Applicability of nano zero valent iron (nZVI) in sono – Fenton process

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Abstract.   Fenton process is one of the advanced oxidation processes (AOPs) used to remove complex organic pollutants in wastewater. In this study, instead of iron sulfate ($FeSO_4$), nano zero valent iron (nZVI) was used as a major source of ferrous iron (Fe^{2+}). In order to enhance the process, ultrasound was utilized in this study. Results show that, with the aid of ultrasound, nZVI produced more Fe^{2+} compared to $FeSO_4$ at pH 2. Furthermore, combination of higher intensity and longer sonication time in Fenton process acceleratde the chemical oxygen demand (COD) removal from palm oil mill effluent (POME). Through the process, 80% of COD content was removed within 2 hours instead of 24 hours of silent degradation.

1. Introduction

In 2012, Malaysia was recorded as second largest world producer of palm oil. As a result of massive production of palm oil, huge amount of palm oil mill effluent (POME) was produced. As POME contains extremely high content of COD, several stages of treatment were required before it can be discharged into the environment. In most cases, anaerobic process was used to treat POME at the primary stage. However, oil millers as well as researchers are still looking for the best treatment method to be applied at the tertiary/polishing level.

One of the options to be consider for tertiary treatment is Fenton process. Study by Kellel [1] and Nieto [2] showed that Fenton process had successfully treated the olive oil mill effluent with similar characteristics to POME. In Fenton process, organic pollutants were attacked by strong oxidant called hydroxyl radical ($OH^{\bullet}$) and produced harmless products. $OH^{\bullet}$ was a result of the reaction between Fe^{2+} and hydrogen peroxide (H_2O_2). The reaction can be written as:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$$
(1)
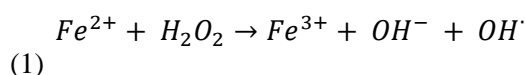
In conventional Fenton process, $FeSO_4$ was utilized as a major source of Fe^{2+} [3], [4]. However, to enhance the process, scholars had combined Fenton with other advanced oxidation processes (AOPs) methods such as photo-Fenton [5], electro-Fenton [6] and ozonation [7]. In addition, some scholars also used ultrasound [8] and nano materials [9] to improve the efficiency of Fenton process.

In this study, we utilized nano zero valent iron (nZVI) and ultrasound to enhance the Fenton process. This paper discuss the effect of pH, ultrasound intensity and its duration on Fe^{2+} production and the successful of sono-Fenton process to remove COD from diluted POME.

2. Method

2.1. Material/chemicals
Hydrogen peroxide (R&M Chemicals, 30%), Sulfuric acid (Merck, 95-97%), Sodium Hydroxide (Merck, M=40g/mol), Iron Sulfate (R&M Chemicals, U.K), nZVI particles (Nanofer Star by NANO IRON).

2.2. Ferrous ion (Fe^{2+}) production
A sono reactor was utilized in order to study the effect of pH, ultrasound intensity and its duration on Fe^{2+} production by nZVI. Using H_2SO_4 (0.1M), 150 ml of distilled water was adjusted to desired pH and 0.09 gram of nZVI was added into the solution. Design of Experiment 5.0 (DOE) software was used to build the experimental design in order to study the effect of pH, ultrasound intensity and it duration on Fe^{2+} production. The mixture was sonicated using ultrasonic probe (Sonic Ruptor 250, 20 kHz, OMNI International) at various intensity and duration as mentioned in table 1. Meanwhile, for comparison purposes, $FeSO_4$ was also used as a replacement for nZVI. The concentration of Fe^{2+} in the solution was determined through 1, 10-Phenanthroline Method [10] and measured using a HACH DR6000 UV- spectrophotometer.

Table 1: Independent variables in Central Composite Design (CCD) using Design of Experiment 5.0 software.

Factor	Units	Low Level (-1)	High Level (+1)
A - pH	pH	2	4
B - Intensity	%	10	50
C - Time	minute	3	10

2.3. Chemical Oxygen Demand (COD) removal test
Before the treatment process began, POME was diluted 25 times. COD content in diluted sample was analyzed by closed reflux method [10] and recorded as 1160 mg/L Using H_2SO_4 (0.5 M), diluted POME was adjusted to pH 2 and 4. 100 ml of diluted POME were then poured into the water-jacketed cylindrical glass sono reactor as pictured in figure 1.
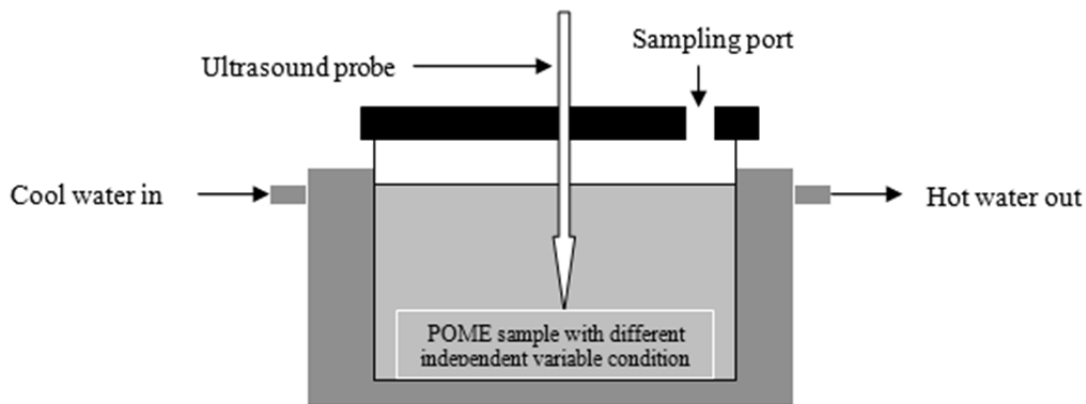
Figure. 1: Water-jacketed cylindrical glass sono reactor.

In every 100 ml diluted POME, 0.4 ml H_2O_2 and 0.06 g nZVI were added. The mixture was sonicated using an ultrasonic probe. The ultrasound intensity and duration setting was generated by DOE software. The independent variables and their levels for the experimental design were shown in table 2.

Table 2: Levels and independent variables for the experimental design.

Experiment	Sonication intensity	Sonication time	pH
	(%)	(min)	
1	20	5	2
2	40	5	2
3	20	15	2
4	40	15	2
5	20	5	4
6	40	5	4
7	20	15	4
8	40	15	4

Immediately after the sonication process, 15 ml of POME was taken out from the reactor for COD testing. The rest of the POME was then placed in an automatic shaker for the silent treatment process to continue. COD testing was done for every 1 hour, 2 hours and 24 hours of silent treatment.

3. Results and discussion

In traditional Fenton process, $FeSO_4$ was used as a major source for Fe^{2+}. Besides Fe^{2+} concentration, the oxidation efficiency of organic pollutants by Fenton process was also very much dependent on pH

of the solution and H_2O_2 concentration [11]. Figure 2 shows the production of Fe^{2+} by $FeSO_4$ and nZVI in an aqueous solution at pH 2.

Due to shockwave and cavitation created by ultrasound irradiation, the nZVI particles were dispersed at high speed inside the POME sample. As a result of rapid collision of nZVI particles, the chemical reactivity was enhanced. Hence, with the support of ultrasound, nZVI produced more Fe^{2+} compared to $FeSO_4$. On the other hand, as $FeSO_4$ was easily dissociated into Fe^{2+} and SO_4^{2-}, ultrasound gives no impact on Fe^{2+} production by $FeSO_4$.

nZVI particle was formed by two unique layers. The outer layer was made up of iron oxides (i.e. FeO) while the inner part comprised of Fe^0 [12]. Iron oxides layer keeps Fe^0 from rapid oxidation, hence prevent the production of Fe^{2+}. Figure 3 shows the Fe^{2+} production by nZVI at different weight and pH of aqueous solution. At pH 3 and 4, very little Fe^{2+} was produced. This was due to the presence of iron oxides layer which protect the core from any oxidation process.
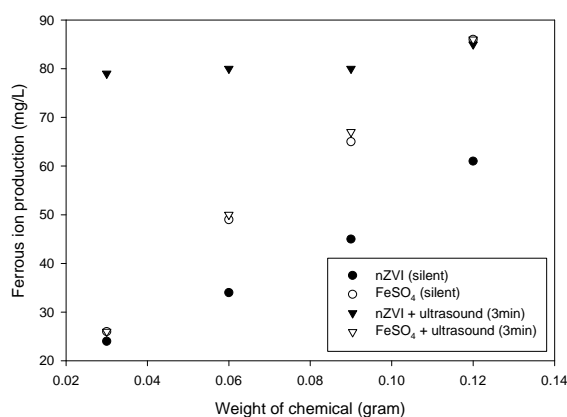

Figure 2: Fe^{2+} production by nZVI and $FeSO_4$ in aqueous solution at pH 2.

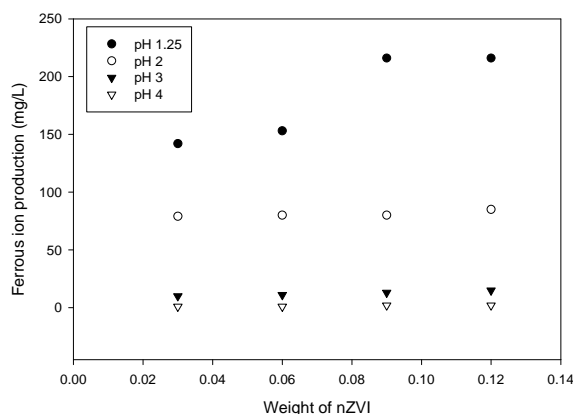**Figure 3**: Fe^{2+} production by nZVI at different weight and pH.

At pH 2, the iron oxides layer was removed and Fe^0 was oxidized. The reaction can be represented as;

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad\qquad (2)$$

At lower pH (i.e. pH 1.25), more Fe^{2+} was produced. This can be explained through excessive H^+ present in the aqueous solution. The reaction occured can be written as;

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \tag{3}$$

$$H_2SO_4 \leftrightarrow H^+ + SO_4^- \tag{4}$$

$$2Fe^0 + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O \tag{5}$$

Besides pH of the aqueous solution, the ultrasound intensity and its duration also play some role in the production of Fe^{2+}. However their impact were not as crucial as pH of the solution. Figure 4, 5 and 6 shows the correlation of pH, ultrasound intensity and ultrasound duration on Fe^{2+} production by nZVI.
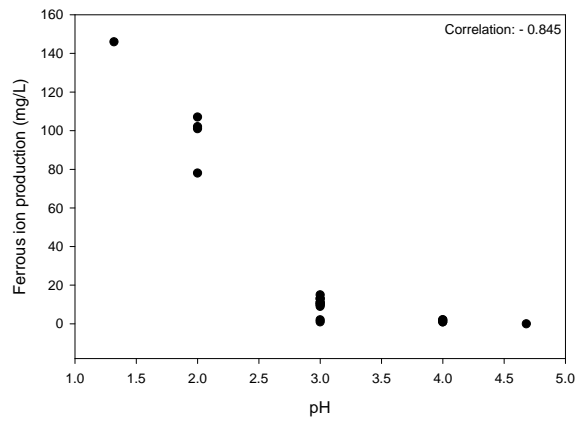

Figure 4: Correlation between Fe^{2+} production and pH of aqueous solution.
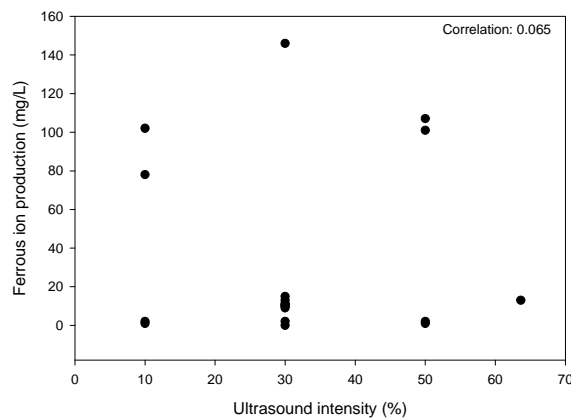

Figure 5: Correlation between Fe^{2+} production and ultrasound intensity.
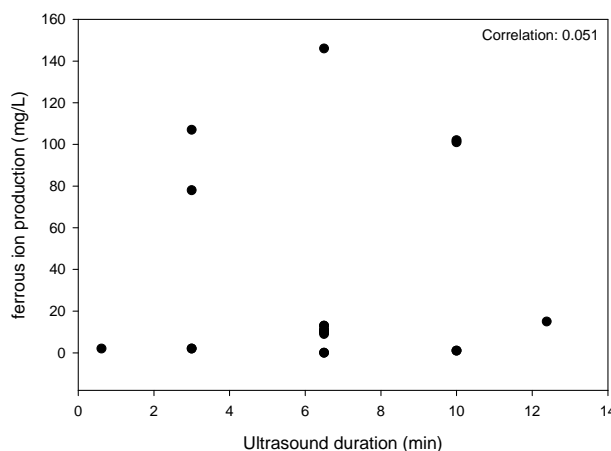
Figure 6: Correlation between Fe^{2+} production and ultrasound duration.

The effect of pH, ultrasound intensity and its duration on Fe^{2+} production from nZVI can be modeed as a linear model. The model demonstrated very low p–values (<0.0001) in the F- test which indicated the significant of the model was very high. Determination coefficient (R^2) of the model showed that 88.3% of the total variability could be explained by the model. Fe^{2+} production by nZVI could be explained by independent variables in term of coded as:

$$\ln(ferrous\ ion + 1.46) = 2.53 - 1.60A + 0.24B + 0.16C \qquad (6)$$

A, B and C in equation (6) referred to the coded values as is in table 1. Figure 7 shows the predicted vs actual values for Fe^{2+} production by nZVI. The model fit very well especially when the aqueous solution was pH 2 and pH 3.
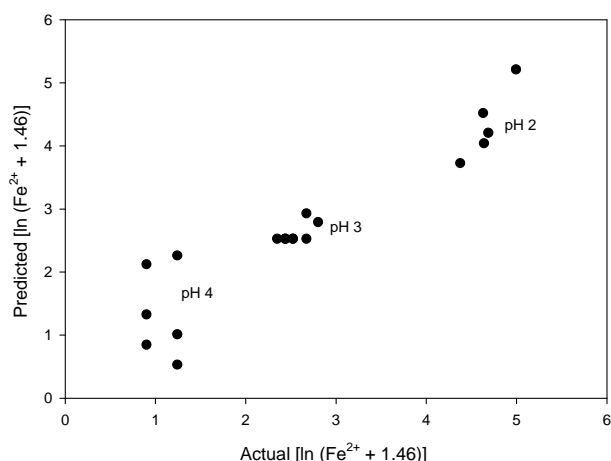

Figure 7: Actual vs. predicted values for Fe^{2+} production by nZVI.

Figure 8(a) – 8(c) demonstrate the effect of ultrasound intensity and pH on Fe^{2+} at three different ultrasound duration (3, 6.5 and 10 min respectively). The graphs clearly show that nZVI produced large amount of Fe^{2+} at pH 2 particularly with the aid of higher intensity and longer ultrasound time.

On the other hand, intensity and duration of ultrasound did not affect the production of Fe^{2+} by nZVI at pH 4. It was due to the presence of iron oxides layer that protected the Fe^0 from oxidation process.
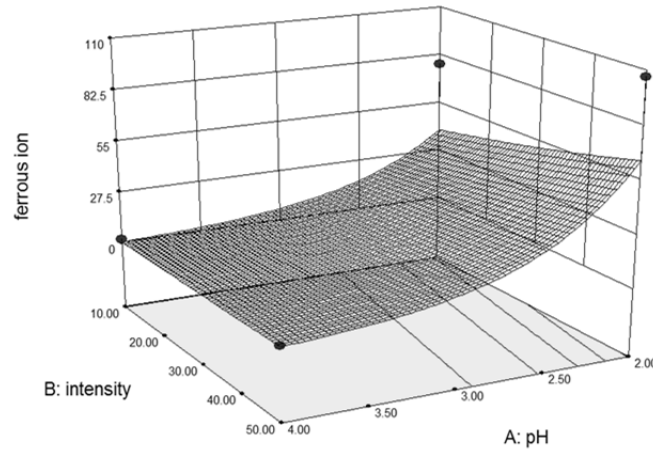

Figure 8(a): The effect of pH and ultrasound intensity on Fe^{2+} production after 3 min of ultrasound.
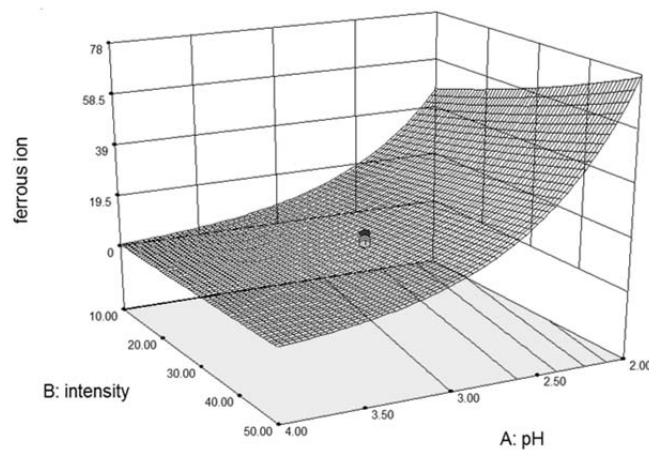

Figure 8(b): The effect of pH and ultrasound intensity on Fe^{2+} production after 6.5 min of ultrasound.
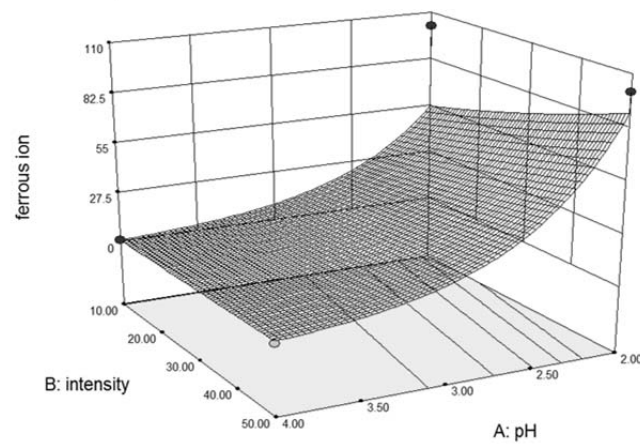

Figure 8(c): The effect of pH and ultrasound intensity on Fe^{2+} production after 10 min of ultrasound.

During COD removal test using diluted palm oil mill effluent (POME), COD readings in all samples were increased immediately after the treatment process except for experiment 4. The results of all experiments setting is represents in Figure 9.
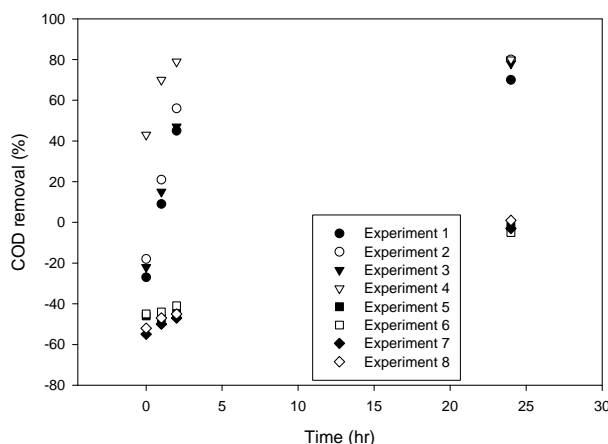

Figure 9: COD removal from diluted POME at different treatment setting.

Increment of COD reading was due to the presence of remaining H_2O_2 in the sample. During COD test, the remaining H_2O_2 was oxidized as well as the organic pollutants in the diluted POME [13]. Hence the COD content in POME arised from the initial value. This scenario clearly happened in samples which were treated at pH 4. As discussed above, obviously very few Fe^{2+} was produced at pH 4. Due to that, production of $OH^•$ was impeded due to the absence of Fe^{2+} and contributed to the excessive amount of remaining H_2O_2 in sample solution.

On the other hand, results showed that COD was removed from POME when they were treated at pH 2. In addition, the removal percentage also increased by time. In this case, the presence of Fe^{2+} in the samples reacted with H_2O_2 to produce $OH^•$. The produced $OH^•$ then attacked the organic pollutants and directly reduced the COD content in solution. After 24 hours of silent degradation, up to 80% of COD was removed from the POME samples.

In contrast, after 24 hours of silent degradation, COD reading in samples treated at pH 4 went back to their initial COD concentration. These indicated that no COD was removed from the diluted POME samples. In these samples, all added H_2O_2 were decomposed into water and oxygen. The decomposition of H_2O_2 as represented in the following equation:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
(7)
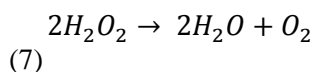
On the other part, ultrasound intensity or ultrasound time gave no significant effect on COD removal efficiency of diluted POME at pH 4. Figure 9 shows that samples which were treated at pH 4 at various ultrasound intensity and ultrasound time resulted in almost the same COD removal. Similar trends were also noticed in experiment 1, 2, and 3. COD removal efficiency for these three treatment conditions was about the same.

However, combination of high intensity and longer ultrasound time can shorten the treatment process time. This clearly happened in experiment 4 where maximum COD removal (80%) was achieved within 2 hours instead of 24 hours of silent degradation. This can be explained by the presence of excessive Fe^{2+} in the solution due to longer exposure to high sonication. As Fe^{2+} determined the rate of the conversion of H_2O_2 to $OH^•$, higher concentration of Fe^{2+} increased the efficiency of the process.

4. Conclusion

Production of Fe^{2+} by nZVI particles only occurred once the iron oxides layer was removed. Removal of iron oxides layer could be done by adjusting pH of the aqueous solution to pH 2. Furthermore, with the aid of ultrasound, nZVI particles were dispersed homogenously in the solution at higher speed. Rapid coalition of nZVI particles had increased its chemical reactivity hence more Fe^{2+} was produced. Thus, nZVI particles could be considered as an alternative source for Fe^{2+} in sono-Fenton process. In addition, utilization of nZVI particles in sono-Fenton process seems to be a promising option for POME treatment. COD contents can be removed faster with the presence of nZVI in sono-Fenton process particularly at higher ultrasound intensity and longer sonication time.

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