Electrokinetic-Induced Phase Separation of Petroleum Wastes: Evaluation of Oil Sediment Behavior and Solids Properties

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Abstract

Electrokinetic-Induced Phase Separation of Petroleum Wastes: Evaluation of Oil Sediment Behavior and Solids Properties

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The disposal of the oily wastes represents a serious threat to the environment. The treatment of such oily wastes poses significant challenges considering their physical and chemical properties. This study focuses on advanced electrokinetic methods as a technology to treat oily sediments through phase separation. The study comprises four objectives which are intimately linked to achieve the overall objective of exploring the electrokinetic method for treatment of water-in-oil emulsions. The first objective is finding the most efficient oil phase separation when four different regimes of electric fields are applied (namely constant direct current (CDC), pulsed direct current (PDC), incremental direct current (IDC) and decremental direct current (DDC)). The second objective is to investigate the factors affecting the electrokinetic process and dewaterability of different types of oily sludge. The third objective is investigating the effect of nanoparticles and synthesized catalysts on the phase separation efficiency within the electrokinetic system. The final objective was to elucidate the various mechanisms underlying the separation of oil, water and solids by thermal analysis of treated samples.

The results showed that the extent and quality of phase separation depend on the regime of electrical current applied. The DDC and IDC regimes resulted in the most efficient phase separation of the oil sediments, and even incurred a highly resolved separation of light hydrocarbons at the top anode.

X-ray photoelectron spectroscopy (XPS) analyses showed a decrease in the concentration of carbon from 99% in centrifuged samples to 63% on the surface of the solids treated by PDC. Wettability alteration studies showed an increase in the level of fine solids in the aqueous phase following electrokinetic treatment thereby enhancing the hydrophilicity of the solids.

The best performance of titanium dioxide (TiO_2) nanoparticles and a synthesized catalyst reactors results were obtained with the synthesized catalyst as compared to the use of TiO_2 nanoparticles. Activation energy emphasized the effect of additives on separation of phases and availability of oil. Hence, the synergistic effects of TiO_2 or synthesized catalyst with electrokinetic treatment can lead to better phase separation and may reinforce the current applications of the electrokinetic method in treating oil sediments.

This thesis is dedicated to my parents

for their continued support and unconditional love,

my beloved wife,

and the new member of our family, Aiden.

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CONTRIBUTION OF AUTHORS

In accordance with the "*Guidelines for Thesis Preparation*", this thesis is presented in a manuscript-based format. A general introduction and literature review are presented in Chapters 1 and 2. Chapter 3 comprises of detailed methodology used throughout this study. Chapters 4-6 include two published articles, and one research article, which is in preparation to be submitted for publication to the *Journal of Environmental Engineering*. The author of this thesis is the primary author of all the manuscripts. In the final Chapter, a general conclusion is presented. Below is a detailed description of the efforts of each contributing author.

Esmaeel Kariminezhad and Maria Elektorowicz, Comparison of constant, pulsed, incremental and decremental direct current applications on solid-liquid phase separation in oil sediments, *Journal of Hazardous Materials*, Volume 358, 2018, Pages 475-483.

Authors' contributions:

Esmaeel Kariminezhad: Designing and running experimental tests, conducting analyses, generating the results and conclusions and writing the manuscript.

Maria Elektorowicz: Defining the electrokinetic processes in oil waste, supervising the research, generating the conclusion and revising the manuscript.

Esmaeel Kariminezhad, Maria Elektorowicz, Effect of various electrokinetic treatment regimes on solids surface properties and thermal behavior of oil sediments, *Journal of Hazardous Materials*, Volume 353, 2018, Pages 227-235.

Authors' contributions:

Esmaeel Kariminezhad: Designing and running experimental tests, conducting analyses, generating the results and conclusions, writing the manuscript.

Maria Elektorowicz: Helping in designing the methodological process, supervising research, generating the conclusion and revising the manuscript.

Esmaeel Kariminezhad and Maria Elektorowicz, Evaluation of synthesized catalyst and TiO2 nanoparticles on the performance of electrokinetic separation of oil sediments, In preparation for submission to the *Journal of Environmental Engineering*.

Authors' contributions:

Esmaeel Kariminezhad: Designing the study, conducting the experimental procedures, analyzing the results, and writing the manuscript.

Maria Elektorowicz: Supervising research work, contributing in the study design and conclusions, revising the manuscript.

Some of the work presented in this thesis have already been published while the remaining will be submitted for publication.

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LIST OF ABBREVIATIONS

Abbreviations	Description
CDC	Constant Direct Current
PDC	Pulsed Direct Current
IDC	Incremental Direct Current
DDC	Decremental Direct Current
API	American Petroleum Institute separator unit
TPI	Tilted Plate Interceptor
API	American Petroleum Institute separator
CPI	Corrugated Plate Interceptor
FFU	Sludge from Flocculation–Flotation Unit
DAF	Dissolved Air Flotation
IAF	Induced Air Flotation Units
W/O	Water-in-Oil
PHCs	Petroleum Hydrocarbons
TPA	Total Petroleum Hydrocarbon
NSO	Nitrogen Sulfur Oxygen
RCRA	Resource Conservation and Recovery Act
EPA	Environmental Protection Agency
AC	Alternating current
DC	Direct current
BTX	Benzene, Toluene, Xylene
SVOCs	Semi-Volatile Organic Compounds
TCLP	Toxicity Characteristic Leaching Procedure
TPH	Total Petroleum Hydrocarbons
TTLC	Total Threshold Limit Concentration
U.S. EPA	United States Environmental Protection Agency

Dehydration	Removal of Insoluble Water from the Crude Oil
Desalting	Removal of Water Soluble Salts from the Crude Oil
SPE	Society of Petroleum Engineers
RCRA	Resource Conservation and Recovery Act
CEPA	Canadian Environmental Protection Act in Canada
EQA	Environmental Quality Act in Quebec
LCA	Life Cycle Assessment
W/O	Water-in-oil
ORS-BAGG	Organic Rich Solids-Biwetted Aggregates
ORS-BUF	Organic Rich Solids-Biwetted Ultra-Fines
ORS-HAGG	Organic Rich Solids-Hydrophobic Aggregates
SEM	Scanning Electron Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
TEM	Transmission Electron Spectroscopy
PAS-FTIR	Photo Acoustic Fourier Transform Infrared Spectroscopy
AC	Activated carbon
BET	Brunauer-Emmett-Teller
CE	Conventional electrical
DW	Deionized water
DW	Distilled water
DBD	Dielectric barrier discharge
DE	Dielectric
GC/MS	Gas Chromatograph/Mass Spectrometer
GE	Ground electrode
IB	Isobutanol
MW	Microwave
P	Power

PCO	Photocatalytic oxidation
ppb	Parts per billion
ppm	Parts per million
SD	Surface discharge
SD	Standard deviation
SIE	Specific input energy
SSA	Specific surface area
T	Temperature
TGA	Thermo-gravimetrical analysis
VOC	Volatile organic compound
WHO	World Health Organization
XRD	X-ray diffraction
SEM	Scanning electron microscopy
US	Ultrasound
UV	Ultra violet

LIST OF SYMBOLS

English Symbol	***Description***
C	Concentration (mass per volume)
D	Dipolar moment
E_c^{CSD}	Energy cost ($kWhm^{-3}$)
EEc	Energy efficiency ($kWhm^{-3}$)
EEi	Energy efficiency ($g\ kWh^{-1}$)
eV	Electron volt
I	Current (mA)
M	Molar mass ($g\ mol^{-1}$)
Mw	Molecular weight ($g\ mol^{-1}$)
Ms	Total mass of sorbent (mg)
$P_{discharge}$	Discharge power (kWh)
S_{BET}	BET surface area ($m^2.g^{-1}$)
SS	Stainless steel
U	Voltage
Wt	weight percent (wt%)

Greek Symbol	***Description***
Å	Angstrom
ε	Dielectric constant ($\varepsilon = Eo/E$)
η	Conversion
Ω	Ohm
ρ	Resistivity (Ω m)
Ø	Diameter (mm)
υ	Bed volume
τ	Residence time
η_b	Adsorption capacity (mmol)
η_t	Single pass removal efficiency (%)

Introduction

1.1 PROBLEM STATEMENT

As the world's conventional oil reserves might have a finite lifetime, interests have spurred in the exploitation of unconventional oil reserves (Hamilton, 2014). However, this has not been the case for Canada due to its capacity to extract oil from oil sands. But in fact, unconventional oil production is an energy-intensive process which can produce more waste compared to conventional methods (Lynam et al., 2015). In addition, the exploitation of oil, though, may have significant adverse impacts on the environment (Sorrell et al., 2010). Oil processing would release toxic materials to water, soil and atmosphere (Allen, 2008a; Allen, 2008b). According to CAPP (2015), oil sands represent 8.5% of Canada's GHG emissions and about 0.12% of global GHG emissions. Thus, oil exploitation industries have to implement a zero-discharge policy and store all process waters for treatment prior to discharge. Although, a considerable amount of waste is produced during the oil refinery processes which would have adverse effects on the environment, these wastes also contain valuable materials that can be recovered further.

The environmental challenges regarding the wastes faced by oil industries are not restricted to the processing stages of extraction and separation only. Oil extraction should be done from soil or underground wells that consist of a complex mixture of sand, clay, minerals, water and oil. The resulting sludge waste called oily sludge represents a serious hazard to the environment if not properly treated and disposed, oily sludge comprised of 30-50% oil, 30-50% water and 10-12% solids, which make them particularly difficult to dewater (Da Silva et al., 2012; Jeeravipoolvarn et al., 2009; Mikula et al., 1996). The high water content contributes to the large volume of materials to be disposed of and render the geotechnical properties of the oily sludge (Snars & Gilkes, 2009). Oily sludge is generally stored in tailing ponds, below ground or above ground with the help of perimeter dikes or lagoons. The storage of huge volumes of oily sludge represents a significant technical challenge on one hand, and their treatment prior to disposal underlies another. Inadequately designed storage structures (insufficient drainage, piping, and overtopping) can significantly affect operation and incur damage to the surrounding environment (Blight, 2009; Rico et al., 2008). This problem can be further exacerbated during other activities such as transport and disposal of oily sludge thereby increasing the risk of severe contamination of water bodies, the demise of aquatic life and heavy metal contamination (Ayotamuno et al., 2007). Oily sludge is generated at every stage of upstream and downstream oil production process (Egazar'yants et al., 2015).

1.2 TECHNIQUES FOR PETROLEUM WASTE MANAGEMENT

Dewatering and separation of oily sludge into its various phases and reuse of resulting separated components are essential steps in promoting sustainable management of oily sludge. Dewatering oily sludge increases its shear strength and reduces the volume of material to be handled. Such processing also minimizes the risk of storage and disposal failure and reduces footprint and water consumption (Farkish & Fall, 2013). Various remediation technologies have been developed for separation of oily sludge components and include incineration/stabilization, centrifugation, solvent extraction, microwave irradiation, ultrasonic treatment, pyrolysis, photocatalysis, chemical treatment and biodegradation (Hu et al., 2013). These treatment technologies can reduce or eliminate hazardous constituents in oily sludge and mitigate its deleterious environmental and health impacts. However, due to the recalcitrant nature of oily sludge, few technologies can reach a compromised balance between satisfying strict environmental regulations and reduce treatment costs.

The electrokinetic method was developed to separate the different phases (water, oil and solids) in oily sludge through the application of low-intensity direct current across a pair of electrode causing electro-osmosis of liquid phase, movement of ions and electrophoresis of charged particles (Elektorowicz & Oleszkiewicz, 2009; Kuo et al., 2011). This method can dewater oily sludge by nearly 63% and reduce the light hydrocarbon content by about 43% (Elektorowicz et al., 2006). In addition, the process may be enhanced through the use of bio-surfactants or reagents to increase contaminant removal rates at the electrodes (Elektorowicz & Boeva, 1996; Elektorowicz & Hatim, 2000). However, so far most of electrokinetic studies on oily sludge have been performed at lab-scale level. A lack of knowledge on the process is preventing its scaling-up to full-scale level. According to Yang et al. (2005a) implementation of this technology at field level can effectively reduce treatment cost.

1.3 RESEARCH OBJECTIVES

The main objective of this project was to further develop an advanced electrokinetic process in separating different phases of oily waste (sediments and sludge). Specific objectives comprise: i) finding the best electro-reactor configuration and operational conditions to increase the separation efficiency of the oil-water-solid mixture; ii) exploring a combination of the electrokinetic process with additives (e.g. nanomaterials, catalysts) to maximize polycyclic aromatic hydrocarbons (PAHs) removal efficiency; iii) generate added-value products (e.g. catalysts produced from oily sludge waste) in view of sustainable development principles ; iv) contribute to knowledge by evaluating complex processes in oil electro-reactors.

Nanoparticle, which has been proposed in this thesis, has become one of the main focus of research and development in contaminant site clean-up in recent years (Karn et al., 2009). Due to their large surface area to weight ratio, nano-sized particles have the capacity to offer faster and more cost-effective solutions since their reaction is much more effective than other materials in soil remediation (Karn et al., 2009). However, to the best of the author's knowledge, the treatment efficiency of an oil-electrokinetic reactor coupled with nano-additives has not been investigated so far. Thus, a separation efficiency of oily sludge/sediments during electrokinetic application with an addition of synthesized catalyst should be also investigated.

Based on the above, the detailed objectives of the proposed research were elaborated as follows.

1- To study different electric field applications for separation of solids, oil and water phases during electrokinetic treatment of oily sludge. The hypothesis is that "*different electrical regimes behave differently in phase separation, including the application of constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC)".*

2- To investigate the effect of intensity of electric field, surfaces charges and surface wettability on electrokinetic process and dewaterability of different types of oily sludge to find optimal treatment performance. The hypothesis is that "*different electrical regimes can affect differently on the surface properties and thermal behaviour of sludge*".

3- To examine the effect of nanoparticles and synthesized catalyst (newly produced from oily sludge) on the separation efficiency of oily sludge in EK treatment. The hypothesis is that "*nanoparticles can improve the separation efficiency by destabilizing the stable emulsions and changing surface properties of solids*".

4- To elucidate the mechanisms underlying the separation of oil, water and solids in oily sludge during electrokinetic separation combined with nanoparticles or/and synthesized catalyst. The hypothesis is that "*electrochemical reaction combined with nanoparticles can effectively change surface properties and decrease activation energy*".

1.4 THESIS ORGANIZATION

Following the introduction and literature review and methodology chapters, this thesis is structured into three chapters describing novel research followed by a chapter of general discussion and conclusions.

Chapter 4 lays the foundation of this research project where an initial hypothesis was formulated and eventually verified as the research unfolded. The first objective of this study was to investigate the effect of different types of electric fields on the electrokinetic-induced separation of oily sludge. A benchtop EK-reactor was operated using lagoon sludge collected from the Suncor full-scale refinery located in Montreal, Canada. As such, the Suncor refinery produces four different types of sludge during its refinery process namely, sludge slurry and catalytic fines (heavy fuels oil tank), lagoon sludge, sludge American Petroleum Institute (API) and Dissolved Air Flotation (DAF) separator units, and separator bottom sludge. However, for this initial study, the effect of different electric field types was investigated for the phase separation of lagoon sludge only due to the difficulty encountered during the centrifugation destabilizing the W/O emulsions. To provide preliminary answers, 5 bench-top electrokinetic reactors were operated. The application of different electric field regimes was evaluated. The solids content of the oil wastes before and after electrokinetic treatment was determined.

Chapter 5 builds on the findings of Chapter 4. Based on the first study, the most efficient electrical regime leading to the best phase separation of the oily sludge was applied for the rest of the study. The EK set-up was operated with the selected electrical regime to test the reactor system in separating different types of sludge from oil refineries. This enabled us to assess the applicability of the system to separate the solids, water and oil from different types of oily sludge. Fresh oily sludge samples were collected from the Suncor full-scale oil refinery in Montreal, and subjected to EK-separation using the designed set-up. The following parameters were monitored before, during and after the EK separation process: water content, solids concentration, light hydrocarbon content, non-volatile hydrocarbon content, pH and wetting properties of the sludge. It is expected that the study outcomes would further help to improve management and treatment strategies for oil sediments by the electrokinetic method. The knowledge gained can help researchers and practitioners to further improve such technology in view of enhancing oil sediment treatment for both resource reuse and compliance to environmental regulations.

Chapter 6 builds on the findings of Chapter 4 and 5 by further examining the effect of nanoparticles and synthesized catalyst on EK treatment of oily sludge. In chapters 4 and 5, the initial material, used for the EK separation process, was the centrifuged oily sludge. In the current study, the effect of nanoparticle addition prior to centrifugation was assessed in view of elucidating whether nanoparticles have a potential to improve the phase separation of oily sludge. Nanoparticles have been extensively used to clean-up of wastes and to define characteristics such as enhanced reactivity, surface area, sub-surface transport and sequestration abilities (Brar et al., 2010; Shan et al., 2009). In the present study, Titanium (Ti) nanoparticles in their metallic were used, due to their ability to increase conduction and convection coefficients, thereby enhancing electrical conductivity (Buongiorno, 2006; Zawrah et al., 2015). A carbon-based synthesized catalyst was also used to assess the improvement of phase separation in EK treatment. Seven 1.5-L electrokinetic reactors with stainless steel electrodes were fabricated. The collected oily sludge was mixed with the synthesized catalyst or nanoparticle solution suspension. To assess the performance of the EK reactors, water, solid content and total petroleum hydrocarbons (TPH) were measured. The ratio of water/solids was also calculated. To elucidate the mechanisms underlying the separation of oil, water and solids in oily sludge during electrokinetic separation combined with nanoparticles or synthesized catalyst a kinetic study was conducted using Thermogravimetric and Differential Thermal Analysis (TGA).

Chapter 7: provides a general discussion of the salient findings of the research and general conclusions of this doctoral thesis.

Background and literature review

2.1 OILY SLUDGE

Oily sludge and sediments are produced at upstream and downstream of petroleum industry processes (Xu et al., 2009). It consists of a complex emulsion of petroleum hydrocarbons (PHCs), water, heavy metals, solid particles and other recalcitrant components. Considered as a hazardous waste in many countries, it represents a serious threat to human health and environment (Hu et al., 2013). Therefore, it is crucial to properly handle and treat oily sludge wastes prior to disposal.

2.2 SOURCES OF OILY SLUDGE

Various wastes are produced from oil and petroleum refineries and can be broadly categorized into oily sludge, sediments, contaminated soils, spent catalysts, chemical waste, and aqueous waste (Bush & Levine, 1992). During the petroleum extraction and process, oily sludge can be produced from both upstream and downstream stages. Processes resulting in the production of upstream sludge include extraction (slop oil at wells), storage and transportation while downstream sludge can result from various operational stages in the refinery process (Fig. 2.1) (Bhattacharyya & Shekdar, 2003). The Resource Conservation and Recovery Act (US RCRA), which is issued by the Environmental Protection Agency (US EPA), identified the main sources of oily sludge and residues under subtitle K. and a number shows the main sources of petroleum oily sludge (Arbuckle et al., 1976). Fig. 2.1 indicate a complete and comprehensive collection of different oily sludge that generate in different processes (Abrishamian et al., 1992; Da Silva et al., 2012; Hu et al., 2013). Canadian environmental protection act in hazardous wastes and hazardous recyclable materials categorized different oily sludge as hazardous wastes and hazardous recyclable materials in two categories of F037 and F038 (CEPA, 2015).

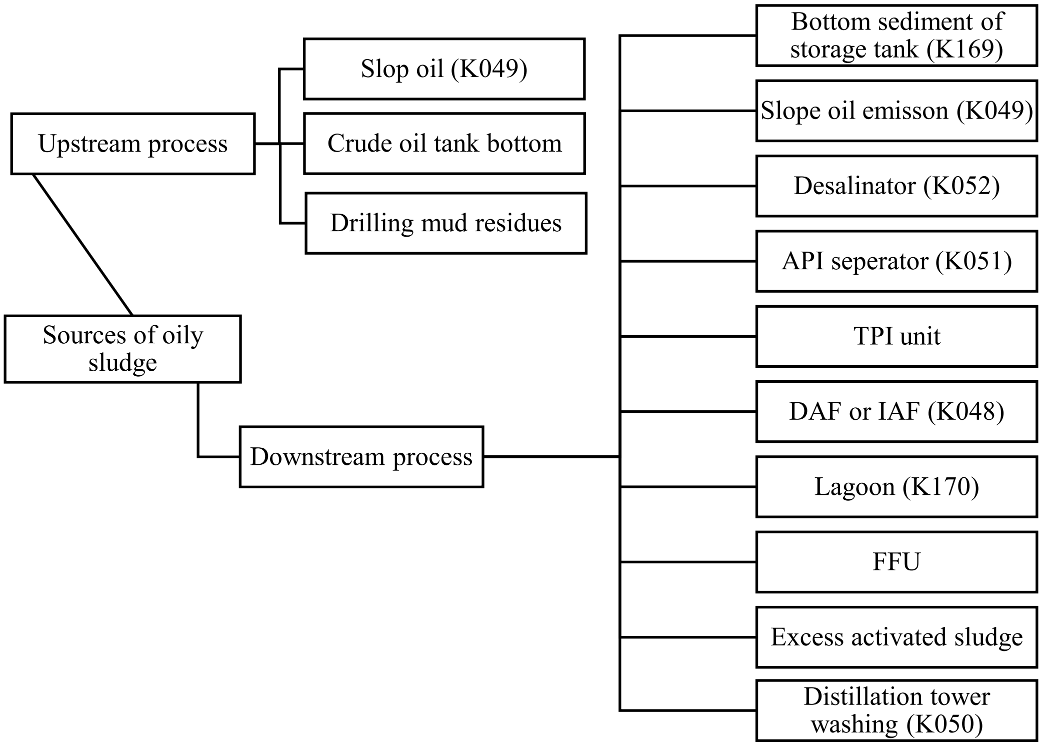


Fig. 2.1. Different sources of oily sludge during refinery process. Legend: API: American Petroleum Institute separator unit; TPI: Tilted Plate Interceptor; FFU: Sludge from flocculation–flotation unit; DAF: Dissolved air flotation; IAF: Induced air flotation units. RCRA code (K. and number) identifies the kind of sludge.

2.3 PRODUCTION OF OILY SLUDGE IN CANADA

About 550,000 tons/d (3.9 barrel/d) of crude oil are extracted in Canada, from which 27% is refined locally, 71% is exported to the U.S. and 2% is exported to overseas (CNEB, 2015). Up to 268,000 tons/d (1.9 barrel/d) of refined oil can be processed by the 15 refineries located in Canada (CFA, 2015). Which can generate around 16,500 tons/day of oily wastes, assuming that waste generation represents 3% of total crude throughput for upstream (Bush & Levine, 1992). In refineries, this amount is around 0.2 % (to 1%) of the oil that has been refined, which can produce at least 536 tons/d of oily sludge depends on the kind of sludge (Van Oudenhoven et al., 1995). According to the Canadian Association of Petroleum Product (CAPP), the extraction and processing of crude oil has been constantly increasing in the eastern and western Canada over the years and is expected to maintain an upward trend in the future (Fig. 2.2). This will result in an accrued production of oily sludge waste which will have serious economic, health and environmental implications.

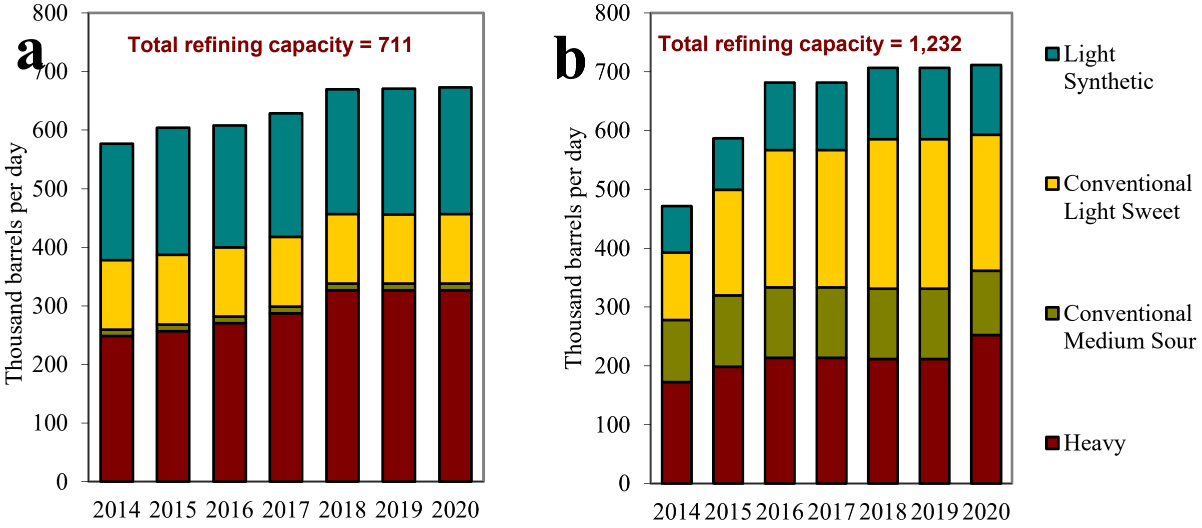


Fig. 2.2. Forecast Canadian crude oil production gross: (a) Western Canada; (b) Eastern Canada (CAPP, 2015)

It has been observed that unconventional means of crude oil extractions methods such as oil sands and shale oil are gaining wider acceptance over conventional methods due to the larger volume of oil that can be extracted (BP, 2016). However, unconventional oil extraction generates low API oils that contain higher concentrations of undesirable resins and Asphaltenes (Mohr & Evans, 2010). Fig. 2.3 indicates the increase of unconventional oil production until 2035 in North America (BP, 2016). North American production expands by 9 Mb/d and supply increases by 49% by 2035. These components increase the volume of sludge wastes, and the handling and disposal cost associated with it altogether. Hence, more advanced technologies are required to treat and/or reduce the quantity of oily sludge wastes.

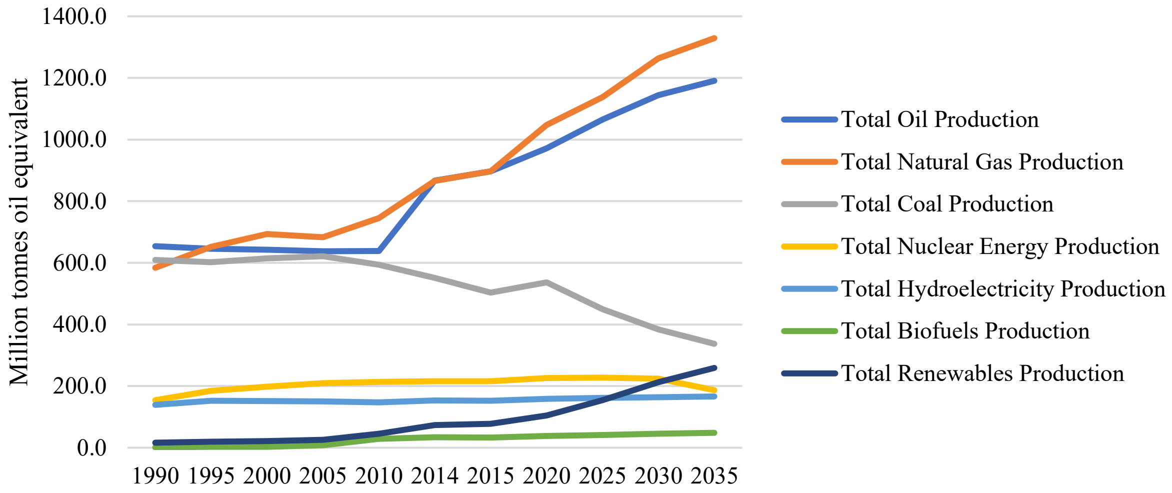


Fig. 2.3. North American energy production gross by BP World Energy outlook booklet till 2035 (BP, 2016)

Currently, centrifugation and chemical treatments are the most commonly applied technologies in Canada to treat oily sludge. However, they are expensive and cost around $100 per cubic meter of oily waste (Chukhareva et al., 2015). The cost in order to treat 8,000 tons/day (9,100 m3/day) of oily sludge will be approximately 900,100 CAD$/day. Therefore, research in the field of oily sludge treatment is crucial to minimize power consumption, capital and operational expenditure, and maintenance cost. While, still the efficiency of these method doesn't show good efficiency on dewatering and emulsion destabilization.

2.4 OILY SLUDGE AND ENVIRONMENT

Oily sludge wastes contain high concentrations of toxic compounds which are harmful to the environment (Hu et al., 2013; Todd et al., 1999). Uncontrolled discharge of untreated oily sludge in the environment can affect soil and water. The high amount of asphaltene and resin in oily sludge has been shown to alter the wettability of soils by reducing its hygroscopic moisture content, water retention and hydraulic conductivity (Manali & Shah, 2013). Studies have shown that high molecular weight compounds from the oily sludge persist in the environment for several years and can form hydrophobic crusts that prevent plant growth or water and air exchange in soils, which is crucial for the survival of soil organisms. They can reduce the diversity of microorganisms which play a crucial role in soil ecosystems (Wake, 2005).

In addition, toxic components in oily sludge wastes can pollute natural water bodies such as lakes and rivers (Wake, 2005). Various studies have reported the contamination of underground water, lakes and rivers by the natural precipitation of oily sludge, which slowly releases its toxic components into the water thereby threatening aquatic life (Bossert et al., 1984; Mishra et al., 2001; Mishra, 1989). Polycyclic aromatic hydrocarbons (PAH) and heavy metals from oily sludge wastes have been shown to decrease fish population due to their toxicity and persistence in the water bodies(Wilson & Jones, 1993) .

Literature has also reported air transmission of oily sludge particles over long distances (Karamalidis & Voudrias, 2007). The possibility of atmospheric pollution through the release of harmful gasses such as BTEX (benzene, toluene, ethylbenzene, and xylenes), methane and propane from evaporation and biodegradation of organic pollutants also poses a serious threat to the natural environment. Inhalation of harmful components emanating from oily sludge wastes can be genotoxic to the human body (Diya'uddeen et al., 2011; Hu et al., 2013).

Storage of oily sludge for a prolonged period of time has been shown to represent a high risk for leakage of oily sludge-related toxic compounds to the environment (Guolin et al., 2009). With the increased production of oily sludge wastes, the risk of environmental pollution incurred by these wastes is becoming higher. That the major health and environmental concern in the disposal of oily sludge are polycyclic aromatic compounds (PAC) because cancer is the major concern from exposure to PAC (Diya'uddeen et al., 2011; Giusti, 2009).

2.5 REGULATIONS FOR OILY SLUDGE DISPOSAL

Due to the hazardous and toxic nature of oily sludge, several regulations have been promulgated for the proper management, handling, storage and disposal of oily wastes. The Resource Conservation and Recovery Act (RCRA) in the USA and Canadian Environmental Protection Act (CEPA) in Canada, enforce the identification, control and/or prevention of toxic substances in the environment. These include oily sludge wastes from refineries.

The CEPA was established in 1999 to address the release of the toxic substance in the environment. This legislation emphasizes on the elimination of persistent organic pollutants (POPs) and bioaccumulative substances from the environment (CEPA, 2015). Petroleum sludge management falls under the Waste Management Act (WMA) which is enforced by the provincial Environment Management of Waste (EMW, 2014). The WMA regulates all aspects pertaining to oily sludge management including, producing, storing, transportation, handling, treatment, destroying, discharging, and disposal of the wastes. In the province of Quebec, disposal of hazardous wastes falls under the Environmental quality Act (EQA). Under this Act, land disposal of oily wastes is prohibited because of their toxic nature. To reduce the hazardous effect of oily wastes, the CEPA has established specific regulations to ensure that all storage tankers or surface impoundments, which treat hazardous wastes, including oily sludge, must be double lined. Reports have shown that oily sludge from refineries which have been disposed of in cement and brick double-lined lagoons or landfills can still be a potential source of atmospheric volatile organic compounds (VOCs) pollution (EPA, 2010). Emission of air pollutants not only creates health risks to the community but also contribute to climate change (CEPA, 2015) .

According to the Fisheries act refineries of Canada (C.R.C., C. 828 — 16 March 2016) the substance that contain: (a) oil and grease; (b) phenols; (c) sulfide; (d) ammonia nitrogen; (e) total suspended matter; and (f) any substance capable of altering the pH of liquid effluent are prescribed as “deleterious substances”. For depositing these deleterious substances need to have authorization from the minister that can be calculated in pounds per barrels of crude oil (Regulations, 2016).

2.6 GENERAL CHARACTERISTICS OF OILY SLUDGE

The general properties of oily sludge are related to the properties of the crude oil extracted. Moreover, it has been reported that different geological formations can lead to the production of crude oils with different chemical compositions, which in turn determine the chemical characteristics of oily sludge wastes produced during refinery (Wang et al., 2010). The geological formation of the terrestrial or marine region from where the oil has been extracted greatly determines the solid composition of the resulting sludge waste and its stability.

Chemically, oily sludge is a complex combination of hydrocarbons consisting predominantly of paraffinic (straight and branched-chain alkanes), naphthenic (cycloalkanes or cycloparaffins), aliphatic and aromatic hydrocarbons, and asphaltenes and nitrogen-sulfur-oxygen (NSO) (Heidarzadeh et al., 2010). The hydrocarbons in oily sludge wastes have carbon numbers that range from four (C_4) to large molecules containing more than sixty carbons (C_{60}). Sulfur, oxygen and nitrogen compounds, organometallic complexes (mainly of nickel and vanadium) and dissolved gasses (mainly hydrogen sulfide), are also found in crude oil and oily sludge wastes (Elektorowicz & Muslat, 2008). Typically, oily sludge can contain total petroleum hydrocarbons (TPH) (20% to 50% by mass), water (30-70%), solids (10-12%), nitrogen and oxygen (1%) and salt (0.1%). Considering only the hydrocarbon component, it has been shown that different refineries can result in oily sludge bearing different composition in hydrocarbons with typically 40-52% alkanes (saturated), 28-31% aromatics, 8-10% asphaltenes, and 7-22% resins by mass (Habibi, 2004). Different types of sludge and their sources are categorized in table 2.1 (EPA, 2010).

Table 2.1. Typical characteristics of different kinds of oily sludge (CEPA, 2015; EPA, 2010)

Type of sludge	Oil%	Water%	Solids %	description
Desalter bottoms	25.5	53	21.5	Inorganic salts, suspended solids, and water-soluble trace metals
Slop oil (lagoon storage)	48	40	12	Emulsion appearance, heavy oily sediments,
API separator sludge	23	53	24	Suspension appearance, with non-mineral skimmed foam and grease
DAF float	13	84	2	Liquid appearance
Tank bottoms	48	13	39	Suspension appearance, raw and dark petroleum product (combustible oils, petroleum asphalt, lubricants)

2.7 PROPERTIES OF OILY SLUDGE – IMPLICATIONS FOR SEPARATION

The separation of the different components in oily sludge waste during treatment largely depends on the physical and chemical properties of the sludge. It is very important to assess the physical characteristics of oily sludge wastes prior to treatment. These include the molecular weight, polarity, PAH content, boiling point, volatility and solubility of the oil component (Elektorowicz & Habibi, 2005). Along with organic components, the presence of several heavy metals has been identified in oily sludge and shown to affect the ionic properties of the sludge waste. The concentrations of these metals vary in the different kinds of oily sludge (Table 2.2) (EQA, 2015).

Table 2.2. The typical range of heavy metal concentrations in oily sludge and liquid oils (EQA, 2015).

Metals	Oily sludge mg/kg	Liquid oil mg/L
Fe	2200- 60200	240
Pb	0.001-565	1
Cd	12	12
Ni	17-480	9
Cu	32-500	5
Zn	7-80	6
V	33	33
Cr	27-480	-

Chemically, oily sludge is a very stable colloidal suspension system as a result of electronegativity and hydration (Guolin et al., 2009). The presence of oil and water, two immiscible liquids, in oily sludge wastes results in the formation of water-oil emulsions. These emulsions are very stable due to the presence of a protective layer of fine clays which prevents the emulsions from coagulation or coalescence. PHC constituents such as asphaltenes and resins act as a natural emulsifier in the layer (Fig. 2.4). Fig. 2.4. the effect of mineral particles in oil emulsion. Where (a) Resin-asphaltene association to form a colloidal aggregate. Asphaltenes interact through hydrogen bonding and π-bond overlap. Through polar functional group interactions, resins solvate asphaltene aggregates to each other. However, Fig. 2.4(b) shows resin-asphaltene colloidal aggregate association to form an interfacial film. Primary asphaltene aggregates cross-link to form a rigid, viscoelastic structure at the oil-water interface. Adsorption of resin/asphaltene aggregates to a hydrophilic particle. As more aggregates adsorb, the particle becomes preferentially wetted by the oil phase ($\Theta > 90°$). Pi bonding and ionic bonding has been found between asphaltene/resin and clay surface adapted from Sullivan and Kilpatrick (2002) and Sparks et al. (2003). There are also other natural emulsifiers in this layer such as fine solids, oil-soluble organic acids and other fine materials that contribute in stabilizing the water-in-oil emulsion (Yang et al., 2008). In addition, asphaltenes and resins contain hydrophilic functional groups that act as lipophilic emulsifiers. The structure of the water-in-oil emulsions is further stabilized by the pH of oily sludge which usually ranges from 6.5-7.5 (Elektorowicz et al., 2006). The formation of these stable water-in-oil emulsions renders the whole separation and treatment process of oily sludge wastes very challenging (Heidarzadeh et al., 2010; Hu et al., 2013). Fig. 2.4 indicates the effects of inorganic solid particles on water and oily sludge emulsion stability (Sparks et al., 2003; Sullivan & Kilpatrick, 2002; Yang et al., 2008). The ratio of asphaltene to resin plays a very important role in the stability of the emulsions and adsorption on the solids.

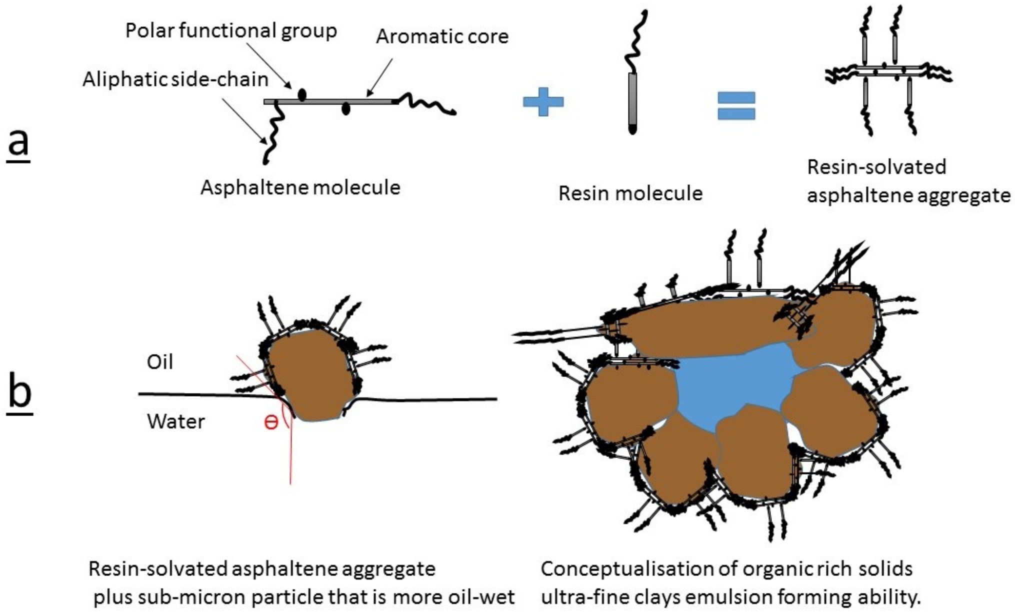


Fig. 2.4. Effect of mineral particles in oil emulsion. (a) Resin-asphaltene association to form a colloidal aggregate, (b) resin-asphaltene colloidal aggregate association to form an interfacial film.

2.8 TECHNOLOGIES FOR OILY SLUDGE TREATMENT

2.8.1 Overview

The management of oily sludge can be divided into three sections: reduction of oily sludge production, recovering of useful fuel from existing oily sludge, and disposal of oily sludge. Since the production of oily sludge wastes is constantly increasing due to the application of unconventional crude oil extraction methods, research in the development of novel technologies is ongoing so as to reduce oil sludge production and/or enhance its treatment (Hu et al., 2015). From a sustainability standpoint, most focus on designing treatment systems to find optimal separation of oily sludge waste components in order to recover valuable fuel. There are different treatment methods for oily sludge wastes; these can be appropriately categorized as disposal, separation and combined methods (Table 2.3).

Table 2.3. Methods for oily sludge treatment

Categories	Methods	References
Disposal	Biodegradation	(Ward et al., 2003)
	Advanced oxidation	(Cui et al., 2009)
	Stabilization and solidification	(Karamalidis & Voudrias, 2007)
	Incineration	(Li et al., 1995)
	Landfill	(Taha et al., 2010)
	Landfarming	(Da Silva et al., 2012)
	Composting or biopile	(Ouyang et al., 2005)
	Bioreactors	(Robles-González et al., 2008)
Separationq	Electrokinetics	(Elektorowicz & Habibi, 2005)
	Microwave irradiation	(Fang et al., 1989)
	Pyrolysis	(Liu et al., 2009)
	Freeze/thaw	(Yang et al., 2008)
	Surfactant EOR	(Abdel Azim et al., 2011)
	Centrifugation	(Cambiella et al., 2006)
	Solvent Extraction	(Taiwo & Otolorin, 2009)
	Froth flotation	(Ramaswamy et al., 2007)
Combined	Electrokinetic + supercritical fluid extraction (SFE)	(Badawieh, 2015)
	Ultrasound + thermochemical	
	Oxidation + pyrolysis	(Zhang et al., 2012)
	Microwave + freeze/thaw	(Jin et al., 2012)
	Bio-surfactant + froth flotation	(Shie et al., 2004)
	Fenton + stabilization/solidification	Rajaković and Skala (2006)
		(Mater et al., 2006)

Each method highlighted in Table 2.3 has its own benefits and disadvantages in terms of its effects on human health, sustainable development and impact on the environmental. In refineries, the methods are mainly chosen based on economic considerations, historical preferences and local geography of the refinery plant (Alshammari et al., 2008). Below are the most commonly used disposal and separation methods by refineries.

2.8.2 Incineration

Incineration involves the combustion of organic wastes using excess air to produce ash, flue gas, and heat. Incinerators reduce the solid mass of original oily sludge by around 85% (Scala & Chirone, 2004). It is widely adopted in large refineries for sludge treatment. The treatment of one ton of oily sludge may cost more than $800 due to the high operation and capital costs treatment method (Habibi, 2004). Rotary kiln and fluidized bed incinerators are the most common types of incinerators. The residence time of oily sludge waste in a rotary kiln incinerator is around 30 min at a temperature range of 980-1200 °C while the residence time of waste in a fluidized bed incinerator can be in the order of days with a temperature range 730-760°C (Scala & Chirone, 2004). Auxiliary fuels are used to improve the combustion efficiency of the wastes and include coal- and coke- water slurry.

The combustion of oily sludge in incinerators can be used as a source of energy for driving steam turbines and represents heat source for different applications. However, sludge incineration has some limitations. The performance of incinerators is largely affected by feedstock quality (hazardous constituents that are resistant to combustion), temperature, residence time, amount and quality of auxiliary fuels, waste feed rates, and combustion condition (Zhou et al., 2009). Usually, the oily sludge is very viscous and needs pretreatment such as heating to decrease the viscosity prior to incineration. On the other hand, some types of oily sludge are less viscous with a high water content that makes combustion difficult to achieve. Gaseous emission (So_x, NO_x, PAH, BTEX, dioxins, and furans) (Li et al., 1995) from incinerators and the heavy metal content in fly and bottom ash residues are toxic and should meet the permissible limits defined by environmental regulations.

2.8.3 Biological methods

The biological method is a common process for remediation of organic pollutants. It involves the use of microorganisms to degrade oily wastes. To accelerate this process different biological methods have been implemented such as land farming, composting and bio-slurry treatment.

2.8.4 Land-farming

Land-farming is a remediation method that involves mixing soil with oily sludge waste. Such mixing leads to different processes that degrade the contaminants in the sludge waste. Biological degradation is the main process, while physical and chemical processes like photo-degradation and evaporation also contribute to the degradation process. Mainly the upper layer of soil is used as it contains active aerobic organisms (Hejazi et al., 2003). This method was first implemented in Europe at the end of the 19th century. However, it has been banned for bioremediation of oily wastes in most North American jurisdictions due to the transfer of pollution (Da Silva et al., 2012). In USA, UK, Canada and Germany, a secure and restricted landfill area with an impermeable layer of compacted clay or high density polyethylene is used to degrade the oily waste. Often the pH, humidity, nutrients (nitrogen, phosphorus and potassium compounds) and aeration of the soil system are controlled to enhance the degradation.

Silva (2009) investigated the land-farming of 1,000 m^2 area at a Brazilian refinery, in which the humidity, nutrient and aeration were controlled. After 225 days the TPH content decreased by 89.6% in the soil and the observed degradation rate was 25.8 mg / (kg day). Hejazi et al. (2003) studied the treatment efficiency of land-farming oily sludge for duration of 12 months. The effects of adding water, nutrient and tilling were compared, and the best treatment was observed with tilling leading to 76% removal of PHCs. Since long chain alkanes such as C_{17} and C_{18} were also found to be degraded, it was concluded that the removal of contaminants may involve other processes than just weathering. Mishra (1989) studied the effect of applying extraneous bacteria consortium (bioaugmentation), and nutrients and water (biostimulation) for a period of 120 days at the field-scale (4000 m^2 area). Both bioaugmentation and biostimulation led to 90% removal of PHCs as compared to the control area where only 17% of degradation was achieved.

Land-farming has some merits such as low capital cost, low energy consumption and simple operation. On the other hand, it requires large land area and is a time consuming process. The major environmental disadvantage of land-farming processes for remediation of oily sludges relates to the large quantities of volatile organic carbons that are released to the atmosphere during the degradation process (Ward et al., 2003). In addition, some of the PAH (benzo pyrene) are capable of accumulating in the food chain and exert similar effects like many organochlorine pesticides. The presence of PHCs and heavy metals can impact negatively on soil microorganisms. Heavy metals have been shown to alter the metabolism and growth of soil microorganisms (Silva, 2009). Consolidating the security of the landfill for land-farming to make it more environmental friendly involves higher costs as compared to conventional land-farming.

2.8.4.1 Biopile

Composting or biopile is a version of land-farming which involves less land area and better control on mixing, moisture content, volatile organic release, and aeration (Da Silva et al., 2012). In this method, the wastes are shoveled into piles of around 2-4 meter height. Aeration is achieved through perforated pipes and mixing through special churning equipment. Addition of organic materials such as wood chips, saw dust and bark have been shown to improve the aeration efficiency (Marín et al., 2006). Wang et al. (2012) applied cotton stalks to aged oily sludge and found an enhanced microbial activity leading to 49.62% removal of TPH in 220 days. On the other hand, they showed that application of large amount urea (3%) as nutrients restricted the diversity and metabolic activity of the microorganisms. Ouyang et al. (2005) studied the effect of bioaugmentation on oily sludge composting over a period of 56 days at ambient temperature and observed 46-53% removal of TPHs. Their control involved conventional composting which removed 31% of the TPHs.

Biopiles can be operated in cold regions (Sub-Antarctica region) as a result of increase in temperature inside the biopile that can reach up to 70 °C as a result of microbial activity (Delille et al., 2004). In comparison to land-farming, VOC emissions can be more controlled. The disadvantages of biopiles include its low treatment capacity, long retention times, low effectiveness under high TPH (> 50 000 ppm) and heavy metal (> 2,500 ppm) concentrations, which are inhibitory to microbial growth. In addition, VOCs may escape to the atmosphere without being degraded. This is why gaseous contents released from biopiles require some levels of treatment (Da Silva et al., 2012; Hu et al., 2013).

2.8.4.2 Bioreactor

Bioreactors have been developed to improve the biological treatment of different liquid effluents from industries. Slurry bioreactors are the most common biological methods for oily sludge waste treatment (Castaldi, 2003). In this method, the oily sludge is mixed with water to make a slurry and increase the amount of solubilized contaminants in order to render them bioavailable. As a result of microbial activities, the pollutants are transformed to carbon dioxide and water or intermediate products that are less toxic such as organic acids and aldehydes (Kim & Weber, 2005). Bio-slurry reactors are usually designed in two configurations namely rotary drum or vertical tank, which is equipped with lifter and impellers for mixing, respectively (Robles-González et al., 2008). Ayotamuno et al. (2007) investigated the possibility of treating bottom storage oily sludge using bio-augmentation method. They added soil as both a source of nutrients and a microbe carrier. It was found that the THC removal from the slurry varied between 63.7% and 84.5%. Ward et al. (2003) used three different bio-surfactant producing microorganisms in their bio-slurry reactor. The sludge concentration was in the range of 1.55- 12.8% and the removal efficiency achieved was 80-99% within 10-12 days of reactor operation.

Advantages of bio-slurry reactors include better control on the operational conditions such as pH, temperature, humidity and efficient mixing. Compared to the classical method of bioremediation, bioreactors can improve the bioaugmentation and biostimulation on enhancing biodegradation of oil hydrocarbons contaminated (Zawierucha & Malina, 2011). In addition, it prevents the direct emission of gaseous pollutants to the environment, which increases environmental safety. It is also applicable on large-scale level. According to Ward et al. (2003), a bioreactor with a capacity of 4.55×10^6 liter has been operated in the Gulf coast refinery (Ward et al., 2003). The system was equipped with air stripping and mechanical agitation and led to 90% of TPH removal. The major drawback of the bio-slurry method is its higher construction and operational costs as compared to the classical bioremediation techniques. On average, the bio-slurry treatment costs above $625 per ton of sludge, while it is only $155 per ton sludge for land-farming (Castaldi, 2003). Optimization of contaminant desorption in bio-slurry to induce bioavailability of contaminants, requires considerable amount of water, from 2 to 20 times the volume of sludge that needs post treatment. The oily sludge contains solids, which may cause operational problems thereby requiring pretreatment (Robles-González et al., 2008).

2.8.5 Advanced oxidation

Advanced oxidation treatment refers to the set of procedures that has been designed to remove organic and some inorganic materials by oxidation through reaction with intermediate radical such as hydroxyl radicals (-OH) (Ferrarese et al., 2008). Organic contaminants are oxidized to water and carbon dioxide or nonhazardous substances such as inorganic salts. There are different oxidation processes that have been used for treatment of biologically toxic or non-degradable materials such as aromatics (PAHs), pesticides, petroleum (PHCs), and volatile organic compounds in wastewater, contaminated soil and oily sludge wastes. These methods involve oxidants such as hypochlorite, ozone, ultrasonic irradiation, Fenton's reagent (H_2O_2), permanganate and persulfate (Collings et al., 2006; Jing et al., 2012a; Mater et al., 2006; Zhang et al., 2012).

In a study conducted by Mater et al. (2006), the applicability of the Fenton process was evaluated on oil-contaminated soil, followed by Portland cement stabilization/solidification. During the Fenton's reaction, hydrogen peroxide (H_2O_2) is decomposed by iron (II) to form hydroxyl radicals

(13 wt% for H_2O_2; 10 mM for Fe^{+2}). The authors achieved the most optimized treatment at a pH of 3, where the PAH decreased from 85475 to 5418 mg kg^{-1} , BTEX decreased from 11,198 to 682 mg kg^{-1} , and total phenol (344 mg kg^{-1}) and surfactant (20 mg kg^{-1}) were completely removed. The oxidation treatment was followed by stabilization/solidification of the remaining waste by Portland cement, which showed enhanced efficiency in immobilizing the recalcitrant and hazardous constituents of the contaminated soil. Ferrarese et al. (2008) investigated the effectiveness of commonly available chemical oxidants such as hydrogen peroxide, modified Fenton's reagent, activated sodium persulfate and potassium permanganate. These oxidizing agents reduced the PAH concentrations from 2,800 mg/kgSS (SS: suspended solids) to less than 100 mg/kgSS. The efficient remediation performance was observed with modified Fenton's reagent, hydrogen peroxide and potassium permanganate, with oxidant dosages about 100 mmols per 30 g sediment sample.

There are other kinds of advanced oxidation techniques such as ultrasonic, supercritical water oxidation (SCWO), wet air oxidation (WAO) and photo-catalytic oxidation (PO). In ultrasonic oxidation, the sonication of water molecules produces intermediate radicals such as hydrogen (H•), hydroxyl (OH•), hydroperoxyl (HO_2•) and hydrogen peroxide (H_2O_2) which can oxidize potential contaminants in oily sludge wastes (Zhang et al., 2012). Ultrasonic has proven to be effective for removing low-concentration organic pollutants from aqueous solutions with the ability to break long-chain or aromatic hydrocarbons into simple hydrocarbons. Compare to thermal methods, ultrasonic is not limited to the shallow soil or sludge sediment but irritated noise problems from ultra-sonication should be considered carefully (Collings et al., 2006). In addition, the ultrasound method needs a lot of water for diluting the contaminants, and consume a significant amount of energy, that reduce its applicability (Jin et al., 2012).

Wet oxidation (WO) is another advanced oxidation which uses oxygen under high pressure (3-25 MPa) and high temperature (150-330 °C) (Jing et al., 2012b). Metal (especially iron) salts are known to be effective catalysts. Jing et al. (2012) investigated the effect of adding Fe^{3+} as catalyst to improve COD removal from oily sludge. The results show that increase in temperature and excess O_2 greatly improve the COD removal rate. The best removal achieved was 88.4% of total COD (4,000-20,000 mg/L) from the oily sludge in 9 min at 330° C. The COD removal was further improved when using both Ni^{2+} and Fe^{3+} in combination. In some studies, hydrogen peroxide has been used as oxidant instead of air at high temperature (Jing et al., 2012b). Catalytic wet air oxidation (CWAO) has been shown to be a good method for COD range of 10,000 to 100,000 but is not cost effective for COD less than 5,000 mg/L (LennTech, 2015).

Supercritical water oxidation (SCWO) uses the critical point of water (375 °C and 22.1 MPa) to produce a single homogeneous phase and convert the H-C-N compounds to water, carbon dioxide and molecular nitrogen (Cui et al., 2009). The application of SCWO for oily sludge treatment has been used by Cui et al. (2009) where the total COD removal of oily sludge was 92%.

Among the advanced oxidation processes, photocatalysis stands out as a promising technology in the treatment of environmental pollutants. In photo catalytic oxidation, UV and sunlight irradiation degrade oxidants added for oily sludge treatment (Yawalkar et al., 2001). The presence of oxygen is necessary for photocatalytic process. The photocatalytic oxidation takes place at the surface of semiconductors (TiO_2) and increase the number of free radicals. The investigation of Da Rocha et al. (2010) shows the capability of 100% PAH removal (218.22 mg/kg total PAHs) from oily sludge in 96 h of photo-catalytic treatment. In this study H_2O_2/UV/TiO_2 was applied to induce the heterogeneous photocatalytic oxidation of the oily waste contaminants.

The above described studies show the capability of advanced oxidation processes to degrade complex mixtures to water and carbon dioxide or to simple composition which have higher bioavailability and solubility. In general, the degradation of oily sludge by advanced oxidation requires less treatment duration than the other methods. On the other hand, treatment with chemical oxidation needs a lot of chemical reagents. To meet the remediation goals, the chemical reagent should be strong enough to attack the most recalcitrant compounds, while high dose could decrease the efficacy. They may also need special equipment that will increase the cost of treatment.

2.8.6 Stabilization/solidification

Stabilization/solidification (S/S) is a common method for the immobilization of inorganic wastes (Al-Futaisi et al., 2007). Stabilization is a chemical technique that reduces the distribution of hazardous waste components by converting them to less soluble, mobile, or toxic forms. Solidification, on the other hand, is the encapsulation of the waste components by forming a solid material. The S/S can take place at the same time by mixing solid additive materials like cement, lime, fly ash, cement kiln dust, blast furnace slag, sulfur, clay, lime, thermoplastic, organic polymerization or any combination of them (Taha et al., 2010). Cement is the most common binder that is used for immobilizing wastes. Most studies carried out on S/S methods involved inorganic wastes due to the inhibitory effect of organic compounds on cement-based binder hydration (Karamalidis & Voudrias, 2007).

Some studies have investigated the application of S/S techniques for the immobilization of organic wastes such as oily sludge. The effect of different additives on the basis of cost, availability of solidification material, quantity and characteristic of materials and leaching behavior of contaminates (heavy metals and organic wastes) has been studied (Al-Futaisi et al., 2007; Karamalidis & Voudrias, 2007; Rozumová et al., 2015). In all of the studies surveyed, the performance of toxicity characteristic leaching procedure (TCLP) revealed that leaching of toxic components after S/S treatment did not exceed the standards (Hu et al., 2013). Taha et al. (2010) investigated the effect of S/S method for the immobilization of oily sludge by different additives and the impact on the leaching threshold TCLP limits established by the U.S. Environmental Protection Agency (USEPA). Different concentration of ordinary Portland cement (OPC), cement by-pass dust (CBPD) and quarry fines (QF). OPC was found to exhibit the highest removal efficiency of toxic components from oily sludge. More precisely, a mixture of sludge, OPC and QF in the ratio of 1:0.5:1.5, and a mixture of sludge and CBPD in the ratio of 1:2, resulted in the highest economical removal efficiency.

Karamalidis and Voudrias (2007) applied cement to stabilize oil and ash from incineration of oily sludge. The results indicated 98% and 93% immobilization of metals in the ash and oily sludge, respectively. They studied the immobilization of real oil refinery sludge in cement-based S/S. Two different kinds of cement namely Portland (I42.5) and blended cement (II42.5) were used. Analyses were performed for total petroleum hydrocarbons, alkanes, and sixteen polycyclic aromatic hydrocarbons (PAH) from the EPA priority pollutants list. Results showed that an increase in the cement level would destabilize the binding capacity of alkanes and increase leaching ability. Addition of I42.5 cement favored immobilization of 5 out of the 16 PAH (such as naphthalene and anthracene) while addition of II42.5 cement favored immobilization of the rest of the aromatic compounds such as: PAHs.

Advantages of the S/S method include the availability of additives, easy application on different wastes, and high efficiency of immobilization of organic and inorganic contaminants in oily sludge. The disadvantage of S/S is that the volume of treated material increases with the addition of additives. The volume of the post-treatment mixture can increase up to four times, which can impact on the handling and disposal costs.

2.8.7 Centrifuge

Sludge derived from refineries, consisting of more than 50% oil and less than 30% solids, can be used for oil recovery processes (USDC, 2015). Recovery of the oil is usually performed by centrifugation, which involves the sedimentation of heterogeneous mixtures at both laboratory and industrial scales. This process can separate immiscible liquids and solids. The components that are denser migrate away from the centrifuge axis and settle at the bottom. In addition, centrifugation is the most common method used in oil refineries to separate different phases of oily sludge. More specifically, the dynamic horizontal decanter centrifuge (solid-bowl) is the common method for treatment of oily wastes. While for other kind of sludges, other than oily sludges, belt-filter presses or plate and frame presses are used (Wakeman, 2007). The added advantage of centrifugation is its ability to separate oily sludge into three phases namely oil, water and solids. In some sludge where stable emulsions are formed between the oil and water phases, a further treatment such as dissolved air flotation unit process coupled with coagulation and flocculation, is required (Hertle, 2012).

Usually, there are some pretreatments for the centrifugation process in order to reduce energy consumption and viscosity of oily sludge. These include injection of steam, direct heating, or addition of organic solvents, demulsifying agent and tensioactive chemicals (Huang et al., 2014). In order to improve the recovery of oil from the centrifuged waste, the remaining solids can be mixed with hot water and re-centrifuged. The properties of oily sludge samples can be very different in some cases leading to water-in-oil (W/O) or oil-in-water (O/W) emulsion. Cambiella et al. (2006) investigated the separation of O/W emulsion using laboratory bottle centrifuge and pilot scale disk-stack centrifuge. To destabilize the emulsion, small amounts of $CaCl_2$ were added as coagulant and its effect studied by monitoring the zeta potential and turbidity. Such approach led to 92-96% oil removal efficiency from the stabilized O/W emulsion. Huang et al. (2014)

developed a model to predict the effect of centrifugation on the oily sludge solids . They used two kinds of common sludge from refineries to validate their model: petroleum sewage sludge (PSS) and oil-tank bottom sludge (OBS). Both samples were sticky, black, and odorous. The predicted particle removal data agreed well with the experimental measurements. The experiments showed the W/O emulsion was in the range of 75% to 86% in the mixture. Preheating (from 20°C to 80°C,) of the PSS decreased the viscosity and improved the particle removal rate by 29%. Solvent addition to the sludge improved the solid particle removal rates to 90% for PSS and 82% for OBS and reduced the amount of W/O emulsion. The results show that viscosity and particle size distribution could influence the model prediction for particle removal efficiency. The various steps involved in the separation of oily sludge by centrifugation is shown in Fig. 2.5 (Hu et al., 2013).

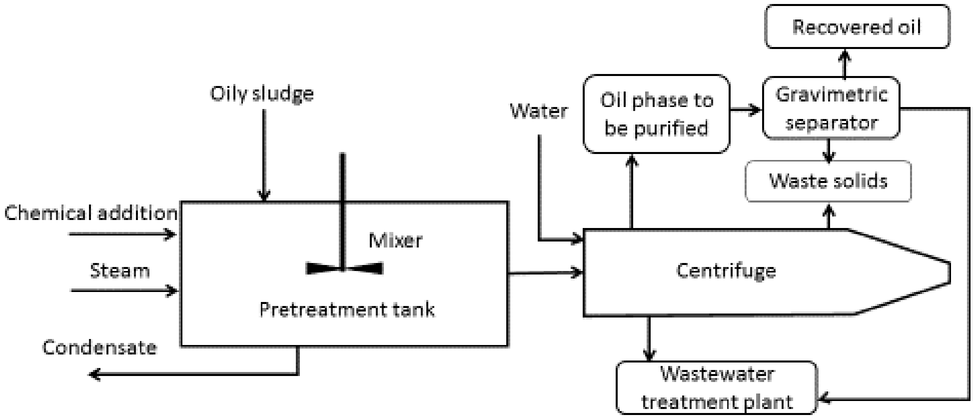


Fig. 2.5. Steps involved in centrifugation of oily sludge adapted from Hu et al. (2013)

Existing centrifuge processes accompanied by heat and chemical additives can improve the oil content to a certain extent. However, there will still be oil in solid residues (5 to 10%) and W/O emulsions (40-60%) present, even after double or triple centrifugation (Badawieh, 2005). Moreover, the application of chemicals such as demulsifying and tensioactive agents has both environmental and cost implications. Centrifugation is a relatively expensive process, especially when extra heat and chemical are supplied to the process. This also relates to the high energy consumption of the equipment to generate strong centrifugation force. Noise pollution is another side effect of the process (Alshammari et al., 2008; Habibi, 2004). The Alpha Laval company in Sweden use the most professional centrifuges to separate oily sludge (Dolphin Centrifuge, 2016).

2.8.8 Solvent extraction

Solvent extraction is usually applied for liquid-liquid and solid-liquid extraction of semi- or non-volatile organic compounds. The type and quantity of solvent used greatly determine the extraction efficiency. It has been used in conjunction with other technologies such as solidification/stabilization or incineration. This method has been reported to be effective in the treatment of sediments, contaminated sludge (with PCBs, VOCs, and halogenated solvents) and petroleum wastes (Hu et al., 2015; Hu et al., 2013).

Abouelnasr and Zubaidy (2008) investigated the solvent extraction efficiency of fuel oil from oily sludge. Methyl ethyl ketone (MEK) and Liquefied Petroleum Gas Condensate (LPGC) have been used in a solvent-to-sludge mass ratio ranging from 1:1 to 6:1 with an optimum ratio of 4:1. The highest amount of recovery was obtained from MEK extraction with almost 39% of the fuel oil recovered. Hu et al. (2015) used different solvents in combination with freeze and thaw processes. Cyclohexane (CHX), dichloromethane (DCM), methyl ethyl ketone (MEK), ethyl acetate (EA), and 2-propanol (2-Pro) were used as solvent in the sludge to solvent ratio of 1:1 to 1:8. Although combination of MEK or EA extraction with freeze/thaw resulted in high extraction efficiency, the amount of heavy metals was increased in the separated oil (Hu et al., 2015). Taiwo and Otolorin (2009) applied hexane and xylene as solvents, which resulted in the recovery of 67.5% of hydrocarbons.

Although solvent extraction is a simple method that does not need any specific equipment it has some disadvantages such as decrease in extraction efficiency for sludge with high clay content and longer contact time. Different types of soil and moisture content can impact on the extraction performance. Solvent extraction has also been shown to concentrate heavy metal content of separated oil. Furthermore, the presence of detergents and emulsifiers in the oily sludge can unfavorably influence the extraction performance (Zubaidy & Abouelnasr, 2010). However, solvents are themselves considered as toxic substances and their presence in treated solids represent an environmental hazard.

2.8.9 Surfactant destabilization

Surfactants can enhance oil recovery by separation of organic pollutants from solid surfaces and changing their wettability in order to destabilize organics. Chemical surfactants or demulsifiers are amphipathic (amphipolar) and can be categorized as anionic, cationic, nonionic, amphoteric and zwitterionic. Amphoteric compounds may only form either a cationic or anionic species depending on external conditions, while zwitterions simultaneously have both ionic states in the same molecule. Surfactants consist of hydrophilic and hydrophobic tails. The hydrophobic tail can comprise of a hydrocarbon, perfluoroalkyl or polysiloxane group. The molecular structure of the tail such as its length or branching can significantly alter the physical behavior of the surfactant (Schramm, 2000).

In environmental applications, neutral or anionic surfactants are preferred because cationic surfactants tend to interact with the soil particles, reducing their effectiveness. The toxicity of surfactants to the soil microorganisms is also very important for remediation and restoration of soils. This is why in recent years the use of natural surfactants or biosurfactants are gaining considerable importance (Elektorowicz et al., 1999; Hu et al., 2013).

Surfactants have been used to demulsify emulsions from petroleum sludge. Various studies revealed the efficiency of nonionic surfactants in destabilizing emulsions (Guolin et al., 2009; Shi et al., 2013; Yang et al., 2005a). Nonionic surfactants are more durable than anionic ones under different conditions. However, both forms of surfactants are nontoxic and have low LD50 (median lethal dose) comparable to sodium chloride (ionic) (Schramm, 2000). Anionic (e.g. sodium dodecyl sulphate [SDS]) and nonionic surfactants (e.g. Corexit 9527, Triton X-100, Tween 80 and Afonic 1412-7) have been shown to dissolve PHCs and increase their concentrations in aqueous phase (Guolin et al., 2009).

Critical micelle concentrations (CMC) of nonionic surfactants are lower than anionic surfactants thereby requiring lesser quantity to induce the same effect. The concentration of surfactant should be more than the CMC in order to have the best effect in interfacial tension lowering. Table 2.4 shows the CMC range for different surfactants. The addition of co-surfactants (.e.g. n-alcohols) can affect the CMC. It has been reported that the CMC decreases with increasing alcohol concentrations, while the addition of urea to micellar solutions tends to increase the CMC, and may even inhibit micelle formation (Schramm, 2000).

Table 2.4. Surfactants and their critical micelle concentration (CMC) (Schramm, 2000).

Surfactant	CMC (Mole)	example
Cationic	$10^{-3} – 10^{-1}$	Alkylpyridinium chloride
Amphoteric	$10^{-3} – 10^{-1}$	Alkyl amino betane
Anionic	$10^{-3} – 10^{-2}$	Sodium dodecyl sulphate
Nonionic	$10^{-5} – 10^{-4}$	Triton X-100

Studies have shown that waxes can stabilize W/O emulsions in oily sludges. Goldman (2001) found that nonionic surfactants comprising of a mixture of dispersants and degreasers resulted in the reduction of the crystalline wax's surface tension (Goldman, 2001; Goldman, 2004). Guolin et al. (2009) used anionic and nonionic surfactants, considered as the two most common surfactants used in cleaning products, to perform separation of oily sludge components. They used sodium dodecylbenzene sulfonate (DBS) and alkyl phenol polyoxyethylene ether (OP-10) as nonionic and ethoxylation alkyl sodium sulfate (Na-AES) as anionic surfactants. These agents were found to 98.75% of the oil from the sludge (Guolin et al., 2009).

Abdel Azim et al. (2011) tested three sets of nonyl phenol ethoxylate (n=9, 11, 13) surfactants to break down petroleum sludge from Al-Hamra Oil Company. They prepared a demulsifier system using surfactants, organic acids (HCl, H_2SO_4 and H_3PO_4) and isopropyl or butyl alcohol as co-surfactants. They found that better demulsification results were obtained with NP-13, and concluded that this may be due to the effect of higher hydrophilic-lipophilic balance (HLB) leading to better solubility. Shi et al. (2013) studied the effect of mixtures of anionic surfactant (sodium dodecyl sulfate (SDS)) and nonionic surfactant (Triton X-100) on the solubility of polycyclic aromatic hydrocarbons (PAHs). They found that most PAHs were transferred to mixed micelles with a mixture of SDS:TX100 in the ratio of 1:9, which they attributed to the lower CMC of the mixed surfactant solution.

Studies also report the enhanced oil recovery from oily sludges by coalescence of emulsions, reduction of the rheological interface properties of the oil and aqueous solution and decrease in interfacial tension. Somasundaran and Zhang (2006) indicated that addition of inorganics such as silicates, phosphates, carbonates and polymers such as lignins, can be used to control the adsorption and the wettability of the system. Meanwhile, they also showed that mixed surfactants perform better than individual ones due to synergetic effects and ability to improve precipitation. A number of factors have been reported to affect the interaction of surfactants with solids and subsequently their wettability (Shi et al., 2013). Some of the more obvious ones include: surfactant structure and concentration, Kinetics, pore surface composition and other factors such as solubility, surfactant stability, presence of co-surfactants, electrolytes, pH, temperature, and solids structure.

2.9 ELECTROKINETIC METHOD FOR OIL SLUDGE SEPARATION

Electrokinetic (EK) is the application of an electric field between two charged phases to separate components in a mixture. It involves a group of physicochemical phenomena such as the transport of charges, action of charged particles, effects of applied electric potential and fluid transport in various porous media, allowing the desired migration or flow of specific components to be achieved (Virkutyte et al., 2002). Recently, the EK phenomena have gained attention due to their:

- Remediation capability of a wide range of toxic pollutants such as heavy metals, radionuclides, and organic compounds.
- Capability for the removal or transfer of contaminants (organics or inorganics) from soil that have low permeability such as clays and silts, alluvial deposits, as well as from various types of sludge.
- Low capital costs (site preparation, installation) and operation costs (power consumption, chemicals use) compared to other methods.

The EK phenomena include electromigration, electroosmosis and electrophoresis, which are all closely related to the transport and migration of different ionic species and chemicals in porous media. Fig. 2.6 visualizes the major phenomena in the electrokinetic transport.

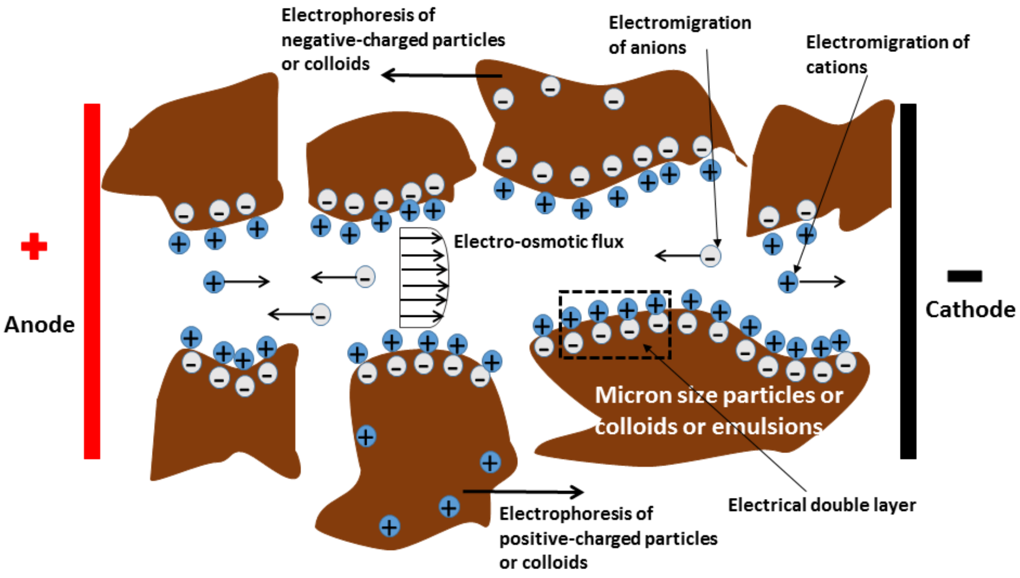


Fig. 2.6. Transport phenomena involve in the electrokinetic separation of oily sludge (adapted from Reddy and Cameselle (2009b)).

There are other reactions that happen during of electric field application on different kinds of samples. They might also include Joule heating, electrochemically enhanced reactions, dipolar coalescence and sedimentation potential (Hill, 2014). Understanding the fundamentals of these phenomena can help to design and implement a functional electrokinetic system for the separation of oily sludge. Two key reactions that affect all EK phenomena are:

a) Decomposition of water in the slurry or sludge, which eventually has enormous implications in the transfer, transport and transformation of oily sludge components.

b) Electrolysis which produces oxygen, and hydrogen ions (H^+) due to oxidation reactions at the anode, leading to a decrease in the pH. Hydrogen gas and hydroxyl (OH^-) ions are also generated at the cathode, thereby increasing the pH. These reactions are described below (Reddy & Cameselle, 2009b):

At anode (oxidation):

$$2H_2O \rightarrow O_{2(gas)} + 4H^+_{(aq)} + 4e^- \qquad E° = 1.299 \qquad \text{(Eq. 2.1)}$$

At cathode (reduction):

$$4H_2O + 4e^- \rightarrow 2H_{2(gas)} + 4OH^-_{(aq)} \quad E° = -0.828\,V \qquad \text{(Eq. 2.2)}$$

$E°$ is the standard electrode potential at a temperature of 298 K.

2.9.1 Main electrokinetic transport phenomena

2.9.1.1 Electromigration

Electromigration or ionic migration is defined as the transportation of ions in solution towards electrodes bearing opposite charges (Elektorowicz & Habibi, 2005). Cations move toward cathode (negative electrode) and anions move toward anode (positive electrode). The migration of ionic metals, polar organic molecules, ionic micelles, and H^+ and OH^- ions generated by electrolysis reactions, are termed as electromigration. Electromigration is closely related to conductivity, porosity, pH gradient, electric potential and the presence of specific ions. Reddy and Cameselle (2009a) provide a comprehensive overview on the relations between these parameters in electromigration.

2.9.1.2 Electroosmosis

Electroosmosis is the motion of liquid induced by an applied electric field across porous materials or any other fluid channel (Reddy & Cameselle, 2009a). It is similar to the advective flow that occurs due to hydraulic gradient that is defined by Darcy’s law. Basically, it is a complex transport mechanism, which is driven by the electric characteristics of a solid surface and liquid, and the interaction between the solid surface and the components in the liquid phase (Reddy & Cameselle, 2009b). Electroosmosis can transport both organic and inorganic contaminants in dissolved, suspended and emulsified forms. Studies have shown that it is the most dominant transport process for organic compounds such as benzene, toluene, xylene and phenolic compounds following the application of electric current (Masliyah & Bhattacharjee, 2006).

The Helmholtz-Smoluchowski theory (H-S theory, 1914) was formulated to describe the flow velocity (veo, cm/s) of particles during and is directly proportional to the zeta potential (ζ, unit cm/ V.s Volt), applied voltage gradient (Ez,, V/s)and permeability (ε, Fa/cm) of the fluid, and inversely proportional to the fluid viscosity (η, Pa/s) (Reddy & Cameselle, 2009a):

$$Veo = -\frac{\varepsilon\zeta}{\eta}E \quad (2.3)$$

Electroosmosis gives rise to Helmholtz double layers which as a cation selective membrane in narrow pore throats of clay minerals (Fig. 2.6 a) (Hill, 2014). The formation of this electrochemical membrane has been exploited to dewater clays and increase the permeability of oily sludge to improve the oil and water separation. Chilingar and Haroun (2014) and Chilingar et al. (1997) have shown that electroosmosis can increase the volumetric flow of components by forty folds in core containing clay and by two to three folds in silica cores. This is interesting because oily sludge has been shown to consist of a mixture of clay and silica (Menon & Wasan, 1988).

Helmholtz double layers can combine together and completely fill the pore throat, thereby hindering the passage of water. Even when the pore throat is not completely occupied by the double layers, the capillary force can prevent non-wetting fluids (hydrocarbons, W/O) from passing the throats (Fig. 2.7b). By decreasing the pH and zeta potential (ζ), the effect of electroosmosis on separation of oily sludge components, can drop considerably (Pamukcu, 2009). In the presence of ionic species, the mass transport by electromigration can be 10 to 300 times greater than electroosmotic advection (Masliyah & Bhattacharjee, 2006).

2.9.1.3 Electrophoresis

Electrophoresis is the transport of bound contaminants and colloidal-sized charged particles as a result of a low direct current or voltage gradient. In soil, mass transport by electrophoresis is negligible compared to electromigration and electroosmosis (Wittle et al., 2011). However, it may become significant in solid particle suspension systems, micelles and colloids (Pamukcu, 2009). Oily sludge consists of 10 to 30% solids that the effect of electrophoresis would be significant in the separation process.

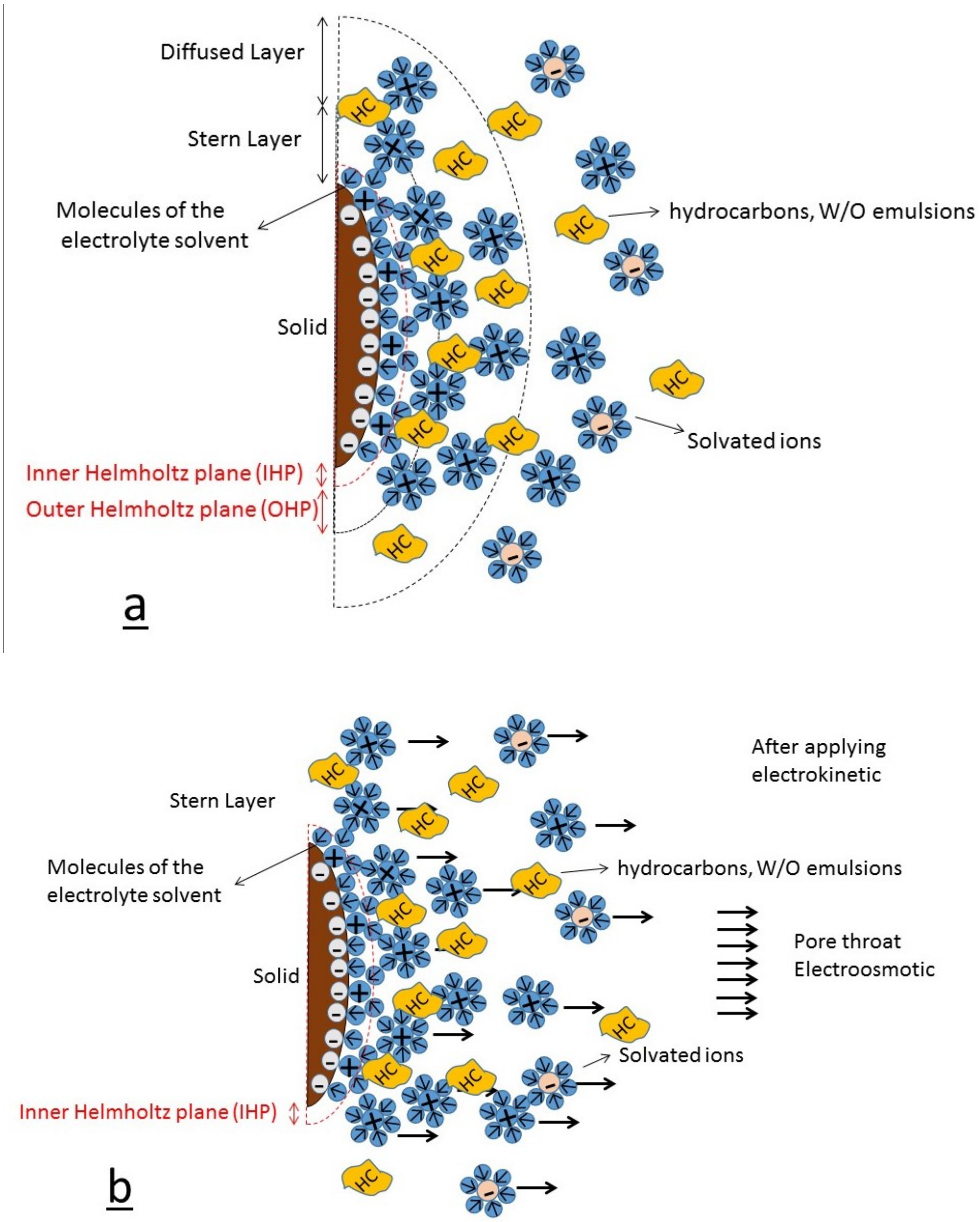


Fig. 2.7. (a) Double layer formation during electroosmosis in clay and restriction of Darcy flow through the center of the pore throat. (b) Electrokinetic transport of the outer Helmholtz layer, modifying the effective pore throat size for fluid flow (adapted from Hill (2014); Miettinen et al. (2010)).

2.9.2 Auxiliary electrokinetic phenomena

2.9.2.1 Electrochemically Enhanced Reactions

The application of an electrical current changes in the potential/pH (Eh/pH) of the system (Hill, 2014). These changes enhance reactions between the pore fluid and matrix materials. Electrochemical enhanced reactions support the breakdown of complex hydrocarbons to simple hydrocarbons. The simpler hydrocarbons have lower viscosities and higher energy compared to the original complex thereby favoring electroosmosis. This mechanism can occur at very low voltage gradients (Hill et al., 2008). These reactions can convey water solubility by increase the polar groups function (like OH) and increase the electroosmosis transportation.

2.9.2.2 Joule Heating

The passage of an electrical current through an oily sludge matrix can lead to localized heating known as Joule heating. Joule heating can effectively increase the temperature of the matrix and fluids and decrease the viscosity of the oil easing the separation process (Hill, 2014).

2.9.2.3 Dipolar attraction

Application of electrical current can polarize the sample matrix. Polarization involves rotation of negative or positive side of charged molecules towards the electrical current. This phenomenon could be more significant in samples having more water emulsions (Hill, 2014). An increase in emulsion intensity decreases the distance between the molecules and increases the chance of coalescence. Polarization is similar to the dielectrophoresis (DEP) phenomena in which the particles do not need to have electrical charges. DEP has been used to separate, sort and transport different types of particles in soil (AES, 2015).

2.10 ELECTROKINETICS AS A TREATMENT TECHNOLOGY FOR OILY SLUDGE

The electrokinetic process uses a low intensity direct current across two electrodes located at each side of the oily sludge medium, causing the electroosmosis of liquid phase, migration of ions and electrophoresis of charged particles in a colloidal system to the respective electrode (Elektorowicz (Elektorowicz et al., 2006; Elektorowicz & Oleszkiewicz, 2009; Kuo et al., 2011). The separation of water, oil and solid components from the oily sludge results from three main electrokinetic-driven mechanisms. Firstly, colloidal aggregates in the oily sludge are broken down under the influence of the electrical field, leading to the movement of colloidal particles of oily sludge and solid phase towards the anode area as a result of electrophoresis, and the movement of the separated liquids (water, oil, remaining emulsion) towards the cathode area as a result of electroosmosis. Secondly, electrocoagulation of the separated solid phase could occur near the anode area, leading to increase solid phase of droplets, thus forming two separated phases of water and oil (Hu et al. 2010). Finally, the separated liquid phase (water and oil, without colloid particles and fine solids) may result in an unstable secondary oil-in-water emulsion which could be gradually electro-coalesced near the cathode area through charging and agglomeration.

Various studies have been conducted on electrokinetic processes to treat oily sludge from refineries. Elektorowicz et al. (2006) studied the effect of different DC voltages on the demulsification of W/O in oily sludge. Using a gradient of 0.5 V/cm, they could achieve 63% removal of the water content and 43% of light oil. Yang et al. (2005b) studied the effect of EK on the separation of oil and water from oily sludge originating from pet food industry. The experiments were conducted in one-liter batch reactors using DC electric fields with different horizontal and vertical electrode positions. The results showed that the solid content of the oily sludge sample increased from 5 to 14%, and the water content removal was more than 40%. Further experiments conducted in 4 L reactors showed an increase in water content removal up to 68%.

The complexity of oily sludge is intimately related to the adsorption of fine particles on the polar active surfaces such as asphaltenes leading to a decrease in the wettability of solids and increase in the stability of W/O (Fig. 2.4). This renders the separation very challenging considering that 106 times more energy is required to separate solid particles from oil-water interfaces as compared to the thermal energy of particles due to Brownian motion. The situation is further compounded by the presence of electric double layer, Van der Waals attractions and capillary interactions (Mahmoud et al., 2010) (Fig. 2.6). Electrokinetic methods have been shown to be able to overcome these molecular constraints to effectively separate the different phases in oily sludge (Habibi, 2004). Besides its capability to separate the different phases in oily sludge, studies have also shown its effectiveness in segregating heavy metals from oily sludge through the application of direct current (DC) supply (Badawieh, 2005). Mass transport effect by ionic migration has always been shown to be higher than the mass transport by electroosmotic advection in low activity soils like silt and clays (Pamukcu, 2009).

Attempts have been made to enhance electrokinetic separation of oily sludge by using surfactants. The use of nonionic surfactant, alkyl polyglucosides (APG), and an anionic surfactant, Calfax 16L-35, were used to investigate their effect on the electrokinetic separation of PAHs (more specifically phenanthrene) from kaolinite soil (Yang et al. 2005). The nonionic surfactant was shown to exhibit better phenanthrene removal efficiency as compared to the anionic surfactant. However, an increase in the amount of surfactant results in a decrease in electroosmotic flow, which decreases the W/O emulsion separation efficiency (Yang et al., 2005a).

EK has also been used to enhance oil extraction from different oil reservoirs. Ansari et al. (2015) studied the effect of EK with low concentration of acid injection at the anode on carbonate oil reservoirs. This process increased the oil recovery by 17-28% compared to high concentration of acid extraction method. The acid addition increases the permeability of the oily sludge, facilitating the EK process, which increases fluid velocity and decreases the viscosity of the oily matrix by decreasing the interfacial tension (surface tension) of emulsions (Ansari et al., 2015b; Ansari et al., 2015c). The overall outcome has enhanced the separation of different phases by an electrokinetic system.

2.10.1 Benefits and limitations of electrokinetic process

Electrokinetic processes constitute several advantages. They are fast and efficient compared to other methods and do not require chemical or additional water (Elektorowicz et al., 2006). They can also remove heavy metals from complex oily sludge matrices (Badawieh, 2005; Pamukcu & Wittle, 1992). In addition, they can be applied to sludge with a low permeability and different compositions, and they do not emit hazardous gaseous components (Hill et al., 2008). Studies have also shown that electrokinetic is capable of inactivating microbial pathogens in the sludge (Esmaeily, 2002).

However, electrokinetic system showed different capabilities but still many electrokinetic studies have been conducted at laboratory or pilot-scale level. Some of electrokinetic methods have been applied at the field scale. Until now, the most applications of electrokinetics are in soil remediation.

Electrokinetic methods have already been used by different governmental agencies such as US Environmental Protection Agency (USEPA), US-Army Environmental Centre, as well as by companies such as Lambda Consult, Electropetroleum Inc., Hak Milieutechniek Company, etc (Cameselle et al., 2013; Lageman & Pool, 2009). Recently this technique has been applied in some Korean and Japanese companies (Chung & Lee, 2009). The cost could range from \$86/m^3 to \$774/m^3 (when surfactants and cosolvents are also used) for nonaqueous phase liquid (NAPL) remediation (Lowe et al., 1999). An average cost for both organic and inorganic electrokinetic remediation is about 200 \$/m^3, but it is site specific, thus, it can vary from less than 100 to more than 400 \$/m^3 (Cameselle et al., 2013). The cost of electrokinetic remediation stayed rather at a low level, while, such treatments as bioremediation, vapor extraction, air sparging, and pump and treat, have been found rather ineffective when applied to low permeability soils in many contaminated sites (Ho et al., 1999).

Electrokinetic techniques showed their capability on enhanced oil recovery too. Possible reasons of delay in application, as suggested by Shang and Lo (1997), which may be due to high power consumption, improperly designed operating systems, corrosion of anodes and difficulties in collecting water drained to the cathode. But above all, there is a limited understanding of the electrokinetic process itself. This is why electrokinetic treatment of sludge is still considered as an "emerging technology" despite it has been used conceptualized sometimes ago (Guo, 2012). To date, due to the paucity of combined knowledge on electromigration, electroosmosis, electrophoresis, and colloid engineering, it is difficult to establish an optimized system for the large-scale application of electrokinetic processes in the treatment of oily sludge.

This project aims at filling existing gaps regarding the electrokinetic technology and providing both theoretical formulations backed by experimental verification of developed hypotheses in order to show the promise of this technique. Oily sludge tends to sequester large quantities of organic and inorganic contaminants, which are often resistant to remediation with traditional technologies due to low hydraulic conductivities. Electrokinetic techniques can overcome this constraint and provide sustainable solutions to oily sludge treatment and oil recovery from refineries. According to Hu et al. (2010), it can even be expected that using oily sludge storage pools as electrokinetic cells in situ or at the field scale could considerably reduce treatment cost of oily sludge from refineries.

2.11 NANO-REMEDIATION STRATEGIES FOR OILY SLUDGE TREATMENT

Nanotechnologies have recently emerged as a key component contributing to technological advances in the petroleum and energy industries. They have brought revolutionary changes in the exploration, drilling, production, enhanced oil recovery, refining, and distribution of oil (Kong & Ohadi, 2010). Due to their large specific surface area, they increase a capability of the environmental remediation (Karn et al., 2009). The main goal of this section is to highlight common studies investigating the effect of nanoparticles on oil contaminants treatment, particularly, on the recovery of PAHs that could be attributed to refinery wastes. Ehtesabi et al. (2013) investigated the effect of different TiO_2 nanofluids to improve the recovery of heavy oil from sandstone cores. They found that a solution of 0.01% anatase with amorphous TiO_2 improved the recovery of heavy oil from 49% to 80%. The presence of hydroxyl groups observed at the surface of TiO_2 nanoparticles, induced partial wettability at the interface of solid-water-oil.

Nanocatalysts have also been applied in the oil industry, especially for upgrading and the recovery enhancement of heavy feedstocks. Recent studies showed the ability of nanocatalyst to enhance transport of components across porous packed beds (Ehtesabi et al., 2013; Onyekonwu & Ogolo, 2010). Nanoparticle micro-emulsions with formulations of Fe, Pt, Ni, Au, Zr, Cd, Pd, Ag and Cu have been tested for their ability to affect sludge matrices (Hashemi et al., 2014). ZrO_2 showed strong alteration the wettability from oil-wet to water-wet surface (Karimi et al., 2012). Similar observation was made in another study, where alumina-based nanofluids was found to change the wettability of sandstone from oil-wet to water-wet (Giraldo et al., 2013). Nanofluids are a relatively new class of fluids comprising of a base fluid with suspended nano-sized particles (1–100 nm). These particles, generally a metal or metal oxides, increase conduction and convection coefficients, allowing for more heat transfer out of the coolant (Saidur et al., 2011).

Usually surfactants destabilize emulsions by decreasing the interfacial tension at the water-oil interface. Metal nano-powders can also show demulsification effects (Fedushchak et al., 2014). Some nano-powders such as AlN (Aluminum nitride) and AlOOH (Boehmite) are highly effective nonionic demulsifiers. Different physical synthesis methods (e.g. by gas-phase synthesis, electric explosion of conductor and electric impulse) can produce different nanopowders. It has been shown that coalescence induced by AlN nanoparticles results from the formation of “hydrophilic bridges" between protective emulsion layers. Following coalescence, the phases separate into water and oil (Fedushchak et al., 2014).

Besides nanocatalysts, silicon nanoparticles have also attracted a lot of attentions in enhanced oil recovery due to their low cost and environmental friendly nature (Safari & Jamialahmadi, 2013). Onyekonwu et al. (2010) studied three different polysilicon nanoparticles (PSNP): lipophobic and hydrophilic nanoparticles (LHPN), hydrophobic and lipophilic nanoparticles (HLPN) and neutrally wet (NWPN). The results showed that the rock wettability and interfacial tension were improved by NWPN and HLPN (Onyekonwu & Ogolo, 2010). Safari et al. (2013) studied different concentrations of HLPN that change the wettability from oil-wet to neutral-wet (90° contact angle), weakly water-wet and water-wet. The best oil recovery resulted from the neutral-wet and weakly water wet wettability (Safari & Jamialahmadi, 2013).

Nanotechnology can contribute to less expensive, and more efficient and environmentally friendly method compared to the application of polymers and surfactants (Ehtesabi et al., 2013). So far, their application in conjunction with electrokinetic treatment of oily sludge from refineries has not been explored. Considering that nanoparticles can alter the wettability of surfaces, reduce interfacial tension and enhance mobility of sludge components, these beneficial attributes may be combined with electrokinetics to achieve better separation of oily sludge and recovery of resources. These will be addressed during this study where the effect of nanoparticles on electrokinetic systems for oily sludge treatment, will be investigated.

Research methodology

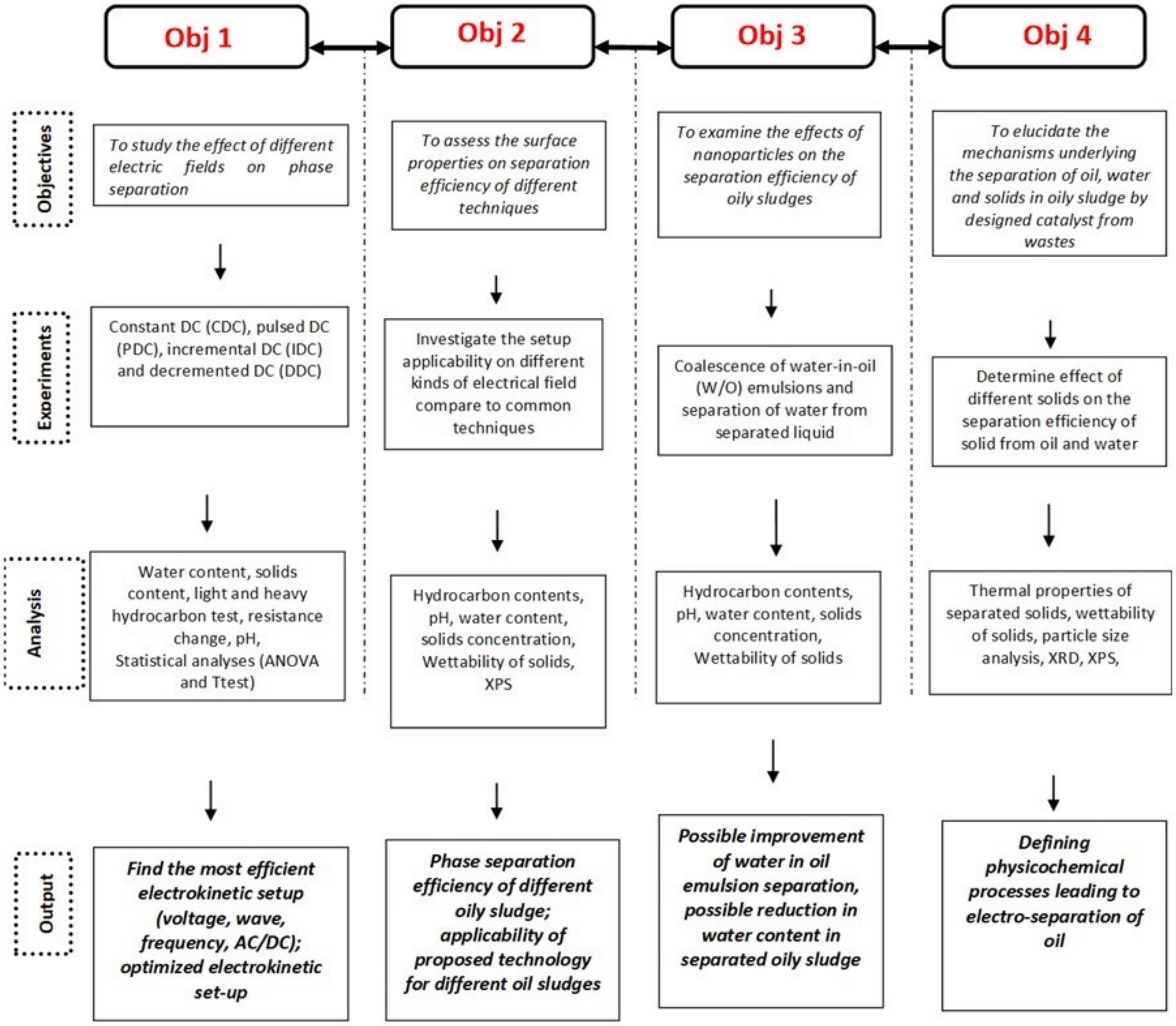
3.1 OVERVIEW

To achieve the aforementioned specific objectives, the research was unfolded over four distinct phases (Fig. 3.1). In the first phase, bench-scale reactors were operated in view of determining the effect of different electric field applications in oily sludge separation. Based on the data gathered, the reactor system was redesigned in next phase of the project by adjusting key operational parameters and the separation efficiency tested using different categories of sludge retrieved and sampled from a full-scale refinery. The efficiency of the separation was assessed by monitoring different factors such as the dewaterability and characteristics of the sludge. In the third phase, the addition of nanoparticles to improve phase separation of the oily sludge has been studied. Finally, potential mechanisms driving the phase separation of oil, water and solids in oily sludge by synthesized catalyst were explored.

3.2 OBJECTIVE 1: STUDY THE EFFECT OF DIFFERENT ELECTRIC FIELDS ON PHASE SEPARATION

3.2.1 Overview

The first objective of this study was to investigate the effect of different regimes of electric field on the electrokinetic-induced separation of oily sludge/sediments. A benchtop EK-reactor was operated using lagoon sludge collected from the Suncor full-scale refinery located in Montreal, Canada. The Suncor refinery produces four different types of sludge during its refinery process namely, slurry and catalytic fines (heavy fuels oil tank), lagoon sediments, sludge American Petroleum Institute (API) and Dissolved Air Flotation (DAF) separator units, and separator bottom sludge. However, for this initial study, the effect of different electric field types was investigated for the phase separation of lagoon sediments only due to their difficulty encountered during the centrifugation destabilizing the W/O emulsions.



	Obj 1	Obj 2	Obj 3	Obj 4
Objectives	*To study the effect of different electric fields on phase separation*	*To assess the surface properties on separation efficiency of different techniques*	*To examine the effects of nanoparticles on the separation efficiency of oily sludges*	*To elucidate the mechanisms underlying the separation of oil, water and solids in oily sludge by designed catalyst from wastes*
Experiments	Constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC)	Investigate the setup applicability on different kinds of electrical field compare to common techniques	Coalescence of water-in-oil (W/O) emulsions and separation of water from separated liquid	Determine effect of different solids on the separation efficiency of solid from oil and water
Analysis	Water content, solids content, light and heavy hydrocarbon test, resistance change, pH, Statistical analyses (ANOVA and Ttest)	Hydrocarbon contents, pH, water content, solids concentration, Wettability of solids, XPS	Hydrocarbon contents, pH, water content, solids concentration, Wettability of solids	Thermal properties of separated solids, wettability of solids, particle size analysis, XRD, XPS,
Output	***Find the most efficient electrokinetic setup (voltage, wave, frequency, AC/DC); optimized electrokinetic set-up***	***Phase separation efficiency of different oily sludge; applicability of proposed technology for different oil sludges***	***Possible improvement of water in oil emulsion separation, possible reduction in water content in separated oily sludge***	***Defining physicochemical processes leading to electro-separation of oil***

Fig. 3.1. Flowchart representing milestones of research methodology

3.2.2 Design of reactor system

Five (5) 1.5 L capacity bench-scale reactors, made up of polyethylene material with the dimensions of 14 cm length, 9 cm width, and 14 cm height, was designed for the electrokinetic experiments (Fig. 3.2a). The polyethylene wall of the reactors was inert and non-reactive to oil and grease, and not conductive of electric current. Two electrodes made of stainless steel with dimensions of 15 cm height, 7.5 cm width, and 1 mm thickness was placed at the two extremities of the reactor chamber. The weight of the electrodes was measured before and after each electric field application in order to check for a possible electrode dissolution. A total of 15 probes (electrical jumpers) was placed in 5 rows to monitor the electric potential across the reactor. Each row was comprised of 3 probes dipped at three different depths: 1, 4 and 7 cm (Fig. 3.2b). The distance between these probes was spaced at 2 cm apart to provide a strategic spatial arrangement for tracking the voltage change across the reactor using the digital multimeter (Mastech-MAS830). A sideline reactor, having the same dimensions without the application of electric fields, was used as a control. The control reactor determined and tracked down factors which may be changed in the system such as sedimentation, evaporation or any other phenomenon. The ambient temperature was kept at 21 °C ±1 °C.

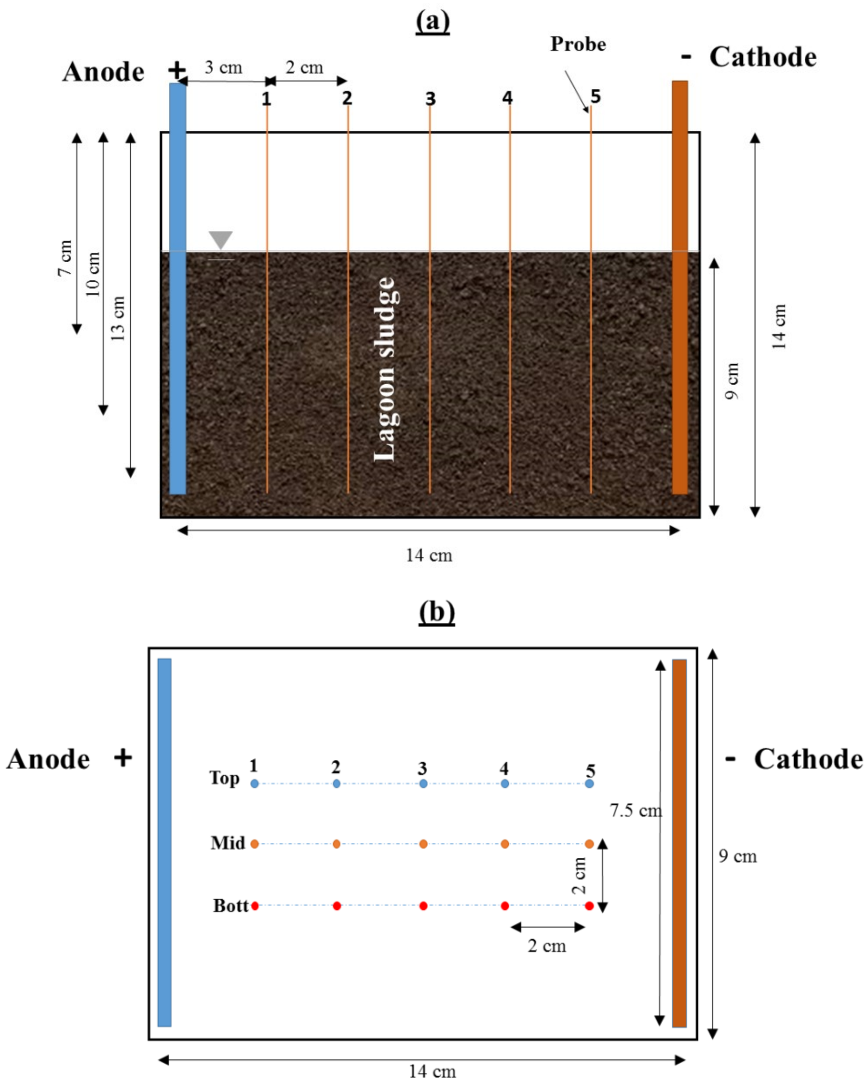


Fig. 3.2. Electrokinetic reactor for Phase1: a; cross section b; top view of the reactor set-up.

The electric current across the electrodes was supplied by a switching mode DC power supply (BK Precision 1902, USA) which converts AC to DC supply. This unit enabled the supply of constant current (CDC). Incremental or decremented DC applied by changing daily the amount voltage (Fig. 3.3 a). In order to create pulsed DC (PDC), a function generator (BK Precision 4001A, USA) was used to produce the DC offset. The power of function generator was increased by an amplifier (model 7224 AE Techron, USA). The amplifier was connected to a 30 Hz Dual Trace Analog Oscilloscope (BK Precision 2120B, USA) to track the electrical function. The Digital Multimeter (Mastech MAS830, USA) was connected to the probes strategically positioned in the EK reactor and was used to monitor and measure the voltage supplied by the different electrical regimes across the electrodes. The overall set-up of the EK reactor system with its different electrical accessories is shown in Fig. 3.3 (a) and (b). Fig. 3.4 (a) and (b) indicates the main components of the EK system.

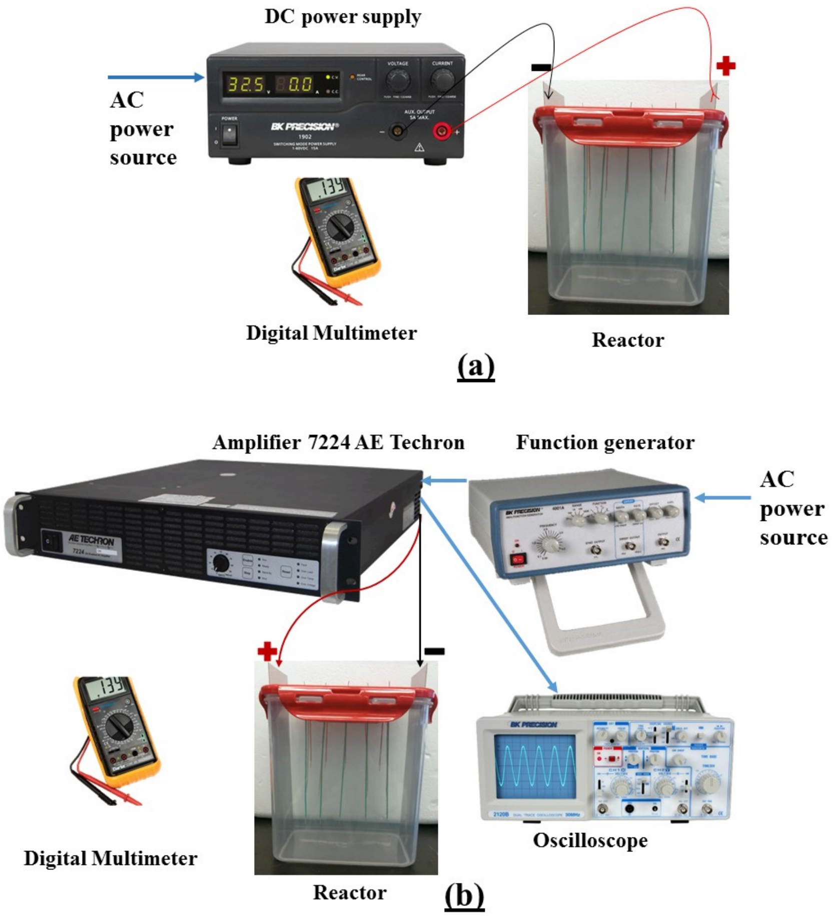


Fig. 3.3. Equipment used in Phase 1: (a) Overall system set-up for EK reactor with electrical accessories to generate CDC, IDC and DDC, (b) Simplified illustration showing main components of EK-reactor system for PDC.

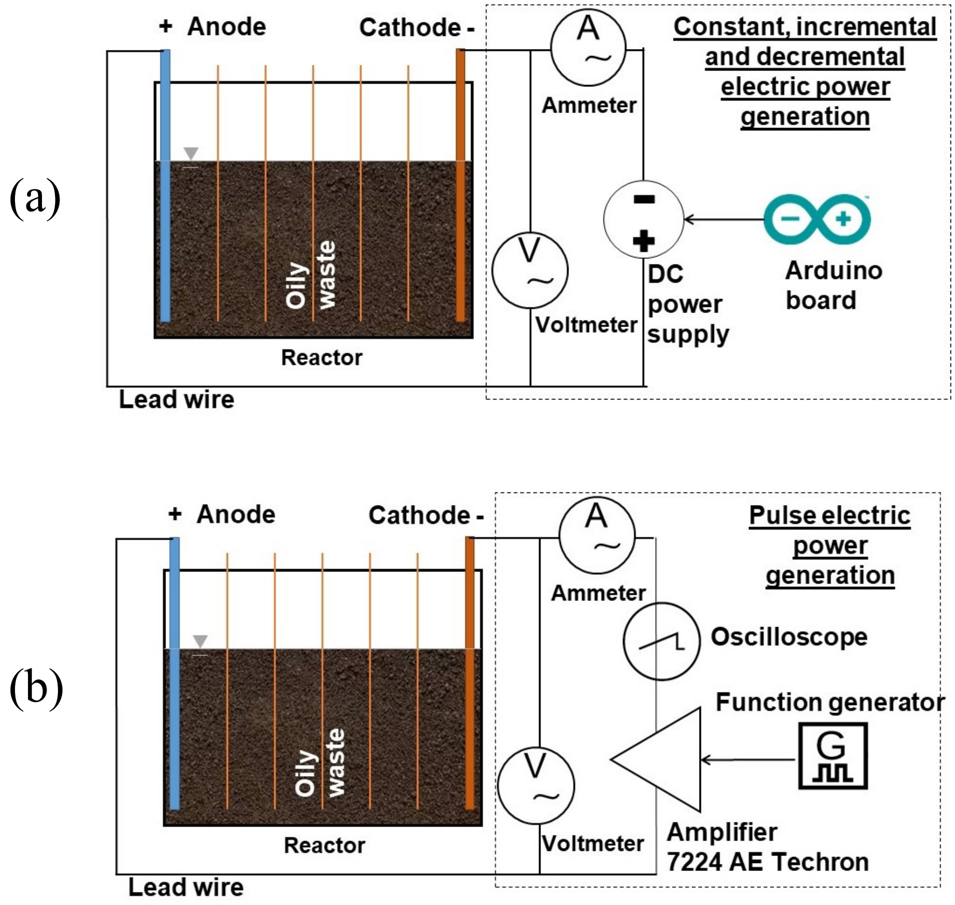


Fig. 3.4. (a) System set-up for electrokinetic reactor with constant direct current (CDC), incremental direct current (IDC) and decremental direct current (DDC) (b) Main components of electrokinetic-reactor system with pulsed direct current (PDC).

3.2.3 Application of different electric field regimes

Electric current was supplied to each reactor cell by means of a DC power supply (BK Precision 1902, USA), and the voltage distribution between the anode and cathode was monitored by direct measurements of the potential between electrodes and each probe electrode. The DC power unit supplied a constant direct current (CDC). A potential gradient of 1 V/cm CDC was applied across the electrodes since this voltage gradient has been shown to be suitable for low conductive sediments (Elektorowicz et al., 2006) and during remediation of contaminated soil (Reddy & Cameselle, 2009a). Previous studies have shown that the application of electrokinetic treatment over a prolonged time results in better separation (Elektorowicz et al., 2006). The optimal runs in the current study showed that about 95% of phase change occurred within the first four days. Incremental direct current (IDC) and decremented direct current (DDC) were applied by programming the voltage with an Arduino board. For both, IDC and DDC, a potential gradient ranging from 0.25 to 1.75 V/cm was applied (Fig. 3.5a). The overall set-up of the reactor system for generating the CDC, IDC, and DDC are shown in Fig. 3.2a and 3.3a.

Pulsed direct current (PDC) was generated using a function generator (BK Precision 4001A, USA) to produce a DC offset. The power of the current was increased by an amplifier (model 7224 AE Techron, USA), which was connected to a 30 Hz Dual Trace Analog Oscilloscope (BK Precision 2120B, USA) to track the electrical function. To generate the PDC, 0.5 V/cm of DC was used in combination with 0.5 V/cm of DC pulse at squared frequencies of 60 Hz with a 1/5 pulse period (Fig. 3.5b). The set-up used for generating the PDC is shown in Fig. 3.2b and 3.3b.

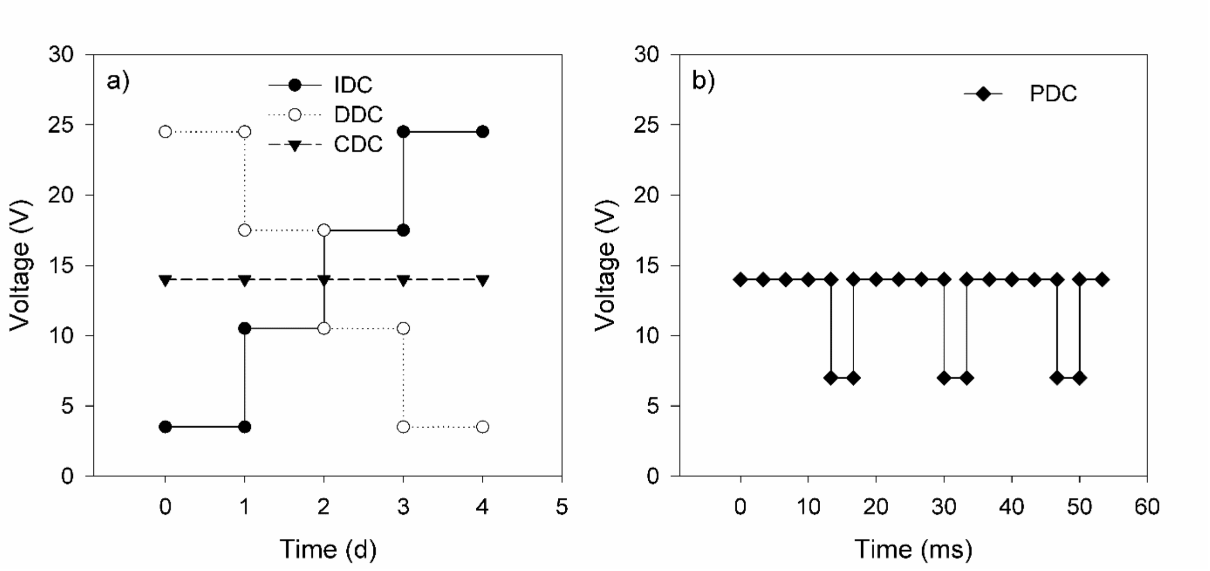


Fig. 3.5. (a) CDC, DDC and CDC, and (b) PDC electrical regimes applied for electrokinetic separation of solid, oil and water in oily sediments.

During initial experiments, the reasonable time period for applying the electric field across the sludge in the EK- reactor was determined over 20 days to evaluate the change of the voltage of the 15 probes placed in the reactor. Based on the findings, electric field application over a period of 4 days was found to correspond to a fast phase separation of the oily sludge while a period of 10 days corresponded to a slow phase separation of the oily sludge components. In subsequence, 4-

day period will be used to evaluate the changes in the voltage, current, and resistance across the oily sludge.

3.2.4 Characterization of EK-treated oily sludge

3.2.4.1 Determination of water content

The oily wastes were centrifuged and resulted in stable water-in-oil emulsions. According to Mao et al. (2016) there are three types of water droplets; (I) emulsified water, (II) dispersed water and (III) free water, where the range of the droplet diameter's are less than 10 µm, 10-60 µm and more that 60 µm, respectively. Around 56% of water content is emulsified and around 44% are dispersed water. Thus, measurement of water content plays an important role to separate all of these small droplets. The water content of the oily sludge before and after the EK treatment was determined in this study based on the standard methods for water in petroleum products and bituminous materials by distillation (ASTM.D95, 2002). This method has been widely used for determining the water content of petroleum products, tar and other bituminous materials in other studies (Teas et al., 2001; Wang et al., 2007). The distillation set-up is shown in Fig. 3.6. The apparatus comprises of a glass still connected to a heater, a reflux condenser, a receiver and a graduated glass trap. The connections between the glass container, trap and receiver are leak-proofed by the use of vaseline. Toluene (Certified ACS, Fisher, 99.5%) was used as a solvent to recover trapped water from the samples. The procedure consisted of the following steps: i) 50 mL of toluene was added to 25 g of oil wastes in the glass still and was well mixed; ii) the mixture was boiled at the azeotropic boiling point and; iii) the volume of distilled water was collected in the graduated glass trap and measured using a graduated cylinder. This represented the amount of water in the oily wastes sample. The water content determination was performed in duplicate for each sample. The amount of distilled water collected in the graduated glass trap represents the amount of water present in the oily sludge sample and is determined based on equation 3.1. The solids content of the oily sludge will then be determined by a gravimetric method based on weight difference before and after the distillation process.

$$\%\, Water\ content\ = \frac{(Volume\ in\ watertrap, ml) - (water\ in\ solvent\ blank, ml)}{Volume\ in\ test\ sample, ml} \times 100$$

(Eq. 3.1)

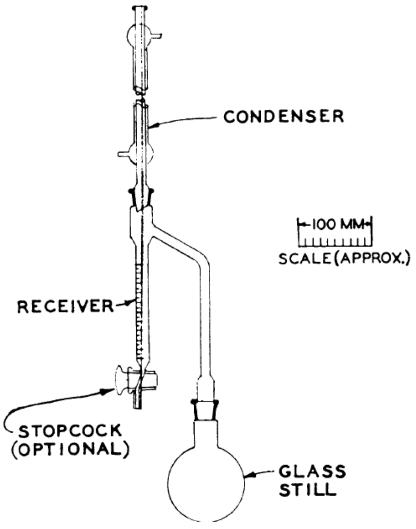


Fig. 3.6: Distillation set-up for the determination of water content in oily sludge (ASTM.D95, 2002)

3.2.4.2 Light hydrocarbon (LH) content

Light hydrocarbons (LHs) are low molecular weight hydrocarbons having boiling points lower than 105 °C (Elektorowicz et al., 2006; Habibi, 2004). The concentration of light hydrocarbons in the oil wastes before and after electrokinetic treatment was determined based on the method of Taiwo and Otolorin (2009). A quantity of the waste sample was weighed in a crucible on an analytical balance (Fisher Scientific ACCU, USA). The sample was then heated in a ventilated oven (Lindberg Blue M, GO1330A, USA) at 105°C for 24 hours, and allowed to cool in a desiccator. The final weight of the sample was measured and used to determine the percentage of light hydrocarbons by Eq.3.2. The procedure was performed in triplicate for each sample.

$$\%\,LH = \frac{Change\ in\ weight}{Weight\ of\ tested\ sample} \times 100 - (\ \%\,water\ content) \qquad \text{(Eq. 3.2)}$$

3.2.4.3 Solids content

The solids content of the oil wastes before and after electrokinetic treatment was determined using Standards Methods (Rice et al., 2012). A portion of the waste sample was weighed in a crucible on an analytical balance and dried at 105 °C in an oven overnight. The crucible was transferred to a muffle furnace (Isotemp, Fisher Scientific, Canada) heated at 550 °C for 3 hours. After cooling to room temperature in a desiccator, the weight of the dried waste sample was measured. The percentage of solids in the sample was calculated by considering the difference in weight of the sample before and after heating as shown in Eq. 3.3.

$$\%\, Solid\ content = \frac{Residue\ remaining\ after\ 550\ \text{°C, g}}{Weight\ of\ tested\ sample, g} \times 100 \qquad \text{(Eq. 3.3)}$$

3.2.4.4 Non-volatile hydrocarbon (NVH) content

The residual hydrocarbons left in the oily sludge sample after drying it at 105 °C for overnight are referred as the non-volatile hydrocarbon content of the sludge. The percentage of NVH was calculated by considering the water, LH and solid contents of the sludge sample using Eq. 3.4.

$$\%\, NVH, \%\, w = 100 - (\%\, light\ hydrocarbon + \%\, solid + \%\, water\ content) \qquad \text{(Eq. 3.4)}$$

3.2.4.5 Organic composition

The organic composition of the oily sludge was determined by sequential solvent extraction using toluene and tetrahydrofuran (THF). This method has been implemented by several authors to extract organic constituents from oily sludge and has yielded good extraction efficiency (Wang et al., 2010). Toluene is used as solvent in the first extraction and THF, which is more polar in nature, is used to recover the rest of organic compounds from the mixture during the second extraction About 25 mg of oily sludge was taken, and the extraction was conducted in a Whatman cellulose extraction thimbles (33X80MM, Fisher Scientific). For the first extraction, 100 mL of toluene was used to reflux the mixture for about 15 h in a Dean-Stark apparatus until (Fisher Scientific) it became colorless. The toluene and aqueous phase were separated from the extractant by using rotary evaporator (Laborota 4000, Heidolph), and the amount of organic compound in the toluene phase was determined (toluene soluble, TS). The extracted sample was placed in the rotary evaporator for 5 minutes in 50 °C at 100 rpm. Then the remaining amount was measured by subtracting the weight of the dish. In the second extraction, the same thimble containing the sample was extracted with 100 mL of THF. The THF-induced reflux extraction was carried out over a period of 15 h. The organic constituents referred to as THS soluble was determined by the weight of the sample that has been left after evaporation. For THF solvent extraction from solution, rotary evaporate set at 35 °C at 100 rpm for 15 minutes. The summation of TS and THS results in the TPH (total petroleum hydrocarbon) of oily sludge.

3.2.4.6 Wetting properties of solids

Oily sludge solids are rich in organics as of oil attachment to the surface of the solid particles. Depending on the solids and organic content of the solid aggregates the particles can be classified as completely hydrophobic (Hydrophobic Aggregate, HAGG) or biwettable (Biwettable Aggregate, BAGG). However, it is not uncommon to have some hydrophobic materials in variable degree in BAGG. In addition, ultra-fine clays (UFCs) may also be present and are the main contributor in intractable solids for stable emulsions of the oily sludge.

Previous studies have assessed the wettability of fine tailings of oil sand by mixing a certain amount of solids with two immiscible liquid phases (Sparks et al., 2003). Toluene has mainly been used as the organic solvent and an aqueous solution of 0.01 M NaCl as the water phase. In this study, the same methodology was applied to determine the wettability of oily sludge but with some modifications. A mixture of 2 mL toluene and 8 mL of water solution was added to 200 mg of dried solids and vortexed for 2 minutes to have a homogenous mixture and put overnight in the fumehood. The wettability of the solids was determined as the percentage of solids present in the aqueous phase by weighting the aqueous phase solids (Binks & Lumsdon, 2000; Somasundaran & Zhang, 2006). In addition, the change of solids wettability over a short period (30 min) and a long period (3 days) of time was investigated. Fig. 3.7 shows a sample that has been prepared by the described protocol for studying the wettability of the solids.

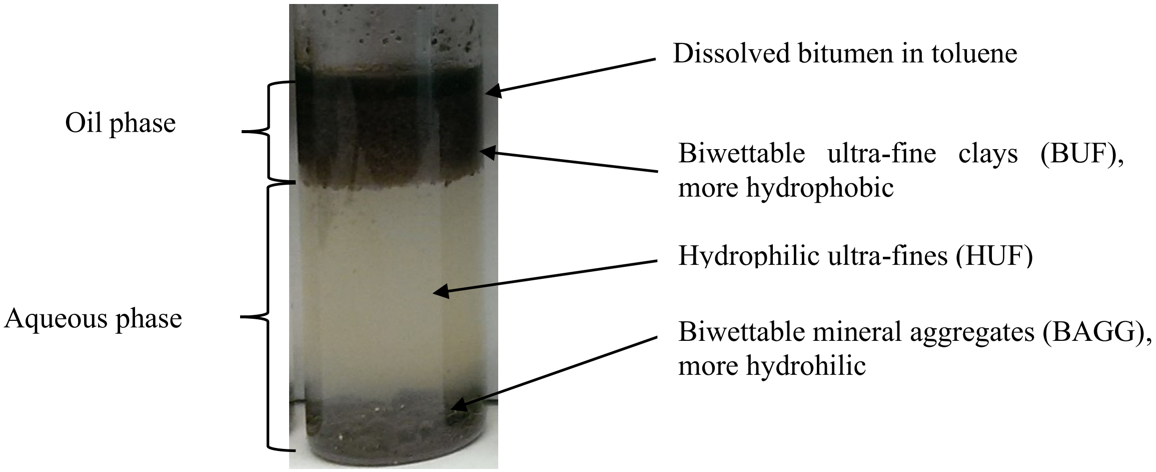


Fig. 3.7. Fractionation of oily sludge solids into organic and aqueous phases

It should be distinguished that the degree of biwettability is variable and some hydrophobic material was also present. XPS (X-ray Photoelectron Spectroscopy) analyzer can indicate the surface functionality and inorganic elements that can clear the reasons to cause the movement of organic-rich solids to the aqueous phase. The weight percentage of solids that move to the aqueous phase show the water wet ratio of the sample.

3.2.4.7 Measurement of pH

pH measurement of the oil waste samples was performed based on the method applied to soil (Science & McKeague, 1978). A solution of 0.01 M $CaCl_2$ was added to the sample in the ratio 1:2 (solution:sample) and vortexed for 2 min. The pH of the resulting mixture was measured using a pH-meter (pH 209, Hanna, Canada).

3.2.4.8 Measurement of electrical parameters

Current intensity (I), potential difference or voltage (V), resistance (R) and conductivity (σ) were continuously monitored across the electrokinetic reactors during the whole duration of the experiment. The electrical amperage was measured by a Non-Contact Multimeter (FW Bell; mA-2000, Canada), while the voltage was measured by a Digital Multimeter (Mastech MAS830, USA). The resistance between two electrodes in a particular reactor was determined based on Ohm's law using the measured voltage (V) and current (I). The conductivity of the oil wastes was measured using a conductivity meter (SensION, Hach). Fifteen probes were strategically positioned along the length of each electrokinetic reactor at different depths, a more representative measurement of the electrical parameters across the reactors was possible. The resistance is V divided by I (A).

Electrical power (P) was calculated in Watts considering an electric current I am bearing a charge of Q Coulomb passing every t seconds through an electric potential difference in Volts. Hence, the electric power was computed by multiplying voltage and amperage. Where Q is an electric charge in Coulombs, t is a time in seconds, I is a electric current in Amperes, V is electric potential or voltage in Volts.

3.2.4.9 Deviation Index (DI) analysis

The evaluation of the efficiency of the four applied electrical regimes (CDC, PDC, IDC, and DCD) with respect to the phase separation of the oil sediments was conducted based on separation criteria. These criteria were defined using the Brown-Forsythe test concept (Zar, 1999). Each value was obtained by subtracting it from the median value and considering the absolute value of the difference. A deviation index (DI) was computed, where the ratio between each two phases is considered as one criterion. The following phase separation criteria were assessed: water/solids, water/heavy hydrocarbons, water/light hydrocarbons, light hydrocarbons/heavy hydrocarbons, heavy hydrocarbons/solids, and light hydrocarbons/solids. These criteria were evaluated for six sections of each electrokinetic reactor. Each criterion was obtained by subtracting the ratio of the phases from the initial ratio of oil phases. Subsequently, the absolute values of the resultant for all six sections of the electrokinetic reactor were summed, and the weighted Deviation Index (DI) separation was computed.

3.3 OBJECTIVE 2: ASSESS THE MECHANISM BEHIND THE OIL/ WATER SEPARATION

Based on the first study, the most efficient electrical regime leading to the best phase separation of the oily sludge was generated. To find out the mechanism behind the oil/ water separation, surface analysis has been conducted. The following parameters was monitored before, during and after the EK separation process: wetting properties, water wet solids and contact angle of the sludge. In addition, besides assessing the dewaterability and its characteristics as described above, the level of carbon and oxygen has been tracked on the surface of the solids.

3.3.1 Characterization of EK-treated oily sludge

The impact of the application of four different regimes of direct current (DC) namely Constant Direct Current (CDC), Incremental Direct Current (IDC), Decremented Direct Current (DDC), and Pulsed Direct Current (PDC), was investigated on the electro-separation of oily sediments from refinery disposal wastes. Changes induced on the surface properties of the solids, their wettability alteration and contact angle were studied before and after application of the electric fields.

3.3.2 Setting-up of electrokinetic reactors

Four (4) 1.5-L electrokinetic reactors with stainless steel electrodes were set up. About 1500 g of lagoon oil sediment, collected from an oil refinery located in Montreal, Quebec, Canada, were placed in each reactor and subjected to the following types of electrical current using a DC power supply (BK Precision 1902, USA): a Constant DC (CDC), an Incremental or Decremented DC (IDC and DDC, respectively) which was generated by adjusting the voltage on a daily basis, and a Pulsed DC (PDC) generated by a function generator (BK Precision 4001A, USA) used to induce a DC offset. The resulting power was increased by an amplifier (model 7224 AE Techron, USA), which was connected to a 30 Hz Dual Trace Analog Oscilloscope (BK Precision 2120B, USA) to track electrical functions. A Digital Multimeter (Mastech MAS830, USA) was connected to electrical probes which were strategically positioned inside the electrokinetic reactors to measure voltage. The CDC reactor was designed by applying a potential gradient of 1 V/cm across the electrodes. The voltage gradient was chosen based on Elektorowicz and Habibi (2005), who found its suitability for very low permeable sludge, like was the case for lagoon sediments used in this study. For both Incremental (IDC) and Decremented (DDC) currents, a potential gradient ranging from 0.25 to 1.75 V/cm was applied while for the pulsed DC (PDC), a 0.5 V/cm current was used in combination with a 0.5 V/cm of DC pulse at squared frequencies of 60 Hz with a 1/5 pulse period. To enable a fair comparison of the effects induced by the four regimes of electrical current, the energy consumption was maintained at less than 2% for all operational scenarios. A control reactor was set up with no potential gradient.

3.3.3 Characteristics of oil sediments

The physicochemical characteristics of the oil sediments sampled from the Montreal oil refinery are shown in Table 1. The lagoon sediment had the highest water content (63.2%), while the slurry and catalytic fines contained only 0.5% of water. Since the lagoon sediment represented the most stable water-in-oil emulsion due to its high-water content, it was selected for the electrokinetic study.

Table 3.1. Characteristics of centrifuged oil wastes from a full-scale oil refinery

Type of waste in Montreal refinery	Water (%)	Light hydrocarbon (%)	Heavy hydrocarbon (%)	Solids (%)	pH	Conductivity (mS/cm)	Density (g/cm^3)	TPH (%)[a]
Slurry and catalytic fines - heavy fuels oil tank	0.50	0.13	39.81	59.56	6.14	92	1.92**	37.50
Lagoon sediment	63.20	15.93	14.83	6.04	7.57	562	1.06	28.40
Sludge API[b] + DAF[c]	45.50	18.32	20.11	16.06	7.69	322	1.21	30.24
Separator bottom	41.70	9.19	20.67	28.44	7.61	290	1.42	25.40

Note: [a] TPH - Total Petroleum Hydrocarbon (represents the organic composition of the oil sediments determined by sequential solvent extraction using toluene and tetrahydrofuran (THF)

[b] API – American Petroleum Institute

[c] DAF – Dissolved Air Flotation

Density of oil sediments was determined based on the mass content of each separated fraction, assuming that the density at 20 °C of water, light hydrocarbons, heavy hydrocarbons, and solids fractions are 0.998 g/m^3, 0.82 g/m^3, 0.93 g/m^3, and 2.6 g/m^3, respectively.

3.3.3.1 Organic composition of oil sediments

The organic composition of the lagoon sediment was determined by sequential solvent extraction (Wang et al., 2010). Toluene was used as a solvent in the first extraction followed by more polar Tetrahydrofuran (THF) to recover the rest of organic compounds from the mixture during a second solvent extraction. About 25 mg of oil sediment was used, and the extraction was conducted in Whatman cellulose extraction thimbles (33X80MM, Fisher Scientific). For the first extraction, 100 mL of toluene was used to reflux the mixture for about 15 h in a Dean-Stark apparatus (Fisher Scientific) until it turned colorless. The toluene and aqueous phases were separated from the extractant using a rotary evaporator (Laborota 4000, Heidolph) at 50 °C for 5 min at 100 rpm (Sparks et al., 2003). The weight of the remaining sample was gravimetrically determined by subtracting the weight of the dish. The thimble containing the sample was then extracted with 100 mL of THF, where reflux extraction was carried out for 15 h. The organic constituents, referred to as THF soluble, was determined by the weight of the sample left after evaporation. For THF solvent extraction from the aqueous phase, the rotary evaporator was set at 35 °C at 100 rpm for 15 min.

3.3.3.2 Wetting properties

Oil sediment solids are rich in organics, which play an important role in the sorption of oil particles to the surface of solid matrices. Depending on their properties and organic content, solid aggregates can be classified as completely hydrophobic (Hydrophobic Aggregate, HAGG) or bi-wettable (Biwettable Aggregate, BAGG). However, it is not uncommon to have hydrophobic materials in varying degrees for BAGG-type solids. Moreover, ultra-fine clays (UFCs) may also be present and represent an additional contributor for stable emulsions in oil sediments.

To determine the wettability of the lagoon sediment, a mixture of 2 mL of toluene and 8 mL of water was added to 200 mg of dried solids, and vortexed for 2 min at 1500 rpm. The resulting homogeneous mixture was incubated overnight in a fumehood at room temperature (Sparks et al., 2003). Sediments were dried in a vacuum oven at 38 °C to reach constant weight (Ukwuoma & Ademodi, 1999). Three types of lagoon sediment samples were dried namely, centrifuged sediment, electrokinetically treated sediment, and toluene-THF extracted sediment. The wettability was determined as the percentage of solids present in the aqueous phase by gravimetry (Jiang et al., 2011; Somasundaran & Zhang, 2006). The change in wettability of the solids was determined over a short period (30 min) and a longer period (3 days). It was expected that some hydrophobic materials were present in the hydrophilic phase and vice versa. Hence, the percentage weight of the solids partitioned to the aqueous phase or the water-wet ratio of the samples was determined. All samples were tested in duplicate.

3.3.3.3 Contact angle measurement

After electrokinetic treatment, the surface hydrophilicity and surface energy change of each sample were evaluated through contact angle measurements of DI water using the sessile drop method (VCA, video contact angle system, AST Products, Inc., Billerica, MA, USA). The right and left angles of the water drop were measured using the software system VCA Optima XE. Pellets of 10 mm were prepared using a laboratory press (Model C12 Ton Benchtop, Carver, Inc., USA). An amount of 0.5 g dried sample was prepared using a vacuum oven to reach a constant weight at 38 °C, and was added to the cast at 25 MPa (Wang et al., 2015). At least three points from the pressed sample were selected for contact angle measurements. An average of the three measurements was reported. This test enabled an evaluation of the solids' surface wettability and emulsion destabilization.

3.3.3.4 X-ray photoelectron spectroscopy (XPS)

Surface measurements using X-ray photoelectron spectroscopy (XPS) can provide an excellent means for probing the first 7 nm of the surface layer solids and indicate surface functionality and inorganic elements that can explain the movement of organic-rich solids to the aqueous phase (Sparks et al., 2003). The Thermo Scientific™ K-Alpha™+ XPS system was used to analyze the surface solids of the lagoon sediment. XPS was performed using an ESCALAB MK II with Mg Kα (hυ= 1253.6 eV) as the excitation source. Pressed samples against a copper adhesive tape were placed in the XPS chamber, which was pumped down to a pressure of 5×10^{-9} mbar. For the analysis, three points were selected on the surface of the sample to have a representative measurement. The resulting XPS spectra were used to identify the surface elemental composition of C_{1s}, O_{1s}, N_{1s}, Fe_{2p}, Al_{2p}, Si_{2p} and S_{2p} of the solid samples.

XPS analysis was also performed to further identify the chemical composition and valances of each sample since typical survey spectra can confirm the presence of different elemental compositions (Li et al.). High-resolution spectra of the main components were extracted and analysed by the XPSPEAK software (version 4.1). The C and O spectra were used to determine the concentration of different bonds. All binding energies were adjusted for specimen charging by referencing C1s to 284.8 eV from adventitious hydrocarbons.

3.3.3.5 Thermogravimetric and differential thermal analysis

Thermogravimetric analysis (TGA) was performed using a TGA Q500 thermal analyzer (TA Instruments, USA) at the temperature range of 29 °C-600 °C with heating rates of 10 °C/min. The air flow rate was maintained at 100 ml min^{-1} through the furnace. An amount of 10 ± 0.01 mg of sediment sample was placed in an Al_2O_3 crucible for each run and subjected to combustion in the thermal analyzer (Liu et al.; Park et al., 2009). Differential Thermal Analysis (DTA) was performed and the Derivative Thermogravimetric (DTG) data, which expresses the rate of weight change due to increasing temperature, were computed using Equation 3.7.

$$DTG = \frac{(m_i - m_{(i-1)})}{(t_i - t_{(i-1)})} \qquad \text{(Eq. 3.5)}$$

where *DTG* is the derivative thermogravimetric (%/min), *m* is the mass (%), *t* is the time (*min*), and *i* is the datum under consideration, The OriginPro (version 9) software was used with the Savitzky- Golay method to reduce noise in the resulting thermograms or DTG curves.

3.3.3.6 X-Ray Diffraction (XRD)

The percentage of crystal structures in the oil sediment samples was determined by X-ray diffraction (XRD; Model D8 Advance, Bruker, Germany) using Cu K-alpha, 0.15418 nm (Bragg-Brentano geometry). X-ray intensity was recorded as a function of 2θ angle in the range of 3.00-70.00 with a step size of 0.02.

3.3.3.7 Optical microscopy

Emulsion droplets were observed and imaged using an optical microscope (OMAX 40X-2000X, USA). One droplet of oil sediment was placed on a microscope slide and UV light was applied to visualize the water-in-oil emulsions.

3.4 OBJECTIVE 3: EXAMINE THE EFFECT OF NANOPARTICLES OR SYNTHESIZED CATALYST ON THE SEPARATION EFFICIENCY OF EK SYSTEM

In the previous phases, centrifuged oily sludge was used as the starting material for the EK separation process. In the current study scope, the addition of nanoparticle or synthesized catalyst prior to centrifugation of oily sludge was assessed to elucidate whether synthesized catalyst or nanoparticles have the potential of improving phase separation of oily sludge.

3.4.1 Preparation of nanoparticles

Anatase (TiO_2) nanopowder was purchased from Sigma Aldrich (ReagentPlus®, Germany) with ≥99% purity, and density of 4.26 g/mL at 25 °C); it was composed of particle size less than 50 nm. A stock suspension of TiO_2 was prepared using deionized water with a neutral pH and subjected to sonification (450 Sonicator, Branson digital sonifier, USA) for 60 minutes to obtain a homogenous distribution of nanoparticles (Taurozzi et al., 2012). To facilitate homogenous dispersion of the nanoparticles, 0.5% of anionic surfactant sodium dodecyl sulphate (SDS) was added (Zawrah et al., 2015). A stock solution of 1000 ppm nanoparticles was prepared and used to generate three concentrations, 50, 100 and 200 ppm, of nanoparticles, which were added to the oily sludge in EK reactors.

3.4.2 Preparation of oil sediments catalyst

To develop the idea to reuse the waste a synthetic catalyst was prepared based on dry oily sludge. About 10 g of oil sludge was grounded into particles in an agate mortar and carbonized in a tube furnace at 600 °C for 4 h under a nitrogen (99.9%) flow of 60 mL/min. No acid wash (Li et al., 2017a) or oxidizing/reducing agent was used to further conditioning the synthesized carbon-base catalyst (CBC) (e.g. removal of ash) in order to have a less costly product. The carbonization process and exposure to N_2 were carried for 4 h since studies showed that this represented the optimum time to have better crystallization and porosity (Khan et al., 2018). Three concentrations, namely, 50, 100 and 200 ppm of CBC were prepared, and subsequently, added to the oily sediments in EK reactors. Surface area was found to be 70.16 m^2/g and 53.23 m^2/g for the synthesized catalyst and TiO_2, respectively.

3.4.3 Characteristics of oil sediments

Fresh lagoon sludge was collected from Suncor, a full-scale oil refinery located in Montreal (QC). The characteristics of the sludge were determined, and the results are shown in Table 3.2.

Table 3.2. Characteristics of non-centrifuged oil sediments from refinery lagoons located in Montreal, Canada.

Parameters	Average Value
Water content (%)	80.12±1.1
Light hydrocarbons (%)	13.00±0.3
Heavy hydrocarbons (%)	5.35±0.23
Solids content (%)	1.53±0.13
pH at 20 °C	7.52±0.04
Conductivity at 20 °C (µS/cm)	10245±374
Density at 20 °C (g/cm^3)	1.06 ± 0.02
Dynamic viscosity at 20 °C (mPa.s)	7.90

Note: Average values reported; n=3, ±: standard deviation

3.4.4 Setting-up of electrokinetic reactors

Seven 1.5 L electrokinetic reactors with stainless steel electrodes were set up (Fig. 3.8). About 1500 g of the collected sludge was mixed with the nanoparticle suspension using a shaker set at 200 rpm for 5 minutes in the dark. The mixing was conducted in the following nanoparticle solution/oily sludge ratios: 50 ml/950 ml, 100 ml/900 ml, and 200 ml/800 ml with a total working volume of 1000 ml. After mixing, sludge with nanoparticles was placed in EK reactors connected to DC power supply (BK Precision 1902, USA). Constant DC (CDC) regime was generated by adjusting the voltage on a daily basis with a potential gradient of 1 V/cm maintained between the electrodes. This voltage gradient was chosen based on Elektorowicz and Habibi (2005), who found its suitability for very low permeable sludge, which was also the case for the lagoon sediment used in this study. Hence, the following EK reactors were set up: Control (without addition of additives), 50 TiO2 (sludge with 50 ppm TiO2), 100 TiO2 (sludge with 100 ppm TiO2), 200 TiO2 (sludge with 200 ppm TiO2), 50 Catalyst (sludge with 50 ppm catalyst), 100 Catalyst (sludge with 100 ppm catalyst), and 200 Catalyst (sludge with 200 ppm catalyst).

After EK treatment for four days, the sampling was conducted (Fig. 3.8) in anode side (1), middle anode area (2), middle cathode area (3) and cathode side (4). The separated liquid was decanted, and solids were characterized as described in the sections below. The results have been compared with the centrifuged treated samples at refinery.

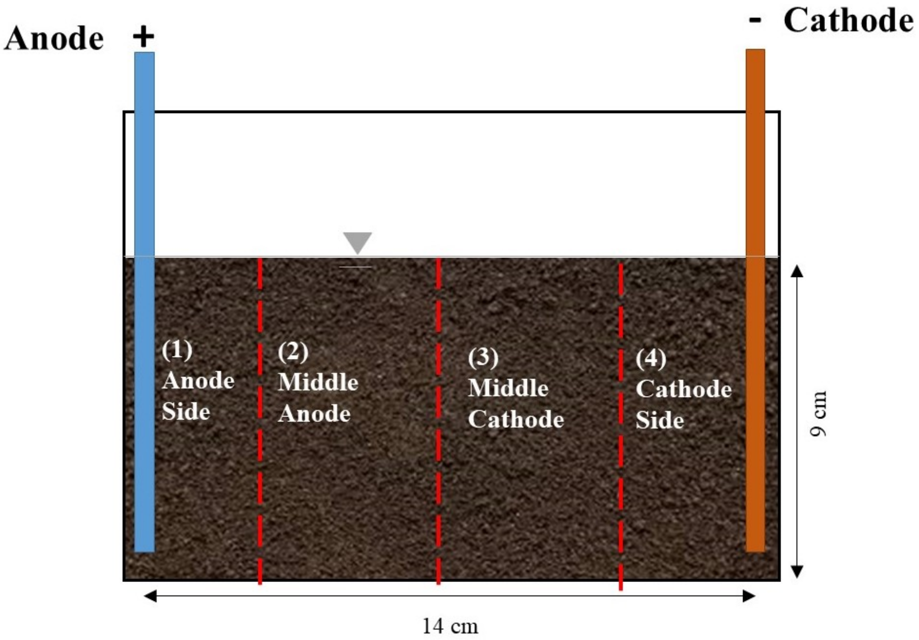


Fig. 3.8. Electrokinetic reactor with oily sediments. Sections of sampling are defined as: (1) anode side, (2) middle anode area, (3) middle cathode area, (4) cathode side.

3.4.5 Solids properties

Oil solids are rich in various forms of organic compounds, which play an important role in the sorption of oil components to the solid matrix. Solids were sampled at the anode, middle anode, middle cathode and cathode for further analyses. Water, solids content and total petroleum hydrocarbons (TPH) were measured according to Kariminezhad and Elektorowicz (2018a). The water to solids ratio was also calculated. For statistical significance, the measurements were conducted in triplicate for each solids sample.

3.4.5.1 Wetting properties

Three types of lagoon sediment samples were dried namely, EK treated, centrifuged, EK + additives. The detailed description of the method used for wetting properties is described in section 3.3.3.2.

3.4.5.2 Contact angle measurement

After EK treatment, the surface hydrophilicity and surface energy change of each sample were evaluated through contact angle measurements of DI water using the sessile drop method (VCA, video contact angle system, AST Products, Inc., Billerica, MA, USA). The detailed description of the method used for contact angle measurement is described in section 3.3.3.3.

3.4.5.3 X-ray photoelectron spectra (XPS)

X-ray photoelectron spectroscopy (XPS) of the surface layer solids provides an excellent means to indicate surface functionality and inorganic elements which can explain the movement of organic-rich solids to the aqueous phase (Sparks et al., 2003). The detailed methodology on XPS analysis of the EK treated samples are provided in section 3.3.3.4.

3.4.5.4 Specific surface area

The specific surface area was calculated by the BET method (Model Autosorb-1 from the company Quanta chrome (USA)). Pore size distribution plots were generated from desorption branch of the generated isotherms based on the ASTM D6556-10 protocol (Li et al.). Surface area was found to be 70.16 m^2/g and 53.23 m^2/g for the synthesized catalyst and TiO_2, respectively.

3.4.5.5 Thermogravimetric and Differential Thermal Analysis

Thermogravimetric Analysis (TGA) was performed on the solids resulting from EK treatment using a TGA Q500 thermal analyzer (TA Instruments, USA). The method used for TGA analysis has been provided in section 3.3.3.5.

3.4.5.6 X-Ray Diffraction (XRD)

The percentage of crystal structures in the EK-treated solid samples was determined by X-ray diffraction. The detailed method has been provided in section 3.3.3.6

3.5 OBJECTIVE 4: ELUCIDATE THE MECHANISMS UNDERLYING THE SEPARATION OF OIL, WATER, AND SOLIDS IN OILY SLUDGE BY KINETICS ANALYSIS

A non-isothermal kinetic study of sediment pyrolysis might be very complicated because of the existence of various elements entering in physicochemical interactions. Kinetic studies were performed by measuring the conversion of the material as a function of temperature for different periods. TGA of the solids sampled in four sections of the reactors was conducted using Helium at a flow rate of 10.0 ml/min, and temperature range of 30 °C to 900 °C with a ramp 10 °C/min. The overall thermal process responsible for the weight loss was described by the following rate expressions:

$$\frac{d\alpha}{dt} = k(P,T)f(\alpha) \qquad \text{(Eq. 3.6)}$$

Where k is the reaction rate constant which includes the effect of temperature (T) and partial pressure of gas (P), t is the time that describes the change in reactivity as well as a change in physicochemical properties of the sample. The conversion of the sludge and f(α) was defined by Eq. (3.7) and (3.8) (Silva et al., 2018).

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_f)} \qquad \text{(Eq. 3.7)}$$

$$f(\alpha) = (1 - \alpha)n \qquad \text{(Eq. 3.8)}$$

where k is the rate constant, α the extent of conversion, n the order of reaction, W_0 the initial weight of the sample, W_t the weight of the sample at time t, and W_f the final weight of the sample at the end of the reaction. Assuming a constant partial pressure, the values of k depended on temperature and, to simplify the calculations, the reaction order (n), which was assumed to be equal to unity (n = 1) (Syed et al., 2011).

$$\frac{d\alpha}{dt} = k(1-\alpha) \qquad \text{(Eq. 3.9)}$$

$$k = Ae^{(-\frac{E}{RT})} \qquad \text{(Eq. 3.10)}$$

Where, A is the Arrhenius constant, E is the activation energy, R is the gas constant and T is the absolute temperature. By combining Eq. (3.0) and (3.10), we obtain:

$$\frac{d\alpha}{dt} = Ae^{(-\frac{E}{RT})}(1-\alpha) \qquad \text{(Eq. 3.11)}$$

For a non-isothermal kinetics expression with linear heating rates, β, Eq. (3.11) becomes

$$\frac{d\alpha}{dt} = \frac{A}{\beta}e^{(-\frac{E}{RT})}(1-\alpha) \qquad \text{(Eq. 3.12)}$$

By integrating Eq. (3.12), taking the natural logarithms, the following expression is obtained:

$$\ln[-\frac{\ln(1-\alpha)}{T_2}] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \qquad \text{(Eq. 3.13)}$$

Using the α and temperature values from the TGA data, a linearized plot of ln[−ln(1 − a)/T 2] versus 1/T was generated (Sonibare et al., 2003). The slope of the produced straight line was equivalent to (-E/R). Thus, multiplying the value by the universal gas constant (R) yielded the activation energy (Ea). The expected accuracy for activation energy was ± 10-15%.

Comparison of constant, pulsed, incremental and decremental direct current applications on solid-liquid phase separation in oil sediments

Connecting Text: Phase separation of oil wastes can mitigate the effects on the environment, by decreasing the volume of hazardous materials and regenerate energy. This study focused on the advanced electrokinetic method as a technology to treat oil sediments from oil refineries and separate them into their individual phase components. The effects of four regimes of electrical field on the phase separation of oil sediments from an oil refinery were investigated, namely constant direct current (CDC), pulsed direct current (PDC), incremental direct current (IDC) and decremental direct current (DDC). The results showed that the extent and quality of phase separation differed based on the regime of electrical current applied, and indicated that different mechanisms such as electroosmosis, electrophoresis, electro-demulsification, and electro-sedimentation might have been involved in the separation process depending on the regime of electrical current. The application of DDC and IDC was found to cause a significant separation of solids by electrophoresis with the movement of almost 70% of solids to the anode of the reactors. The DDC and IDC regimes resulted in the most efficient phase separation of the oil sediments, and even incurred a highly resolved separation of light hydrocarbons at the top anode.

The results of this study have been published in the *Journal of Hazardous Materials*:

Esmaeel Kariminezhad, Maria Elektorowicz, Comparison of constant, pulsed, incremental and decremental direct current applications on solid-liquid phase separation in oil sediments, Journal of Hazardous Materials, Volume 358, 2018, Pages 475-483.

4.1 INTRODUCTION

Oily waste is produced as a result of various petroleum industrial processes including crude oil exploration and refinery. In technical terms, oily waste produced during the refining process (downstream) is classified as non-specific hazardous waste (EPA, 2005) while extraction and exploration (upstream) waste belong to a category of special hazardous waste (RCRA, 2016). Management of oil wastes resulting from industrial processes is gaining more and more attention since it represents a serious threat to human health and environment, and is considered as a hazardous waste in many countries (Hu et al., 2013; Xu et al., 2009). Thus, proper handling and treatment of oily wastes prior to disposal is required. According to the Brundtland Commission Report, it is imperative to implement sustainable development and properly manage such hazardous materials in order to avoid serious environmental catastrophes (Sharma & Vredenburg, 1998).

In general, oily waste consistency varies but generally comprises of an emulsion of petroleum hydrocarbons (PHCs), water, heavy metals, solids and different recalcitrant components. Separation and dewatering of oily waste components and their potential reuse represent a potential avenue for promoting sustainable management of this hazardous material. Dewatering improves phase separation and increases shear forces while reducing the volume of material to be handled. Such processing also minimizes the risk of storage failure and reduces footprint (Farkish & Fall, 2013). Various technologies have been developed for oily waste treatment and include incineration/stabilization (Li et al., 1995; Rozumová et al., 2015), centrifugation (Cambiella et al., 2006), solvent extraction (Zubaidy & Abouelnasr, 2010), microwave irradiation (Rajaković & Skala, 2006), ultrasonic treatment pyrolysis (Liu et al., 2009), photo-catalysis (Da Rocha et al., 2010), thermochemical treatment (Jin et al., 2012) and biodegradation (Ward & Singh, 2003). These treatment technologies have been shown to reduce hazardous constituents in oil sludge and mitigate their deleterious impacts on the environment and human health. But still, there are stable emulsions containing water and hydrocarbons that can resist treatment and increase the volume of waste disposal. Due to the recalcitrant nature of oil sludge, only a few technologies can reach a compromised balance between satisfying strict environmental regulations while consuming a significant amount of energy or chemical and water (Hu et al., 2013). The problem is compounded by the presence of interstitial water which binds oily sludge making flocs with poor settleability.

Existing techniques have not been shown to be substantially efficient in inducing dewatering of such matrix containing a significant amount of interstitial water (Guo et al., 2011).

The electrokinetic method was developed in order to separate stable phases (water, hydrocarbons, and solids) through the application of low-intensity direct current between electrodes causing electroosmosis of liquid phase, movement of ions and electrophoresis of charged particles (Elektorowicz et al., 2006; Lima et al., 2012). This method has been shown to dewater oil sludge by nearly 63% and reduce the light hydrocarbons content by about 43% (Elektorowicz & Habibi, 2005). Electrokinetic treatment, compared to other methods, has a low amount of water consumption for treatment (Elektorowicz et al., 2006; Jin et al., 2012; Xu et al., 2009).

Despite successful application of electrokinetic treatment of oil sludge, the impacts of various types of electrical field on phase separation have not been investigated. Furthermore, most of the research work associated with the electrokinetic method have focused on oil sludge from food industries (Yang et al., 2005b) and wastewater treatment plants (Ibeid et al., 2015; Mahmoud et al., 2010). Water-in-oil emulsions produced by refineries are more challenging to treat and present the most interesting matrix for oil recovery from petroleum wastes. This study investigates the application of electrokinetic treatment of water-in-oil system produced downstream under the influence of four different direct electrical current regimes. Electrokinetic methods affect the chemical bonds in solids and emulsions by changing acidity through electrokinetic processes. Electrical measurements were conducted to assess the phase separation process.

4.2 EXPERIMENTAL PROCEDURE

The experimental procedure and operation are explained in detail in section 3.2; therefore here, only some of the specific points during the adsorption tests are highlighted.

4.3 MATERIALS AND METHODS

4.3.1 Oil sediment

Four different types of oily waste are generally produced in refineries: slurry fines, lagoon sediments, dissolved air flotation (DAF) and American Petroleum Institute (API) sludge and separator bottom. These wastes include a considerable amount of oil (20 to 40 %). Since lagoon waste has been shown to display the highest stability after centrifuge treatment. Lagoon oil waste samples forming very stable emulsions were collected from an oil refinery located in Montreal, Canada, and were used in the current study for performing the electrokinetic analyses.

4.3.2 Reactor setup

Five 1.5 L capacity polyethylene bench-scale electrokinetic reactors were designed bearing a dimension of 14 x 9 x 14 cm (l x w x h) to perform the electrokinetic experiments. Approximately 1500 g of well-mixed oily sediments collected from the refinery were placed in each of the five reactors. Two stainless steel electrodes (an anode and a cathode) were inserted at the extremities of each reactor to supply power (Fig. 4.1). A total of 15 probes, also known as electrical jumpers, were placed in 3 rows with 5 probes along the length of each reactor to monitor the electrical potential change in three dimensions. The 3 sets of probes were dipped in the sediments at three different depths: 1, 4 and 7 cm. The distance between the inserted probes were 2 cm apart to provide a strategic spatial arrangement for tracking the voltage intensity across the electrokinetic reactors. The probes were connected to a Digital Multimeter (Mastech MAS830, USA) for monitoring the voltage distribution between the electrodes upon application of different electrical regimes. A sixth sideline reactor containing the same sediments, and bearing the same design and operational configuration, but without any electric field, was used as a control. The ambient temperature was kept at 21 °C ±1 °C.

4.3.3 Deviation Index (DI) analysis

The evaluation of the efficiency of the four applied electrical regimes (CDC, PDC, IDC, and DCD) with respect to the phase separation of the oil sediments was conducted based on separation criteria. These criteria were defined using the Brown-Forsythe test concept (Zar, 1999). Each value was obtained by subtracting it from the median value and considering the absolute value of the difference. A deviation index (DI) was computed, where the ratio between each two phases is considered as one criterion. The following phase separation criteria were assessed: water/solids, water/heavy hydrocarbons, water/light hydrocarbons, light hydrocarbons/heavy hydrocarbons, heavy hydrocarbons/solids, and light hydrocarbons/solids. These criteria were evaluated for six sections of each electrokinetic reactor. Each criterion was obtained by subtracting the ratio of the phases from the initial ratio of oil phases. Subsequently, the absolute values of the resultant for all six sections of the electrokinetic reactor were summed, and the weighted Deviation Index (DI) separation was computed.

4.4 RESULTS AND DISCUSSION

4.4.1 Physicochemical properties of oil sediments

A comprehensive physicochemical and chemical characterization of the lagoon sediments used in this study is provided in Table 4.1 The density of oil sediments was determined based on the mass content of each separated fraction, and assuming density of water, light hydrocarbons, heavy hydrocarbons and solids fractions at 20 °C to be 998 kg/m^3, 820 kg/m^3, 930 kg/m^3 and 2,600 kg/m^3, respectively (Wang et al., 2010).

Table 4.1. Characteristics of pre-centrifuged oil sediments from refinery lagoons located in Montreal, Canada.

Parameters	Average Value
Water content (%)	63.20±2.4
Oil (by solvent extraction/wt., %)	22.60±1.1
Light hydrocarbons (%)	15.93±0.9
Heavy hydrocarbons (%)	14.83±1.2
Solids content (%)	6.04±0.4
pH at 20 °C	7.57±0.14
Conductivity at 20 °C (µS/cm)	562±14
Density at 20 °C (g/cm^3)	1.06±.02

Note: Average values reported; n=3, ±: standard deviation

4.4.2 Effect of different electric field regimes on electrokinetic separation

The characteristics of the oil sediments were monitored through non-destructive and destructive analyses to evaluate phase separation induced by constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC). Non-destructive testing was performed to measure resistance change in the sediment matrix during the experiment, while destructive testing included conductivity, pH, and phase separation assessment after completion of each experiment.

The mass of oil sediments varied negligeably before and after the electrokinetic treatment, showing that weight loss by evaporation of water or other volatile components was insignificant. After four days of experimentation, the weight of the sediments decreased by only 0.73%, 0.41%, 0.52% and

0.57% following the application of CDC, PDC, IDC, and DDC, respectively. However, an accumulation of water at the cathode, and an increase in the stiffness of the sediment matrix at the anode were observed for all electrokinetic treatments.

4.4.3 pH

The electrokinetic treatment induced a change in pH as a result of oxidation and reduction reactions at the anode and cathode, respectively, and is in agreement with Eq. (4.1) and (4.2).

Anode (oxidation) reactions:

$$2H_2O \rightarrow O_{2(gas)} + 4H^+_{(aq)} + 4e^- \qquad E° = 1.299\,V \qquad \text{(Eq. 4.1)}$$

At cathode (reduction) reactions:

$$4H_2O + 4e^- \rightarrow 2H_{2(gas)} + 4OH^-_{(aq)} \qquad E° = -0.828\,V \qquad \text{(Eq. 4.2)}$$

$E°$ is the standard electrode potential at a temperature of 298 °K.

Measurement of pH was made at six sections of each reactor, namely top, middle and bottom anode, and top, middle and bottom cathode. Following the application of the different electrical currents over a 4-day period, a reduction in pH was observed for all lagoon sediments close to the anode due to acidification. The average initial anodic pH was 7.57, and decreased to an average of 3.22, 3.45, 3.06 and 3.43 following the application of CDC, PDC, IDC, and DDC, respectively (Fig. 4.1). On the other hand, alkalization occurred at the cathode and the pH increased to an average of 10.38, 10.81, 10.89, and 11.84 following the application of CDC, PDC, IDC, and DDC, respectively (Fig. 4.1). In some cases, a pH gradient was observed in the vertical section of the reactors especially at the anode. The lowest pH was measured at the bottom anode and the highest pH was recorded at the top cathode during the application of the DDC as a result of vertical movement of water. pH can play an important role in electrokinetic applications, especially in electrocoagulation process. In addition, pH has been shown to have an effect on demulsification to some extent (Rodrigues Pires da Silva et al., 2015) and to affect acidity which can alter the chemical bonds in solids and improve phase separation (Guo et al., 2011).

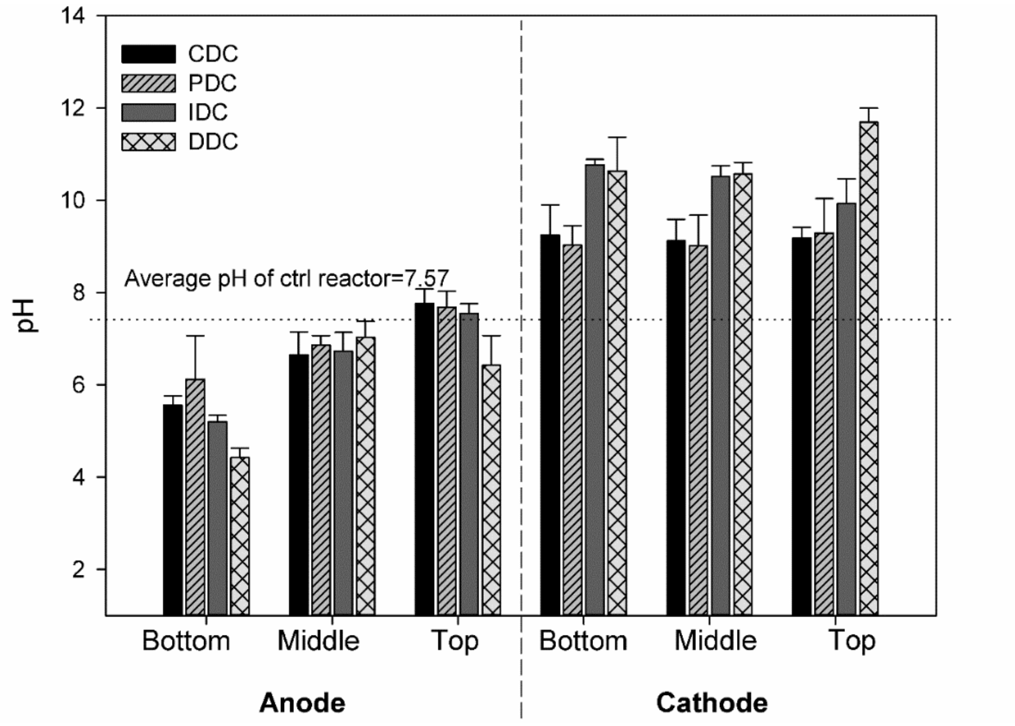


Fig. 4.1. pH in different sections of electrokinetic reactor with oil sediments treated with constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC) (average values reported, n=3).

Previous electrokinetic studies in soil or municipal sludge have been shown to induce the formation of pH gradients which can effectively increase the hydraulic flow, electroosmotic, electrophoretic and ionic migration in the treated matrix (Acar et al., 1995; Elektorowicz & Oleszkiewicz, 2012; Mahmoud et al., 2010). A pH gradient between electrodes can be caused by the production of H^+ and OH^- ions. These ions can affect the zeta potential at low concentrations and alter the double layer of solids that interface with the liquid phase. Studies involving oil extraction from refinery reservoirs by the electrokinetic method have shown an increase in pH at the cathode, which led to a reduction in interfacial tension, and an increase in the solubility of PAHs (Yang & Lee, 2009), enhancing ion exchange and double layer expansion (pore throat enlargement and permeability enhancement) (Alklih et al., 2014; Pamukcu et al., 2016). These changes are believed to enhance the separation of oil waste phases. Ansari et al. (2015a) showed that an increase in acid concentration enhanced displacement efficiency and permeability due to increased electroosmotic, electromigration and electrophoretic effects.

4.4.4 Electrical parameters

4.4.4.1 Electrical conductivity

Electrical conductivity (EC) is dependent on active ions found in a particular matrix. It is related to the water content, and mineral ion species in the matrix (Scott et al., 1967). While the presence of ions increases electrical conductivity, hydrocarbons in oil sediments decrease the conductivity of the matrix due to low dielectric constant. Monitoring the electrical conductivity and/or resistivity changes across the electrokinetic reactor can provide valuable insights about the motion of different oil phases.

EC measurement in the oil sediments after electrokinetic treatment showed an overall increase in conductivity from the anode to the cathode (Fig. 4.2). Such EC gradient may be indicative of water movement towards the cathode due to electroosmotic phenomena as well as mobilization of polar particles and their electrophoretic movement towards the anode. Elektorowicz et al. (2006) also observed that the water content decreased considerably at the anode area over time. Shrestha et al. (2012) found that the type of clay and its respective content have a significant effect on electrically induced hydrocarbon mass transport.

The variation of EC across the electrokinetic reactor hints to a change in the properties of the sediment matrix and the induction of a dewatering process. Among the four electrical current regimes, IDC and DDC induced the highest conductivity at the bottom cathode, (860 and 842 μS/cm, respectively). A significant change in EC at the cathode from top to bottom (92 to 842 μS/cm) following the application of DDC shows its efficiency in causing vertical and lateral separation of phases. Contrary to DDC system, IDC maintained a relatively high EC from the top to the bottom of the cathode area and increased the formation of water-in-oil emulsions at the top of the cathode (Fig. 4.3). The increase in EC is indicative of the commutation of water molecules and their possible evacuation through the cathode. The established EC gradients in all the reactors induced an effective phase separation in the oil sediments by all the electrical current fields.

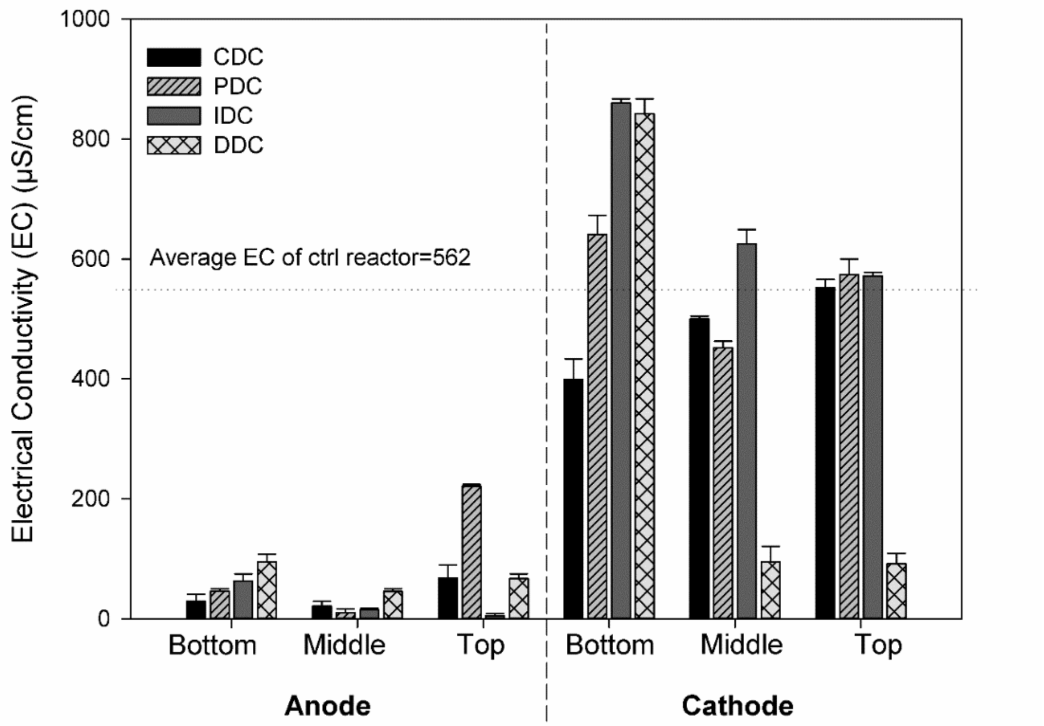


Fig. 4.2. Electrical conductivity (EC) in different sections of the oil sediment matrix following electrokinetic treatment with constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC) (Average values reported, n=3).

4.4.4.2 Current intensity

Monitoring of the electrical intensity in the oil sediments showed a gradual decrease over time for the CDC, PDC, and DDC (Fig. 4.3). This may be explained by a decrease in conductivity and an increase in resistance due to water transport towards the cathode and an accumulation of solids at the anode of the reactor. Additionally, activation and concentration polarization phenomena related to the production of O_2 and H_2 gases, and H^+ and OH^- transport (Eq. (4) and (5)) (Virkutyte et al., 2002) may have also contributed to the increasing resistance in the reactor leading to a reduced electrical intensity. It has also been shown in a previous study involving non-neutralized acidic or alkaline conditions, that the current dropped over time following electrokinetic treatment (Virkutyte et al., 2002).

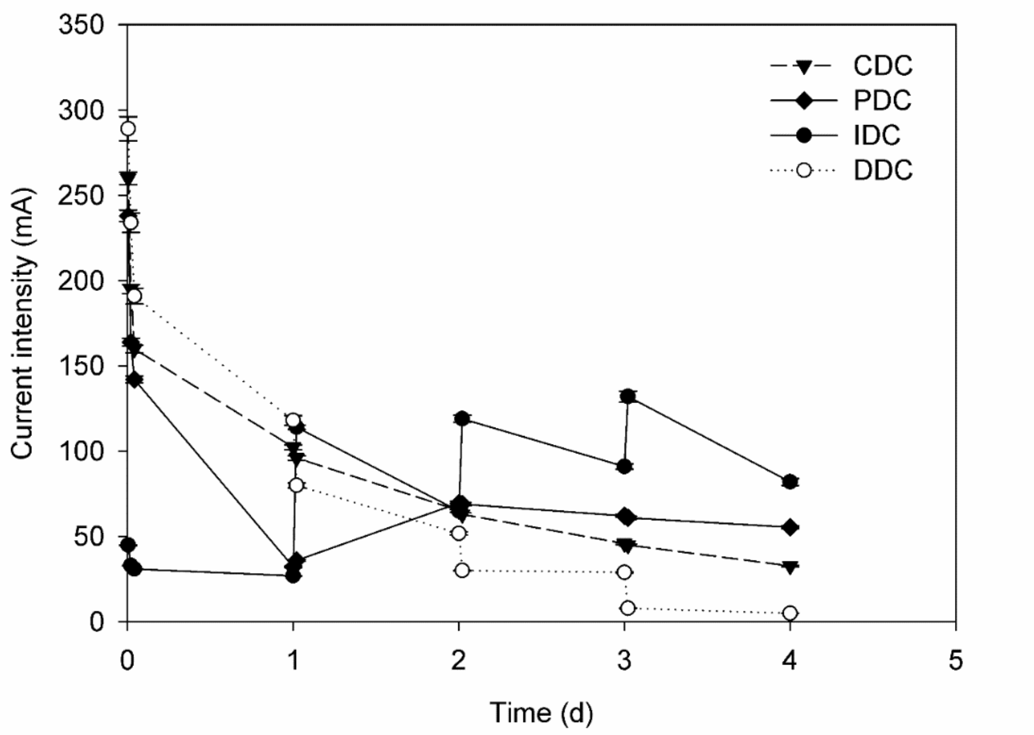


Fig. 4.3. Electrical current intensity (I) of oil sediments after electrokinetic treatment with constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC) (Average values reported, n=3).

After 4 days of treatment, it was found that the PDC reactor maintained a higher electrical intensity as compared to the CDC and PDC supply, although it dropped sharply on Day 1 of the experiment. This may be due to an accrued concentration of ions present in the interstitial water, and breakdown of water-oil emulsions, which maintained the electric current intensity (Glendinning et al., 2007). The DDC reactor showed the highest decrease in electrical intensity change from 289 mA at Day 0 to 5 mA at Day 4. Conversely to the other electrical regimes, the IDC reactor showed a consistent increase in electrical intensity from 31 mA (Day 0) and increased by approximately 100 mA each day.

The application of the above different electrical supplies appears to have induced different mechanisms in separating the phases in the complex oily sediment matrix. Dissolution of the iron anode produces ions with the high valent state. These ions undergo oxidation while low valent state ions will be re-oxidized. There are different metal species such as Ni, Al, Ti, Co and Ag in oily sediments that may undergo oxidation during electrokinetic treatment. Oxidation or reduction of ions may result upon application of different electrical currents, and this will impact on the electrical conductivity of the oily sediment.

4.4.4.3 Electrical resistivity

Electrical resistivity was calculated based on Ohm's law using the voltage differential between probes and amperage of each system (Urish, 1983). The 3D distribution of resistance in each electrokinetic reactor was obtained from the measurements of the probes which were strategically placed across the reactors - at the bottom, middle and top parts.

4.4.4.3.1 CDC reactor

Following the application of the CDC, the resistance showed incremental trends over time (Fig. 4.4a). This was correlated with a decrease in electrical current as observed in section 3.4.2 Such increase in resistivity over time may have resulted from oil electro-demulsification and subsequent water removal from the cathode, ion migration and polarization. Compared to the middle and top sections of the reactor, the bottom layer of the oily sediment showed a lower resistance across the reactor. This could have been due to the vertical movement of phases as a result of electro-demulsification. High resistance was observed at the anode due the accumulation of solids at the surface of the anode, and electrophoretic movement of solids towards the anode. A previous study showed that electrophoresis plays an important role in increasing the resistance at the anode area over time (Elektorowicz & Hatim, 2000; Virkutyte et al., 2002). Similar phenomena may have induced a decrease in electrical resistance at the cathode in the electrokinetic reactors.

4.4.4.3.2 PDC Reactor

The PDC reactor showed a generally increasing trend in electrical resistance over time (Fig. 4.4b). However, the electrical resistance measured at different points in the PDC reactor was lower as compared to the other electrokinetic reactors. Such lower resistance may be explained by less transport of water molecules towards the cathode, and the desorption of metals from the solids, rendering more ions available for electro-migration to take place (Rajić et al., 2013). The electrical resistance was higher at the anode due to the accumulation of solids loaded with heavy hydrocarbons. Resistance change at the cathode was lower than at the anode because of electroosmotic migration, which increased the water content at the cathode. Overall, all the three stratifications (bottom, middle and upper layers) showed an increase in electrical resistance over the 4-day period. The differences in resistivity in the three layers showed that the electrokinetic treatment induced phase separation with a lower resistance at the bottom due to an increase in water content as a result of demulsification of water-in-oil emulsions, and horizontal and vertical movements of solids and water.

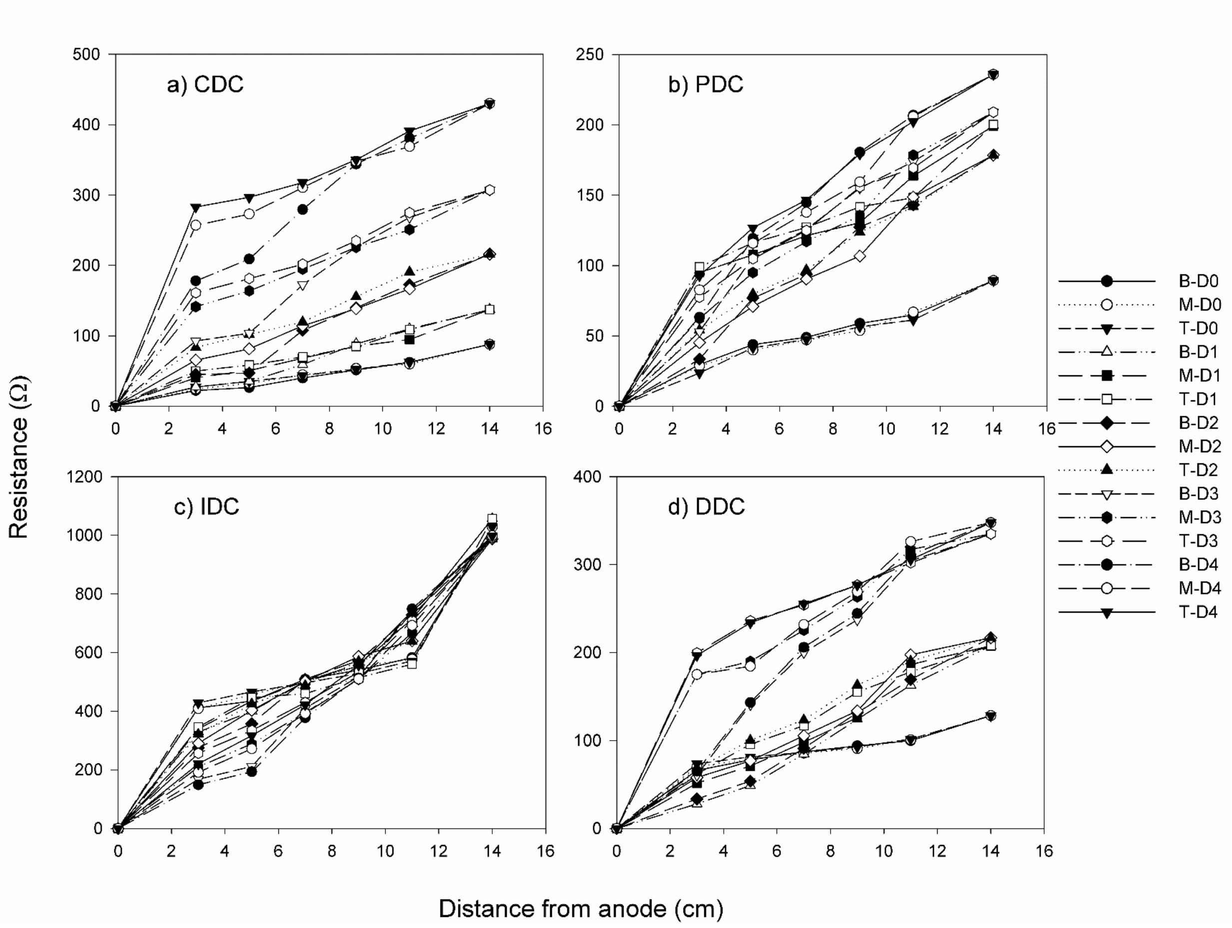


Fig. 4.4. Electrical resistance profiles of lagoon oily sediments in different sections of the electrokinetic reactors supplied with CDC, PDC, IDC and DDC. Note: Bottom (B), Middle (M), Top (T), Day (D), constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC).

4.4.4.3.3 IDC reactor

The IDC reactor displayed a different electrical resistance trend compared to the CDC and PDC reactors as a result of an incremental change in voltage potential with time. The resistance increased toward the cathode, while it decreased at the anode (Fig. 4.4c). However, at both electrodes, a general decrease in electrical resistance was observed over time. A high resistance (1,057 Ω) was measured at low voltage potential close to the electrodes and may be attributed to the accumulation of solids or resistance polarization. However, analysis of bottom, middle and top layer resistance profiles does not show much difference over time. The highest resistance change between the stratifications was observed on Day 4, and may be indicative of the destabilization of emulsions and movement of water molecules to the bottom of the reactor, movement of oil molecules to the top, and movement of solids to the anode at high current intensity.

4.4.4.3.4 DDC reactor

Based on the profiles of the DDC reactor, it was found that the electrical resistance increased over time along with an increase in the slope of the profiles (Fig. 4.4d). In addition to an increase in resistance over time, the difference in electrical resistance between the layers also increased. Application of the DDC resulted in a better separation of the phases which may be attributed to the low resistivity at the bottom of the reactor and high resistivity at the top layer. In comparison to the IDC and PDC electrical regimes, the DDC induced less resistivity across the reactor. The difference in resistance at 3 cm from the anode between the bottom and top layers was 131 Ω, while the maximum difference in resistance between the bottom and upper layers for the other reactors was 122 Ω, 105 Ω and 29 Ω for IDC, CDC, PDC, respectively. Resistivity changes across different layers may indicate demulsification, and horizontal and vertical movements of phases. A steeper slope of the resistance profiles shows that electrophoretic phase separation may be occurring. In contrast to the other types of electrical current, DDC appears to have induced clear horizontal movement of solids.

4.4.5 Phase separation

The efficiency of the different electrical regimes in inducing separation of the different phases (water, solids and hydrocarbons) in the oil sediments was assessed. Insights about the different phenomena involved in the phase separation such as electroosmosis, electrophoresis, demulsification, and vertical and horizontal particle movement were also studied. Application of different electrical regimes may alter the mechanisms involved during the electrokinetic treatment and the extent of separation of the different phases in the oil sediment. Phase movement was studied by determining the amount of water, light and heavy hydrocarbons, and solids in different sections of the electrokinetic reactor.

4.4.5.1 CDC reactor

The different phases monitored during the study period following the application of CDC are shown in Fig. 4.5a. The CDC increased the water content at the cathode from 63% to 68%. Such increase in water content can be mainly attributed to electroosmotic movement of molecules at the cathode. On the other hand, the amount of solids was found to increase at the anodic side from 6.0% to 9.2 %, possibly due to electrophoretic movement of solid particles. The effect of electro-demulsification was not significant as shown by the low degree of vertical movement.

4.4.5.2 PDC reactor

The effect of PDC on phase separation is shown in Fig. 4.5b. The water content at the bottom cathode reached 74% showing an enhanced effect of the pulsed current to induce electroosmotic movement of water in the oil sediments. In addition, a good vertical separation of light hydrocarbons was observed at the cathode increasing from 16% to 28%; however, such vertical phase separation was not significant at the anode. A direct correlation was found between the heavy hydrocarbon content and the accumulated solids at the anode indicating that the heavy hydrocarbon particles were mostly adsorbed to the solid matrix. Such correlation has been previously observed in other studies (Sparks et al., 2003; Sullivan & Kilpatrick, 2002).

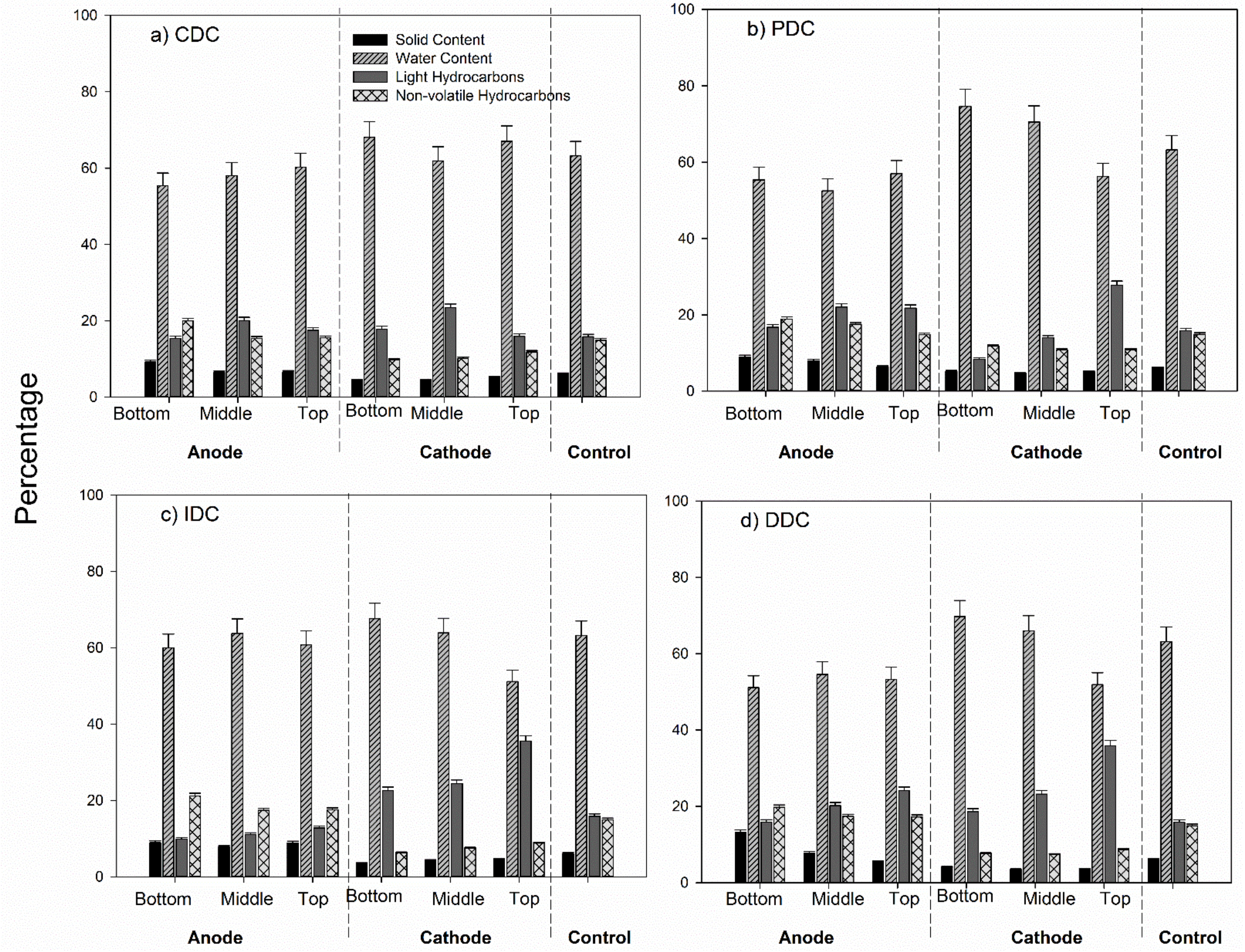


Fig. 4.5. Phase separation in the different sections of the electrokinetic reactor after 4 days electrokinetic treatment by constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC). The Control refers to the sample in the reactor prior to the application of the different electrical currents (average values reported, n=3).

4.4.5.3 IDC reactor

The separation of the different phases in the IDC reactor is shown in Fig. 4.5c. The solids content at the bottom, middle and top part of anode was similar (8.9%, 7.0%, and 8.9%, respectively) indicating a uniform horizontal movement of particles across the reactor. The percentage of light hydrocarbons increased at the cathode after application of the IDC from 16% to 36%. Previous studies have shown that Joule heating requires the highest potential (voltage) gradient, while electrochemically enhanced reactions such as electromigration, electrophoresis, and electroosmosis, require intermediate energy at a particular voltage gradient (Hill, 2014). By applying an IDC with varying voltage gradient, these mechanisms might have taken place in a dissimilar order compared to the other regimes. Application of electric current may have increased the temperature by a few degrees which were sufficient to induce electro-demulsification. Disintegration of heavy hydrocarbons as a result of the IDC may have contributed to the cumulative amount of light hydrocarbons and a decrease in the heavy hydrocarbon content at the anode.

4.4.5.4 DDC reactor

The phase separation induced by the DDC is shown in Fig. 4.5d. An increase in acidity of the oil sediments at the anode was observed, which may have caused free ions to adsorb onto the surface of the solids. The amount of non-volatile hydrocarbons was found to decrease at the cathode as compared to the anode. On the other hand, the percentage of light hydrocarbons increased in the system, especially at the cathode. According to Conway (2013), any fluctuation in a local electric field will result in the discharge of stored energy, similar to discharging a super capacitor. Such discharge can potentially induce the breakdown of complex hydrocarbon molecules, resulting in simpler product molecules or release of simpler molecules from the emulsion traps. This may explain the increase in the amount of light hydrocarbons in the DDC reactor from 16% to 23%. Light hydrocarbons were transported toward the cathode with water and accumulated at the bottom of the cathode area. This may be an important aspect to consider when designing an electrokinetic treatment system operated on a DDC for oil sediments.

On Day 4, the separation of phases was also confirmed through other electrical measurements (Fig. 4.6). The cumulative resistance from the anode toward cathode reflects the distribution of different fractions of the oil sediment in X-Z coordinates. It was assumed that the distribution in X-Y plane is constant. Fifteen points were considered in each reactor for determining the resistivity between the electrodes. The contour-lines in Fig. 4.6 show concentration levels of the measured matrix such that concentrate lines of high resistance at the anode show solids accumulation in that specific area. The CDC and DDC reactors have similar resistance distribution with the exception of the cathode where a higher concentration of electrically low resistance hydrophilic compounds accumulated. Contrary to the PDC, the IDC reactor showed disbanded areas with variable cumulative resistance. This observation may indicate a uniform flow of the oil components with variable resistance. It also shows the impact of the IDC on destabilizing and dispersing the sediments leading to phase separation. The contour plots also show that the solids accumulated mostly at the bottom anode while water molecules moved to the cathode area. Transition areas can be associated with light and heavy hydrocarbons separation which occurred within the 4 experimental days. According to Fig. 4.6c, the IDC induced changes in the oil sediments in a way that more concentrated contour-lines occurred close to the electrodes. It is possible that electrically low resistance water molecules did not have enough time to move adequately between the electrodes.

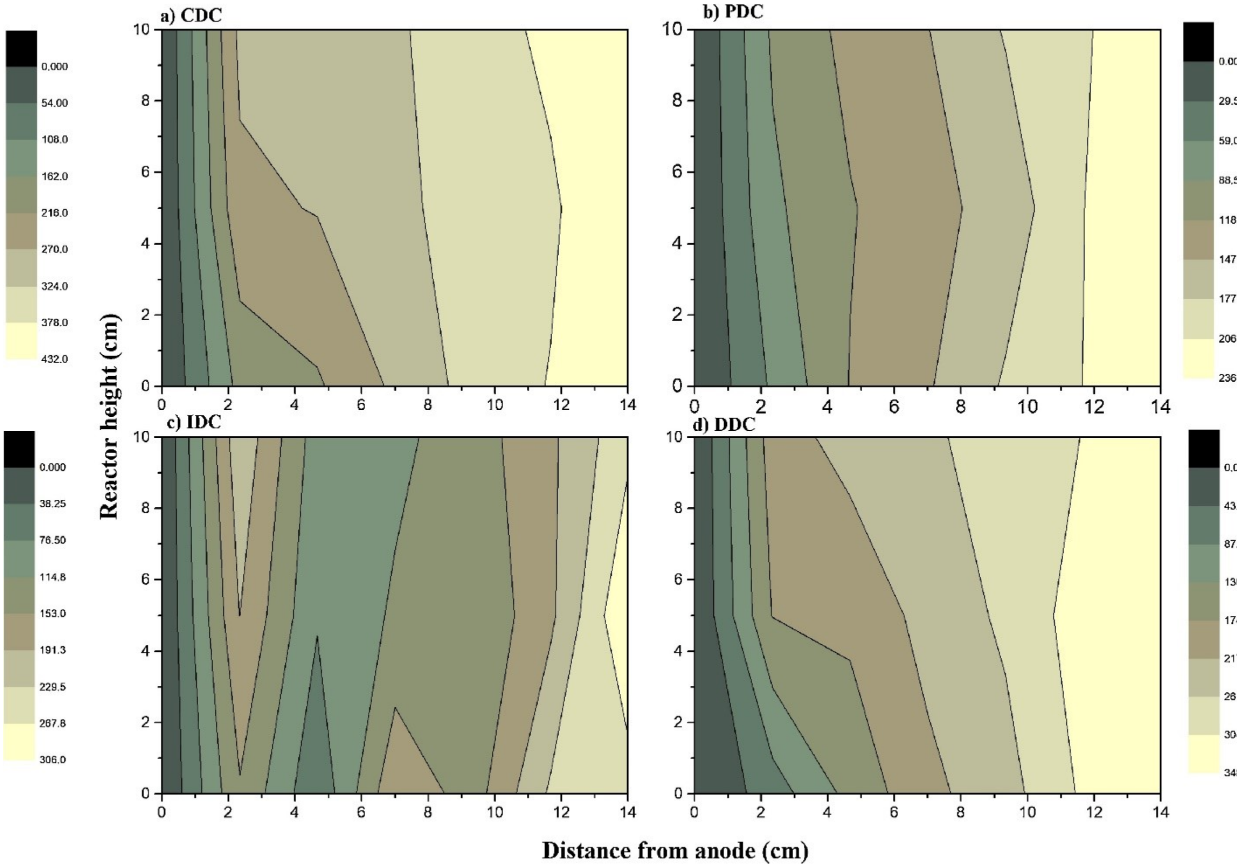


Fig. 4.6. Electrical resistance patterns across electrokinetic reactors after 4 days of treatment with CDC, PDC, IDC, and DDC. Note: constant DC (CDC), pulsed DC (PDC), incremental DC (IDC) and decremented DC (DDC).

Based on the computed deviation indices (DI), it was found that the DDC and IDC reactors displayed the highest separation weights (80.51 and 76.71, respectively) (Table 4.2). The separation efficiencies by the different applied electrical fields were as follows (from lowest to highest): CDC > PDC > IDC > DDC. This is an important information to consider when designing and operating an electrokinetic treatment system for oil sediments.

Table 4.2. Deviation Index (DI) for assessment of separation efficiency.

Criteria	Deviation Index (DI)			
	CDC	PDC	IDC	DDC
Water/solids	18.50	18.84	24.08	30.38
Water/ heavy hydrocarbons	8.33	8.27	15.15	15.28
Water/light hydrocarbons	3.79	11.56	9.55	7.78
Light hydrocarbons /heavy hydrocarbons	2.89	2.85	9.07	7.24
Heavy hydrocarbons /solids	1.09	1.51	2.70	2.87
Light hydrocarbons /solids	6.06	5.88	16.16	16.97
Total	40.66	48.91	76.71	80.51

Note: DI - Deviation Index compared to original oil sediments

4.5 CONCLUSION

The effect of different electrical field regimes was investigated in the phase separation of oily sediments by electrokinetic treatment. Oily sediments are the most significant solid wastes generated from the petroleum and oil refinery industry, which constituted a complex emulsion of hydrocarbons, water, and solid particles. The current study showed that DDC and IDC were the most effective in separating the solid and liquid phases in oily sediments. DDC and IDC were effective in separating and recovering light hydrocarbons from oil sediments.

4.6 ACKNOWLEDGEMENT

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Effect of various electrokinetic treatment regimes on solids surface properties and thermal behavior of oil sediments

Connecting Text: Developing the findings of Chapter 4, we further explored the ability of electrokinetic process to separate the different phases through the electroosmotic movement of the liquid phase, migration of ions and electrophoretic movement of charged particles in a colloidal system. Sediments from oil refineries represent a complex mixture of oil, water, sand, mineral matter and metastable emulsions. However, not much is known about the effect of the electric field regimes on the surface properties of solids in the oil sediments and their behavior. In this study, the effect of four different types of electrical current on the surface properties of oil sediments was investigated, namely constant direct current (CDC), pulsed direct current (PDC), incremental direct current (IDC) and decremental direct current. X-ray photoelectron spectroscopy (XPS) analyses showed a decrease in the concentration of carbon from 99% in centrifuged samples to 63% on the surface of the solids in the PDC-treated oil sediment. Wettability alteration results showed an increase in the level of fine solids in the aqueous phase following electrokinetic treatment thereby enhancing the hydrophilicity of the solids. A significant change in carbon and oxygen-containing functionalities at the surface solids of the DDC-treated sediment was also observed. Thermogravimetric analyses (TGA) confirmed the ability of electrokinetic treatment in separating the phases by shifting the thermogram profiles towards lower temperatures.

The results of this study have been published in the *Journal of Hazardous Materials*:

Esmaeel Kariminezhad, Maria Elektorowicz, Effect of various electrokinetic treatment regimes on solids surface properties and thermal behavior of oil sediments, Journal of Hazardous Materials, Volume 353, 2018, Pages 227-235

5.1 INTRODUCTION

The environmental challenges associated with the treatment and disposal of wastes generated by petroleum industries are related to all stages of processing, extraction and transportation. Residual sediments from oil wastewater are generally stored in tailing ponds, below or above the ground. The storage of a huge volume of oil sediments, and their treatment prior to disposal represent a significant technical challenge. Inadequately designed storage structures such as drainage, piping, and overtopping, can significantly affect operation and incur damage to the surrounding environment (Blight, 2009; Rico et al., 2008). This problem can be further exacerbated during other activities such as transport and disposal of oil sediments, thereby increasing the risk of water body contamination and the demise of aquatic life (Ayotamuno et al., 2007). Oil sediments and slurries represent a complex matrix comprising of 30-50% oil, 30-50% water and 10-12% solids (Da Silva et al., 2012; Jeeravipoolvarn et al., 2009; Mikula et al., 1996). A high water content contributes to the large volume of the material to be disposed of and renders the geotechnical properties of the oil sediments more intricate (Snars & Gilkes, 2009).

Chemically, oil slurries and wastewaters are very stable suspensions as a result of electronegativity and hydration of colloidal components (Guolin et al., 2009). The presence of immiscible liquids in oily wastes, results in the formation of water-in-oil emulsions. These emulsions are metastable due to the presence of a protective layer of fine clay which prevents them from coagulation or coalescence. Petroleum hydrocarbons (PHCs) such as asphaltenes and resins act as natural emulsifiers in these protective layers. Among other natural emulsifiers are various fine materials and oil-soluble organic acids that contribute to the stabilization of water-in-oil emulsions (Yang et al., 2008). Asphaltenes and resins contain hydrophilic functional groups that act as lipophilic emulsifiers. The structure of the water-in-oil emulsions is further stabilized by the pH of oil slurries which usually ranges between 6.5 and 7.5 (Elektorowicz et al., 2006). The formation of these stable water-in-oil emulsions poses a significant technical challenge for the separation and treatment of oil sediments (Heidarzadeh et al., 2010; Hu et al., 2013; Kilpatrick, 2012). The surface properties of solids in oil sediments also play an important role in the stability of the emulsions. Chen et al. (2017) showed the effect of non-uniform particles with varying hydrophobicity on emulsion stabilization. The ratio of asphaltenes to resins influence the stability of emulsions and their adsorption to solids (Sparks et al., 2003; Sullivan & Kilpatrick, 2002). Mineral particles show a significant effect on the emulsion stability (Binks & Lumsdon, 2000), while resins and asphaltenes associate to form colloidal aggregates (Sullivan & Kilpatrick, 2002). Asphaltenes interact through hydrogen bonding and π-bond overlap. Resins solvate asphaltene aggregates through polar functional group interactions. However, asphaltene colloidal aggregates associate to form an interfacial film. Primary asphaltene aggregates cross-link to form a rigid, viscoelastic structure at the oil-water interface. The process is further complicated by the adsorption of resin/asphaltene aggregates to hydrophilic particles. As more aggregates adsorb, the particles become preferentially wetted by the oil phase ($\Theta > 90°$). The presence of ionic bonding has also been shown between asphaltene/resin and clay surface (Sparks et al., 2003; Sullivan & Kilpatrick, 2002).

Considering the composition and structural complexity of oil sediments, their management can be divided into three categories: reduction of volume, recovery of useful fuels, and appropriate disposal (Hu et al., 2013). Different techniques have been developed to manage oily wastes such as centrifugation (Cambiella et al., 2006), solvent extraction (Zubaidy & Abouelnasr, 2010), microwave irradiation (Rajaković & Skala, 2006), ultrasonic treatment pyrolysis (Liu et al., 2009), photo-catalysis (Da Rocha et al., 2010), thermochemical treatment (Jin et al., 2012) and biodegradation (Ward & Singh, 2003). However, these techniques involve high maintenance, energy consumption and cost, long processing time, low separation of oil, and production of toxic by-products (Hu et al., 2013). These drawbacks are due to the presence of a large amount of stable emulsions as a result of solids covered with hydrocarbons which tend to resist treatment. Pre-treatment of oily sediments can be useful in destabilizing recalcitrant emulsions and increase the treatment efficiency. The electrokinetic process has been shown to be a cost-effective remediation technology to treat both organic and inorganic contaminated soils (Reddy & Cameselle, 2009a). It involves the application of a low voltage DC to a porous medium to separate different phases (water, hydrocarbons and solids) through electroosmosis and electrophoresis driven by an electric field. Recently, electrokinetic techniques have been applied to enhance the remediation oil-contaminated soils (Lim et al., 2016). This method can dewater oil sediments by nearly 63% and reduce light hydrocarbon content by about 43% (Elektorowicz et al., 2006). Studies have shown that an increasing frequency and magnitude of the applied DC voltage can effectively improve the phase separation of oily sediments (Ghazanfari et al., 2012; Pamukcu et al., 2016). However, so far no comparative study has been conducted to investigate the performance of different electrical types and the associated effects on solids surface properties.

The purpose of this research was to investigate the effects of electrokinetic processes on the surface properties of oil sediment conglomerates under different electrical current applications in lab-scale operated electrokinetic reactors. It is expected that the study outcomes would further help to improve management and treatment strategies for oil sediments by the electrokinetic method.

5.2 METHODOLOGY

The experimental set-up design and operation are explained in detail in section 3.3; therefore here, only some of the specific points during the adsorption tests are highlighted.

The application of four different types of direct current (DC) namely Constant Direct Current (CDC), Incremental Direct Current (IDC), Decremented Direct Current (DDC), and Pulsed Direct Current (PDC), was investigated on the electro-separation of oily sediments from refinery disposal wastes. Changes induced on the surface properties of the solids, their wettability alteration and contact angle were studied before and after application of the electric fields.

5.2.1 Setting-up of electrokinetic reactors

Four (4) 1.5-L electrokinetic reactors with stainless steel electrodes were set up. About 1500 g of lagoon oil sediment, collected from an oil refinery located in Montreal, Quebec, Canada, were placed in each reactor and subjected to the following types of electrical current using a DC power supply (BK Precision 1902, USA): a Constant DC (CDC), an Incremental or Decremented DC (IDC and DDC, respectively) which was generated by adjusting the voltage on a daily basis, and a Pulsed DC (PDC) generated by a function generator (BK Precision 4001A, USA) used to induce a DC offset. The resulting power was increased by an amplifier (model 7224 AE Techron, USA), which was connected to a 30 Hz Dual Trace Analog Oscilloscope (BK Precision 2120B, USA) to track electrical functions. A Digital Multimeter (Mastech MAS830, USA) was connected to electrical probes which were strategically positioned inside the electrokinetic reactors to measure voltage. The CDC reactor was designed by applying a potential gradient of 1 V/cm across the electrodes. The voltage gradient was chosen based on Elektorowicz and Habibi (2005), who found its suitability for very low permeable sludge, like was the case for lagoon sediments used in this study. For both Incremental (IDC) and Decremented (DDC) currents, a potential gradient ranging from 0.25 to 1.75 V/cm was applied while for the pulsed DC (PDC), a 0.5 V/cm current was used in combination with a 0.5 V/cm of DC pulse at squared frequencies of 60 Hz with a 1/5 pulse period. To enable a fair comparison of the effects induced by the four types of electrical current, the energy consumption was maintained at less than 2% for all operational scenarios. A control reactor was set up with no potential gradient.

5.3 RESULTS AND DISCUSSION

5.3.1 Wetting properties of oil sediments

Understanding the wettability of solids is important for oil recovery. The oil versus-water wetting preference may influence many aspects of reactor performance and oil recovery techniques. In the present study, the wetting properties of centrifuged sediment solids, toluene/THF solvent-extracted solids, and electrokinetically treated solids were evaluated (Fig. 5.1). The centrifuged sediments were found to contain 35% of water-wet solids while the solvent-extracted solids comprised of 57% of water-wet solids. The solids subjected to electrokinetic treatment, on the other hand, showed a varying extent of solids wettability depending on the electrical regimes applied and the location across the reactor. The DDC reactor showed the lowest water-wet condition at the top anode (~33% which was lower as compared to centrifuged solids) while the IDC resulted in the highest solids wettability at the bottom cathode (~75%). Hence, the application of the different electrical fields resulted in a change in the proportion of the water-wet solids in the sediment. It has been shown in a previous study that heterogeneous surface wettability can effectively alter the stability and dynamics of oil-in-water emulsions (Meng et al. 2016), with sediments having higher proportion of water solids forming less stable emulsions. The kinetic stability of emulsions is a consequence of small droplet size and the presence of interfacial films around the water droplets. Demulsification is very common in matrices containing unstable emulsions (Schramm, 2006). Electrokinetic treatment appeared to have altered the wettability of the sediment solids and increased the rate of solids sedimentation and demulsification of stable emulsions thereby inducing phase separation in the oily sediment.

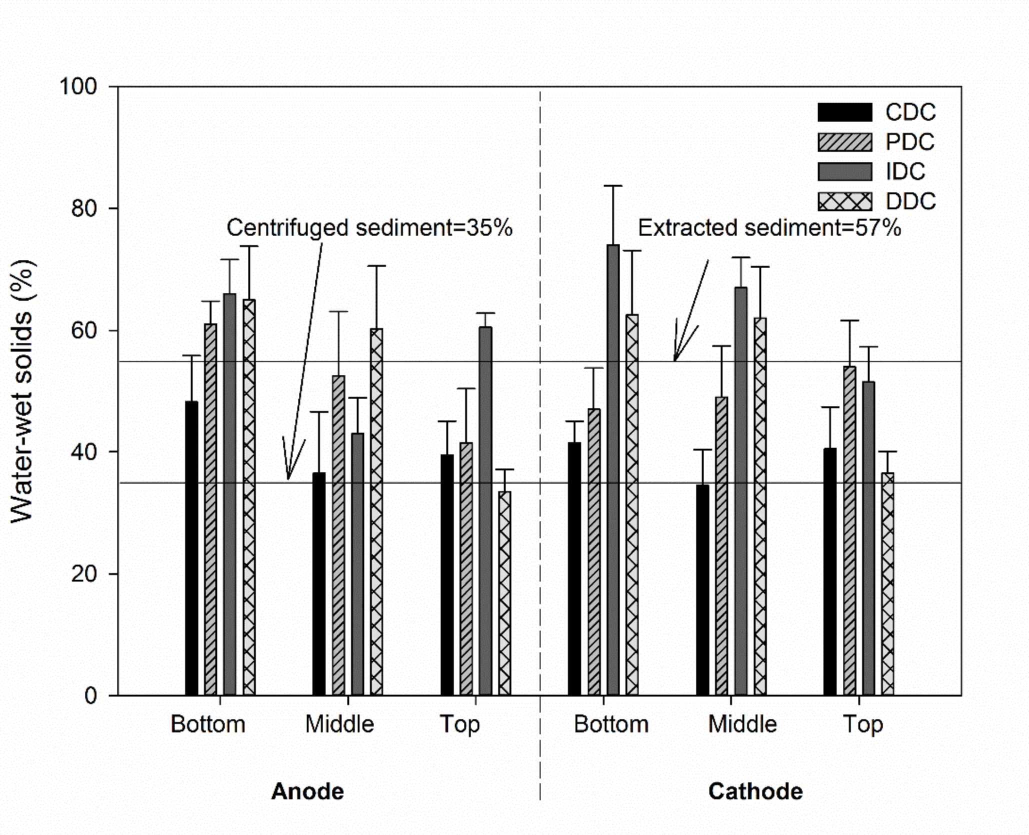

Fig. 5.1. Percentage (%) of water-wet solids in electrokinetically treated oil sediments. Centrifuged and toluene/THF extracted sediments were used as controls. CDC - Constant Direct Current, IDC - Incremental Direct Current, DDC – Decremented Direct Current, and PDC - Pulsed Direct Current. All samples were analyzed in triplicate (n=3).

The mechanisms involved in the wettability of solids may be complicated (Donaldson & Alam, 2013). One of the most important influential parameters is pH gradient resulting from the production of H^+ and OH^- ions. These ions have been shown to affect the zeta potential at low concentrations and alter the double layer of solids that interface with the liquid phase. Such alteration in structure and properties, in turn, impacts on the process of electrocoagulation and demulsification (Guo et al., 2011; Rodrigues Pires da Silva et al., 2015). In the present study, the pH of the sediments decreased to ~3 on the anode side and increased to ~10 on the cathode side. Similar observations have been reported in studies involving oil extraction from refinery reservoirs by the electrokinetic method where an increase in pH at the cathode led to a reduction in interfacial tension and an increase in the solubility of PAHs thereby enhancing ion exchange and double layer expansion (pore throat enlargement and permeability enhancement) (Alklih et al., 2014; Pamukcu et al., 2016). Ansari, et al. (2015) showed that an increase in acid concentration enhanced displacement efficiency and permeability due to increased electroosmotic, electromigration and electrophoretic effects. Similar mechanisms are believed to have induced a change in the wetting properties of the sediments in the present research.

5.3.2 Wettability alteration

The change in the wetting state of solids is an important aspect to consider during phase separation of oil sediments. One of the ways to assess wettability alteration is through the measurement of contact angle which is defined as the point at which the oil and water interface meet at the solid surface. It can effectively be used to analyze the alteration of surface wettability as it measures the shift in solid's surface affinity of one fluid to another (Morrow & Buckley, 2011). In general, a contact angle value greater than 90° indicates an oil-wet state while a contact angle of less than 90° describes a water-wet state. The neutral state is determined by a contact angle that is about 90°. The results showed that the four types of electrical current resulted in a contact angle greater than 90 ° which is indicative of an oil-wet state, except for the PDC which induced a water-wet state at the bottom anode ($\theta < 90°$). However, all the samples analyzed for the different electrical applications across the reactors showed contact angles of less than the centrifuged control sample (i.e. < 109.4°). Hence, the applied electrical currents induced a shift from more oil-wet towards more water-wet conditions. The solids at the bottom anode in the PDC reactor displayed the highest change in contact angle relative to the centrifuged sediment control (from 109.4° to 87.5°) and, hence showed the highest wettability alteration of its solids surface (Fig. 5.2).

The change in contact angle and wettability induced by the electrokinetic treatment may have been the result of modification in functional groups at the surface of the solids as well as the bonding formation between organic compounds such as asphaltenes and resins. Based on the wettability measurements, it appears that application of electrical currents led to the demulsification and dewatering of the oil sediments. The results of the contact angle measurements and wetting properties of the solids point to a decrease in the hydrophobicity of the solids' surface, a destabilization of the emulsions and a general tendency towards more water-wet solids. As shown in previous studies, a slight change in contact angle can result in a marked difference in the solid wetting properties and emulsion stability (Sullivan & Kilpatrick, 2002). Moreover, acidification of the solids might have resulted in the increase in higher hydrocarbon concentration at the anode(Li et al., 2005). The release of oil molecules from the surface renders the solids more water-wet, a condition which can effectively destabilize emulsions and minimize the coagulation of hydrocarbons and solid particles (Gu et al., 2003). Another mechanism which can drive the release of hydrocarbons attached to the electric double layer is viscous coupling that has been shown to separate the oil phase from bulk water by electroosmosis (Pamukcu et al., 2016).

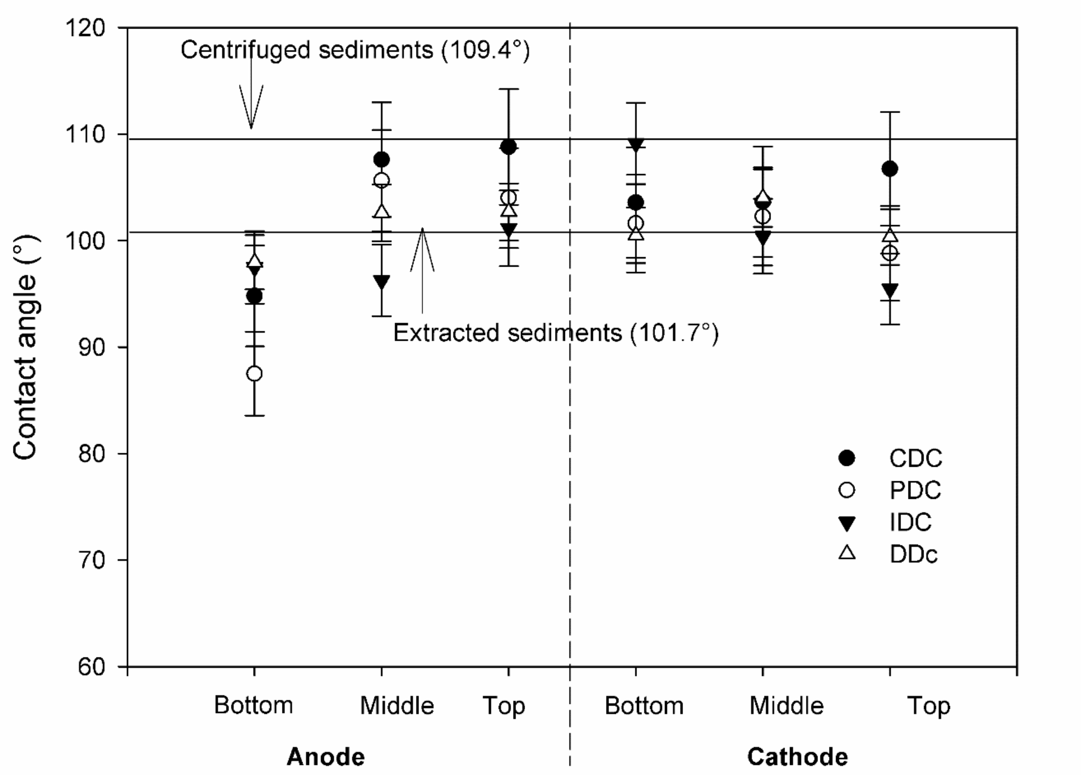

Fig. 5.2. Comparison of contact angles of electrokinetically treated oil sediments across the reactors. Centrifuged and toluene/THF extracted sediments were used as controls. CDC - Constant Direct Current, IDC - Incremental Direct Current, DDC – Decremented Direct Current, and PDC - Pulsed Direct Current. All samples were analyzed in triplicate (n=3).

5.3.3 Elemental properties of surface solids

XPS measurements were performed to study the elemental composition of the surface solids of the oil sediments. The anodic sediments were analyzed because most of the solids migrated to the anode following the application of the electric currents, and were, therefore, more representative of the overall solids surface properties. In addition to the electrokinetically treated sediments, the control samples (centrifuged and solvent-extracted solids) were also analyzed. Carbon was found to be the dominant chemical element in all electrokinetically treated sediments (Fig. 5.3). The carbon composition of the centrifuged sample was strongly concentrated at the surface with the percentage reaching 98%. The solids treated with the PDC showed the highest carbon content as compared to the other electrokinetic treatments.

Oxygen was the second most abundant element, after carbon, in all the electrokinetically treated samples with the DDC reactor showing the highest oxygen element level as compared to the other treatments and controls. According to previous studies, the presence of oxygen increases hydrophilicity of surface solids (Li et al., 2017a). The centrifuged sediments were found to contain a low level of oxygen as compared to the other sediment types. This shows that electrokinetic treatment and solvent extraction with toluene/THF caused an increase in the composition of oxygen in the surface solids. Studies have shown that a minor change in elemental composition of surface solids can induce a marked change in hydrophobicity/hydrophilicity and adsorption. Sivakumar and Somasundaran (1994) showed that even by changing the position of methyl and sulfonate groups on the aromatic rings can result in a change of the surface properties by several orders at the solid/liquid interface and alter the wettability of solids. In addition, the amount of acidic impurities (O, OH, C-O, C=O) in the oily waste can affect the oil and water interfacial tension [24, 31, 32].

The analyzed solids samples were also found to contain N, Fe, Al and Si (Fig. 5.3). The presence of Al and Si has been shown to enhance the hydrophilicity of surface solids (Sparks et al., 2003). Metal species such as Ni, Al, Ti, Co and Ag in oily sediments may also undergo oxidation during electrokinetic treatment (Virkutyte et al., 2002). Oxidation or reduction of ions induced by electrical currents may impact on the surface properties of oil sediments.

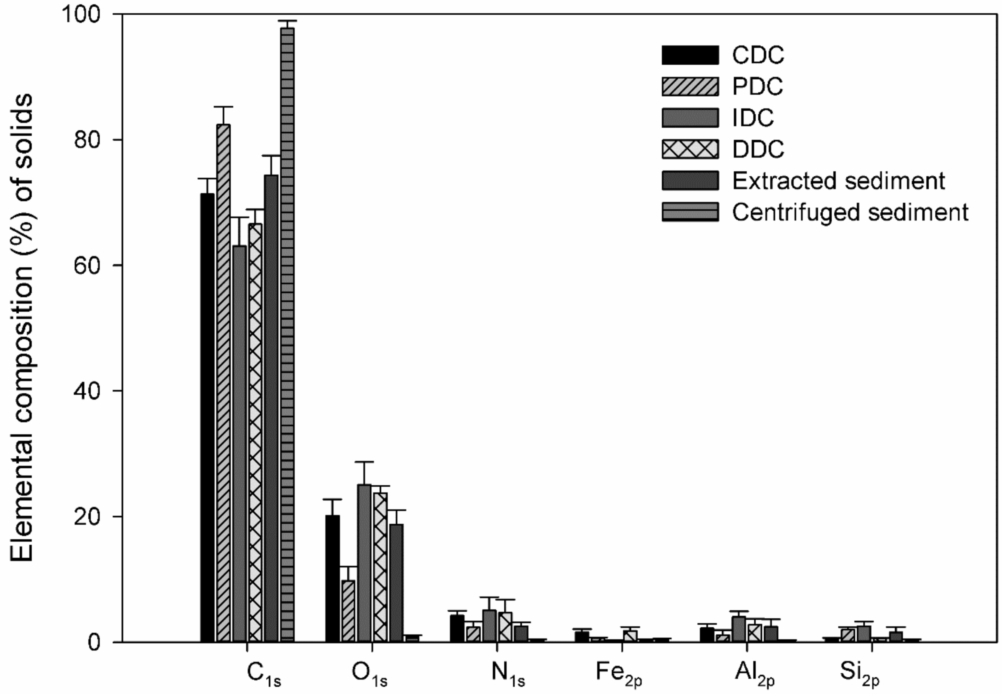

Fig. 5.3. XPS-determined elemental compositions of surface solids following electrokinetic treatment with CDC, PDC, DDC, and IDC. The elemental composition of the controls (centrifuged and solvent-extracted solids) are also shown. All samples were analyzed in triplicate (n=3).

Since the samples contained mainly carbon and oxygen, their bonding properties were investigated based on high-resolution binding energies from the XPS profiles. The element C, O and H have been shown to be mainly involved in particle wettability (Woche et al., 2017). In general, liquid transport is favored in a matrix with predominantly hydrophilic surfaces and is reduced with increasing percentage of hydrophobic surfaces. The approach in the present research has been adopted in previous studies to evaluate the percentage of different carbon-oxygen bonding (Al-Futaisi et al., 2007; Wang et al., 2010). Considering the carbon-containing functionalities, all the samples analyzed showed more or less similar profiles of C_{sp2} and C_{sp3} composition except the DDC reactor which showed a significant decrease in these elements (Table 5.1). On the other hand, the PDC reactor sediment contained the highest C-O-H/C-O-C bonding, while the solvent-extracted solids had the least composition of C-O-H/C-O-C bonding.

Table 5.1. Surface bonding properties of electrokinetically treated, centrifuged and solvent-extracted solids.

Sample	Carbon-containing functionalities (%)				Oxygen-containing functionalities (%)				
	C_{sp2}	C_{sp3}	C-O-H, C-O-C	O-C=O	O=C	O=C-OH	O-C=O	OH/-O-	chemisorbed oxygen
CDC	44.52	43.19	11.29	1	57.71	42.29	<1	<1	<1
PDC	36.7	24.68	38.62	<1	41.29	41.25	17.46	<1	<1
IDC	41.11	44.14	13.36	1.39	22.63	49.7	26.53	<1	1.14
DDC	<1	16.71	32.64	50.63	<1	32.50	27.32	2.18	37.87
Centrifuged sediments	44.86	33.20	21.58	0.36	36.37	22.81	30.54	10.27	<1
Extracted sediments	35.43	39.37	0.01	25.18	46.17	41.72	<1	11.96	<1

Note: Solids at the bottom anode were considered for assessment of the surface bonding properties of the electrokinetically treated sediments.

The change in some of the oxygen-containing functional groups was significant in the electrokinetically treated sediments as compared to the controls. The DDC sediment contained the lowest level of O=C bonding (<1%), but the highest level of chemisorbed oxygen (37.87%). Chemisorption of oxygen on the solids' surface following the application of DDC may explain the increased wettability of the sediment and enhanced efficiency of the phase separation. According to Aria (2013) chemisorbed oxygen can effectively increase the concentration of oxygenated groups by a process similar to oxidation as well as the O/C ratio and hydrophilicity. Woche et al. (2017) reported that a high O/C ratio is intimately linked to an enhanced surface wettability. Therefore, as the results showed enhance in surface wettability is not just related to the O/C ratio, type of carbon and oxygen functionalities had an effect on wettability. On the other hand, the presence of hydroxyl groups is indicative of demulsification during electrokinetic treatment and their accumulation at the cathode shows a decrease in the oil and water interfacial tension (Somasundaran & Zhang, 2006). DDC treated sediment showed the presence of hydroxyl groups (2.18%) as compared to the other electrical treatments where such presence was almost undetected (<1%). These observed phenomena may explain the efficiency of the DDC in inducing the most significant phase separation of the oil sediments (Chilingar et al., 1970).

5.3.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to evaluate the thermal properties of the solids across the electrokinetic reactors. Controls (non-centrifuged and centrifuged) were also analyzed. The thermograms for all samples showed a decrease in mass as the temperature increased (Fig. 5.4). Such loss in mass may have resulted from vaporization or chemical reaction forming gaseous products. The decomposition of the samples for all treatments and controls was not stepwise but entailed rather more or less constant decrease in mass. Volatile compounds such as water, residual solvents or low molecular weight hydrocarbons are evolved at relatively low temperatures while heavier hydrocarbons are subjected to combustion at higher temperatures. Based on the thermograms, it can be deduced that the analyzed samples consisted of different hydrocarbon fractions. In conventional fractionation, hydrocarbons can be divided to naphtha (boiling point <177 °C), kerosene (177 °C <boiling point < 343 °C), gas oil (343 °C <boiling point < 525 °C), vacuum residues(525 °C < boiling point < 700 °C) and cokes (boiling point >700 °C) (Yoon et al., 2009). The extent of weight loss over temperature for the CDC, IDC, PDC and DDC treated sediments differed across the different positions in the reactors hinting about the presence of different solid composition which may have resulted from their movement inside the reactors following the application of the different electrical currents. However, the thermal decomposition rates in terms of slopes shown in Fig. 5.5, were roughly the same for all the samples. The least weight loss (64%) was observed at the anode of the DDC reactor, which may have been due to the electrophoretic movement and sedimentation of solids toward the anode. Conversely, most weight losses occurred at the top cathode of the DDC reactor after 170 °C indicating the presence of a high concentration of hydrocarbons at that location.

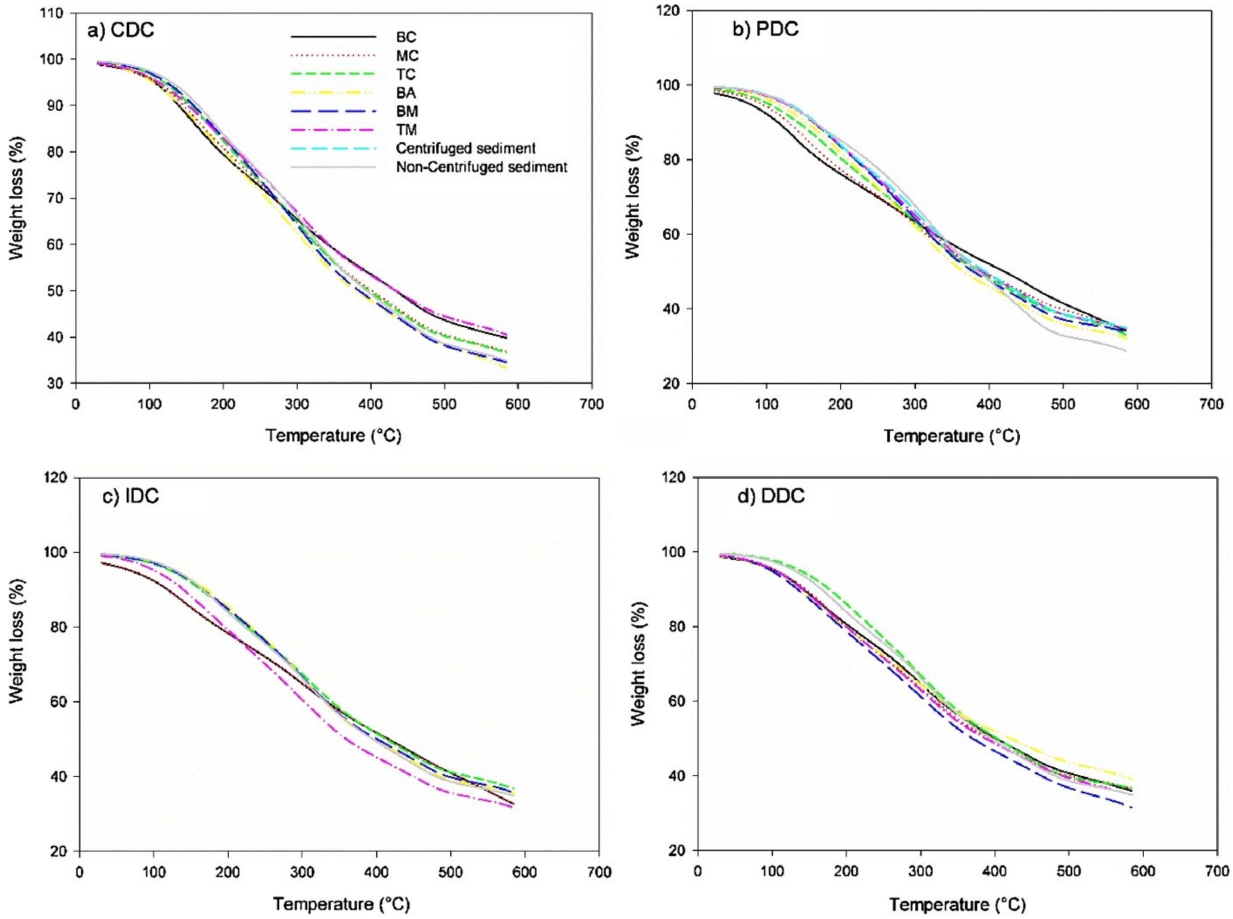

Fig. 5.4. Thermogravimetric analysis (TGA) curves of electrokinetically treated oil sediments with CDC, PDC, IDC, and DDC. Thermograms for the controls (non-centrifuged and centrifuged) are also shown. BC-bottom cathode, MC-middle cathode, TC-top cathode, BA-bottom anode, MA-middle anode, and TA-top anode.

To study the transformation undergone by the solids, differential thermogravimetric analyses (DTA) were performed (Fig. 5.5). All generated thermograms depicted roughly 3 troughs between 30 °C to 600 °C temperature range which may correspond to three phases. The first phase involved the vaporization of water and light hydrocarbons which occurred below 170 °C. Similar observations have been made by previous authors (Deng et al., 2016; Park et al., 2009). Non-centrifuged and centrifuged sediments showed similar thermal profiles indicating that centrifugation did not affect the solids. On the other hand, application of electrical currents shifted the curves to the left showing a change in the composition of the solids toward more light hydrocarbons. In the second phase, the volatile matter may have been discharged and combusted between 170 °C and 350 °C. Similar observations have been made by other studies (Deng et al., 2016; Li et al., 2017b). Most of the variations in the thermogram profiles occurred during this phase for the different electrokinetically treated sediments. Horizontal and vertical movements of the matrix such as movement of water to the cathode and bottom side of the reactors may explain such fluctuation. The third phase may have involved the oxidation and combustion of heavy organics between 350 °C and 600 °C. Such processes have been described by other authors during electrokinetic investigation of oil sediments (Park et al., 2009). The thermogram profile for the top cathode of the DDC reactor showed the least differential thermogravimetric variation hinting about a more homogeneous distribution of hydrocarbons in that location of the reactor.

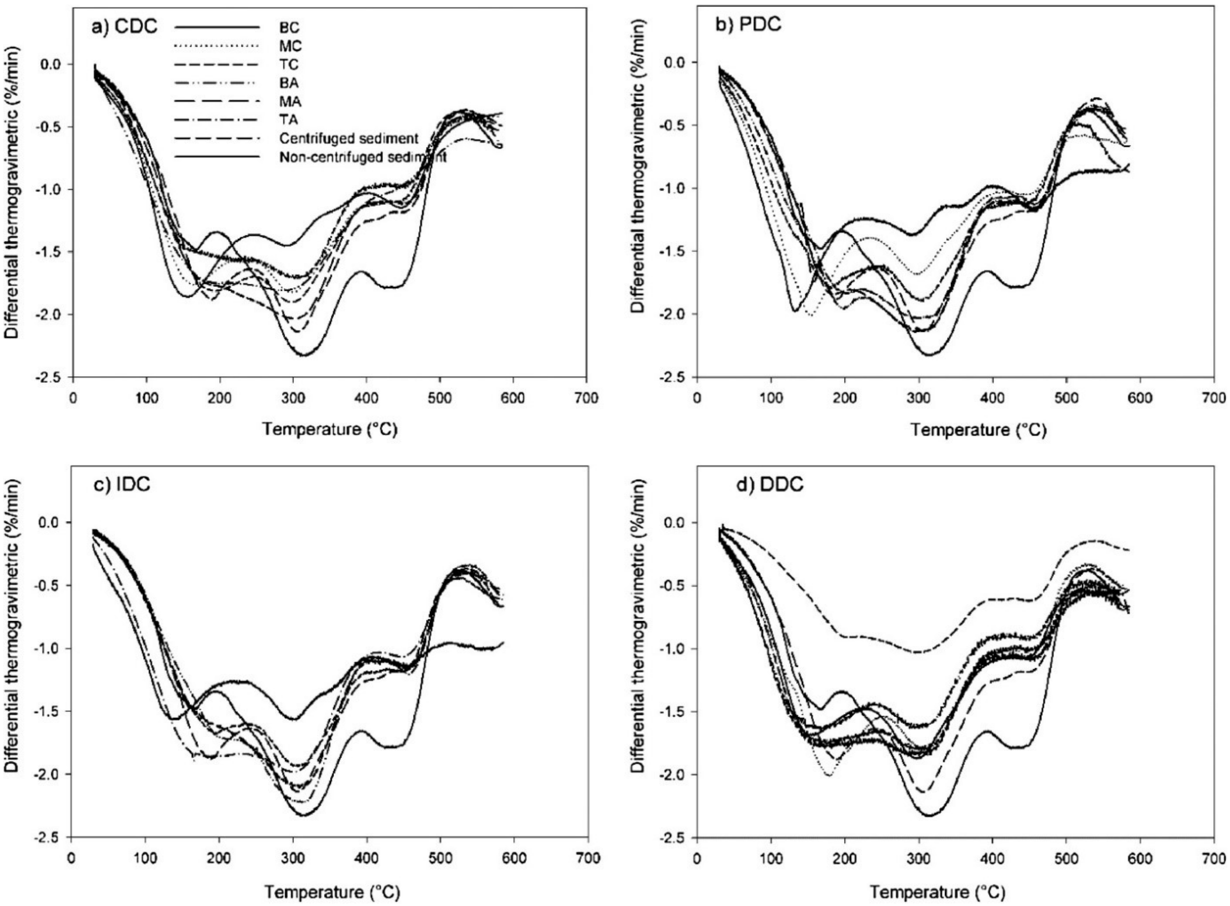

Fig. 5.5. Differential thermogravimetric (DTG) curves for electrokinetically treated oil sediments with CDC, PDC, IDC and DDC. The thermograms of the controls (non-centrifuged and centrifuged solids) are also shown. BC-bottom cathode, MC-middle cathode, TC-top cathode, BA-bottom anode, MA-middle anode, and TA-top anode.

5.3.5 Mineral composition

Since the DDC induced the most movement of solids to the anode, XRD analysis was performed on the resulting sediment sample to assess its mineral composition. The results show that quartz and feldspar (which include albite and calcian) were the most abundant minerals found in the DDC treated and control sediments (Table 5.2). Initial solids (non-centrifuged) contained 52.9 % of quartz and 47.1% of feldspar. After centrifugation, the concentration of quartz increased to 62.6% while the level of feldspar decreased to 37.4%. The main change in mineral composition was observed following the application of the DDC. The percentage of feldspar and quartz decreased at the bottom anode, while the composition of calcium sulfate, calcite, hematite and maghemite increased at the same electrode. Such change may have resulted from electrophoretic processes and the destabilization of the water-in-oil emulsions. The composition of feldspar significantly decreased to less than 1% at the top cathode while the level of calcium sulfate, calcite, hematite and magnetite increased.

Table 5.2. Mineral composition (%) of solids in non-centrifuged, centrifuged and DDC-treated oil sediments.

	Mineral composition (%)						
Sample	Feldspar	Quartz	Calcium Sulfate	Calcite	Hematite	Magnetite	Maghemite
Non-centrifuged	47.1	52.9	<1.0	<1.0	<1.0	<1.0	<1.0
Centrifuged	37.4	62.6	<1.0	<1.0	<1.0	<1.0	<1.0
DDC-treated BA	16.2	32.1	29.2	7.0	5.6	<1.0	10.0
DDC-treated TC	<1.0	20.0	19.8	36.2	2.3	21.2	<1.0

Note: DDC-Decremented Direct Current; BA-bottom anode; TC-top cathode

5.3.6 Microscopic analysis

The water-in-oil emulsion droplets from the non-centrifuged, centrifuged and DDC-treated oil sediments were visualized under the microscope (Fig. 5.6). Non-centrifuged samples contained different sized fine and coarse emulsion droplets (Fig. 5.6a). After centrifugation, most of the emulsion droplets decreased in size (< 5µm) forming a homogeneous matrix with finely dispersed droplets (Fig. 5.6b). A decrease in droplet size is associated with an increase in the kinetic stability of the emulsion, and is indicative of emulsification (Burakova et al., 2017). Application of the DDC to the centrifuged samples resulted in the coalescence of the finely dispersed emulsion droplets forming larger droplets (Fig. 5.6c). Hence, electrokinetic treatment caused spontaneous destabilization of the emulsion, a feature which is highly desirable in phase separation. The disappearance of small droplets and enlargement of droplets resulting in polydispersed coarse emulsions can affect the rheological properties of the sediment matrix and facilitate phase separation.

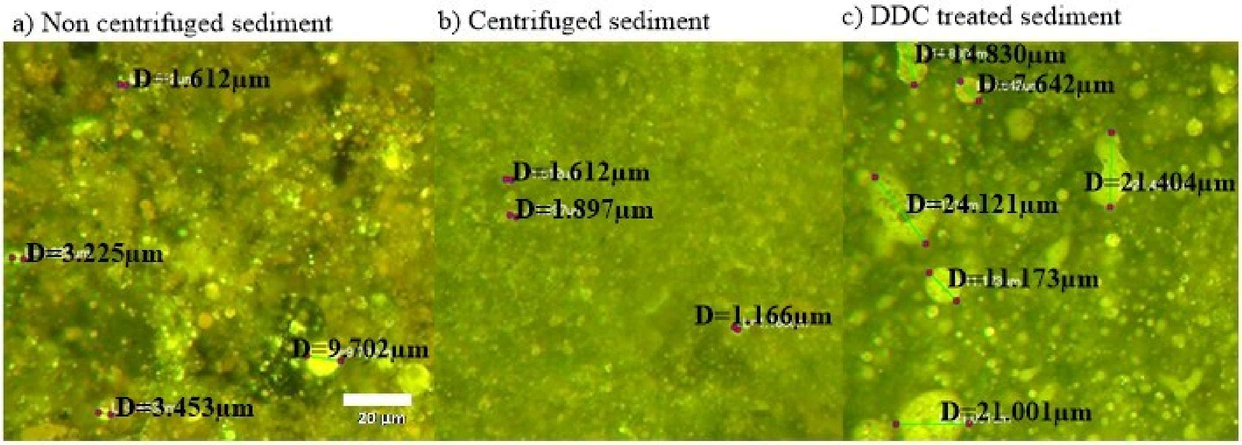

Fig. 5.6. Photomicrograph images of non-centrifuged (a), centrifuged (b), and DDC-treated (c) oil sediments. D-diameter.

5.4 CONCLUSION

The experimental data presented in this research showed that all four different types of electric currents (CDC, PDC, IDC and DDC) induced changes in the physical and chemical characteristics, and thermal behavior of the solids in the oil sediments during electrokinetic treatment. However, the DDC showed the highest efficiency in separating the different phases in the oil sediments. Changes in surface properties induced by reaction of electrolysis products, electroosmotic flow of the oil phase by viscous coupling and electrophoretic movement of solids to the anode were involved in the phase separation of the oil sediments.

5.5 STATEMENT OF NOVELTY

The paper assesses the impacts of incremental, decremental, pulse, and constant direct current on solids surface wettability alteration of oil sediments. To our knowledge, such data have never been generated for petroleum wastes. We show that this approach results in a better solids treatment than the conventional methods such as centrifugation and solvent extraction. The Journal of hazardous materials has been chosen because this new technique can be applied directly to petroleum waste define as hazardous materials (K048, K049 by The Resource Conservation and Recovery Act) which is significantly important for the petroleum industry, environmental engineers, ecologist and chemical engineers.

Evaluation of synthesized catalyst and TiO2 nanoparticles on the performance electrokinetic separation of oil sediments

Connecting Text: Further developing on the findings of chapters 4 and 5, in Chapter 6 the efficiency of the electrokinetic separation of oil waste phases was investigated in presence of titanium dioxide (TiO_2) nanoparticles and a synthesized carbon-based catalyst. Seven lab-scale electrokinetic reactors were operated. Three of the reactors contained Nano TiO_2 in oil sediments prior to electrokinetic separation at concentration of 50, 100 and 200 ppm. Another set of three reactors were used to treat oil sediments mixed with 50, 100 and 200 ppm of the synthesized carbon-based catalyst. A control reactor, where electrokinetic separation was conducted without additives was simultaneously operated. The results have also been compared with the centrifuged sample obtained from the oil refinery. The samples were subjected to wettability analysis, X-ray photoelectron spectroscopy (XPS), Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric (DTG). It was observed that the addition of Nano TiO_2 and synthesized carbon-based catalyst significantly improved the water removal and volume reduction capacity of the electrokinetic method. Better performance results were obtained with the synthesized catalyst compared to Nano TiO2. Hence, the synergistic effects of TiO_2 or synthesized catalyst with electrokinetic treatment can lead to better phase separation and may reinforce the current applications of the electrokinetic method in treating oil sediments.

The results of this research will be submitted to the Journal of *Environmental Engineering* under the title: “Evaluation of synthesized catalyst and TiO_2 nanoparticles on the performance electrokinetic separation of oil sediments”. The paper will be authored by Esmaeel Kariminezhad and Maria Elektorowicz.

6.1 INTRODUCTION

The activities of upstream and downstream petroleum industry result in the production of a significant amount of oil wastes. Uncontrolled disposal of these wastes represents a serious threat to the environment (Hu et al., 2013; Todd et al., 1999). The high amount of asphaltene and resin present in oily sludge wastes has been shown to alter the wettability of soils by reducing their hygroscopic moisture content, water retention and hydraulic conductivity (Manali & Shah, 2013). High molecular weight compounds from oily sludge have also been found to persist in the environment for a long period. Furthermore, they can form hydrophobic crusts that prevents the growth of plants or hinders water and air exchange in soils, which are crucial for the survival of soil organisms. This situation can significantly reduce the diversity of microorganisms playing a crucial role in soil ecosystems (Wake, 2005). Polycyclic aromatic hydrocarbons (PAH) contained in the petroleum waste are also of concern because of potential carcinogenic or teratogenic effects (Diya'uddeen et al., 2011; Giusti, 2009).

Storage of oily sludge and sediments for a prolonged period of time may present a high risk for leakage of hazardous compounds to the environment (Guolin et al., 2009). In conventional techniques, oil sediments are stored for a long period before they are treated and disposed. Studies have also shown that storage of oily waste can lead to air transmission of oily particles over long distances (Karamalidis & Voudrias, 2007). The possibility of atmospheric pollution through the release of volatile hydrocarbons (VOCs) also represents a risk to the natural environment and human health (Diya'uddeen et al., 2011; Hu et al., 2013).

It has been observed that unconventional means of crude oil extraction processes (e.g. oil sands and shale) are gaining wider acceptance over conventional methods due to the larger volume of oil that can be produced (BP, 2016). However, unconventional extraction techniques generate low API (American Petroleum Institute) oils that contain higher concentrations of undesirable resins and asphaltenes (Mohr & Evans, 2010). In North America, it is expected that the oil production will increase by 9 Mb/d by 2035, representing an increase of 49% compared to the actual situation (BP, 2016). This will significantly increase the volume of sludge wastes, and the handling and disposal costs associated with it. Hence, more advanced technologies are required to efficiently treat and/or reduce the quantity of oily sludge waste in order to reduce their impacts on environmental receptors.

The electrokinetic (EK) method has emerged as an effective way of treating oily sludge waste by altering the physical and chemical characteristics, as well as thermal behavior of the solids in oil sediments after centrifugation (Kariminezhad & Elektorowicz, 2018b). The electric field distorts and thus weakens the film of emulsifier surrounding the water droplets. And change in voltage weakening the film so that it breaks more easily when droplets collide (Bobra, 1990). In the current study, the effect of nanoparticles or synthesized carbon-based catalysts in combination with EK treatment has been assessed in view of elucidating whether nanoparticles or synthesized carbon-based catalysts have a potential to improve the phase separation in oil sediments. The electric field disturbs the interfacial film by rearranging the polar molecules, thereby weakening the rigid film and enhancing coalescence. At the same time interfacial material like nano particles can move the minerals that tend to form a rag layer, especially siderite, pyrite, magnetite, rutile, and anatase, from the oil/water interface to the underflow (Kailey & Behles, 2015).

Nanoparticles have been extensively used for clean-up of wastes and combine characteristics such as enhanced reactivity, surface area, sub-surface transport and sequestration abilities (Brar et al., 2010; Shan et al., 2009). In the present research, titanium (Ti) in its metallic form and a synthesized carbon-based catalysts have been used, due to their ability to increase conduction and convection coefficients, thereby, enhancing electrical field (Buongiorno, 2006; Zawrah et al., 2015). Major factors influencing the enhancement of electrical conductivity are pH value in relation to isoelectric point (IEP), as well as monodispersity. Previous studies showed that nanoparticles can act as demulsifiers by bridging protective layers in emulsions (Fedushchak et al., 2014). Nanoparticles can also change the wettability of solids and penetrate low permeable layers within solids (Karimi et al., 2012; Kariminezhad & Elektorowicz, 2018a). Studies show the effectiveness of nanocatalysts in viscosity reduction of bitumen compared to the cases in which no nanoparticles were implemented (Hashemi et al., 2014). Metallic nanoparticles exhibit pronounced demulsifying behavior and bear a unique morphology that allows it to change the wettability of solids (Fedushchak et al., 2014). Titanium dioxide (TiO_2) also has the capability to alter the wettability of solids and is rather inexpensive and environmentally friendly (non-toxic and having catalytic ability). Titanium dioxide is also stable in the presence of different ionic salts (Ehtesabi et al., 2013).

Carbon can be chemically functionalized and/or decorated with metallic nanoparticles and enzymes to impart or improve novel catalytic activity (Lam & Luong, 2014). Metal carbon catalyst like the Al2O3/ carbon showed the ability to convert cellulose into sugar alcohols (Wilson & Lee, 2014). Charged nano particles can attract more polar components from the oil bulk to adsorb the nano particles' surface. This synergistic effect reduced considerably the polar components' concentration in the bulk (Xu et al., 2018), which further increased the water chemical potential in the oil and decreased the chemical potential difference between the bulk oil and bulk water, thus led to less water trapping and droplets. Injecting particles 1-100 nm in size reduced the viscosity of oil, allowing for greater mobility of fluids and better separation (Ayatollahi & Zerafat, 2012).

To the best of our knowledge, there are no studies about combing the effect of nanoparticles with EK system on separation efficiency, emulsion destabilization and water removal from oil sediments. This study evaluates the addition of a new synthesized carbon-based catalyst to improve the separation efficiency. The results have been compared with the control EK reactor without additives and with centrifuged samples obtained from the oil refinery.

6.2 METHODOLOGY

The experimental set-up design and operation are explained in detail in sections 3.4 and 3.5.

6.3 RESULTS AND DISCUSSION

6.3.1 Efficiency of EK treatment

The efficiency of EK application was assessed by the reduction in volume of the sludge matrix after treatment. The centrifuged residual solids were determined by measurng the weight before and after EK treatment. The highest volume reduction (82.5%) was achieved in reactor with 200 ppm synthesized carbon-based catalyst (Fig. 6.1) which suggests better demulsification in this reactor compared to the others. The control reactor (EK treatment without additives) had the lowest volume reduction showing the importance of synthesized catalyst or nano TiO_2 in changing the surface properties of the solids (Ehtesabi et al., 2013). The water droplets become polarized and tend to align themselves with the lines of electric force. In so doing, the positive and negative poles of the droplets are brought adjacent to each other. Electrical attraction brings the droplets together and causes them to coalesce (Xu et al., 2018).

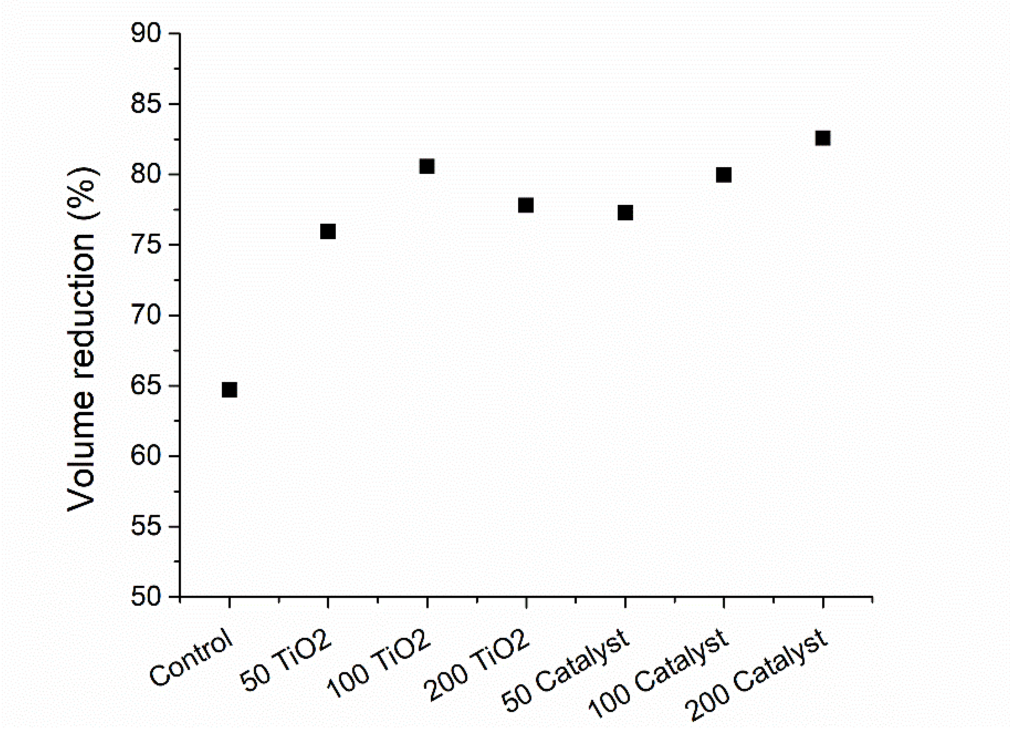

Fig. 6.1. Comparison of water wet solids in 4 sections of EK reactor compared with initial sediments and centrifuged sediments. Control (without addition of additives), 50 TiO_2 (sludge with 50 ppm TiO_2), 100 TiO_2 (sludge with 100 ppm TiO_2), 200 TiO_2 (sludge with 200 ppm TiO_2), 50 Catalyst (sludge with 50 ppm catalyst), 100 Catalyst (sludge with 100 ppm catalyst), and 200 Catalyst (sludge with 200 ppm catalyst).

6.3.2 Non-destructive analyses

The characteristics of the oil sediments were monitored through non-destructive analysis to evaluate phase separation induced by EK with different concentrations of TiO_2 or synthesized carbon-based catalyst (Fig. 6.2). The non-destructive analysis was done based on measuring resistance change in the sediment matrix during the experiment. Destructive testing included conductivity and phase separation assessment after completion of each experiment. The resistance difference was measured at the bottom and the top layer of each reactor. At the beginning of the process (Day 0), no resistivity difference was observed. After 2 days of operation (Day 1 and Day

2) a significant change in the resistivity was found. This suggests that the separation of water, oil, and solids may have been induced by processes such as electro-demulsification and electro-sedimentation (Kariminezhad & Elektorowicz, 2018b). The higher slope on the anode side of all reactors indicates electrophoretic movement of solids toward to the anode (Kariminezhad & Elektorowicz, 2018a). Unlike other reactors where there was no significant difference between the resitivity in the top and bottom layer, reactor with 200 ppm catalyst showed a different trend at the start of the EK treatment, where an obvious difference in resistivity was observed. This might be due to the presence of the synthesized carbon-based catalyst, which may have contributed in the destabilization of emulsions, thereby resulting in sedimentation of solids.

The separation of charges is known as the interfacial electrical double layer. Electrical field can shrinkage the double layer. This shrinkage can decrease the stability of the emulsions. These charge may originate from several sources such as: (1) inclusions of extraneous atoms in the lattice structure, (2) dissolution of slightly soluble atoms at the surface of water, (3) chemical reaction (chemisorption) of ions in water with surface atoms forming complex polar molecules on the surface, or (4) exposure of metallic oxides at the surface which react with water to form surface ions. These are some of the major causes of surface charges; others are recognized in suspensions of particles and flocculants in water (Hunter, 2013).

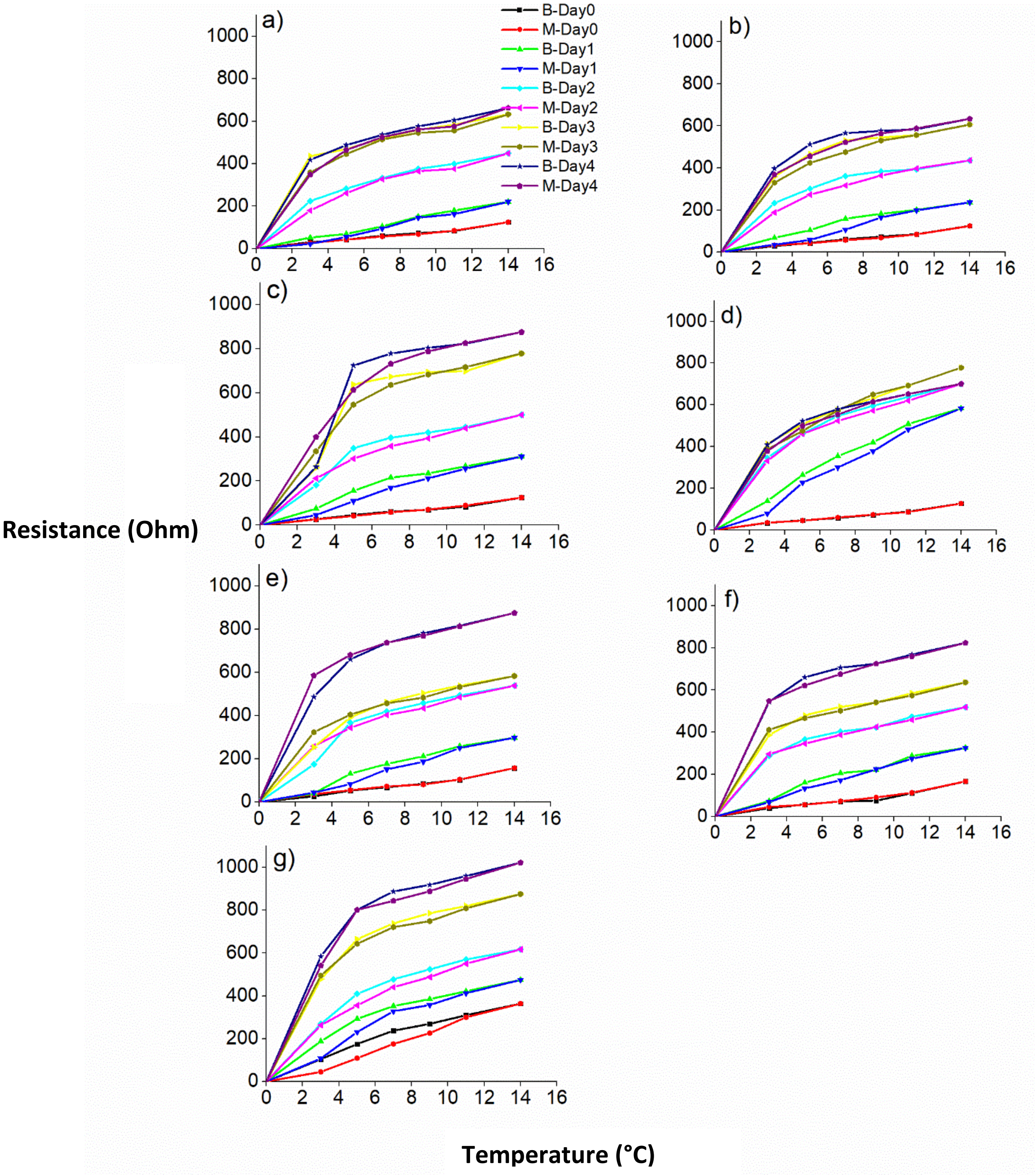

Fig. 6.2. Non-destructive resistance analysis during EK treatment of the sludge. a) Control (reactor without any nanoparticles or catalyst), b) 50 TiO_2 (sludge with 50 ppm TiO_2), c) 100 TiO_2 (sludge with 100 ppm TiO_2), d) 200 TiO_2 (sludge with 200 ppm TiO_2), e) 50 Catalyst (sludge with 50 ppm catalyst), f) 100 Catalyst (sludge with 100 ppm catalyst), and g) 200 Catalyst (sludge with 200 ppm catalyst).

6.3.3 Solids behavior after EK treatment

Solids in oil sediments and sludge are the main contributors to emulsion's stability. Destabilization of such emulsions is possible by changing the solids surface properties. The efficiency and mechanisms behind the EK treatment of oil sediments were evaluated by measuring water/solids ratio, solids wettability, contact angle, and XPS analyses (Fig. 6.3). The results were compared with EK treated samples without additives and centrifuged samples obtained from the oil refinery. The results indicate that the water/solids ratio was significantly changed due to addition of nanoparticles or synthesized carbon-based catalyst after EK treatment in all reactors. The initial water/solids ratio before EK treatment was 52.5%; it decreased to 10.46% after centrifugation and further reduced to 5% with EK treatment (without addition of additives). Additon of TiO_2 and synthesized carbon-based catalyst further decreased the water/solids ratio. The lowest ratio was observed for reactor with 200 ppm of catalyst with a value of 3.38%. The majority of solids after EK treatment migrated to the anode (Fig. 6.3a). The matrix at the anode in all the reactors had lower water/solids ratio compared to the 10.46% of centrifuge treated sample (control). The water-solids separation efficiency was assessed by changing the concentrations of both nanoparticles and the synthesized carbon-based catalyst from 50 to 200 ppm. EK reactor with synthesized carbon-based catalyst of 200 ppm demonstrated the best separations of solids among all EK reactors containing additives while reactor with 100 ppm TiO_2 showed the best performance among the reactors using only TiO_2.

To evaluate the effect of electrokinetic phenomena (e,g, electroosmosis and electrophoresis) on the separation process, the change in pH in the reactors was monitored (Figure 6.3b). Reduction in interfacial tension and an increase in the solubility of PAH can occur when the pH gradient increases (Yang & Lee, 2009). Acidity can change chemical bonds on solids surface (Guo et al., 2011) and improve the demulsification (Kariminezhad & Elektorowicz, 2018b). Due to the application of electric field, electrolysis takes place and H^+ and OH^- ions are generated at anode and cathode, respectively, leading to a pH gradient (Cameselle et al., 2013). In the present study, all reactors had similar trends of the pH distribution, with a low pH at the anode and a high pH at the cathode.

Solids wettability analysis showed more water-wet solids and better separations (Fig 6.3c). Change in the wettability of a rock surface from oil-wet to water-wet or water-wet to strongly water-wet would increase the oil mobility (Onyekonwu & Ogolo, 2010). The EK reactor with 200 ppm of synthesized catalyst displayed more water-wet solids leading to better separation of phases. The division of reactor content on 4 sections between electrodes permitted to assess water-wet solids distribution due toelectrokinetic phenomena (Kariminezhad & Elektorowicz, 2018a). Section 4 of the EK reactor with 100 ppm TiO_2 nanoparticles and EK reactor with 200 ppm of synthesized carbon-based catalyst had the highest water-wet solids of 66% and 63%, respectively (Figure 4.c) due to electroosmosis. The TiO_2 concentration of 100 ppm affected the wetting properties of the solids by increasing the water-wet solids from 32.5 % to 53% in section 1 due to electrophoretic movements (Kariminezhad & Elektorowicz, 2018b). Ehtesabi et al. (2013) suggested that wettability alteration (from super hydrophobic to super hydrophilic) occures when using TiO_2 nanoparticles. In this process, at the surface of TiO_2 nanoparticles, the water molecules occupy oxygen vacancies and produce OH groups, which make the surface hydrophilic.

Contact analysis was applied to a section close to the anode ,where more than 70 % of the solids were moved (Fig. 6.3d). Sections 1 and 2 (anode) in all of the reactors showed a lower solid contact angle compared to the centrifuge treatment. Closer to anode the contact angle reached the lowest value in all reactors; which suggests the ability of the EK system to change the surface properties of the solids. By adding the synthesized catalyst in section 1 (instead of TiO_2), the contact angle values decreased further. The contact angle is an indicator of of stable solids in oil wastes (Kariminezhad & Elektorowicz, 2018b); as previous studies showed, with decreasing the contact angles, the water/solids ratio increased (Kariminezhad & Elektorowicz, 2018b), leading to better separation of phases in oily sludge.

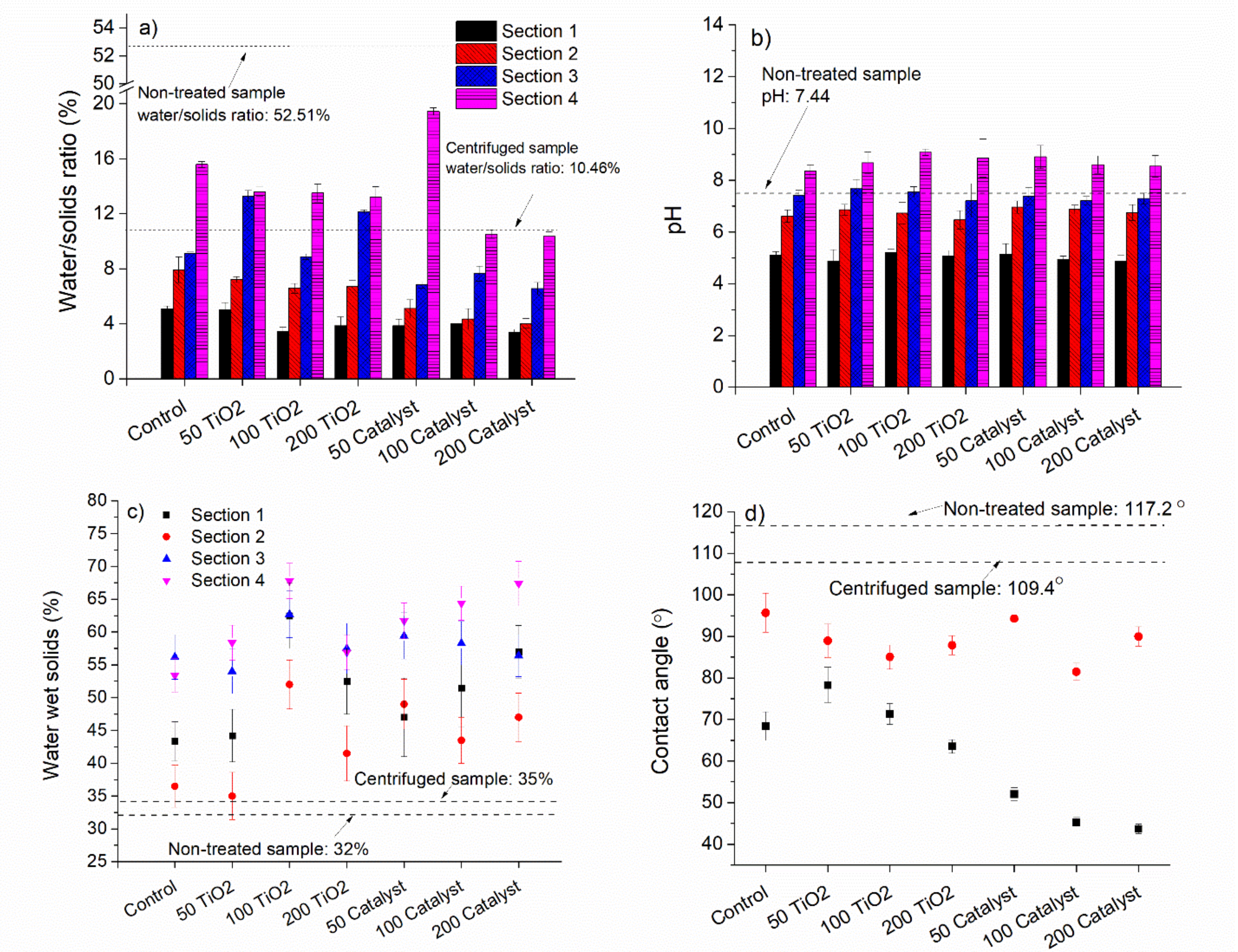

Fig. 6.3. Distribution of: a) Water/solids ratio, b) pH, c) water wet solids, d) contact angle degree in four sections of all EK rectors, legend in panel a also applies to panel b and legend in panel c also applies to panel d. Anode side (section 1), middle anode (section 2), middle cathode (section 3) and cathode side (section 4).

One possible cause of changes in contact angle and wettability during electrokinetic treatment might be due to the modification of functional groups at the solids surface. Also, bond formation between organic compounds such as asphaltenes and resins might be another possible reason. Based on the wettability measurements, it appears that application of additives beside electrical currents led to the demulsification and dewatering of oil sediments. The results of the contact angle measurements and wetting properties of the solids led to a decrease in the hydrophobicity of the solids' surface, destabilization of the emulsions and more water-wet solids. As shown in previous studies, a slight change in contact angle can result in a noticeable difference in the solid wetting properties and emulsion stability (Kariminezhad & Elektorowicz, 2018b). The electric field disturbs the interfacial film by rearranging the polar molecules, thereby weakening the rigid film and enhancing coalescence. At the same time interfacial material like nano particles can move the minerals that tend to form a rag layer, especially siderite, pyrite, magnetite, rutile, and anatase, from the oil/water interface to the underflow (Kailey & Behles, 2015).

XPS measurements were performed to study the elemental composition of the surface solids of the anodic oil sediments where most of the solids migrated due to electrokinetic phenomena ; therefore, the anodic oil sediments were used as a representative for overall solids surface properties. According to the XPS results (Table 6.1), the concentration of carbon, being the dominant chemical element in all electrokinetically treated sediments, decreased on the surface of the solids at section 1 of reactors with 100 ppm TiO_2 (74%) and with 200 ppm synthesized carbon-based catalyst (49%) compared to the untreated sample that was around 99%. The presence of TiO_2 on the surface of solids in section 1 (anode side) of the reactor specifies the ability to use TiO_2 as a demulsifier for water-in-oil emulsions. The presence of Ti^{2+} and Fe^{2+} might increase the production of hematite, maghemite, and anatase. According to Kailey and Behles (2015) TiO_2 can decrease the stability of water-in-oil emulsions. Oxygen was the second most abundant element, after carbon, in all samples. In EK reactor containing 200 ppm catalyst the highest oxygen element level of almost 40% was observed compared to other reactors and the control reactors. According to previous studies, the presence of oxygen increases the hydrophilicity of surface solids (Li et al., 2017a). These results can confirm the lowest water content of remaining solids in the anode side in Fig. 6.3a. The analyzed solids showed some N, Fe, Al and Si contents (Table 6.1). Studies show that the presence of Al and Si have an impact on enhancing the hydrophilicity of solids surface (Sparks et al., 2003). The results confirmed that addition of catalyst and nanomaterial does not change category of sludge classification.

Table 6.1. Elemental compositions (XPS-determined) of solids surface in the anode area in EK reactors with 100 TiO_2 ppm and 200 ppm synthesized carbon-based catalyst. Surface properties of catalyst is also provided.

Elements %	Produced Catalyst	Section 1 of 100 TiO_2	Section 1 of 200 Catalyst
C1s	54.57*	74.44	49.67
O1s	25.46	18.31	39.86
Fe2p	0.80	1.68	2.54
N1s	3.07	2.21	2.66
Cl2p	0	0.77	0.97
Si2p	4.50	1.22	2.36
S2p	0.71	1.55	1.1
Ti2p	0.08	0.49	0
P2p	2.20	0	1.2
Al2p	6.47	0	0
Ca2p	1.74	0	0
Mg1s	0.60	0	0
Na1s	0.23	0	0

Note: *values are arithmetical means of 3 experimental runs

6.3.4 Thermalgravimetric analysis of EK treated samples

Thermogravimetric analysis (TGA) was used to evaluate the thermal properties of the solids across the electrokinetic reactors including the controls (EK treatment without additives and centrifuged samples obtained from refinery). All thermograms showed a decrease in mass when the temperature was increased (Fig. 6.4). The main reason behind decreasing mass might be due to vaporization and chemical reactions that yield volatile products. The mass loss for all samples (treatments and controls) was not stepwise but involved a constant decrease. Similar results were also obtained in chapter four of this thesis, where it was demonstrated that water vapor and volatile compounds such as residual solvents or/and low molecular weight hydrocarbons vaporized at relatively low temperatures while heavier hydrocarbons were subjected to combustion at higher temperatures. Based on the thermograms, it can be concluded that the analyzed samples consisted of different hydrocarbon fractions. Their presence led to different extents of weight loss in each section of the reactors. Although, the lowest weight loss (reached to 48% of initial weight) was observed at the anode of the reactor with 100 ppm of synthesized carbon-based catalyst, the reactor with 200 ppm of synthesized carbon-based catalyst, had a low weight loss (of almost 42% of initial weight) at both sections 1 and 2 (anode side). The water droplets become polarized and tend to align themselves with the lines of electric force. In so doing, the positive and negative poles of the droplets are brought adjacent to each other. Electrical attraction brings the droplets together and causes them to coalesce (Xu et al., 2018). Thermal decomposition showed less weight loss at the anode in all reactors, which may have been due to electrophoretic movement and sedimentation of solids toward the anode. The difference between the weight losses in different reactor sections confirmed the separation of phases in the EK reactors. Reactors with catalyst showed more difference in weight loss compared to reactors supplemented with TiO_2.

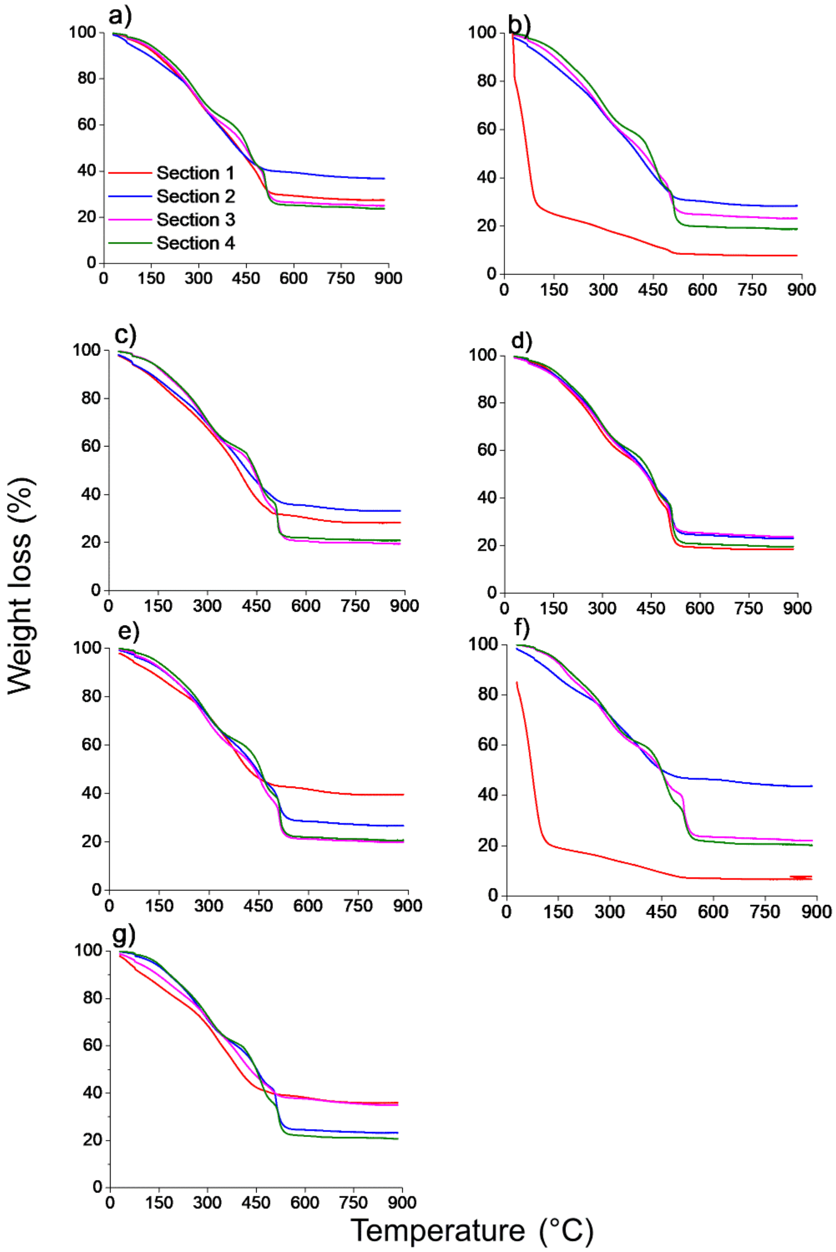

Fig. 6.4. Thermogravimetric analysis (TGA) curves of electrokinetically treated oil sediments in four sections of the reactors with TiO_2 and synthesized catalyst, a) Control (reactor without any nanoparticles or catalyst), b) 50 TiO_2 (sludge with 50 ppm TiO_2), c) 100 TiO_2 (sludge with 100 ppm TiO_2), d) 200 TiO_2 (sludge with 200 ppm TiO_2), e) 50 Catalyst (sludge with 50 ppm catalyst), f) 100 Catalyst (sludge with 100 ppm catalyst), and g) 200 Catalyst (sludge with 200 ppm catalyst). Anode side (section 1), middle anode (section 2), middle cathode (section 3) and cathode side (section 4).

Differential thermogravimetric analyses (DTA) evaluated the transformations undergone by solids in the EK reactors (Fig. 6.5). The thermograms show 3 distinct stages between 30 to 600 °C due to existence of three troughs: <170 °C, between 160 and 380 °C and between 380 and 600 °C.

6.3.4.1 Elimination of moisture stage

The weight loss in this stage is 18–20wt.% (except section 4 of reactor b and f) of the original weight; the proximate analysis shows that there is 80.12wt.% of moisture in non-treated sample, so it can be concluded that the major fraction of volume reduction of reactors is mainly related to vaporization of water and light hydrocarbons which occurs below 160 °C. Similar observations have been made by previous authors (Deng et al., 2016; Kariminezhad & Elektorowicz, 2018b; Park et al., 2009). The shift of the curves towards the left (Fig. 6.5) indicates a change in the composition of the solids toward lighter hydrocarbons. Similar observations were also observed in chapter 4 of this thesis where different electrical regimes were applied to oily sludge.

6.3.4.2 Lower temperature stage

A second stage of mass decrease is observed between 160 and 380 °C and involves a very important weight loss (around 35wt.% of the original weight) mainly related to volatilization and decomposition of volatile matter in the oil sludge. Most of the variations in the thermogram profiles occurred during this phase for the different electrokinetically treated oily sludge. Horizontal and vertical movements of the matrix such as movement of water to the cathode and bottom side of the reactors may explain such fluctuations. The DTG curves in the second stage contain several peaks. One possible reason for the multi-peak curves might be due to the presence of complex organic matter available in the sludge and their different boiling points and physical or chemical properties (Deng et al., 2016; Liu et al., 2009).

6.3.4.3 Higher temperature stage

A third stage of mass decrease is observed between 380 °C and 600 °C with a relatively small weight loss (around 12wt.% of the original weight). The temperature corresponding to maximum weight loss rate in this stage is at 500°C (Fig. 6.5). The weight loss of oil sludge in this temperature range might be mainly attributed to the oxidization of heavy organic compounds into low-molecular-mass gas and oil products. It was observed that the final pyrolysis residue is approximately 53–55wt.% of the original weight. Studies have shown that all of these phenomena are closely related to the structure characteristics and the surface properties of the oil sludge particles (Cheng et al., 2018; Park et al., 2009).

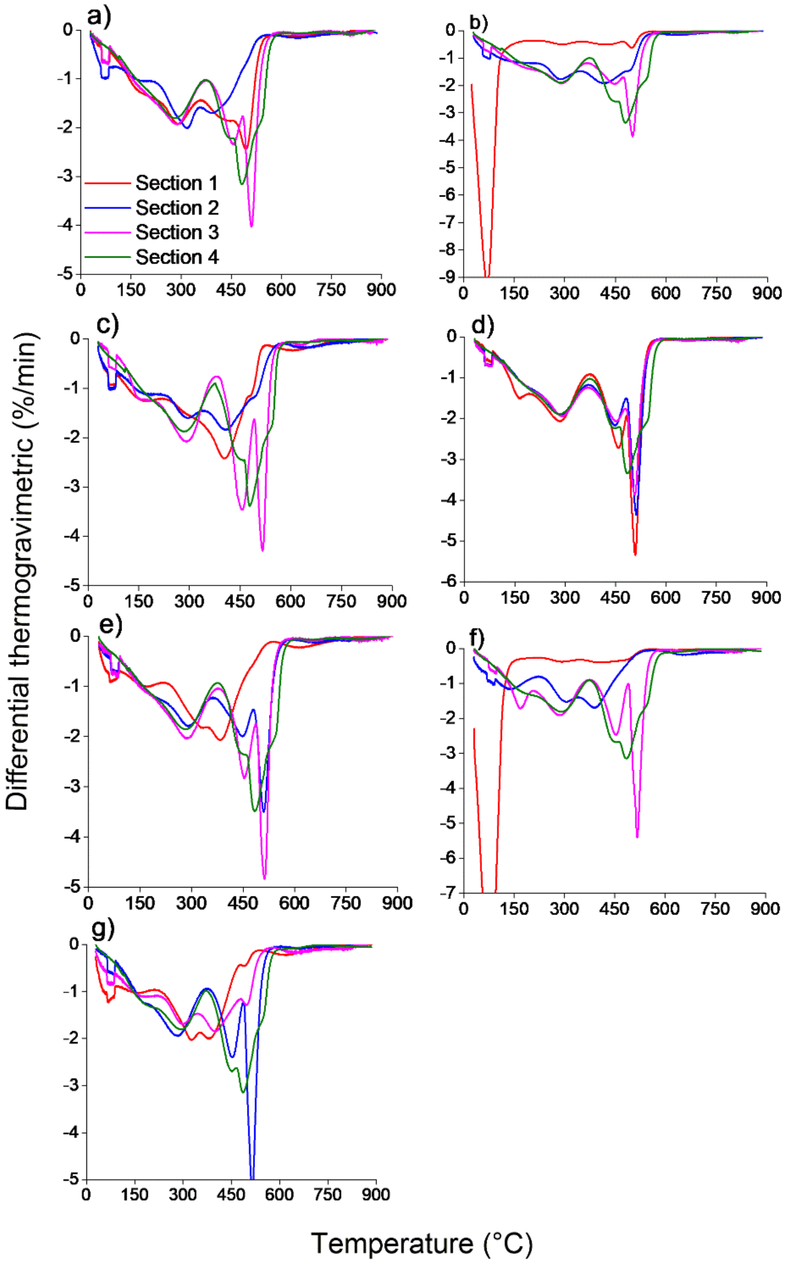

Fig. 6.5. Differential thermogravimetric (DTG) curves for electrokinetically treated oil sediments in four sections of the reactor with TiO_2 and synthesized catalyst. a) Control (reactor without any nanoparticles or catalyst), b) 50 TiO_2 (sludge with 50 ppm TiO_2), c) 100 TiO_2 (sludge with 100 ppm TiO_2), d) 200 TiO_2 (sludge with 200 ppm TiO_2), e) 50 Catalyst (sludge with 50 ppm catalyst), f) 100 Catalyst (sludge with 100 ppm catalyst), and g) 200 Catalyst (sludge with 200 ppm catalyst). Anode side (section 1), middle anode (section 2), middle cathode (section 3) and cathode side (section 4).

6.3.5 Analysis of kinetics

Kinetic studies were performed by measuring the conversion of the material as a function of temperature over different periods. Activation energy can give detailed information about the critical energy required to surmount an energy barrier and start a reaction (Eq. 3.15). To measure the activation energy, the region should be divided into the sections including the peaks which represent the maximum rate loss of mass. Measured activation energy of samples at 4 sections of the reactor is presented in Table 2. The mass-loss process of treated samples could be divided into three steps: the first step occurs between 25 and 160 °C, where water volatilizes; in the second step, relatively light organic substances volatilize and desorb at 160 to 380 °C, while the third step is between 380 and 600 °C, where the heavy organic substances crack.

The results showed that activation energy changed in all sections of the reactors. For all treatments, the activation energy decreased comparing to the control reactors. Reactor with 200 ppm of synthesized carbon-based catalyst showed the lowest activation energy among all the reactors. Generally, it is believed that a supplemental catalytic activity lowers the activation energies. This is assigned to combined effects of the heat transfer at different heating rates and kinetics of the decomposition, resulting in the delayed effects of the decomposition. The addition of catalysts decreased the stability of the emulsions and in turn, lowered the activation energy. The metallic additives can lower the bond energy by attacking the heteroatoms in asphaltene (Pu et al., 2015) and fracture these weakened bonds by the effect of electrokinetic. Table 2 shows the activation energy for all samples in the third region were much higher than those in the first and second regions; this might be due to the lower concentration of volatile materials and higher content of fixed hydrocarbons in asphaltene (Ghazanfari et al., 2012). Such molecules are heavy and more heat resistant; thus, almost all mass was lost in the third region while a little was lost in first and second regions.

Fully understanding the EK mechanism and catalytic mechanism during treatment process is extremely difficult due to occurrence of a series of complex and consecutive physical and chemical reactions. Based on Table 6.2, it could be pointed out that the type of additives can determine the catalytic efficiency. For all the reactors unlike the control reactor (with EK and without additive), the activation energy decreased in all regions which shows more availability of the components and better separation of phases. The reactor with 200 ppm catalyst showed the lowest activation energy compared to the other reactors which was between 51-68 kJ/mol in the first region, comparing to 91-118 kJ/mol in the control reactor (EK treatment without additive). The activation energy in the third region in reactor with 200 ppm catalyst was 314-345 kJ/mol. These results indicate a better separation of oil phases from solid phases and destabilization of emulsions. Among reactors with TiO_2 additive, the reactor with 100 ppm TiO_2 resulted in the lowest activation energy in the first and second regions.

Table 6.2. The activation energy in 4 sections of the reactors

Reactor	Sections in reactor*	Activation energy (kJ/mol)		
		First region (25 and 160 °C)	Second region (160 to 380 °C)	Third region (380 to 600 °C)
Control without additives	1	97	274	401
	2	91	267	387
	3	118	324	468
	4	103	311	427
50 ppm TiO_2	1	78	221	367
	2	74	214	359
	3	83	289	412
	4	85	278	423
100 ppm TiO_2	1	65	195	341
	2	60	187	320
	3	74	214	364
	4	78	206	337
200 ppm TiO_2	1	75	204	340
	2	73	197	347
	3	74	224	345
	4	68	191	330
50 ppm catalyst				
	1	77	208	340
	2	79	241	384
	3	84	274	421
	4	75	214	364
100 ppm catalyst				
	1	60	187	308
	2	58	165	292
	3	79	228	347
	4	71	211	321
200 ppm catalyst				
	1	51	174	324
	2	68	190	314
	3	54	187	345
	4	65	182	321

Note: *Anode side (section 1), middle anode (section 2), middle cathode (section 3) and cathode side (section 4).

6.4 CONCLUSION

In this study, seven lab-scale electrokinetic reactors were operated. The separation of phases took place in all reactors. In each EK system, the water/solids ratio decreased below values detected in the centrifuged samples obtained from the oil refinery. It was determined that wettability (water-wet solids) had a direct relationship with the separation efficiency of oil sediments. The main catalytic effect of synthesized catalyst was increasing the hydrophilicity of solid surfaces compared to without nanocatalyst. Increase in oxidation happened by using combined nanocatalyst and EK that has been confirmed by XPS analysis. Furthermore, EK reactor containing 200 ppm of synthesized catalyst had the lowest water/solids ratio. The water/solids ratio reached 3.38% in section 1 at anode area, which is three times lower than those achieved by centrifugation, a most popular industrial method of oil sludge treatment. The results from XPS confirmed the ability of EK to change the solids surface properties and destabilize oil emulsions (oil sediments). TGA data confirmed the better separation of synthesized catalyst compared to TiO_2 nanoparticles. The lower activation energy in the reactor with 200 ppm of catalyst showed better separation of phases and demulsification of oil suspension. Overall, the combination of 200 ppm synthesized catalyst with electrokinetic treatment can lead to better phase separation and water removal from oil sediments.

Conclusions and recommendations

7.1 CONCLUSIONS

The present research showed the feasibility of the application of electrokinetic (EK) to treat petroleum waste, specifically, oil sediments produced by Suncor oil refinery. EK treatment of oil sediment found to be successful in its demulsification and separation of phases such as hydrocarbons, water, and solids. The current study showed that the electrokinetic method was effective at room temperature with practically low energy consumption.

Among the applied electrical regimes, DDC and IDC were found to be the most effective in inducing phase separation in oily sediments. The DDC and IDC electrokinetic processes increased the amount of light hydrocarbons by 43% and 21%, respectively. This showed that DDC can be effective in separating and recovering light oil from oil sediments. Deviation Index (DI) analyses confirmed that DDC and IDC were the most effective electrical regimes to induce separation of heavy hydrocarbon/water, light hydrocarbon/solids, and water/solids. Nondestructive resistance analyses allowed the assessment of the separation efficiency of the different phases and shed light in the involved separation mechanisms such as demulsification, horizontal and vertical movements of particles. Application of PDC incurred a low resistivity to the current passing through the reactor as a result of a low pH change between electrodes. DDC favored electro-sedimentation, demulsification and electroosmosis of molecules, while PDC promoted significant vertical movements of water, but IDC mainly resulted in a horizontal separation of light hydrocarbons.

In Chapter 5, the results showed that all four different types of electric currents (CDC, PDC, IDC and DDC) induced changes in the physical and chemical characteristics, and thermal behavior of the solids in the oil sediments during electrokinetic treatment. However, the DDC showed the highest efficiency in the separating the different phases in the oil sediments. Wettability, contact angle and elemental analyses by XPS revealed the transport of molecules under the applied electric fields to enhance the recovery of oil from stable emulsions. Changes in surface properties induced by reaction of electrolysis products, electroosmotic flow of the oil phase by viscous coupling and electrophoretic movement of solids to the anode were involved in the phase separation of the oil sediments. The stability of the water-in-oil emulsions were closely linked to the carbon and oxygen functionalities of the surface solids. The release of oil molecules from the surface, following the application of the different electric fields, rendered the solids more water-wet, thus destabilizing the emulsions and reducing the coagulation of hydrocarbons and solids. The application of electrical currents induced a change in the contact angle at the oil-water and solids interface. Although a minor change in the contact angle was observed, this led to a marked difference in the properties of the surface solids. The elemental composition and types of bonding (O, OH, C-O-H, C-O-C, O-C=O, O=C, O=C-OH…etc.) were affected by the application of the electrical currents, which in turn impacted on the solids wettability, hydrophilicity and interfacial tension between oil and water. The thermogravimetric analysis (TGA) curves shifted to the left following the application of electrical currents indicating a change in the composition of the solids with higher light hydrocarbons. The mineral composition of the electrokinetically treated sediments were altered causing a destabilization of emulsions and facilitating the phase separation of the oil sediments.

In Chapter 6, seven lab-scale electrokinetic reactors were operated. Separation of phases took place in all the reactors. In each EK system, the water/solids ratio decreased below the values detected in the samples than the control. It was determined that wettability (water-wet solids) has a direct relationship with the separation efficiency of oil sediments. Application of both nano-TiO_2 and synthesized catalyst showed enhancement of the electrokinetic method applied to oil sediment treatment. TGA data confirmed the better separation of synthesized catalyst compared to nano TiO_2. In conclusion, the combination of synthesized catalyst with electrokinetic treatment can lead to a better phase separation and water removal from oil sediments. EK reactor with 200 ppm synthesized catalyst had the lowest water/solids ratio. Water/solids ratio reached 3.38 in section 1 at anode, which was three times lower than those achieved by centrifugation, a most popular industrial method of oil waste separation technique. Activation energy of all treated samples support the efficiency of additives for better separation of phases and demulsification of emulsions. When the water-wet solids concentration increases, there was a better separation of phases in the EK reactor. XPS confirmed the change of the solids surface properties and the ability of EK to destabilize oil emulsions.

7.2 CONTRIBUTION TO ORIGINAL KNOWLEDGE

This study provides a more comprehensive understanding of the effects of electrical current application in altering the surface characteristics of solid particles contained in oil sediments, and the associated mechanisms involved in phase separation to improve oil recovery efficiency and reduce potential pollution caused by oil sediment residues. The present work has contributed to the following:

- Demonstrated the feasibility of applying different mode of electrical current for the electrokinetic treatment of oily sludge; identified the best suitable mode of electrical field for oily sludge treatment.
- Find optimal electrokinetic technology for the treatment of different types of oily sludge produced at the different stages of oil processing. The impacts of incremental, decremental, pulse, and constant direct current on solids surface wettability alteration of oil sediments were assessed. To the author's knowledge, such data has never been generated for petroleum wastes. This approach resulted in a better solids treatment than the conventional methods such as centrifugation and solvent extraction. The developed new technique can be applied directly to petroleum waste define as hazardous materials (K048, K049 by The Resource Conservation and Recovery Act), which is a significant achievement in the domains of petroleum industry, ecology, environmental and chemical engineering.
- Found the effects of nanoparticles as well as the synthesized carbon-based catalyst on destabilization of emulsions and wettability of oily sludge solids during electrokinetic treatment.
- Defined changes of solid surface properties considering the oil and water separation produced by the combined effect of electrokinetic with nanoparticles or with synthesized carbon-based catalyst.

7.3 RECOMMENDATIONS FOR FUTURE WORK

- This study was conducted on a small scale electrokinetic reactor for phase separation of oily sludge. Evaluating the performance of a pilot-scale or a full-scale electrokinetic reactor for evaluating phase separation of oily sludge is a subject that needs further research.

- In this study lagoon sludge collected from the full-scale refinery was used to evaluate the phase separation efficiency. Further research can be conducted on the other types of sludge available in oil refineries for example slurry and catalytic fines from heavy fuel tank, sludge from API, sludge from DAF or sludge from separator bottom.
- In this study for finding optimal electrokinetic reactors different kind of electric regimes were applied. For further optimizing the reactors an evaluation of energy performance and cost analysis should also be considered.
- In this study to prepare the carbon-based catalyst, lagoon sludge collected from full-scale refinery was used. The effect of different kind of sludge available at oil refineries (slurry and catalytic fines from heavy fuel tank, sludge from API, sludge from DAF or sludge from separator bottom) for preparation of carbon-based catalyst should also be further investigated.
- Evaluating the adsorption capacity of the synthesized carbon-based catalyst for light and heavy hydrocarbon removal should also be considered in the future.

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