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DIFFERENT ELECTRICAL REGIMES TO DEMULSIFY OIL SLUDGE - WETTABILITY INDICATOR

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Abstract: Extraction and refinery of oil by oil-producing industries result in the production of a huge amount of oil sludge which disposal might present a threat to the environment. The treatment of oil sludge is challenging due to its physical and chemical properties. Among these properties, a stable emulsion is one of the main obstacles to an effective treatment. Adsorption of asphaltenes and resins on the surface of solids drastically increases the hydrophobicity of the solid particles and produces meta-stable water-in-oil emulsions. In this study, an electrokinetic (EK) approach was employed to decrease the double layer thickness and destabilize emulsions to facilitate the separation of water from oil phase. Four different types of electrical fields were applied to test their impact on the stability of water-in-oil emulsions. They are: constant direct current (CDC), pulsed DC (PDC), incremental DC (IDC) and decremental DC (DDC). Furthermore, the effectiveness of DDC and IDC methods remarkably improved demulsification compared to the sequential solvent extracted oil sludge with toluene and tetrahydrofuran. Wettability alternation analyses showed an increase in the population of fine solids in the aqueous part following EK treatment which in turn led to the higher hydrophilicity of the solids. The applied DDC and IDC fields enhanced the wettability towards water-wet solids and were better than the other tested configurations, which can result in better solid-oil phase separation.

1 INTRODUCTION

The environmental challenges regarding the treatment and disposal of waste generated by oil industries are not restricted to the processing stages of extraction and separation only. For example in upstream, oil extraction conducted from geological strata produces a complex mixture of sand, clay, minerals, water and oil. The resulting oil sludge represents a serious hazard to the environment if not properly treated and disposed. Oil sludge might be comprised of 30-50% oil, 30-50% water and 10-12% solids, and forms a complex matrix which is difficult to dewater (Mikula et al., 1996;Jeeravipoolvarn et al., 2009;Da Silva et al., 2012). The high water content contributes to the large volume of material to be disposed of and renders the geotechnical properties of the oil sludge more intricate (Snars and Gilkes, 2009).

Oil sludge is generally stored in tailing ponds, below or above ground with the help of perimeter dikes or lagoons. The storage of huge volumes of oil 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 (Rico et al., 2008;Blight, 2009). This problem can be further exacerbated during other activities such as transport and disposal of oil sludge thereby increasing the risk of severe contamination of water bodies, the demise of aquatic life and heavy metal contamination (Ayotamuno et al., 2007).

Chemically, oil 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 oil sludge wastes, results in the formation of water-in-oil emulsions. These emulsions are meta stable due to the presence of a protective layer of fine clay which prevents the emulsions from coagulation or coalescence. Petroleum hydrocarbons (PHCs), such as, asphaltenes and resins act as natural emulsifiers in these protective layers. There are also other natural emulsifiers in these layers such as fine solids, oil-soluble organic acids and other fine materials that contribute to the stabilization of water-in-oil emulsions (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 oil 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 oil sludge to be very challenging (Heidarzadeh et al., 2010;Hu et al., 2013).

Surface properties of solids in oil sludge play important roles on the stability of the emulsion. Chen et al. (2017) show the effect of ununiform particles with varying hydrophobicity on the emulsion stabilization that can be an example of solids on the oil sludge. The ratio of asphaltenes to resins plays a very important role in the stability of the emulsions and adsorption on the solids (Sullivan and Kilpatrick, 2002;Sparks et al., 2003). Mineral particles show a significant effect on the emulsion stability, while resins and asphaltenes associate to form colloidal aggregates. Asphaltenes interact through hydrogen bonding and π-bond overlap. Through polar functional group interactions, resins solvate asphaltene aggregates to each other. 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 compounded by the adsorption of resin/asphaltene aggregates to hydrophilic particles. As more aggregates adsorb, the particles become preferentially wetted by the oil phase ($\Theta > 90°$). Ionic and π-bondings have been found between asphaltene/resin and clay surface (Sullivan and Kilpatrick, 2002;Sparks et al., 2003).

Electrokinetic (EK) method show the ability to remediate organic and inorganic contaminated soil and recently much attention had been shifted on the usage of EK remediation for oil contaminated soil (Lim et al., 2016). For the first time, the EK method was developed to separate the different phases (water, oil and solids) in oil 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 (Kuo et al., 2011). This method can dewater oil sludge by nearly 63% and reduce the light hydrocarbon content by about 43% (Elektorowicz et al., 2006). The effect of EK separation, however, has not been studied on the fine solid particles in oil sludge.

The aim of this project was to further explore the effect of EK processes on the surface properties of oil sludge conglomerates. Thus, wettability alternation of solid particles is possible due to electro-demulsification processes, the wettability was examined as an indicator of destabilization of oil sludge. Study was conducted by the application of different direct current (DC) operation regimes to the sludge originated from a refinery disposal pond. Changes induced on the surface properties of solids, wettability alternation and contact angle were studied before and after application of the electric fields. It was assumed that the study outcomes would help to improve management of oil sludge which can be beneficial to environment, soil and water pollution.

2 MATERIALS AND METHODS

2.1 Setting-up of an electrokinetic reactor

To achieve the above-mentioned objectives, the 1-L electrokinetic (EK) reactor was set up by supplying an electric current across two electrodes by a DC power supply (BK Precision 1902, USA) which converts an AC to a DC. This unit enabled the supply of a constant direct current (CDC). Incremental or decremented DC was applied by adjusting the voltage on a daily basis. In order to create pulsed DC (PDC), a function generator (BK Precision 4001A, USA) was 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 the electrical function. A Digital Multimeter (Mastech MAS830, USA) was connected to the probes which were strategically positioned in the EK reactor, and used to monitor and measure the voltage supplied by the different electrical configurations across the electrodes.

2.1.1 Application of different electrical regimes

EK studies were conducted using lagoon sludge sampled from an oil refinery located in Montreal, Quebec, Canada. A control reactor was set up with no potential gradient. A Constant DC (CDC) reactor was designed by applying a potential gradient of 1 V/cm across the electrodes. This gradient of voltage was chosen based on Elektorowicz and Habibi (2005), who found its suitability for very low permeable sludge, which was the case for the lagoon sludge used in this current study. For both Incremental and Decremented currents (IDC and DDC), 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 of DC was applied in combination with a 0.5 V/cm of AC pulse at squared frequencies of 60 Hz with a 1/5 pulse period.

2.2 Characterization of solids in oil sludge

2.2.1 Sequential solvent extraction solids

A two step solvent extraction has been used to evaluate the efficiency of EK systems (Mochida et al., 1986;Wang et al., 2010). The first extraction was performed using 25 g of oil sludge with 100 mL of toluene, while the mixture was boiled under reflux for 15 hrs in a Dean-Stark apparatus (Kimble KIMA Soxhlet Apparatus, Fisher Scientific). The second extraction was conducted with 100 mL more polar tetrahydrofuran (THF) over a period of 15 hrs. The extracted solids from solvent extraction was subjected to different examinations as described below to compare with other EK methods.

2.2.2 Wetting properties of solids

Oil sludge solids are rich in organics, which plays important roles in the sorption of oil particles to the surface of the solid matrix. Depending on the solids and organic content in 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 degrees for the BAGG-type solids. In addition, ultra-fine clays (UFCs) may also be present and they are an additional contributor in intractable solids for stable emulsions in oil sludge.

In order to assess wettability, a mixture of 2 mL toluene and 8 mL of water was added to 200 mg of dried solids, then vortexed for 2 minutes at a maximum speed of 1500 rpm to have a homogenous mixture, and incubated overnight in the fumehood at room temperature (Sparks et al. 2003). Dried sludge in this study was prepared by using a vacuum oven to reach a constant weight at 38°C (Ukwuoma and Ademodi, 1999). Three kinds of sludge were dried. First, original sludge is the sludge that has not been treated. Second are sludge samples treated with different EK techniques. Third is the extracted sludge with toluene and THF to have comparison between EK and solvent extraction. All three kinds of sludge were dried by this technique. The wettability of the solids was determined as the percentage of solids present in the aqueous phase by weighting the aqueous phase solids (Somasundaran and Zhang, 2006;Jiang et al., 2011). In addition, the change of solids wettability over a short period (30 min) and a long period (3 days) of time was investigated.

The degree of biwettability is variable, thus, it is expected that some hydrophobic materials will also be present in the hydrophilic phase and vice versa. Therefore, the percentage weight of the solids that were partitioned to the aqueous phase which show the water-wet ratio of the sample was evaluated. These tests have been applied twice to each sample for more representative results. The emulsions stability could be evaluated by the results from this analyse.

2.2.3 Contact angle measurement

The surface hydrophilicity and surface energy change in each sample after EK treatments were assessed 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 system software (VCA optima XE). 10 mm pellets were prepared with laboratory press (Model C12 Ton Benchtop, Carver, Inc., USA). 0.5 g of dried sample was added to the die, and 25 MPa pressure was applied to prepare the pellets (Wang et al., 2015). At least three points from the pressed sample were selected for contact angle measurements; an average of three measurements was reported. The purpose of this test is to have a comparison and a evaluation on the solids surface wettability and emulsion destabilization.

3 RESULTS AND DISCUSSION

All EK regimes, as defined in section 2.1.1, were able to destabilize oil sludge but at different extents. Figure 1 shows an example of a demulsified oil sludge sample prepared for further wettability tests. The samples from different reactors have been prepared like the one in Figure 1 to study the effects of solids wettability on the emulsion stabilities. Though this analyse, the comparison can be done on the destabilization ability of different EK technique and solvent extraction.

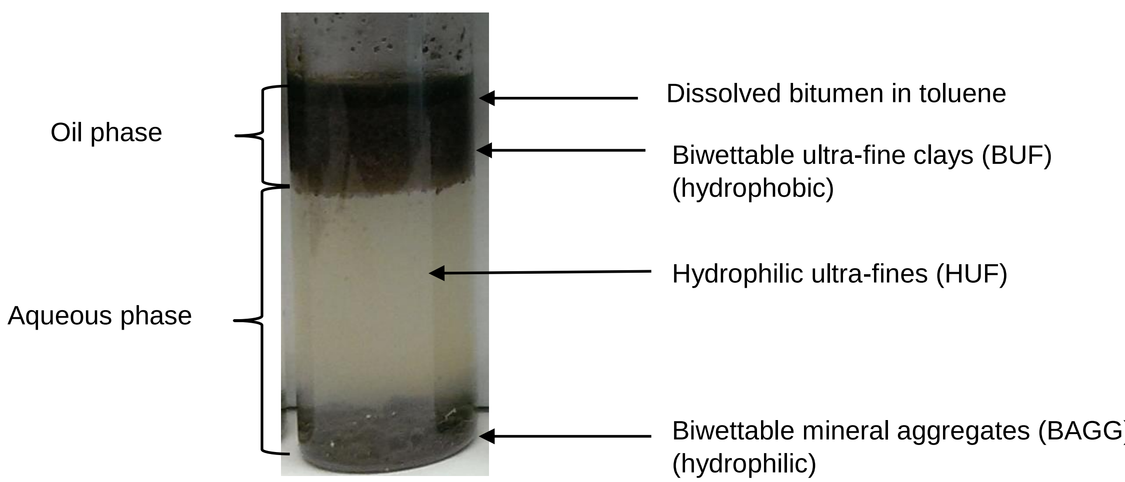

Figure 1: Fractionation of oil sludge solids into organic and aqueous phases

3.1 Wetting properties comparison between original, solvent extracted and EK-treated oil sludge solids

To evaluate the wettability alteration of solids with EK treated sludge, wettability analyses have been applied. The results from wettability analyses have been compared with two samples; original (control) sludge solids and solvent extracted sludge solids that have been extracted by toluene and THF. Solids from original sample showed no significant changes over short and long periods of time. By evaluating the changes through time the stability of emulsions was found to decrease. This was mainly due to the effect of the applied electrical field on the ion concentration on the surface of solids.

For the long-time testing, when the separation of phases was complete, solids from different sections of the reactor showed different behaviours. At the bottom anode, which included most of the solids, the wettability showed clear changes of solids wettability to water-wet compared to the original control sludge. Under the PDC, IDC and DDC electrical regimes, the water-wet portion of solids increased more than sequential extracted oil sludge solids. Most of the solids at the bottom cathode showed better water-wet properties compared to the original control. The DDC reactor showed the most alternation in water-wet conditions at the bottom and middle parts of the reactor. For all the reactors, the water-wet percentage increased to more than 60%. The top points of reactors had low amounts of solids that were mostly oil wet. The IDC reactor exhibited an interesting change in the water-wet behavior at the bottom section of the reactor where it had the highest movement of solids to the anode side. Subsequently, it was concluded that both horizontal and vertical mobilisation of particles vs. water takes place under EK treatment (Figure 2).

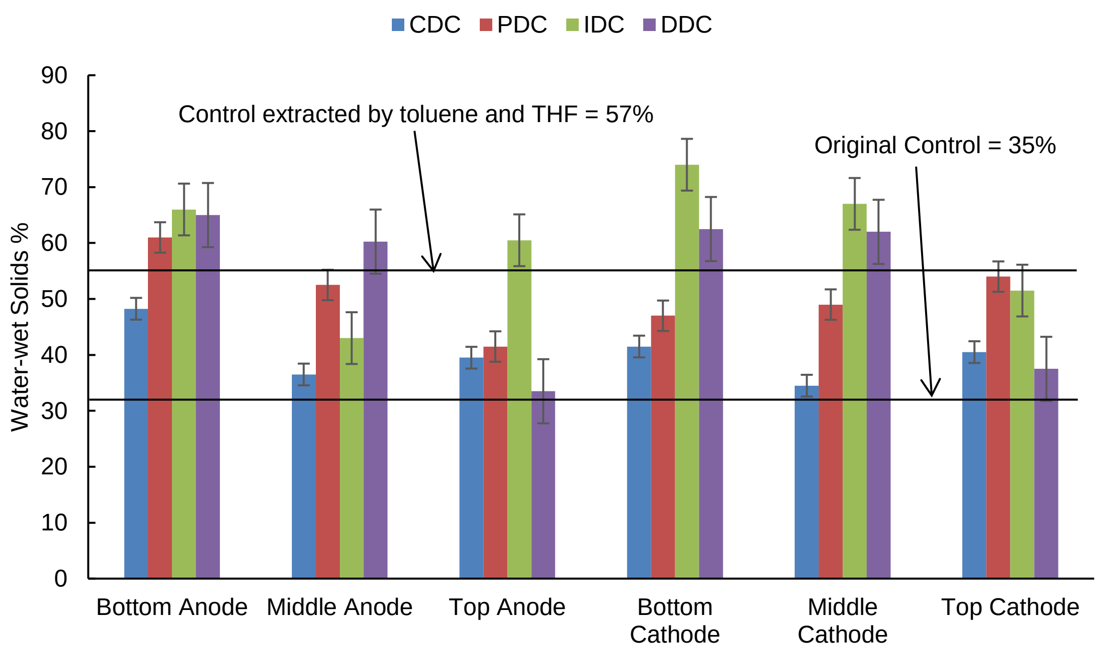

Figure 2: Percentage of solids that migrated to the aqueous phase in the four reactors following application of different electrical regimes.

3.2 Contact angle

The contact angle measurements of the dried solids confirmed the wettability alternation of the solids from oil-wet to water-wet for all four electric regimes. As mentioned before, most of the solids moved to the bottom anode side in the IDC and DDC reactors (Figure 2). Thus, the wettability alternation (contact angle) changes were significant for the bottom anode solids (Figure 3). PDC reactor configuration showed the most alternation on the solid surface properties. As indicated before, the wetting properties of solids were observed for the IDC and DDC reactors followed by the PDC reactor, which all of them had more decrease on contact angle degree compare to the toluene/THF extracted control.

Hence, the current study shows that EK treatment can have a significant impact on the wettability alternation of fine solids in oil sludge. These changes might occur due to changes in functional groups at the surface of the solids as well as the bonding formation between organic compounds, mainly asphaltenes and resins. Subsequently, wettability analyse can serve as an adequate indicator of demulsification and dewatering of oil sludge. Comparison between contact angle and wetting properties of solids showed that decrease on the hydrophobicity of surface destabilize the emulsions and make more water wet solids. The minor change on the contact angle can make a marked difference in the solids and emulsions stability.

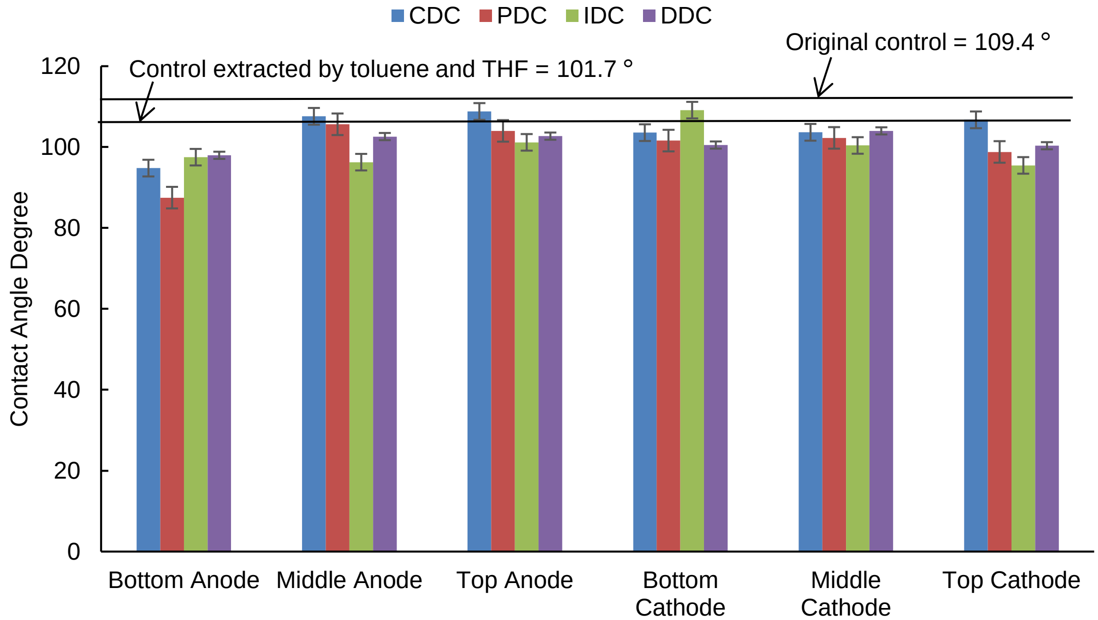

Figure 3: Comparison of contact angle degree of solids in different section of each reactor with original and control extracted solids by toluene and THF.

4 CONCLUSION

In this study, different configurations of DC electrical regimes were applied to oil sludge treatment. It was found that they all induce changes to the surface properties of the fine solids. For all the tested EK systems, the solids wetting properties changed to water-wet and the changes even surpass the sequential solvent extracted solids. It was concluded that wettability is a valuable indicator of water-in-oil emulsion destabilisation that can play an important role in oil sludge treatment and volume reduction. The results have been confirmed by contact angle analyse that almost in all sections of reactors the contact angle of the solids decreased even lower than the solids that have been solvent extracted. The DDC and IDC electrical regimes induced the highest extent of solids movement to the anode side and wettability alternation to water-wet. Hence, they can be applied as advanced treatment technology to destabilise oil sludge emulsions. In comparison between contact angle and wetting properties it can be determined that minor change on the contact angle can make a marked difference in the solids and emulsions stability.

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References

Ayotamuno, M., R. Okparanma, E. Nweneka, S. Ogaji and S. Probert (2007). Bio-remediation of a sludge containing hydrocarbons. *Applied energy*, **84**(9): 936-943.

Blight, G. (2009). Geotechnical engineering for mine waste storage facilities, CRC Press.

Chen, Q., I. Stricek, M. R. Gray and Q. Liu (2017). Influence of hydrophobicity distribution of particle mixtures on emulsion stabilization. *Journal of Colloid and Interface Science*, **491**: 179-189.

Da Silva, L. J., F. C. Alves and F. P. de França (2012). A review of the technological solutions for the treatment of oily sludges from petroleum refineries. *Waste Management & Research*, **30**(10): 1016-1030.

Elektorowicz, M. and S. Habibi (2005). Sustainable waste management: recovery of fuels from petroleum sludge. *Canadian Journal of Civil Engineering*, **32**(1): 164-169.

Elektorowicz, M., S. Habibi and R. Chifrina (2006). Effect of electrical potential on the electro-demulsification of oily sludge. *Journal of colloid and interface science*, **295**(2): 535-541.

Guolin, J., L. Ming and Q. Shaopeng (2009). The Use of Nonionic and Anionic Surfactant in the Treatment of Oily Sludge. Energy and Environment Technology, 2009. ICEET'09. International Conference on, IEEE.

Heidarzadeh, N., S. Gitipour and M. A. Abdoli (2010). Characterization of oily sludge from a Tehran oil refinery. *Waste Management and Research*, **28**(10): 921-927.

Hu, G., J. Li and G. Zeng (2013). Recent development in the treatment of oily sludge from petroleum industry: A review. *Journal of Hazardous Materials*, **261**(0): 470-490.

Jeeravipoolvarn, S., J. Scott and R. Chalaturnyk (2009). 10 m standpipe tests on oil sands tailings: long-term experimental results and prediction. *Canadian geotechnical journal*, **46**(8): 875-888.

Jiang, T., G. J. Hirasaki, C. A. Miller and S. Ng (2011). Wettability Alteration of Clay in Solid-Stabilized Emulsions. *Energy & Fuels*, **25**(6): 2551-2558.

Kuo, C.-H., H.-Y. Chang, C.-P. Liu, S.-H. Lee, Y.-W. You and J.-J. Shyue (2011). Effect of surface chemical composition on the surface potential and iso-electric point of silicon substrates modified with self-assembled monolayers. *Physical Chemistry Chemical Physics*, **13**(9): 3649-3653.

Lim, M. W., E. V. Lau and P. E. Poh (2016). A comprehensive guide of remediation technologies for oil contaminated soil — Present works and future directions. *Marine Pollution Bulletin*, **109**(1): 14-45.

Mikula, R. J., K. L. Kasperski, R. D. Burns and M. D. MacKinnon (1996). Nature and fate of oil sands fine tailings. *Advances in Chemistry Series*,(251).

Mochida, I., K. Sakanishi, Y. Korai and H. Fujitsu (1986). Two-stage catalytic up-grading of vacuum residue of a Wandoan coal liquid. *Fuel*, **65**(8): 1090-1093.

Rico, M., G. Benito, A. Salgueiro, A. Díez-Herrero and H. Pereira (2008). Reported tailings dam failures: a review of the European incidents in the worldwide context. *Journal of Hazardous Materials*, **152**(2): 846-852.

Snars, K. and R. Gilkes (2009). Evaluation of bauxite residues (red muds) of different origins for environmental applications. *Applied Clay Science*, **46**(1): 13-20.

Somasundaran, P. and L. Zhang (2006). Adsorption of surfactants on minerals for wettability control in improved oil recovery processes. *Journal of petroleum science and engineering*, **52**(1): 198-212.

Sparks, B., L. Kotlyar, J. O'Carroll and K. Chung (2003). Athabasca oil sands: effect of organic coated solids on bitumen recovery and quality. *Journal of Petroleum Science and Engineering*, **39**(3): 417-430.

Sullivan, A. P. and P. K. Kilpatrick (2002). The effects of inorganic solid particles on water and crude oil emulsion stability. *Industrial & Engineering Chemistry Research*, **41**(14): 3389-3404.

Ukwuoma, O. and B. Ademodi (1999). The effects of temperature and shear rate on the apparent viscosity of Nigerian oil sand bitumen. *Fuel Processing Technology*, **60**(2): 95-101.

Wang, C., M. Geramian, Q. Liu, D. G. Ivey and T. H. Etsell (2015). Comparison of Different Methods To Determine the Surface Wettability of Fine Solids Isolated from Alberta Oil Sands. *Energy & Fuels*, **29**(6): 3556-3565.

Wang, J., J. Yin, L. Ge, J. Shao and J. Zheng (2010). Characterization of Oil Sludges from Two Oil Fields in China. *Energy & Fuels*, **24**(2): 973-978.

Yang, X., W. Tan and Y. Bu (2008). Demulsification of asphaltenes and resins stabilized emulsions via the freeze/thaw method. *Energy & fuels*, **23**(1): 481-486.