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Evaluation of Applying Solvent Extraction and Iron Nanoparticles for Oily Sludge Recovery and Upgrading Based on Sludge Specifications

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ABSTRACT: Due to its wide range of hazardous hydrocarbons and even heavy metal ions, oily sludge has become a great environmental challenge which must be dealt with quite quickly. As a result, ther have been numerous efforts during recent years to develop an efficient method for sludge recovery. The current research studies the effectiveness of solvent extraction with toluene and Fe_2O_3 nanoparticles for recovery and upgrading of oily sludge. Having employed Design of Experiment (DOE), it has found optimum conditions for sludge recovery with solvent extraction, namely a temperature of 55°C and mixing time of 17 minutes with solvent to sludge ratio of 6.4/4.2. Under these conditions, the sludge recovery has been 37%, which is the maximum available with toluene. Furthermore, it has studied the effectiveness of Fe_2O_3 nanoparticles for improvement of sludge pyrolysis efficiency in order to upgrade the oily sludge, wherein it has been observed that nanoparticles can significantly decrease the temperature and time of reaching maximum conversion during sludge pyrolysis process. The temperature and time of reaching to the maximum conversion, by means of gamma Fe_2O_3 nanoparticles, is about 200°C and 1200 s, respectively, which is lower than the condition in which pure sludge is being pyrolyzed.

Keywords: Oily sludge, recovery, upgrading, solvent extraction, iron nanoparticles.

INTRODUCTION

Oily sludge is one of the most critical challenges of oil industries, wherein a noticeable amount of it is produced in both upstream and downstream processes (Wang et al., 2017). It is estimated that 1 ton of oily sludge is being produced for every 500 tons of processed crude oil (Hu et al., 2013). Generally, oily sludge is a stable emulsion, containing solid particles, oily hydrocarbons, and metal ions with different compositions (Elektorowicz and Habibi, 2005). Having a significant amount of hydrocarbons and heavy metal ions turn the disposal of oily sludge into a challenge for which serious environmental regulations have been made. Therefore, there have been numerous efforts to develop efficient methods of sludge disposal or recovery (Wang et al., 2015). Since the major part of oily sludge is consisted of valuable oily hydrocarbons, recovery methods are more preferable than disposal ones (e.g. solidification and stabilization), thanks to economic benefits the latter have for the whole process, enabling hydrocarbon reuse (Shie et al., 2000). However, it is necessary to have sufficient information about the physical and chemical properties of the sludge in order to choose the most suitable method of recovery.

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A common approach for chemical analysis of oily sludge is to measure four different groups of hydrocarbons, namely (1) Saturated, (2) Aromatics, (3) Resins and (4) Asphaltenes, together known as SARA. These hydrocarbons are categorized based on their molecular weight, boiling point, and solubility in different solvents (Klein et al., 2006). Paraffin and cyclic alkanes are saturated hydrocarbons, while the three other categories (aromatics, resins, and asphaltenes) are a collection of different molecular types, whose molecular weight, aromaticity, and composition of heteroatom molecules rise when moving from aromatics to Asphaltene (Premuzic and Lin, 1999). The precipitated oily sludge in the petroleum storage containers are mainly consisted of heavier parts of crude oil such as paraffin and Asphaltene accompanied by water and solid sediments in minor amounts (Kim et al., 2004). Temperature and pressure drop in the movement of fluid from the tank to the outside is the main reason of paraffin precipitation (Erickson et al., 1993). On the other hand, asphaltenes are precipitated when lighter hydrocarbons such as n-pentane and n-heptane are present in the oil (Escobedo and Mansoori, 1997). Thus, it can be concluded that chemical properties and composition of each component play a key role in separation of each hydrocarbon group; therefore, it is quite necessary to have sufficient knowledge concerning the chemical composition of oily sludge in order to choose the most appropriate method of recovery.

Numerous methods have been proposed and developed for oily sludge recovery. Centrifuge (Cambiella et al., 2006) recovery by surfactants (Mao et al., 2015), thaw and freeze method (Zhang et al., 2012), pyrolysis (Liu et al., 2015) and solvent extraction (Hu et al., 2015) are among the methods, greatly applied for oily sludge recovery. Although each method has advantages and disadvantages, solvent extraction has displayed higher efficiency in hydrocarbon recovery (Zubaidy and Abouelnasr, 2010). Moreover, due to feasibility of solvent recovery and reuse, this method is environmentally safer than the others, being economically more beneficial due to its low operational costs as well (Taiwo and Otolorin, 2009). In order to reach higher degrees of recovery and sludge purification, recovery methods must usually be accompanied by an upgrading method that facilitates higher hydrocarbon recovery (Bartilucci et al., 1989).

Biological degradation (Lazar et al., 1999) by means of biosurfactants (Yan et al., 2012) as well as application of membrane technologies (Padaki et al., 2015) are the most important efforts, which have been carried out in order to develop an effective method for oily sludge upgrade with high efficiency and low operational costs. However, development of nanotechnology along with quick expansion of nanomaterials' application in different fields (esp., environmental protection and resources recovery) (Liu, 2006) has attracted researchers' attention towards nanostructures for hydrocarbon recovery and sludge upgrade (Guo et al., 2015, Almao, 2012). There have been some successful efforts of using nanoparticles for hydrocarbon recovery during recent years. For instance, Nassar et al. (2011) studied the impact of Fe, Co, Ti, Mg, Ca, and Ni oxide nanoparticles on asphaltene adsorption and oxidation, achieving the following trend for efficiency of utilized nanoparticles: $CaO > Co_3O_4 > Fe_3O_4 > MgO > NiO > TiO_2$. Sahebnazar et al. (2017) applied zero-valent Fe nanoparticles in order to upgrade the oily sludge recovery and managed to have separation efficiency increased by 27%.

The research has conducted a detailed study on the specification and composition of the oily sludge, sampled from Iran oil fields, and based on its results, solvent extraction with toluene and nanoseparation with gamma Fe_2O_3 nanoparticles have been studied as recovery and upgrade methods, respectively. In order to find the best operational conditions for solvent extraction process so that it could lead to maximum recovery percentage, the study applied experimental design with Response Surface Methodology (RSM). In order to evaluate the catalytic effect of iron nanoparticles on hydrocarbon recovery and sludge upgrading processes, thermogravimetric analysis (TGA) has been utilized to study the impacts of nanoparticles on kinetics of sludge upgrade.

MATERIALS AND METHODS

The studied oily sludge in this research were sampled and separated from Iran oil fields. For the purpose of sampling, the research employed a polycarbonate pipe, 2 m long and 10 cm in diameter, equipped with a rubber inner piston. Considering the geographical conditions of the sampling zone, five different samples from different points were made and labelled A, B, C, D, and E. Besides, in order to have a homogenous sample, a good representative of each point, sampling was done from the surface up to the depth of 1 m in the soil. Regarding the variety of sampling points, these five samples can be good indices of the oily sludge of the whole field.

The first step of recovery process design involved determination of chemical and physical properties of the oily sludge along with its chemical composition. Table 1 shows the standard methods for determination of chemical and physical properties of the sludge, important in recovery process design.

Table 1. Standard methods for measuring physical and chemical properties

Specification	Standard method of measurement
Density	ASTM D4052 (Azad et al., 2012)
Ash Content	ASTM D482 (Demirbaş, 2003)
Heat Value	ASTM D240 (Mofijur et al., 2013)

Density is one of the key parameters for separation processes like solvent extraction. Moreover, density can provide a vision about the percentage of light hydrocarbons in the sludge matrix. Also, ash content is quite useful to study the kinetic effect of nanoparticle, via TGA. What is more, heat value can be a good index of the potential of recover of the hydrocarbons. The greater the heat value of the sludge, the higher the recovery of hydrocarbon potential and the more economical, the whole process.

Oily sludge composition measurement is divided into two steps. In the first, the composition of different groups of hydrocarbons is determined by SARA tests, wherein saturated, aromatic, resin, and asphaltene hydrocarbons content in the oily sludge is measured (Lima et al., 2014).

The standard method of IP-143 was followed so that SARA hydrocarbons could be determined (Kord and Ayatollahi, 2012). This method employed gas chromatographer, equipped with flame ionization detector (FID) to scan the quartz rods, the length and diameter of which were 15.2 cm and 1 mm, respectively, all coated with silica particles homogenously. FID functioned with pure hydrogen, with a flow rate of 160 ml/min, as well as air, with a flow rate of 2 L/s.

The oily sludge dissolved in dichloromethane (DCM) whose concentration was 20 mg/L. About 10 to 20 micrograms of the sample got poured onto the activated rods. Then, the sample was exposed to hexane for 30 minutes, to toluene for 10 minutes, and to the 95:5 mixture of DCM and methanol for 4 minutes, respectively. Between each step, the rods got dried with air for about 3 minutes (Fan et al., 2002). Then, saturated, aromatic, resin, and asphaltene hydrocarbons composition in the sludge sample was determined by pick graphs, resulted from chromatography.

The second step for studying the composition of oily sludge is to determine some trace elements that noticeably affect the recovery process. Although the composition of metals like Li, V, Ni, Ti, and Na are minor in oily sludge, even such minor contents can be significantly effective on the efficiency of recovery methods. In order to determine these metals' composition in the samples, ASTM D5863 was utilized, being based on atomic mass spectroscopy (Ancheyta et al., 2002). Potassium is another metallic element that can be influential, even in slight amounts, on both solvent extraction and nanoparticles effectiveness, which is due to its fairly high chemical activity (Lin et al., 2002). Potassium content is determined by ASTM D7111-16 (Faber and Brodzik, 2017). Similarly, sulfur is potential to have destructive effects on the performance of nanoparticles and the solvent in solvent extraction process, due to its capability of making thiol bonds. Besides, presence of sulfur molecules in the process environment increases the level of corrosion (Fang et al., 2008). In order to measure the sulfur content in the oily sludge sample, UOP 864 standard method has to be employed.

For measuring the hydrocarbon recovery percentage, the first step is to make a proper mixing between solvent and sludge. For so doing, a solvent (toluene) and sludge sample with definite ratio got blended, using (RTC Baic, Germany) heater-stirrer. The composition of each sample after the mixing was determined by gas chromatography. The temperature of FID in these experiments was 300°C with N_2, used as the carrier gas.

There are numerous operational parameters which can significantly affect the efficiency of solvent extraction process. One of the main purposes of this research is to optimize them so that it can obtain maximum hydrocarbon recovery from oily sludge. Temperature, solvent to sludge ratio, mixing time, mixing velocity, and pressure are the most important factors to directly affect the performance of solvent during extraction. Therefore, designing some experiments seems to be necessary to find the optimum conditions. Thanks to their more intense impact than the other parameters, the research chose temperature, mixing time, and solvent to sludge ratio, using Response Surface Methodology (RSM) to design the experiments and analyze the results.

A set of mathematical operations and statistical techniques, RSM is used to make experimental models. It was first invented by Box and Draper (1987) to model the experimental responses; however, it gradually was developed to model numerical experiments as well. Application of RSM not only decreases the experiments' costs, but simplifies a big complicated problem to smaller and simpler problems (Kim and Na, 1997). There are two common models to design RSM experiments: Central Composite Design (CCD) and Box-Behnken Design (BBD) (Ferreira et al., 2007, Cho and Zoh, 2007). The number of tests are usually more, in the former (CCD) than the latter (BBD), thus covering a greater range of effects are covered (Muthukumar et al., 2004). The current research employed CCD to design the experiments by RSM. Table 2 shows the results of experiments' design for toluene, considering temperature, mixing time, and solvent to sludge ratio as the key parameters that affect the solvent extraction process.

According to the results from Table 2, 31 different runs were proposed for toluene in which hydrocarbon recovery had to be measured experimentally. Then, according to the values of hydrocarbon recovery in each run, the optimum conditions for obtaining the maximum percentage of recovery was determined.

Fe_2O_3 nanoparticles, used in this research, were bought from (Neutrino®, Iran) and their specification can be seen in Table 3.

To determine the size and specifications of Fe_2O_3 nanoparticles, SEM was performed, using MIRA3 (TESCAN, US). SEM magnitude was set at 200 kx and the scale remained 200 nm. Figure 1 shows the SEM of Fe_2O_3 nanoparticle.

Table 1. The results of *DOE* using RSM with CCD model

Run Order	Temperature (°C)	Time (min)	Solvent	Sludge	Recovery (%)
1	37.500	15	5	5	29.41
2	50.000	10	6	6	49.80
3	50.000	10	4	4	33.33
4	37.500	20	5	5	36.86
5	25.000	15	5	5	36.47
6	50.000	10	4	4	24.93
7	50.000	15	5	5	32.01
8	37.500	15	5	5	25.46
9	50.000	20	4	6	40.73
10	37.500	20	6	4	30.19
11	37.500	15	5	5	28.82
12	25.000	20	6	4	43.96
13	37.500	15	5	5	23.73
14	50.000	20	4	4	28.03
15	37.500	10	6	6	26.35
16	50.000	15	5	5	35.39
17	25.000	15	5	5	40.06
18	37.500	15	5	5	28.23
19	25.000	10	6	4	29.42
20	37.500	10	6	4	25.68
21	50.000	15	5	5	26.26
22	37.500	15	5	6	25.09
23	37.500	10	5	5	28.23
24	25.000	20	4	4	35.49
25	37.500	20	4	6	40.09
26	25.000	15	6	5	34.12
27	50.000	15	4	5	39.39
28	37.500	20	6	6	27.46
29	25.000	10	4	6	31.17
30	25.000	20	6	6	36.07
31	37.500	10	4	6	28.93

Table 2. Fe_2O_3 Nanoparticles specifications

Formula	Fe_2O_3
Phase	Gamma
Purity	99%
Average Particle size	30 nm
SSA[*]	50 m^2/g
Morphology	Spherical
Density	5.24 g/cm^3
Appearance	Red brown powder
Molecular weight	159.69 g/mol

[*] Specific surface area

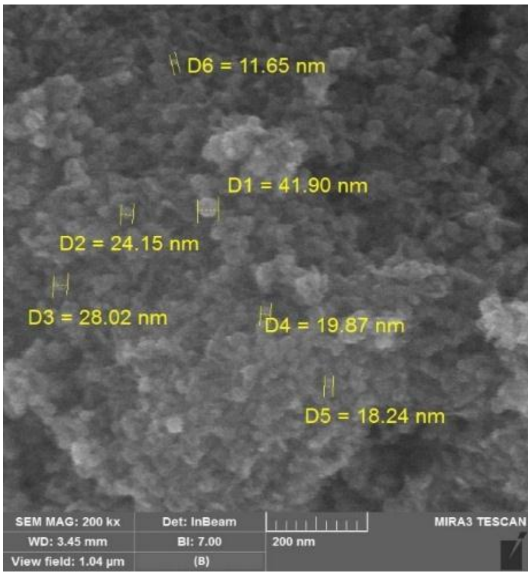

Fig. 1. SEM image of Fe_2O_3 nanoparticle

As it can be seen in Figure 1, Fe_2O_3 nanoparticle size fluctuated between 11nm and 25nm.

TGA is a thermal method for kinetic study of the pyrolysis process that simultaenously can give useful information concnering the range of hydrocarbons in the sample (Liu et al., 2015). In this study, TGA was perofrmed by METTLER TOLEDO, Switzerland, using 70 µL alumina oxide as the standard solution. The heating rate equal to 20°C/min got selected thanks to its similarity to the real conditions in industrial scale. The temperature rose from 25° to 600°C, covering nearly all hydrocarbons which were valuable to be recovered and reused. To avoid nanoparticles agglomeration, the mixture of nanoparticle and oily sludge was ultrasonicated for 30 minutes in 50°C.

RESULTS AND DISCUSSION

Table 4 shows the results of sludge specification for five samples A, B, C, D, and E, being five different sampling points.

It can be concluded from Table 4 that in all five samples, the majority of the hydrocarbon content was consisted of saturated hydrocarbons, which are usually valuable and worth getting recovered. This justifies the use of recovery and upgrading methods. Moreover, the lower amounts of heavy asphaltene compounds, which make distillation and hydrocarbon reuse difficult, was another reason for the methods to be economically reasonable to recover the oily sludge, studied in this research. Besides, minor amounts of metals and sulfur shows that recovery and upgrading process could be performed without any chemical interfering effects of these elements.

Table 3. The specification of oily sludge samples from different points of sampling

Sample / **Specification**	**Results**				
	A	**B**	**C**	**D**	**E**
Saturated hydrocarbon content (mass %)	47.3	46.5	62.4	50.3	49.8
Aromatic hydrocarbon content (mass %)	23.7	20.7	13.4	20.9	19
Resin hydrocarbon content (mass %)	21.6	22.1	17.4	22.3	24.1
Asphaltene hydrocarbon content (mass %)	7.4	10.7	6.8	6.5	7.1
Density* (g/ml)	1.283	1.315	1.259	1.180	1.087
Ash Content (mass %)	40.6	55.2	39.9	41.3	43.4
Li Content (mg/Kg)	9.6	4.7	5.4	9	9.7
V Content (mg/Kg)	47	27	26	48	53
Ni Content (mg/ Kg)	9.5	4.8	5.4	9	9.7
Ti Content (mass %)	0.12	0.10	0.07	0.12	0.16
Na Content (mass %)	0.65	0.54	0.97	0.82	0.81
K Content (mass %)	0.30	0.20	0.20	0.25	0.36
Sulfur Content (mass %)	1.5	1.7	1.1	1.3	0.1
Heat Value (MJ/Kg)	13.565	7.090	5.895	7.685	**

*Measured at 25 °C
** It was impossible to be measured

Mineral ions such as Na and K increase the salinity of the sludge, causing great challenges in the process of recovery and upgrade. Low amounts of Na and K in the studied samples shows that the salinity level of the sludge was not too high to bring any challenge for the recovery process and put the whole process at the risk of corrosion.

In order to avoid repetition of the experiments and considering the similarity between the composition of the five samples, a homogenous sample with equal composition of samples A, B, C, D, and E was produced via mixing them. The tests of solvent extraction and upgrade with nanoparticles was carried out, using this combined sample.

Considering the results of DOE in Table 2, the experiments of liquid extraction were designed for toluene and the optimum point got determined. The regression of 0.9652 for DOE results indicates great sufficiency and accuracy of the proposed model by RSM. Figure 2 shows the normal distribution of the data for toluene.

Figure 2 shows the results distribution and deviation from the normal line. As it can be seen in this figure, there was no significance difference between the results of the model and the normal distribution (the diameter line), showing the model's validity for experiment design. As the results got closer to the normal lines, the model would become more sufficient for designing the experiments and the results would be more accurate.

Figure 3 illustrates the graph of sequence of the experiments for oily sludge extraction with toluene. Obviously, there was no rational relation between the results, showing that the runs were totally random and the model was valid in this way, too.

The R^2 coefficient which stands above 0.95 and the negligible deviation between R^2 and R-adjusted shows great accuracy of the results from the suggested model by CCD method.

Figure 4 shows the effects of mixing time and temperature on hydrocarbon recovery with toluene from the oily sludge sample, studied in this research.

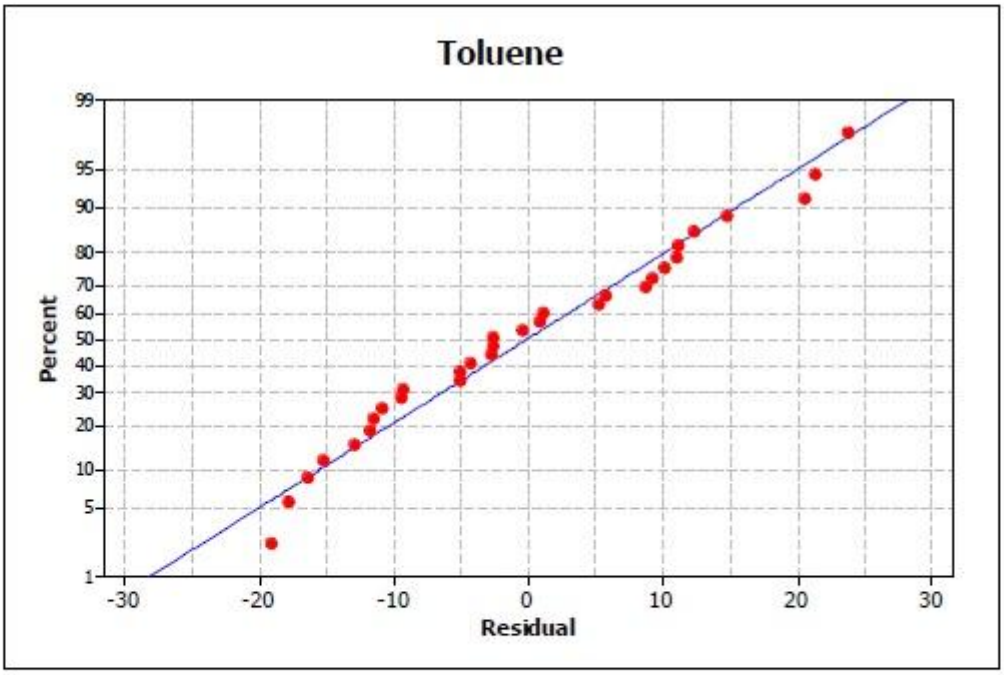

Fig. 2. Normal distribution graph of the data for solvent extraction with toluene

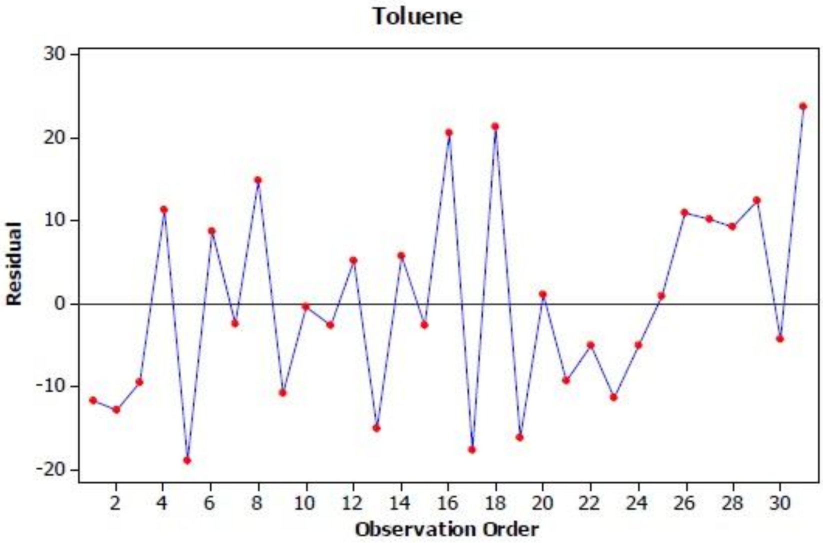

Fig. 3. The graph of sequence of experiments for oily sludge extraction with toluene

Table 5. presents the analysis of variance (ANOVA) for the statistical model.

Level	N	Mean	SD
19.825	1	28.230	*
25	8	38.970	8.337
37.5	13	30.099	7.305
50	8	37.201	9.551
55	1	26.260	*

$R^2 = 0.9652$

R-adjusted = 0.9326

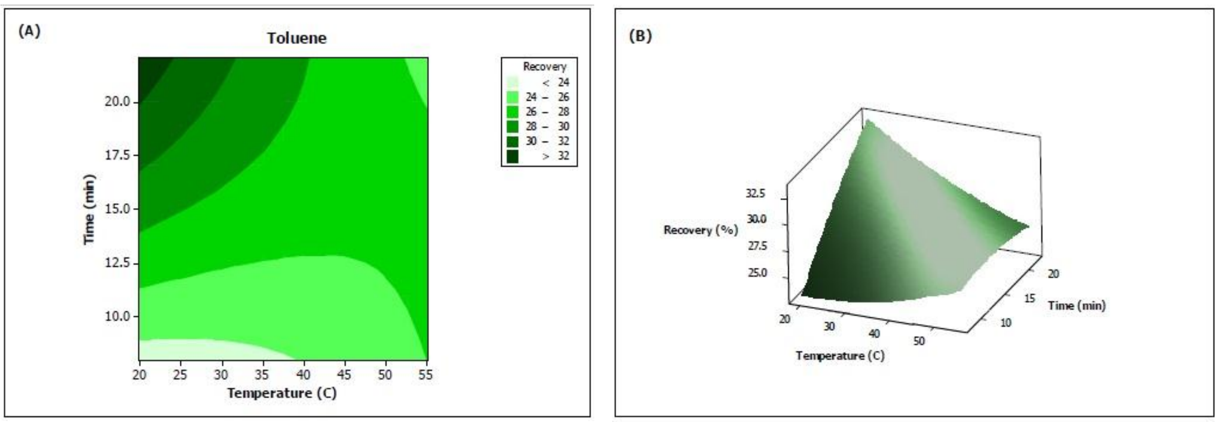

Fig. 4. (A) Surface plot of sludge recovery with toluene for time and temperature; (B) contour plot of sludge recovery with toluene for time and temperature;

As it can be seen in Figure 4, toluene recovered hydrocarbon more efficiently in higher temperatures. Since toluene is a non-polar solvent, its affinity towards non-polar compounds was higher. Furthermore, non-polar compounds of oily sludge like asphaltene and long-chain compounds have higher boiling points in comparison to polar compounds; therefore, as the temperature rose, the composition of non-polar compounds grew. With polar compounds evaporated, their undesirable interactions with toluene molecules reached a minimum level, and the recovery percentage of non-polar hydrocarbons increased consequently.

As for the mixing time, a similar trend was observed. It was reasonable to expect that as the mixing time rose, more hydrocarbons dissolved in the solvent and the recovery percentage increased, consequently. Based on Figure 4, one can conclude that a temperature of about 50°C and greater time of mixing provided better conditions to obtain higher recovery percentage.

Figure 5 shows the effects of solvent to sludge ratio for toluene.

According to Figure 5, the greater the solvent to sludge ratio, the better the hydrocarbon recovery. In a zone wherein the amounts of solvent and sludge were close to one another, i.e., solvent to sludge ratio was about 1, the minimum recovery percentage occurred; however, in zones wherein solvent amount surpassed the sludge, the recovery percentage increased subsequently and predictably.

According to the results from Figures 4 and 5, the optimum conditions to achieve maximum recovery percentage could be determined as Table 5. In such conditions, the solvent extraction test with toluene was applied and the obtained value for hydrocarbon recovery under these was 37.24%.

Fe_2O_3 nanoparticles were used to improve the kinetics of the oily sludge recovery, with TGA used to study the effects of nanoparticles on sludge upgrade. Figure 6 shows the effect of Fe_2O_3 nanoparticles on the degree of conversion in sludge pyrolysis process.

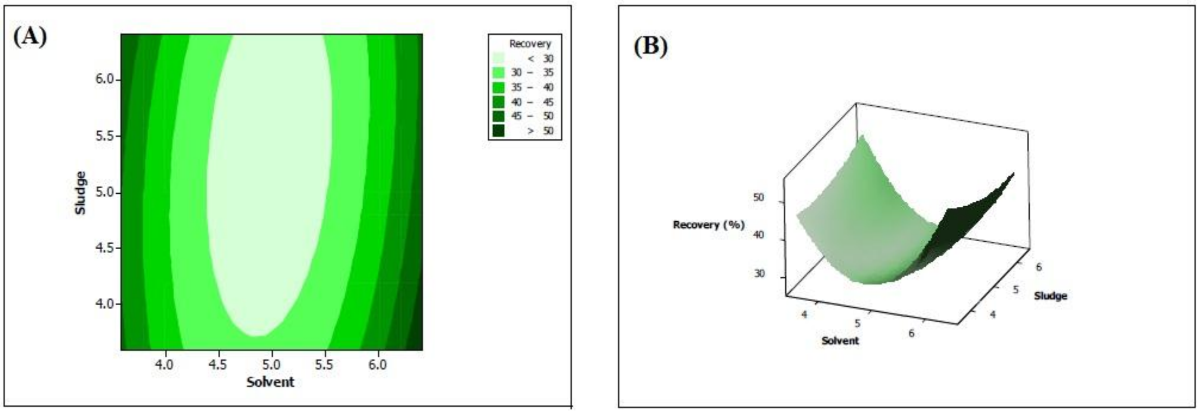

Fig. 5. (A) surface plot of sludge recovery with toluene for solvent to sludge ratio; (B) contour plot of sludge recovery with toluene for solvent to sludge ratio

Table 6. Optimum conditions for toluene in order to obtain maximum hydrocarbon recovery from oily sludge

Parameter	Optimum Value
Temperature (°C)	55
Mixing time (min)	17
Solvent to sludge ratio (wt:wt)	6.4 / 4.2

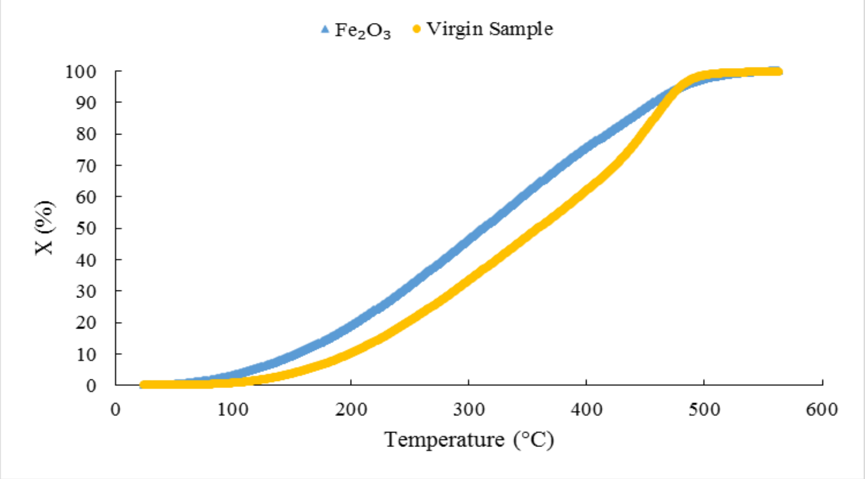

Fig. 6. The effect of Fe_2O_3 nanoparticles on the trend of conversion degree vs temperature in oily sludge pyrolysis

X is the degree of conversion, calculated as following:

$$X = \frac{w}{w_i - w_\infty} \tag{1}$$

where w is the weight of pyrolyzed fraction of the sample and w_i and w_∞ stand for initial weight and the weight of unpyrolyzed sludge, respectively (Kim et al., 2013).

Figure 6 shows that through the use of Fe_2O_3 nanoparticles, the temperature of reaching the maximum degree of conversion plummeted. In other words, when Fe_2O_3 nanoparticles were added to oily sludge, the conversion in lower temperatures reached the maximum conversion. Besides, as illustrated in Figure 7, using Fe_2O_3 nanoparticles decreased the temperature of maximum rate of conversion in oily sludge pyrolysis. Moreover, the system performed with maximum rate in a wider temperature range. According to Figure 7, the sample with nanoparticles reached the maximum rate of conversion at about 200°C, while the maximum rate of conversion for untreated sample occurred at 480°C.

Furthermore, using nanoparticles reduced the time of reaching the maximum rate of conversion, according to Figure 8.

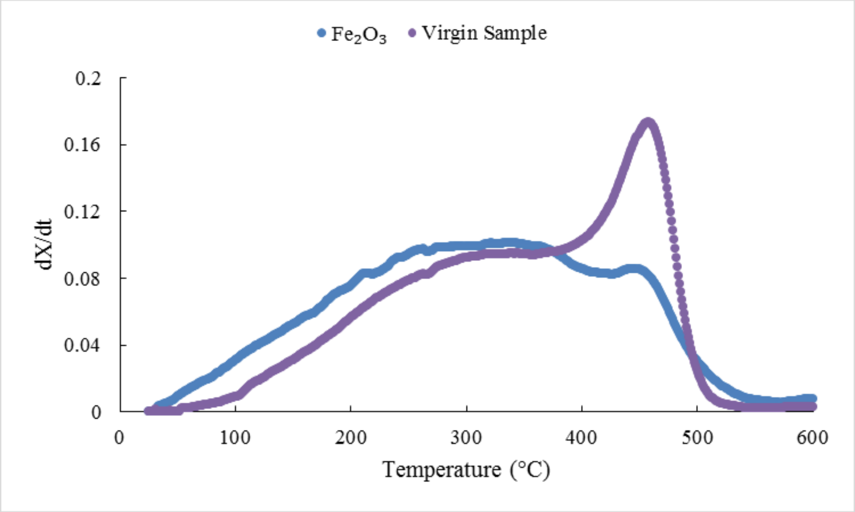

Fig. 7. Influence of Fe_2O_3 nanoparticles on the rate of conversion in oily sludge pyrolysis

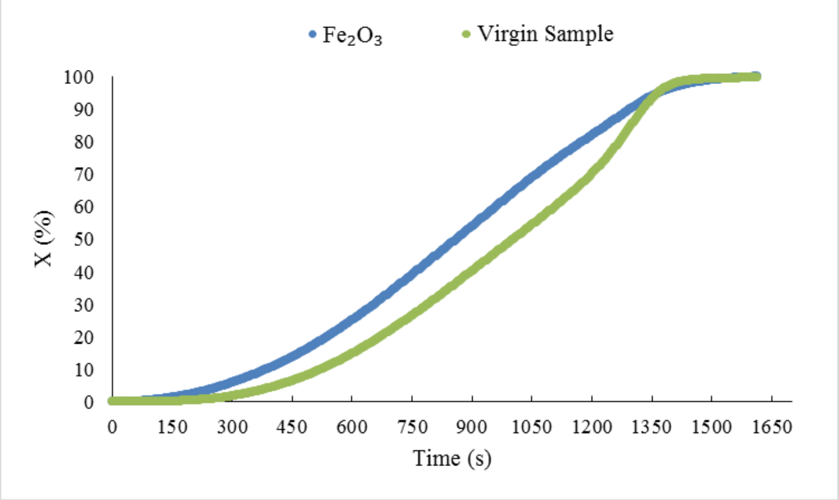

Fig. 8. Effects of Fe_2O_3 nanoparticles on the time of conversion in oily sludge pyrolysis

It can be concluded from this figure that the system reached its maximum conversion in a shorter period of time, when nanoparticles were being used in comparison to the untreated sample. The time of maximum conversion for the sample with Fe_2O_3 was about 1200 s, while for virgin sample is about 1400s.

The results of TGA for oily sludge with Fe_2O_3 nanoparticles show that using nanoparticles has catalytic effect on oily sludge pyrolysis and can be a good method for sludge upgrading in order to obtaining higher degrees of conversion and hydrocarbon recovery percentage subsequently.

CONCLUSION

Oily sludge is a great environmental challenge as it has different hydrocarbons, e.g. asphaltene and aromatics. However, with an effective recovery method, not only can the destructive influences of oily sludge be mitigated, but hydrocarbon reuse can economically be beneficial also. Therefore, a proper method of sludge recovery is necessary. The present research studied feasibility of solvent extraction with toluene as the recovery method, using Fe_2O_3 nanoparticles for sludge upgrade. Applying toluene for sludge recovery under the optimum condition can recover about 37% of the hydrocarbons, present in the oily sludge. Furthermore, using Fe_2O_3 nanoparticles can noticeably increase recovery percentage in lower temperatures with sludge pyrolysis, due to its significant catalytic effect. Fe_2O_3 nanoparticles provide appropriate surface area for hydrocarbon molecules to be adsorbed and separated from the sludge mixture during pyrolysis process.

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