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EFFECTS OF TITANIUM DIOXIDE NANOPARTICLES AND SYNTHESIZED CATALYST ON PERFORMANCE OF ELECTROKINETIC SEPARATION OF OIL SEDIMENTS

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Abstract: Sediments from oil refineries consist of a complex mixture of oil, water, sand, mineral matter and metastable emulsions. Separation of phases from water-in-oil emulsion still represents a major challenge in petroleum and oil industries including the minimization of rag layers below supernatant oil to effectively demineralize and dehydrate the resulting waste. In the current research, the efficiency of the electrokinetic separation of oil waste phases has been investigated in presence of titanium dioxide (TiO_2) nanoparticles and a synthesized catalyst. Seven lab-scale electrokinetic reactors were operated. Three of the reactors involved the addition of 50, 100 and 200 ppm of Nano TiO_2 to the oil sediment prior to electrokinetic separation. Another set of three reactors were used to treat sediment mixed with 50, 100 and 200 ppm of a synthesized catalyst. A control reactor which contained only the oil sediment devoid of any TiO_2 nanoparticles and the synthesized catalyst was also operated. For all the reactors, vertical samples were collected at four positions with two sampling points near the anode and cathode, respectively. The samples were subjected to wettability analysis, X-ray photoelectron spectroscopy (XPS), and Thermogravimetric Analysis (TGA). It was observed that the addition of Nano TiO_2 and synthesized catalyst significantly improved the water removal and volume reduction capacity of the electrokinetic method. Better performance results were, however, obtained with the synthesized catalyst as compared to the use of TiO_2 nanoparticles. In comparison with the control reactor, the optimal water/solid ratio was achieved using 100 ppm of Nano TiO_2 (reduction from 52.51 to 3.45), and 200 ppm of engineered catalyst (water/solid ratio from 52.51 to 3.38). Wettability analysis and XPS data showed that the electrokinetic treatment induced a change on the surface of the solids which became more water-wet at the anodic side of the reactors. Sediments impregnated with Nano TiO_2 or synthesized catalyst showed higher level of wettability as compared to the control. TGA data also showed a better phase separation during electrokinetic treatment when Nano TiO_2 or synthesized catalyst was used. 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.

Keywords: Oil sediment, Oil emulsions, Electrokinetic treatment, Nanoparticles, Synthesized catalyst

1 INTRODUCTION

The extraction and refinery of oils by oil-producing industries result in the production of a significant amount of oil wastes which disposal represents a serious threat to the environment (Todd et al., 1999, Hu et al., 2013). Uncontrolled discharge of untreated oily sludge 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 and Shah, 2013). Studies showed 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).

Storage of oily sludge for a prolonged period of time might carry a high risk for leakage of oily sludge-related hazardous compounds to the environment (Guolin et al., 2009). With the increased production of oily 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 hydrocarbons (PAH) because cancer is the major concern from exposure to PAH (Giusti, 2009, Diya'uddeen et al., 2011). In conventional techniques oil sediments are stored for a long period, then, the treatment methods are applied. Literature has also reported air transmission of oily sludge particles over long distances (Karamalidis and Voudrias, 2007). The possibility of atmospheric pollution through the release of volatile hydrocarbons (VOCs) based on treatment methods also carries risk to the natural environment and human health (Diya'uddeen et al., 2011, Hu et al., 2013).

Electrokinetic (EK) method shows the ability to changes in the physical and chemical characteristics, and thermal behavior of the solids in the oil sediments after centrifugation (Kariminezhad and Elektorowicz, 2018). In the current study, the effect of nanoparticle addition prior to centrifugation will be assessed in view of elucidating whether nanoparticles have the potential for improving the phase separation of oil sediments. 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 (Shan et al., 2009, Brar et al., 2010). In the present study, titanium (Ti) and a synthesized catalyst in its metallic forms has been used, due to its 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. The effect of particle surface charge and IEP is also exposed to varying thermal conductivity (Zawrah et al., 2015). Previous studies also showed that some nanoparticles can act as demulsifiers by bridging protective layers in emulsions (Fedushchak et al., 2014). Moreover, nanoparticles are able to change the wettability of solids and penetrate the low permeable layers of solids (Karimi et al., 2012, Kariminezhad and Elektorowicz, 2018). Metallic nanoparticles has been shown to exhibit pronounced demulsifying behavior and bears a unique morphology that allows it to change the wettability of solids (Fedushchak et al., 2014). Titanium dioxide (TiO_2) has also capability of changing the wettability of solids and are rather inexpensive and environmentally friendly (non-toxic and catalytic ability) way. It is also stable in the presence of different ionic salts (Ehtesabi et al., 2013).

Based on such facts, the EK system was enhanced with synthesized catalyst and titanium dioxide (TiO_2) in order to improve phase separation and water removal from oil sediments in this study. Presence of metallic nanoparticle in the oil sediments permitted to produce nanoparticles from the waste that could be used as a catalyst in the separation process. The aim of this project was to explore the ability of EK enhanced by nanoparticle to destabilize water-in-oil emulsions.

2 MATERIALS AND METHODS

2.1 Setting-up of an electrokinetic system

The lagoon sediment has high water content (80%), and it belongs to the group of the most stable water-in-oil emulsions. Since usually the separation process of water is not very efficient, such emulsion was investigated. Fresh lagoon sludge collected from the Montreal full-scale oil refinery, was mixed with nanoparticle solution (1000ppm) using shaker set at 200 rpm in 5 minutes and preserved in the dark. The mixing was conducted in three ratios of nano-solution/sludge: 50ml/950 ml, 100ml/900ml, and 200ml/800ml.

Three of the reactors prepared with of 50, 100 and 200 ppm of Nano TiO_2 and three other reactors were used to treat sediment mixed with 50, 100 and 200 ppm of a synthesized catalyst. A control reactor which contained only the oil sediment devoid of any TiO_2 nanoparticles and the synthesized catalyst was also operated. Control reactor and 6 other reactors are designed in constant DC according to Kariminezhad and Elektorowicz (2018). Following the mixing period, the mixtures were placed in EK-reactors. A control EK-reactor without nanoparticles has been also prepared. A constant voltage gradient was applied to all reactors. The reactors were designed with a possibility of water drainage out of the system. The characteristics of sediments were determined as described in the Kariminezhad and Elektorowicz (2018) and the efficiency of phase separation was compared with the treated sediments devoid of nanoparticles as well as with sediments treated at full scale by a conventional method in the refinery. X-ray photoelectron spectroscopy (XPS), and Thermogravimetric Analysis (TGA) data was used to analyze the material generated by the process. This permitted to determine whether the addition of nanoparticles can effectively help to improve the EK separation of phases, mostly water, from the oily matrix. In addition, it was also allowed to compare the separation efficiency obtained with the different nanoparticles (TiO_2 and synthesized catalyst).

2.2 Characterization of solids in oil sediments

2.2.1 Solids properties

Oil waste solids are rich in various forms of organic compounds, which play an important role in sorption of oil component to the solid matrix. Samples of solids settled at the bottom of the reactors were collected r in four sections for further analyses. Water, solids and TPH (total petroleum hydrocarbons) have been measured according to (Kariminezhad and Elektorowicz, 2018). The ratio of water/solids has been calculated. Water-wet solids measured according to the (Kariminezhad and Elektorowicz, 2018). In all the analysis the test has been done on three points regarding the QA/QC. An average of the three measurements was reported.

2.2.2 Thermogravimetric Thermal Analysis

Thermogravimetric Analysis (TGA) can indicate the amount of mass loss in different temperature that indicates the water and solids movement in the reactor. TGA was performed using a TGA Q500 thermal analyzer (TA Instruments, USA) at the temperature range between 29 °C and 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 Al2O3 crucible for each run and subjected to combustion in the thermal analyzer (Liu et al., Park et al., 2009).

2.2.3 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 methodology was according to Kariminezhad and Elektorowicz (2018).

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3 RESULTS AND DISCUSSION

After applying the EK, separation of the reactor content took place and the liquid part has been drained from the solid part. The left sedimented solids divided into 4 sections, where section 1 was located close to the anode side while section 4 close to the cathode side. To find the most efficient process in separation, water/solids ratio, water-wet solids, XPS and TGA analyses have been conducted.

3.1 Solids behavior after treatment

To evaluate the efficiency and the mechanisms behind the EK treated oil sediments, water to solids ratio analyses has been applied. All the results compared with original samples and centrifuge treated samples in the refinery. The results indicate that the water/solids ratio had significantly changed due to EK treatment in all reactors. The ratio before treatment was 52.5, decreased to 10.46 after centrifuging, while reached 3.38 in EK reactor G. Majority of solids after EK treatment moved to the anode area and as the results show (Figure 1) section 1 in all reactors has better results compared to the centrifuging technique. Evaluating of the separation efficiency was conducted through assessing the changing of the concentrations of nanoparticles and catalyst. Such changes showed mostly improvement in phase separation. EK reactor C with 100 ppm TiO_2 showed the best performance, and EK reactor G with 200 ppm catalyst demonstrated the best separations of solids overall. Water/solids ratio fund to be lower than centrifuged samples in all sections of the EK reactor (Figure 1).

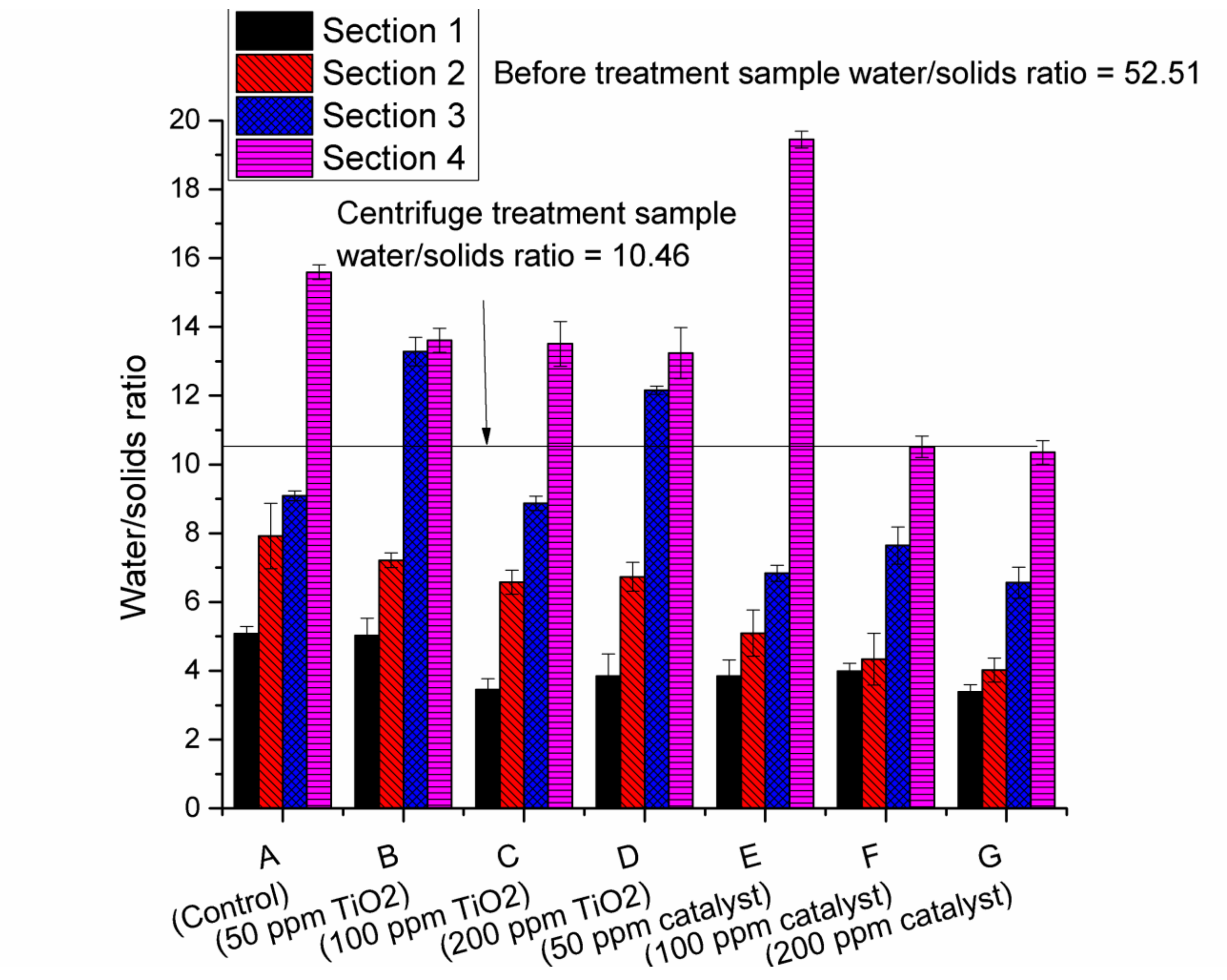


Figure 1: Water/solids ratio of treated samples in 4 sections of enhanced EK reactors compared with a centrifuge treated sample and control EK reactor

Results from solids wettability analysis show the relation of having more water-wet solids and better separations. EK reactor C with TiO_2 nanoparticles and EK reactor G with designed catalyst again showed more water-wet solids and confirmed the possibility of better separation. In the majority of the reactors section, the fourth section has more water wet solids compare to others due to electroosmotic flow. Section 4 of EK reactors C and G have the highest water-wet solids of 66% and 63%, respectively (Figure 2). The TiO_2 concentration of 100 ppm had the best ability to change the wetting properties of solids by increasing the water wet solids from 32.5 % to 53% in section 1 of the reactor due to electrophoretic flow.

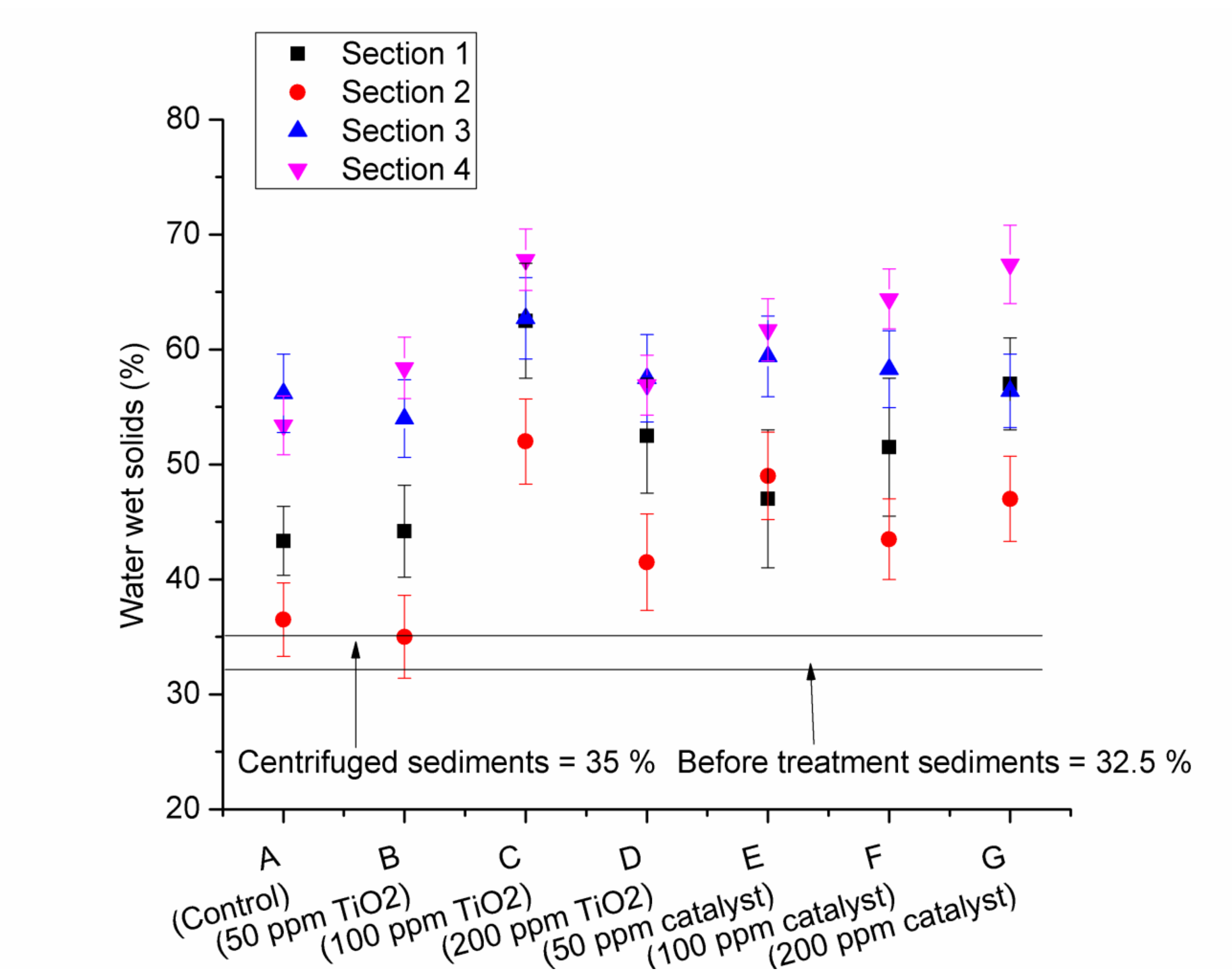


Figure 2: Comparison of water wet solids in 4 sections of each enhanced EK reactor compared with initial sediments and centrifuged sediments

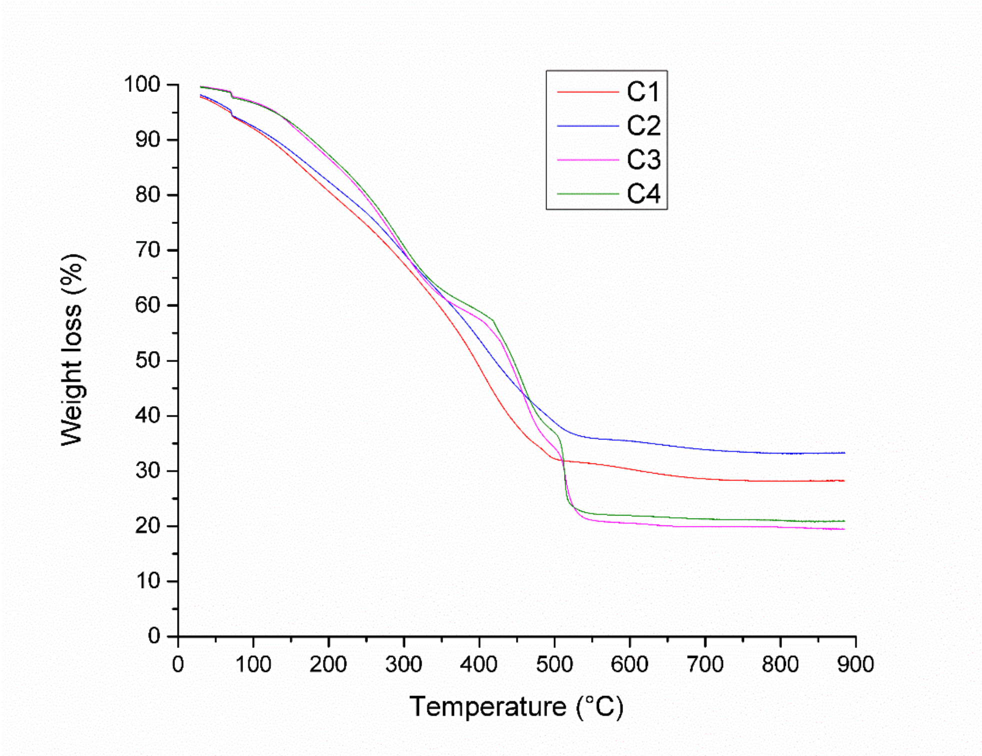
3.2 XPS and TGA results

According to the XPS results (Table 1), the concentration of carbon decreased on the surface of solids at section one of reactor C (C1=74%) and reactor G(G1=49%) sections compared to the untreated sample that was around 99%. Presence of Ti on the surface of solids at section one of the reactor specifies the ability to use TiO_2 as a demulsifier for water-in-oil emulsions. Presence of Ti and Fe can increase the chance on the production of hematite, maghemite, and anatase. According to Kailey et al., it can decrease the stability of water in oil emulsions (Kailey and Behles, 2015).

Table 1: XPS-determined percentage of elemental compositions of surface solids following electrokinetic treatment of solids in the anode side of reactor C and G

Elements %	Section one of reactor C	Section one of reactor G
C1s	74.44	49.67
O1s	18.31	39.86
Fe2p	1.68	2.54
N1s	2.21	2.66
Cl2p	0.77	0.97
Si2p	1.22	2.36
S2p	1.55	1.1
Ti2p	0.49	0
P2p	0	1.2

Thermal properties of 4 sections in reactor C and G has been studied. Difference between weight loss in different sections confirmed the separation of phases in the EK reactors. In sections 3 and 4 of reactor C (C3, C4), the presence of more heavy oil is confirmed because of the weight loss continue after 450°C and reach to constant at 550°C. Reactor G showed less weight loss, which can confirm better separation of oil and water from the sediments. Most of the compounds in the sedimented samples after treatment in section 1 of EK reactor G are the solids that confirmed the better separation efficiency in this reactor.



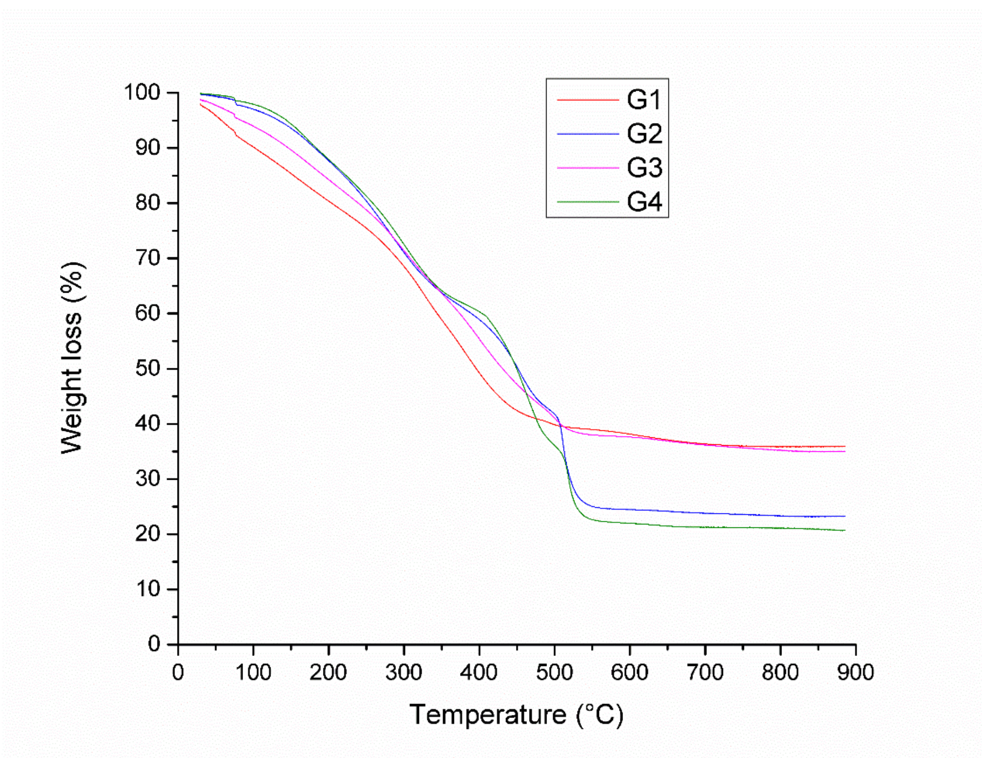


Figure 3: Thermogravimetric analysis (TGA) curves of electrokinetically treated oil sediments in the four sections of reactor C and G

4 CONCLUSION

In this research, seven lab-scale electrokinetic reactors were operated. Separation of phases took place in all of the reactors. In each EK systems, the water/solids ratio decreased below values detected in the samples that are treated with the centrifuge technique. It was determined that wettability (water-wet solids) has a direct relationship with the separation efficiency of oil sediments. When the water-wet solids concentration increase there is a better separation of phases in the enhanced EK reactor. EK reactors F and G that contained 100 and 200 ppm synthesized catalyst, respectively, had the lowest water/solids ratio. Water/solids ratio reached 3.38 in section 1 which is three times lower than those achieved by centrifuging technique a most popular industrial method of oil waste treatment. XPS confirmed the change of the solids surface properties and the ability to destabilize stable oil emulsions. TGA data confirmed the better separation of synthesized catalyst compares to nano TiO_2. In conclusion, the combination of TiO_2 or synthesized catalyst with electrokinetic treatment can lead to better phase separation and water removal from oil sediments.

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References

Brar, S. K., M. Verma, R. D. Tyagi and R. Y. Surampalli (2010). "Engineered nanoparticles in wastewater and wastewater sludge – Evidence and impacts." Waste management 30(3): 504-520.

Buongiorno, J. (2006). "Convective transport in nanofluids." Journal of Heat Transfer 128(3): 240-250.

Diya'uddeen, B. H., W. M. A. W. Daud and A. R. Abdul Aziz (2011). "Treatment technologies for petroleum refinery effluents: A review." Process Safety and Environmental Protection 89(2): 95-105.

Ehtesabi, H., M. M. Ahadian, V. Taghikhani and M. H. Ghazanfari (2013). "Enhanced heavy oil recovery in sandstone cores using tio2 nanofluids." Energy & fuels 28(1): 423-430.

Fedushchak, T., A. Akimov and V. Kuvshinov (2014). "Metal nanopowder demulsifiers." Russian Journal of Physical Chemistry A 88(5): 827-830.

Giusti, L. (2009). "A review of waste management practices and their impact on human health." Waste management 29(8): 2227-2239.

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.

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.

Kailey, I. and J. Behles (2015). "Evaluation of the Performance of Newly Developed Demulsifiers on Dilbit Dehydration, Demineralization, and Hydrocarbon Losses to Tailings." Industrial & Engineering Chemistry Research 54(17): 4839-4850.

Karamalidis, A. K. and E. A. Voudrias (2007). "Cement-based stabilization/solidification of oil refinery sludge: Leaching behavior of alkanes and PAHs." Journal of Hazardous Materials 148(1-2): 122-135.

Karimi, A., Z. Fakhroueian, A. Bahramian, N. Pour Khiabani, J. B. Darabad, R. Azin and S. Arya (2012). "Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications." Energy & fuels 26(2): 1028-1036.

Kariminezhad, E. and M. Elektorowicz (2018). "Comparison of constant, pulsed, incremental and decremental direct current applications on solid-liquid phase separation in oil sediments." Journal of Hazardous Materials.

Kariminezhad, E. and M. Elektorowicz (2018). "Effect of various electrokinetic treatment regimes on solids surface properties and thermal behavior of oil sediments." Journal of Hazardous Materials 353: 227-235.

Liu, G., H. Song and J. Wu "Thermogravimetric study and kinetic analysis of dried industrial sludge pyrolysis." Waste management(0).

Manali, D. and M. Shah (2013). "BIOREMEADIATION OF OILY SLUDGE-A REVIEW."

Park, Y. C., J.-Y. Paek, D.-H. Bae and D. Shun (2009). "Study of pyrolysis kinetics of Alberta oil sand by thermogravimetric analysis." Korean journal of chemical engineering 26(6): 1608-1612.

Shan, G., S. Yan, R. Tyagi, R. Y. Surampalli and T. C. Zhang (2009). "Applications of nanomaterials in environmental science and engineering: review." Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management 13(2): 110-119.

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.

Todd, G. D., R. L. Chessin and J. Colman (1999). Toxicological profile for total petroleum hydrocarbons (TPH), US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

Wake, H. (2005). "Oil refineries: a review of their ecological impacts on the aquatic environment." Estuarine, Coastal and Shelf Science 62(1): 131-140.

Zawrah, M. F., R. M. Khattab, L. G. Girgis, H. El Daidamony and R. E. Abdel Aziz (2015). "Stability and electrical conductivity of water-base Al2O3 nanofluids for different applications." HBRC Journal.