nitrate) breakthrough data with the two-region model (see Figure 5.24). This implies that the fraction of immobile regions (less that 4% of the total column pore volume), if present at all, is apparently not very significant for the transport of the conservative tracer. The value of v^m and D^m are equal to v/f and D/f, respectively. The parameters k_f, k_b and the mass transfer coefficient, α, were estimated by curve fitting to the measured BTC data. The value of the maximum adsorption capacity S_{max} was used from the Table 5.2. In Figures 5.17-5.23, the two-region nonequilibrium model provides the experimental data a fit similar to that of the nonlinear, reversible first-order kinetic model. This implies that the two-region model does not successfully describe the underlying data.

Attempts to simulate the transport of Cu(II) in the soil column have thus met with only limited success. The general shapes of the experimental BTCs could be simulated, but additional methods must be developed to provide better estimates of the model parameters in order to improve agreement with experimental dada.

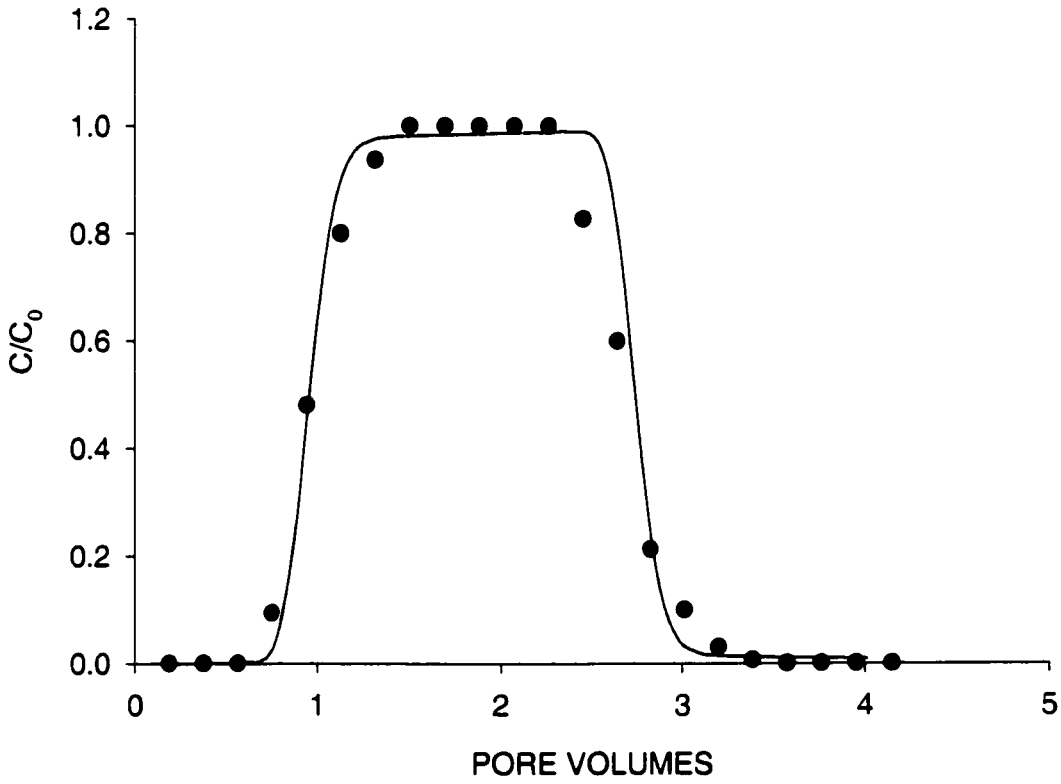

Figure 5.24 Observed and fitted BTC for sodium nitrate in soil column used to estimate *f*. Solid line is model fitted BTC, and solid circles are experimental data.

CHAPTER SIX

Conclusions and Recommendations

6.1 Conclusions

Batch and column experiments were conducted for the investigation of the effects of surfactants on the sorption and transport of Cu(II) in soil. In addition, mathematical models were used to simulate the sorption isotherms obtained from the batch experiments, and to describe the transport of Cu(II) in a soil column in the presence of surfactants, respectively. The conclusions obtained from this study are as follows:

1. The anionic surfactant (SDS) was found to decrease the retention of Cu(II) on the soil surface. Greater Cu(II) removal was observed as the SDS concentration continued to increase above the CMC. It is suggested that counterion binding and precipitation-dissolution are the likely mechanisms of enhancing Cu(II) displacement by anionic surfactant (SDS). In the presence of the nonionic surfactant (Triton X-100), only a small enhancement in Cu(II) extraction was observed relative to distilled water alone. The possible mechanism for the extraction of Cu(II) by Triton X-100 is precipitation - dissolution. Both SDS and Triton X-100 were observed to be more effective in the removal of Cu(II) under increasingly acidic conditions. In the moving fluid, the adsorption of Cu(II) is still decreased in the presence of surfactants in solution. The position and shape of Cu(II) elution BTCs were significantly affected by the presence of surfactants in solution and by change in pH.

2. Both Freundlich and Langmuir sorption models successfully described the sorption isotherms obtained in the batch experiments. A correlation between solution type and the partition coefficient (K_f) or maximum sorption capacity (S_m) has been demonstrated using Freundlich or Langmuir sorption isotherms.

3. The batch-generated adsorption isotherms were found to be different quantitatively from those calculated in column experiments. The possible explanations may be that experiment conditions for batch experiments did not reflect the sorption conditions that occur during transport.

4. The sorption processes of Cu(II) in the soil column is shown to be nonequilibrium. Both a first-order kinetic model and a two-region model are not capable of describing the entire experimental BTC in most instances.

6.2 Recommendations

1. This study focuses on the description of sorption and transport of Cu(II) in the presence of surfactants in soil. It is felt that one should also investigate the abilities of surfactants to remove heavy metals from the contaminated soil. For example, the uncontaminated soil packed in a column may be spiked with $CuSO_4$ at an ionic strength of 0.01M $NaNO_3$. The contaminated soil can be stored at room temperature for a period and then find the abilities of surfactants to remove the Cu(II) adsorbed onto the surface of soil.

2. The models used in this study do not depend on a particular reaction mechanism. It is felt that one may also use the multireaction and multicomponent approaches to model the sorption and transport of Cu(II) in the presence of surfactants in soils.

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