Avestia Publishing
International Journal of Environmental Pollution and Remediation
Volume 2, Issue 2, Year 2014
ISSN: 1929-2732
DOI: 10.11159/ijepr.2014.006

Investigation of Impact Factors on the Treatment of Oily Sludge using a Hybrid Ultrasonic and Fenton's Reaction Process

Ju Zhang[1], Jianbing Li[1*], Ronald W. Thring[1], Guangji Hu[1], Lei Liu[2]
[1]Environmental Engineering Program, University of Northern British Columbia,
3333 University Way, Prince George, British Columbia, Canada V2N 4Z9
jzhang5@unbc.ca; jianbing.li@unbc.ca;thring@unbc.ca; hug@unbc.ca
[2]Department of Civil and Resource Engineering, Dalhousie University,
1360 Barrington St., Halifax, Nova Scotia, Canada B3H 4R2
lei.liu@dal.ca

Abstract - *In this study, a hybrid ultrasonic and Fenton's reaction process (US/Fenton) was applied for oily sludge treatment. The impacts of four different factors on the reduction of total petroleum hydrocarbons (TPH) in oily sludge were investigated. These include the initial sludge content, the molar ratio of hydrogen peroxide to iron (H_2O_2/Fe^{2+}), the ultrasonic power, and the ultrasonic treatment duration. Taguchi experimental design method was used to arrange laboratory experiments. The results indicated that a TPH reduction rate of up to 88.1% was reached with an initial sludge content of 20 g/L, a H_2O_2/Fe^{2+} molar ratio of 4:1, an ultrasonic treatment time of 5 min, and an ultrasonic power of 60 W. The initial oily sludge content and ultrasonic treatment duration were found to be the most significant factors affecting the US/Fenton treatment of oily sludge.*

***Keywords*:** Advanced oxidation, Fenton's reaction, oily sludge, petroleum hydrocarbons, ultrasound.

1. Introduction

As one of the major wastes generated in the petroleum industry, oily sludge is a complex mixture consisting of water, inorganic solid particles, and various petroleum hydrocarbons (PHCs). In particular, it contains a large amount of heavy PHCs, such as long-chain alkanes and alkenes, polycyclic aromatic hydrocarbons, asphaltenes, and resins [1, 2]. Due to the complicated composition and high concentration of heavy PHCs, the direct disposal of oily sludge could pose serious threats to the environment, and thus it needs effective treatment. Among various technologies, advanced oxidation processes (AOPs) have been recognized potential treatment approaches to effectively degrade the recalcitrant compounds [3]. During AOP processes, a large amount of hydroxyl radicals (·OH) can be generated through various methods (e.g., ultrasonic irradiation, ultraviolet radiation, photo-catalysis, ozonation, and/or Fenton's reaction) [4]. The hydroxyl radicals are strong and non-selective oxidants which can oxidize various recalcitrant organic compounds. The final products of reaction include carbon dioxide, short-chain organic compounds, and inorganic ions, which are usually less toxic and favourable for biodegradation [5]. Among various AOPs, ultrasonic irradiation (US) and Fenton's reaction have been widely applied to a variety of fields. Ultrasonic treatment can generate •OH radicals due to the acoustic cavitation which involves the formation and subsequent expansion of micro-bubbles under the periodic pressure variations [6]. The Fenton's reagents, usually hydrogen peroxide (H_2O_2) and ferrous (Fe^{2+})

Date Received: 2013-09-20
Date Accepted: 2014-02-12
Date Published: 2014-04-09

materials, can react with each other to generate sufficient hydroxyl radicals, while H_2O_2 serves as an oxidizing agent and the ferrous (Fe^{2+}) compound works as a catalyst for reaction [7].

In general, there is a similarity between the pollutant oxidation mechanisms among various AOPs, and it is thus expected that the combination of individual AOPs might achieve better results as compared to a single AOP. In fact, the combination of ultrasonic irradiation and Fenton's reaction has recently received increasing attention. In the hybrid AOP process, hydroxyl radicals can be generated by the decomposition of H_2O_2 which also converts Fe^{2+} ions into Fe^{3+} ($Fe\text{-}OOH^{2+}$). Meanwhile, the application of ultrasonic energy could isolate Fe^{2+} from $Fe\text{-}OOH^{2+}$, and the isolated Fe^{2+} could in turn react with H_2O_2 to generate hydroxyl radicals. As a result, the iron catalysts could be regenerated during the hybrid process of combining ultrasonic irradiation with Fenton's reaction, and this hybrid method can be more effective in degrading recalcitrant compounds. For example, Neppolian et al. [8] reported that the degradation rate of para-chlorobenzoic acid (p-CBA) was 7.3×10^{-3} min^{-1} under the combined process of ultrasound and Fenton's reaction as compared to the value of 4.5×10^{-3} min^{-1} under the process of only using 20 kHz ultrasound. Sun et al. [9] investigated the combined ultrasonic and Fenton's reaction process for the decolorization of acid black 1 (AB1) solution, and found that the optimal concentration of Fe^{2+} was 0.025 mM when the concentration of H_2O_2 was 8.0 mM. Virkutyte et al. [10] examined the effect of ultrasonic and Fenton's reaction process on the degradation of naphthalene when the mineral iron in soil was used as the catalyst, and they observed that the optimal degradation efficiency of naphthalene reached 97% at an ultrasonic power of 400 W when 600 mg/L of H_2O_2 was added into the soil with an initial naphthalene concentration of 200 mg/kg. In spite of the advantages of oxidizing recalcitrant organic compounds, these reported AOP studies mainly focused on the degradation of individual contaminants; very few studies have applied the hybrid AOP process to treat a mixture of hazardous organic compounds such as oily sludge.

The objective of this study is then to investigate the application of a combined ultrasonic and Fenton's reaction process (US/Fenton) to treat refinery oily sludge. The Taguchi experimental design method was used to plan the laboratory experiments and to examine the effects of different factors on the treatment performance, which is indicated by the oxidation of petroleum hydrocarbons. These factors include the initial oily sludge content in the treatment system, the molar ratio of H_2O_2 to Fe^{2+}, the ultrasonic power, and the ultrasonic treatment duration. The results could provide a sound basis for developing more efficient and economically competitive methods for oily sludge treatment.

2. Materials and Methods

2. 1. Oily Sludge and Chemicals

$FeSO_4 \bullet 7H_2O$ (from Sigma) and H_2O_2 (30% w/w) solution were used as Fenton's reagents. The oily sludge was obtained from the crude oil tank bottom in an oil refinery plant in western Canada, and was kept at 4 °C in a capped stainless-steel bucket before use. Table 1 lists the summary of its characteristics. The TPH content was measured according to the method described in Zhang et al. [11], water content was measured using ASTM D1744 [12], the solid content was calculated based on the measurement of TPH and water, and metal elements were measured using Inductively Coupled Plasma (ICP) analysis based on the ASTM D5185 [13].

Table 1. Characteristics of oily sludge.

Parameter	Concentration	Parameter	Concentration
TPH (by mass)	61%	Barium(mg/kg)	2,136
Water content (by mass)	24%	Iron (mg/kg)	6,339
Solid content (by mass)	15%	Zinc (mg/kg)	209
Sodium (mg/kg)	76	Copper (mg/kg)	43
Potassium (mg/kg)	423	Lead (mg/kg)	19
Magnesium (mg/kg)	432	Chromium (mg/kg)	11
Aluminium (mg/kg)	999	Nickel (mg/kg)	9
Calcium (mg/kg)	1,145		

2.2. Experimental Design

The ultrasonic apparatus used in this study was a 20-kHz Misonix Sonicator 3000 generator with a titanium sonic probe, and the ultrasonic power could be adjusted from 0 to about 75 W. For the hybrid ultrasonic and Fenton's reaction process, the impacts of four different factors were investigated. They include the initial oily sludge content in the treatment system, the molar ratio of H_2O_2 to Fe^{2+} (H_2O_2/Fe^{2+}), the ultrasonic power, and the ultrasonic treatment duration. Each factor was examined at 3 levels, and a Taguchi orthogonal experimental design method [14] was used to arrange the experiments through a L27 array (Table 2). This method can allow for the examination of both the main effects of each factor and the interaction effects between factors. There were 27 experimental runs (L1-L27), and each run was replicated twice. For each test, a constant volume of H_2O_2 (i.e. 15 mL) was used, and a given amount of oily sludge was added into a 100-mL beaker with 10 mL of de-ionized water. A final total liquid volume of 25 mL was thus obtained after adding 15 mL of H_2O_2 solution, which was gradually added to avoid rigorous reaction. The sludge amount for each test (e.g., 0.5 g, 1.0 g, 1.5 g) was determined by multiplying the specified sludge content in Table 2 by the liquid volume (i.e. 25 mL). The amount of $FeSO_4 \bullet 7H_2O$ added to the beaker was calculated based on the molar ratio of H_2O_2 /Fe^{2+} for each test (Table 2). During the experiment, the ultrasonic probe was placed under the liquid to start ultrasonic irradiation with an ultrasonic power as specified in Table 2. After initiating the ultrasonic treatment, the H_2O_2 solution (i.e. a total volume of 15 mL) was gradually added into the beaker at a rate of about 15, 5, and 3 mL/min for the 1-, 3-, and 5-min ultrasonic treatment durations (Table 2), respectively,

Table 1. L27 array obtained from Taguchi experimental design.

Experimental test #	Sludge content (g/L)	Molar ratio of H_2O_2 /Fe^{2+}	US time (min)	US power (W)
L 1	20 (level 1)	4:1 (level 1)	1 (level 1)	20 (level 1)
L 2	20 (level 1)	4:1 (level 1)	3 (level 2)	40 (level 2)
L 3	20 (level 1)	4:1 (level 1)	5 (level 3)	60 (level 3)
L 4	20 (level 1)	10:1 (level 2)	1 (level 1)	40 (level 2)
L 5	20 (level 1)	10:1 (level 2)	3 (level 2)	60 (level 3)
L 6	20 (level 1)	10:1 (level 2)	5 (level 3)	20 (level 1)
L 7	20 (level 1)	50:1 (level 3)	1 (level 1)	60 (level 3)
L 8	20 (level 1)	50:1 (level 3)	3 (level 2)	20 (level 1)
L 9	20 (level 1)	50:1 (level 3)	5 (level 3)	40 (level 2)
L 10	40 (level 2)	4:1 (level 1)	1 (level 1)	40 (level 2)
L 11	40 (level 2)	4:1 (level 1)	3 (level 2)	60 (level 3)
L 12	40 (level 2)	4:1 (level 1)	5 (level 3)	20 (level 1)
L 13	40 (level 2)	10:1 (level 2)	1 (level 1)	60 (level 3)
L 14	40 (level 2)	10:1 (level 2)	3 (level 2)	20 (level 1)
L 15	40 (level 2)	10:1 (level 2)	5 (level 3)	40 (level 2)
L 16	40 (level 2)	50:1 (level 3)	1 (level 1)	20 (level 1)
L 17	40 (level 2)	50:1 (level 3)	3 (level 2)	40 (level 2)
L 18	40 (level 2)	50:1 (level 3)	5 (level 3)	60 (level 3)
L 19	60 (level 3)	4:1 (level 1)	1 (level 1)	60 (level 3)
L 20	60 (level 3)	4:1 (level 1)	3 (level 2)	20 (level 1)
L 21	60 (level 3)	4:1 (level 1)	5 (level 3)	40 (level 2)
L 22	60 (level 3)	10:1 (level 2)	1 (level 1)	20 (level 1)
L 23	60 (level 3)	10:1 (level 2)	3 (level 2)	40 (level 2)
L 24	60 (level 3)	10:1 (level 2)	5 (level 3)	60 (level 3)
L 25	60 (level 3)	50:1 (level 3)	1 (level 1)	40 (level 2)
L 26	60 (level 3)	50:1 (level 3)	3 (level 2)	60 (level 3)
L 27	60 (level 3)	50:1 (level 3)	5 (level 3)	20 (level 1)

2.3. Sample Analysis

The sample in the beaker after US/Fenton treatment was transferred into a 50-mL tube for centrifugation for 30 min in order to separate the solid from liquid for the analysis of PHCs within the two phases [15]. After centrifugation, the supernatant was transferred into a separating funnel for liquid extraction, and the solid residue left in the centrifugation tube was used to extract PHCs. The liquid and solid extraction procedures as well the chemical solvents used can be found in Zhang et al. [11]. The extracted solution was then analyzed for PHCs using a Varian CP-3800 Gas Chromatograph with flame ionization (GC-FID). The GC analysis conditions and procedures can be found in Zhang et al. [11] The TPH reduction rate (η) was used to analyze the efficiency of the US/Fenton process, based on the measured TPH mass in the system before and after treatment (M_0 and M_A):

$$\eta = \frac{M_A - M_0}{M_0} \times 100\% \tag{1}$$

2.4. Experimental Data Analysis

Statistical analyses including signal to noise (S/N) ratio analysis and ANOVA were used to analyze the experimental data. The S/N ratio was evaluated using the following equation [14]:

$$\mathrm{S/N} = -10 \log \sum_{i=1}^{n} \left(\frac{1}{y_i^2} \right) / n \tag{2}$$

where S/N denotes the performance statistic, y_i denotes the observed data, n is the number of observations. The unit of S/N ratio is decibels (dB). The higher the S/N ratio, the better the result is.

3. Results and Discussion

3. 1. Degradation of PHCs in Sludge by using the Hybrid US/Fenton Process

The reduction of individual petroleum hydrocarbons (PHCs) fraction in oily sludge after US/Fenton treatment was examined (Fig. 1), where fraction 1 (F1), fraction 2 (F2), fraction 3 (F3) and fraction 4 (F4) was defined as the group of PHCs from C6 to C10, C10 to C16, C16 to C34, and C34 to C50, respectively. It can be found that the US/Fenton process achieved a F2 fraction reduction in the range of 43.3% to 93.1%, a F3 fraction reduction in the range of 33.3% to 86.9%, and a F4 fraction reduction in the range of 11.8% to 90.1%, respectively. The decomposition of long-chain hydrocarbons (i.e. F4 fraction) was generally less than those of the other two PHCs fractions, indicating that short-chain PHCs are more prone to be destructed by this hybrid oxidation process. All of the highest PHCs reduction occurred for treatment L3, but the reduction of the F3 fraction was less than that of F4 fraction. This might be caused by the accumulation into F3 fraction of intermediate products from the decomposition of the heavier F4 fraction. The lowest F2 reduction (i.e. 43.3%), F3 reduction (i.e. 33.3%) and F4 reduction (i.e. 11.8%) occurred for treatment L22 (i.e. corresponding to the lowest ultrasonic power and treatment duration level), L27 (i.e. corresponding to the lowest ultrasonic power level), and L1 (i.e. corresponding to the lowest level for all the four factors), respectively. Fig. 2 presents the reduction results of TPH in oily sludge for all of the experiments. The TPH reduction rate was in the range of 51.9% to 88.1%, 42.3% to 83.9%, and 36.0% to 81.3% for experiments with low (i.e. test # L1 to L9), medium (i.e. test # L10 to L18), and high initial sludge contents (i.e. test # L19 to L27), respectively. It is obvious that the initial oily sludge content could affect the treatment performance of the hybrid US/Fenton process. Among all of the 27 experimental runs, the highest TPH reduction rate of 88.1% was observed for treatment L3, with an initial sludge content of 20 g/L, a molar ratio of H_2O_2/Fe^{2+} of 4:1, an ultrasonic treatment time of 5 min, and an ultrasonic power of 60W.

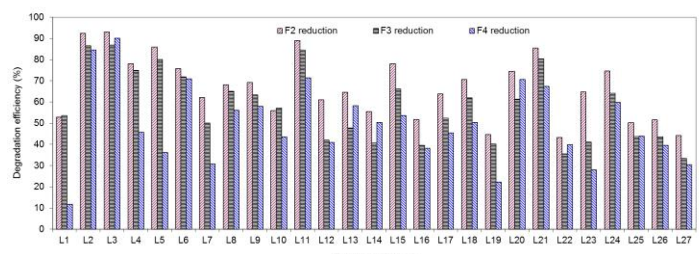

Figure 1. Reduction of PHCs fraction in oily sludge through US/Fenton process.

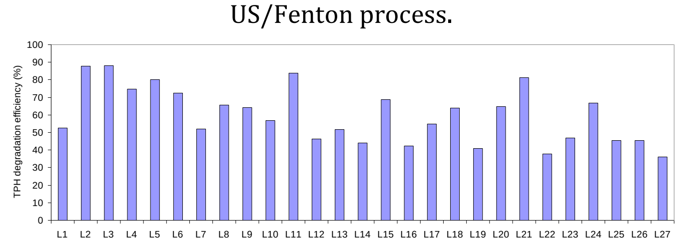

Fig. 2 Reduction of TPH in oily sludge through US/Fenton process.

3. 2. Impact of US/Fenton Operating Factors on the TPH Reduction

Fig. 3 presents the main effect plot which shows the contribution to S/N ratio change from variation in an impact factor from one level to another. It can be found that the S/N ratio decreased with the increase of initial oily sludge content and the increase of H_2O_2/Fe^{2+} ratio, but increased when the ultrasonic irradiation time was extended. The S/N ratio increased when the ultrasonic power increased from level 1 to level 2, but decreased when the ultrasonic power increased from level 2 to level 3. This indicates that further increase of ultrasonic power after level 2 didn't further promote the TPH reduction. The greater change in S/N ratio occurred when sludge content and ultrasonic treatment duration increased from level 1 to level 3, indicating that sludge content and ultrasonic treatment time were the most significant factors on TPH reduction. As shown in Fig.3, the optimal condition (when the highest S/N ratio occurs) for TPH reduction using US/Fenton process would be a sludge content of 20 g/L, a H_2O_2/Fe^{2+} molar ratio of 4:1, an ultrasonic irradiation time of 5 min, and an ultrasonic power of 40 W.

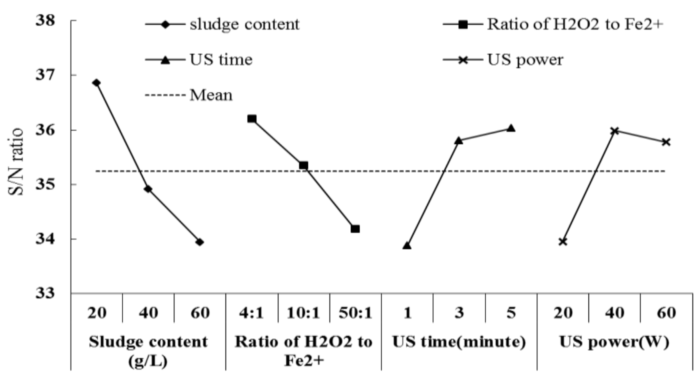

Figure 3. Main effects of factors on the reduction of TPH in oily sludge.

Fig. 4 presents the two-factor interaction effects on TPH reduction in oily sludge when using the US/Fenton process. In the interaction plot, the levels of one factor are set on the x-axis and a separate line stands for the mean S/N ratio of each level for the other factor. A larger vertical distance between the factor point and the mean S/N ratio line indicates a stronger interaction between that factor and the corresponding factor set on the x-axis. However, if the lines are parallel to each other, there is no interaction between them. Since each factor was examined with three levels in this study, three curves were displayed in each plot. The degree of interaction between the factors depends on the departure of a curve from the trend of another curve. It was observed in Fig. 4(c) that the interaction between H_2O_2/Fe^{2+} ratio and the ultrasonic treatment duration was greater than that between other factors, and a greater TPH reduction was obtained with a H_2O_2/Fe^{2+} ratio of 4:1 and an ultrasonic treatment time of 3 min.

In addition to S/N ratio analysis, the analysis of variance (ANOVA) was also carried out to verify the impacts of various factors and their interactions on the TPH reduction in oily sludge. The ANOVA was implemented by using MINITAB 16, and the results are shown in Table 3. Several parameters were generated during the ANOVA process, including the degree of freedom (DF), the sequential sums of squares (Seq SS), the adjusted sum of squares (Adj SS), and the adjusted means squares (Adj MS). F-test was performed with 95% confidence interval, and it was verified that oily sludge content and ultrasonic treatment duration had significant impacts on TPH reduction (e.g., their P values were less than 0.05 as shown in Table 3). The other two factors (with P values greater than 0.05) did not show significant impacts on the US/Fenton treatment performance. The ANOVA results also illustrated that a higher interaction existed between H_2O_2/Fe^{2+} ratio and ultrasonic treatment duration (with P value of 0.332), but there was no significant interaction between the factors to affect TPH degradation.

Table 3. ANOVA for TPH reduction using US/Fenton process.

Sources	DF	Seq SS	Adj SS	Adj MS	F	P
Sludge content	2	39.646	39.646	19.823	8.34	0.019
H_2O_2/Fe^{2+} ratio	2	18.395	18.395	9.1975	3.87	0.083
Ultrasonic treatment duration (US time)	2	24.982	24.982	12.491	5.25	0.048
Ultrasonic power (US power)	2	22.422	22.422	11.211	4.72	0.059
Sludge content*H_2O_2/Fe^{2+} ratio [(a)]	4	5.597	5.597	1.3994	0.59	0.684
Sludge content*US time [(a)]	4	2.595	2.595	0.6488	0.27	0.885
H_2O_2/Fe^{2+} ratio*US time [(a)]	4	13.544	13.544	3.3861	1.42	0.332
Residual error	6	14.262	14.262	2.377		
Total	26	141.444				

(a)* denotes the interaction between two factors

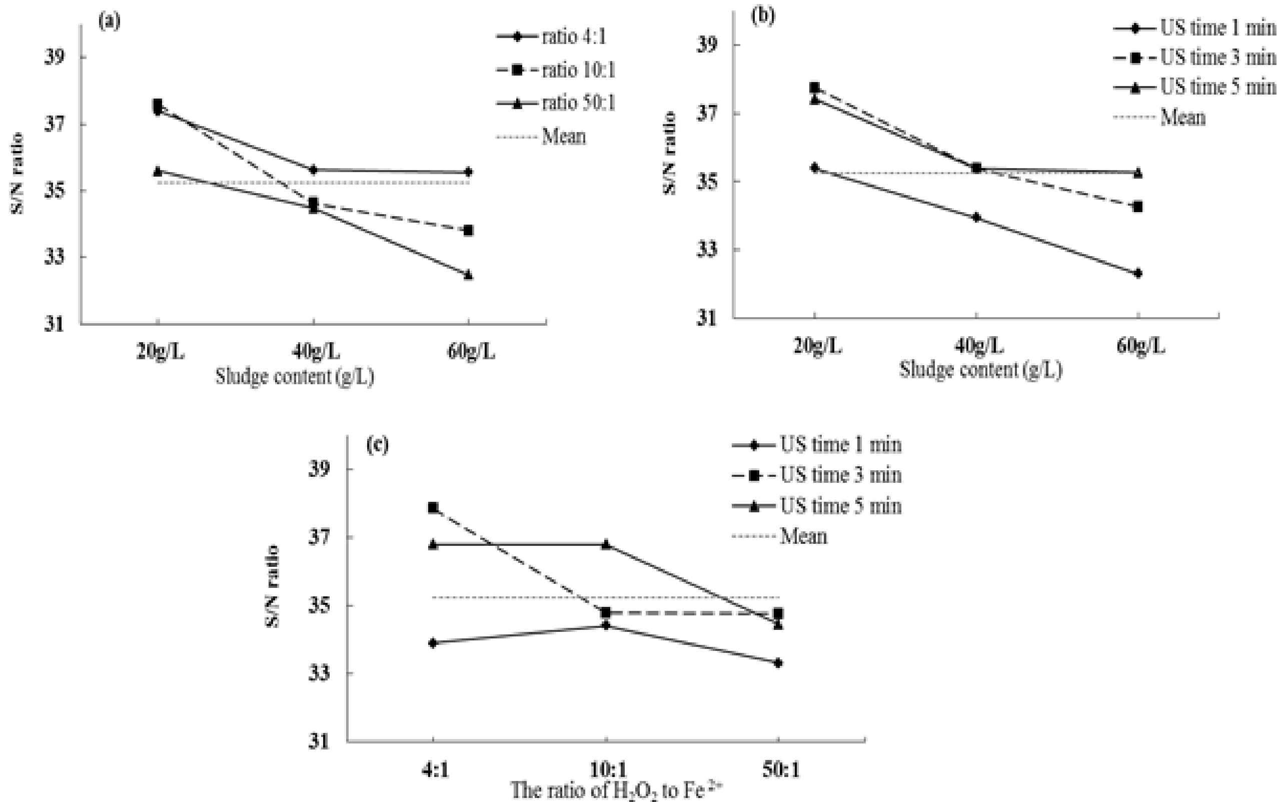

Figure 4. Interaction effects of factors on TPH reduction in oily sludge: (a) interaction between initial sludge content and H_2O_2/Fe^{2+} ratio, (b) interaction between initial sludge content and ultrasonic treatment duration, (c) interaction between H_2O_2/Fe^{2+} ratio and ultrasonic treatment duration.

3. 3. Discussion

As illustrated in Fig. 3 and further verified by ANOVA, the initial oily sludge content had a significant impact on the performance of the US/Fenton process. On one hand, when the initial oily sludge content was high, more PHCs would be in the form of a non-aqueous phase or attached to the solid particles. This would decrease the contact of hydroxyl radicals with PHCs, and thus the TPH reduction would decrease. When the initial sludge content was high in the US/Fenton treatment system, the viscosity of bulk liquid also increased. The increased viscosity could lead to the impedance of the formation and collapse of cavitation bubbles, and thus decrease the ultrasonic desorption of petroleum hydrocarbons [16]. For example, the TPH reduction rate ranged from 51.9% to 88.1% at level 1 (i.e. 20 g/L), from 42.3% to 83.9% at level 2 (i.e. 40 g/L), and from 36.0% to 81.3% at level 3 of sludge content (i.e. 60 g/L), respectively. This was consistent with many other studies. Virkutyte et al. [10] investigated the ultrasonic assisted oxidation of naphthalene-contaminated soil combining with a Fenton-like process, and they observed a higher degradation efficiency (94-97%) with lower initial naphthalene concentration (200 mg/kg), but the efficiency decreased to 58-76% when the initial naphthalene concentration was doubled (i.e. 400 mg/kg). On the other hand, the yield of oxidation intermediates could increase when the initial sludge content increased, and the accumulation of intermediates might affect the degree of PHCs degradation. Lin et al. [17] examined the oxidation rate of azo dyes at high initial concentration under ultrasonic irradiation with Fenton-like reagents, and they found that a lower degradation efficiency was due to the formation of recalcitrant by-products. Since oily sludge is a mixture of many complex PHCs, the intermediates (e.g., carboxyl acids, alkene, ketones) could be accumulated when a large amount of PHCs were oxidized. The resistance to further decomposition might increase due to the accumulation of more oxidation intermediates. Consequently, a lower TPH reduction efficiency was observed in this study when the initial sludge content increased.

In spite of the above discussion, a relatively higher TPH reduction rate was still observed at a higher level of initial sludge content (i.e. 60 g/L). For example, TPH reduction reached 66.7% and 81.3% for experimental run L24 and L21, respectively (Fig. 2). This might indicate the complicated effects of other factors on the US/Fenton process or other interactions of factors. As the initial sludge content increased, more solid particles were brought into the treatment system, and they could also provide more interfacial areas for the formation of OH• radicals and thus the occurrence of free radical reactions [18]. Moreover, it was reported that many metal components could serve as catalysts to trigger the chain oxidation reactions similar to reactions associated with the Fenton process [18]. Many metals elements, such as Fe, Al, Ca, Cu, Zn, were found in oily sludge. These metals might serve as other sources of catalysts for Fenton-like reactions to improve the TPH reduction. In addition, ultrasonic treatment duration had a positive impact on TPH reduction when using the US/Fenton process. In general, the benefit of applying ultrasonic irradiation during Fenton's reaction process is mainly to enhance the contact of hydroxyl radicals (OH•) with PHCs compounds. The increase in ultrasonic treatment time could help the desorption of PHCs from solid particles and the dispersion of these hydrophobic compounds into the bulk liquid. In the meantime, the micro-jets generated from the heterogeneous sludge treatment system by ultrasonic irradiation could enhance the transfer of OH• radicals towards the solid-liquid interface where PHCs are attached. As a result, a higher TPH reduction rate could be achieved under US/Fenton's process when a longer ultrasonic treatment (i.e. 5 min) was applied.

Moreover, the abundant intermediates of $Fe\text{-}OOH^{2+}$, which are related to Fenton's reactions, can be decomposed into Fe^{2+} and hydroperoxyl ($HO\bullet^{2+}$) by ultrasonic irradiation. With longer ultrasonic treatment duration, more Fe^{2+} could be regenerated to engage in the reactions with H_2O_2, leading to the production of more hydroxyl radicals. Another benefit from prolonged ultrasonic irradiation is that it might facilitate the decomposition and cleavage of more petroleum hydrocarbons. Although the ANOVA results did not confirm the significant impact of H_2O_2/Fe^{2+} ratio on TPH reduction when using US/Fenton's process, it is still worth further investigating the effect of this ratio. Many studies have examined the impact of the H_2O_2/Fe^{2+} ratio on wastewater treatment when using Fenton's reaction process alone, and reported a wide range of optimal ratios. Casero et al. [19] reported the optimal molar ratio was 5 to 40 by the use of Fenton's reagents to degrade aromatic amines in wastewater, and Tekin et al. [20] found that the molar ratio was between 150 and 250 when using Fenton's reaction process for pharmaceutical wastewater treatment. In this study, the highest TPH reduction rate was achieved when the H_2O_2/Fe^{2+} ratio was 4:1, and the existence of extra Fe^{2+} might play an important role in the oxidation of PHCs by reactions with intermediate radicals (carboxyl radicals) [21]. In fact, other studies have indicated that the mineralization of organic compounds can be increased with the increase of Fe^{2+} [22].

4. Conclusion

In this study, a hybrid ultrasonic and Fenton's reaction (US/Fenton) process was applied to treat refinery oily sludge. Four different factors were examined for their effects on the performance of the US/Fenton process. These factors include the initial oily sludge content in the treatment system, the molar ratio of H_2O_2/Fe^{2+}, the ultrasonic treatment duration, and the ultrasonic power. Taguchi experimental design method was used to arrange laboratory experiments for investigating the impact of these factors. It was found that a TPH reduction rate of up to 88.1% was reached with a sludge content of 20 g/L, a H_2O_2/Fe^{2+} ratio of 4:1, an ultrasonic power of 60 W, and an ultrasonic treatment duration of 5 min. The sludge content and ultrasonic treatment duration had significant impacts on the reduction of petroleum hydrocarbons, while the other two factors didn't show significant impacts. A higher TPH reduction was generally observed to be associated with a lower initial sludge content and a longer ultrasonic treatment duration. Although there was no significant interaction between factors with respect to TPH reduction, the interaction effect between ultrasonic treatment duration and H_2O_2/Fe^{2+} ratio was relatively higher than that between other factors. In summary, the combination of ultrasonic irradiation with Fenton's reaction can effectively reduce petroleum hydrocarbons in oily sludge within a short treatment period, and its treatment efficiency could be improved by appropriate combination of different factor levels.

References

[1] D. Ramaswamy, D. D. Kar, S. De "A study on recovery of oil from sludge containing oil using froth flotation", Journal of Environmental Management, 85, 2007, 150-154.

[2] G. J. Hu, J.B. Li, G.M. Zeng "Recent development in the treatment of oily sludge from petroleum industry: a review", Journal of Hazardous Materials, 261, 2013, 470-490.

[3] R.P. Gogate, B.A. Pandit "A review of imperative technologies for wastewater treatment II: hybrid methods" Advances in Environmental Research, 8, 2004, 553-597.

[4] A.R. Torres, F. Abdelmalek, E. Combet, C. Petrier, C. Pulgarin "A comparative study of ultrasonic cavitation and Fenton's reagent for bisphenol A degradation in deionised and natural waters", Journal of Hazardous Materials, 16, 2007, 546-551.

[5] G.Y. Adewuyi "Sonochemistry in environmental remediation. 1 combinative and hybrid sonophotochemical oxidation processes for the treatment of pollutants in water" Environmental Science & Technology, 39, 2005, 3409-3420.

[6] M. Mohajerani, M. Mehrvar, F. Ein-Mozaffari "Recent achievements in combination of ultrasonolysis and other advanced oxidation processes for wastewater treatment" International Journal of Chemical Reactor Engineering, 8(R2), 2010, 1-78.

[7] J.J. Pignatello, E. Oliveros, A. MacKay "Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry" Critical Reviews in Environmental Science & Technology, 36(1), 2006, 1-84.

[8] B. Neppolian, J. Park, H. Choi "Effect of Fenton-like oxidation on enhanced ocidative degradation of para-chlorobenzoic acid by ultrasonic irradiation" Ultrasonics Sonochemistry, 11, 2004, 273-279.

[9] J-H. Sun, S-P. Sun, J-Y. Sun, R-X, Sun, L-P. Qiao, H-Q. Guo, M-H. Fan "Degradation of azo dye acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation" Ultrasonics Sonochemistry, 14, 2007, 761-766.

[10] J. Virkutyte, V. Vickackaite, A. Padarauskas "Sono-oxidation of soils: degradation of naphthalene by sono-Fenton-like process." Journal of Soils and Sediments, 10, 2010, 526-536.

[11] J. Zhang "Treatment of Refinery Oily Sludge using Ultrasound, Bio-surfactant, and Advanced Oxidation Processes" M.Sc. Thesis, University of Northern British Columbia, Prince George, Canada, 2013.

[12] ASTM "Standard test method for determination of water in liquid petroleum products" by Karl Fischer reagent, ASTM D1744, 1992.

[13] ASTM "Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils" by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ASTM D5185, 2009.

[14] G. Taguchi "System of Experimental Design" White Plains, New York, 1987.

[15] Q.X. Huang, X. Han, F.Y. Mao, Y. Chi, J.H. Yan "A model for predicting solid particle behaviour in petroleum sludge during centrifugation" Fuel, 117, 30, 2014, 95-102.

[16] G.S. Gaikwad, B.A. Pandit "Ultrasound emulsification: effect of ultrasonic and physicochemical properties on dispersed phase volume and droplet size" Ultrasonics Sonochemistry, 15(4), 2008, 554-563.

[17] J.J. Lin, X.S. Zhao, D. Liu, Z.G. Yu, Y. Zhang, H. Xu "The decoloration and mineralization of azo dye C. I. Acid Red 14 by sonochemical process: rate improvement via Fenton's reactions" Journal of Hazardous Materials, 157, 2008, 541-546.

[18] Y.L. Pang, Z. Abdullah, S. Bhatia "Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater" Desalination, 277, 2011, 1-14.

[19] D.S. Casero, S. Rubio, D. Perez-Bendito "Chemical degradation of aromatic amines by Fenton's reagent" Water Research, 31, 1997, 1985-1995.

[20] H. Tekin, O. Bilkay, S.S. Ataberk, H.T. Balta " Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater" Journal of Hazardous Materials, 136, 2006, 258-265.

[21] C. Mansano-Weiss, H. Cohen, D. Meyerstein "Reactions of peroxyl radicals with $Fe(H_2O)_6^{2+}$" Journal of Inorganic Biochemistry, 91, 2002, 199-204.

[22] J.R. Watts, C.P. Stanton "Mineralization of sorbed and NAPL-phase hexadecane by catalyzed hydrogen peroxide", Water Research, 33(6), 1999, 1405-1414.