

Removal of Pb(II) ions in the aqueous solution by photo-Fenton method

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Abstract

Photo-Fenton for decreasing concentration of Pb(II) ions in the aqueous solution is systematically studied. The photo-Fenton process was carried out by batch technique, under UV light. The influences of the process operating parameters were evaluated. The results of the research demonstrated that by photo-Fenton process, the concentration of Pb(II) ions in the aqueous solution can be decreased, that may be through oxidation mechanism by OH radicals. The decrease is found to be dictated by Fe²⁺ and H₂O₂ concentrations, as well as by the pH and the irradiation time. For 25 mg/L of Pb(II) in the 100 mL solution, the optimum condition of the oxidation is obtained to be 10 mmole of Fe²⁺, 200 mmole of H₂O₂, pH 3, and 90 mins of the reaction time. It is also confirmed that the oxidation of Pb²⁺ by OH radical has formed the undissolved PbO₂, that is less toxic and easier to be handled. The oxidation well fits to the first order reaction with the rate of the reaction is as much as 0.07 mmole/min.

Keywords: Photo-Fenton, Pb²⁺, oxidation, removal.

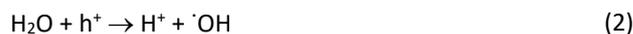
1. Introduction

The release of heavy metals into wastewater through human and industrial activities has become a major problem both to humans and aquatic lives. Among heavy metals, lead (Pb) is ranked in the 5 main hazardous heavy metals (Harrison and Laxen, 1981), that has harmful effects on human health, especially for children (Harrison, and Laxen, 1981; NRC Committee on Lead in the Human Environment, 1980). Further, high lead level has been reported to cause organs and brain damaged, and mental retardation (NRC Committee on Lead in the Human Environment, 1980). Lead as Pb²⁺ is frequently found in the industrial wastewater of manufactures of paint, battery, and pigment, and metal plating activity (NRC Committee on Lead in the Human Environment, 1980).

To remove of Pb²⁺ ions in the water, adsorption (Yao *et al.*, 2016; Asuquo *et al.*, 2017; Mahmoud *et al.*, 2016; Soliman *et al.*, 2016) and biosorption methods (Chen *et al.*, 2010; Yuvaraja *et al.*, 2014; Ayoub *et al.*, 2013) have been frequently attempted. Those methods were found

to be simple and effective (Yao *et al.*, 2016; Asuquo *et al.*, 2017; Mahmoud *et al.*, 2016; Soliman *et al.*, 2016; Chen *et al.*, 2010; Yuvaraja *et al.*, 2014; Ayoub *et al.*, 2013), however the toxic property of the Pb²⁺ remains existed. Accordingly, when the adsorbents have been exhausted with the toxic Pb²⁺, they become solid toxic waste. This creates new environmental problem that needs further treatment.

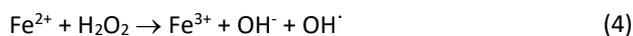
It has been reported an effort to covert the toxic Pb²⁺ into the less toxic PbO₂ through oxidation reaction, that is called as photocatalytic oxidation (Tanaka *et al.*, 1986; Chen and Ray, 2001; Wahyuni *et al.*, 2015). In this method, TiO₂ photocatalyst in water media is exposed with UV light that results in OH radical, as presented by reactions (1) and (2).



The hydroxyl radical ($\cdot\text{OH}$) acts as a strong oxidizing agent assigned by standard oxidation potential (E°) as much as 2.8 V, that is higher than other oxidants such as ozone ($E^\circ = 2.0$ V) and H₂O₂ ($E^\circ = 1.8$ V) (Fujishima *et al.*, 2000). The high strength of the hydroxyl radicals ($\cdot\text{OH}$) can induce Pb²⁺ oxidation (Tanaka *et al.*, 1986; Chen and Ray, 2001; Wahyuni *et al.*, 2015), as illustrated by reaction (3), as well as degrade a large number of organic compounds (Reza *et al.*, 2017; Ajmal *et al.*, 2014; Dariani *et al.*, 2016; Zuo *et al.*, 2014; Gautam *et al.*, 2016; Shukla *et al.*, 2009; Choquette-Labbé *et al.*, 2014; Grabowska *et al.*, 2012; Turki *et al.*, 2015) effectively. However, due to the heterogeneous system, the photocatalysis process faces light entering inhibition when large dose of the TiO₂ powder is used (Reza *et al.*, 2017; Dariani *et al.*, 2016; Gautam *et al.*, 2016), leading to the less effective photooxidation.

There is a homogeneous oxidation method that also provides $\cdot\text{OH}$ radicals called photo-Fenton. Photo-Fenton method involves the use of Fenton's reagent, that is a combination of Fe²⁺ and H₂O₂, with UV light exposure (Babuponnusami and Muthukumar, 2014; Joseph and

Katoch, 2016; Kavitha and Palanivelu, 2004, 2005; Huang *et al.*, 2010; Kusi *et al.*, 2006; Tony and Bedri, 2014; Zazouli *et al.*, 2012; Azhdarpoor *et al.*, 2015; Wahyuni *et al.*, 2016; Shaban *et al.*, 2017; Çiner, 2017; Ali and Ameta, 2013). In this process, H_2O_2 is decomposed catalytically by Fe^{2+} at acidic pH, yielding hydroxide ion (OH^-) and hydroxyl radical ($\cdot\text{OH}$) (reaction 4). While the Fe^{2+} ion is transformed into Fe^{3+} ions (reaction 5) that can further reacts with hydroxide ion (OH^-) to form hydroxylated ferric ions ($\text{Fe}(\text{OH})^{2+}$) (reaction 6). In the presence of UV light, H_2O_2 is also decomposed into OH radicals (reaction 7) (Kavitha and Palanivelu, 2004). It is clear that a lot number of OH radicals can be provided, that promote more effective oxidation. Additionally, since the chemicals exist as dissolved species, the light entering into the solution is not screened, that should result in the high photooxidation.



Based on the ability in providing OH radicals, photo-Fenton method has been intensively studied for removal of wide range of organic pollutants including phenols (Kavitha and Palanivelu, 2004; Huang *et al.*, 2010; Kusi *et al.*, 2006), nitrophenol (Kavitha and Palanivelu, 2005), car wash wastewater (Tony and Bedri, 2014), and organic compounds in leachates (Joseph and Katoch, 2016; Zazouli *et al.*, 2012) and in sludge (Azhdarpoor *et al.*, 2015), as well as for surfactant in the laundry waste water (Wahyuni *et al.*, 2016), and dyes in water (Shaban *et al.*, 2017; Çiner, 2017; Ali and Ameta, 2013). However, so far there is no study of photo-Fenton method to decline the concentration of Pb(II) ion in the water through oxidation mechanism that has been reported.

Under the circumstance, in this present paper, photooxidation of Pb(II) by the use of Fenton's reagent assisted with UV light is addressed. The oxidation power of Fenton reagent depends very much on the operating parameters, including the initial substrate concentration, Fe^{2+} concentration, H_2O_2 concentration, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ mole ratio, pH and process time (Babuponnusami and Muthukumar, 2014). Therefore, it is necessary to find the optimal process parameters through laboratory treatability tests.

2. Experiment

2.1. Chemicals

The chemicals used were ferrous sulfate, hydrogen peroxide 30% v/v, and lead nitrate with analytical grade that were purchased from E. Merck and were used as received. The aqueous solutions were prepared by using twice distilled water. Sodium hydroxide and hydrochloric acid received from Aldrich, were used for adjusting the pH of the solutions.

2.2. Photo-Fenton process

All experiments were carried out in duplicate and batch technique. A 250 mL Beaker glass was filled with 100 mL of solution containing 10 mg/L Pb^{2+} , Fe^{2+} 10 mmole/L and H_2O_2 200 mmole/L. The beaker glass was placed in the photoprocess apparatus, as illustrated by Figure 1, that was equipped with UV lamp with 250-350 nm of the wavelength. Then the UV lamp was turned on to start the photo-process, and the process was proceeded for 90 mins, that was accompanied by magnetically stirring. After a period of time as desired, the reaction was quit and the light brown turbid solution was formed in the solution. By filtration of the turbid solution through Whatman 42 paper filter, the clear solution was obtained.

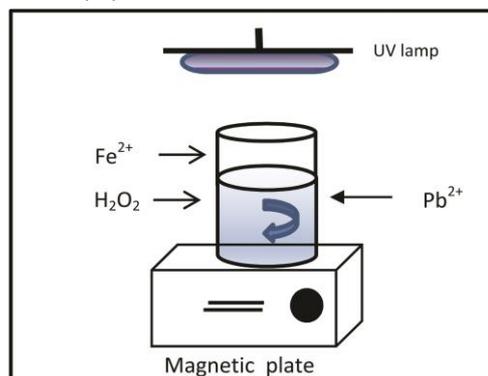


Figure 1. The simplified schematic diagram of a lab-scale photo-Fenton process

The solid on the paper filter was dried at 110°C for 2 h, and then it was analyzed by SEM-EDX instrument to identify its chemical composition. Meanwhile the solution was analyzed by using GBC type-AAS to determine the concentrations of Pb(II) left in the solution. The amount of Pb^{2+} removal is calculated by using formula below:

$$\frac{\text{Co} - \text{Cl}}{\text{Co}} \times 100\%$$

Co: the initial concentration of Pb(II) in the solution, Cl: the concentration of Pb(II) left in the solution.

The same procedure was repeated with various of Fe^{2+} and H_2O_2 concentrations, the irradiation time, system pH, and the initial concentration of Pb(I). When one operating variable was varied, the other variables were adjusted to be constant.

3. Results and Discussion

3.1. The influence of Fe^{2+} concentration

The amount of Fe^{2+} is one of the primary parameters that influences the effectiveness of the photo-Fenton process (Kavitha and Palanivelu, 2004; Huang *et al.*, 2010). In Figure 2. the influence of Fe^{2+} concentration on the effectiveness of the photo-Fenton process is displayed ($\text{H}_2\text{O}_2 = 200 \text{ mmol/L}$, $\text{pH} = 3$, $\text{time} = 90 \text{ mins}$). It is observed that the increase of the Fe^{2+} concentration promotes the removal of Pb^{2+} ion up to reach the maximum level. Increasing Fe^{2+} concentration provides more amount of Fe^{2+} ions in the solution, that results in the higher amount of the hydroxyl radical, as described by reaction (4). This explains the fact that higher removal of Pb(II) is observed.

The negative effect on the removal of Pb(II) appears when the concentration of Fe²⁺ is more than the optimum level. The excessive Fe²⁺ ion produces larger amount of Fe³⁺ ions (reaction 4) that further allows them to react with hydroxide ions formed from reaction (4), to form Fe(OH)₃ precipitate, as seen in reaction (8) (Kavitha and Palanivelu, 2004; Huang *et al.*, 2010).



The precipitate formation creates turbid solution that can inhibit the light entering into the solution (Babuponnusami and Muthukumar, 2014; Joseph and Katoch, 2016; Kavitha and Palanivelu, 2004; Huang *et al.*, 2010; Kusi *et al.*, 2006). The effect of this situation is a decrease in OH radical formation, that further diminishes of the Pb(II) removal. In addition, the precipitate can also further contribute to a significant increase in total dissolved solids (TDS), that requires further treatment of the effluent before its discharge to the receiving water. This finding is in a good agreement with the previous observations elsewhere (Joseph and Katoch, 2016; Kavitha and Palanivelu, 2004; Huang *et al.*, 2010; Tony and Bedri, 2014; Azhdarpoor *et al.*, 2015; Wahyuni *et al.*, 2016; Çiner, 2017; Ali and Ameta, 2013).

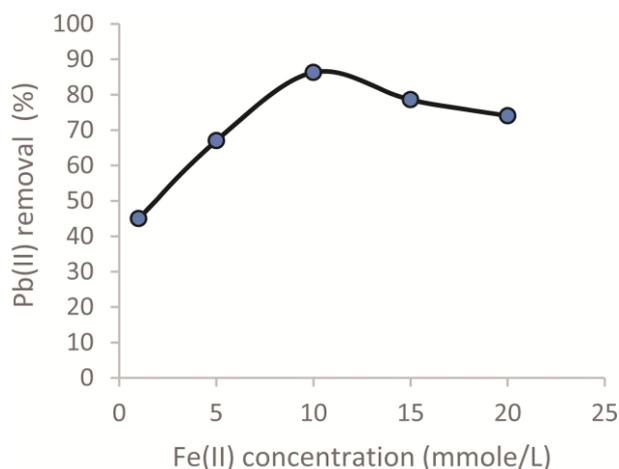


Figure 2. The influence of Fe(II) concentration on the removal of Pb(II) in the solution

The decrease of Pb(II) concentration can be caused by 2 possible reactions, that are reduction of the dissolved Pb²⁺ into undissolved Pb⁰, or oxidation of the dissolved Pb²⁺ into Pb(IV) formed as the undissolved PbO₂ (Harrison and Laxen, 1981). The reduction of Pb²⁺ into Pb⁰ is impossible thermodynamically (Harrison and Laxen, 1981), so that the diminishing concentration by oxidation of Pb(II) by OH radicals (reaction 3) is favored, to form the solid PbO₂. The same result of the solid PbO₂ has also been obtained from the photopoxidation of Pb(II) ion by OH radicals that was provided by TiO₂ under exposure of UV light (Tanaka *et al.*, 1986). Furthermore, in this research, during the photo-Fenton process, light brown solid was observed.

To find out the compounds in the light brown solid, the solid was also analyzed by SEM-EDX instrument, and the result is presented as Figure 3. From the figure and the table along with, it is informed that Fe, Pb, S and O elements are existed in the solid. The elements respectively may represent Fe(OH)₃ (brown colored), PbO₂, and SO₄ (from FeSO₄ reagent as source of Fe²⁺) compounds. It is confirmed that Pb(II) has been oxidized into PbO₂ with relatively low amount. The low amount of PbO₂ product was resulted from the low the initial concentration of Pb(II), that was 10 mg/L in 100 mL solution.

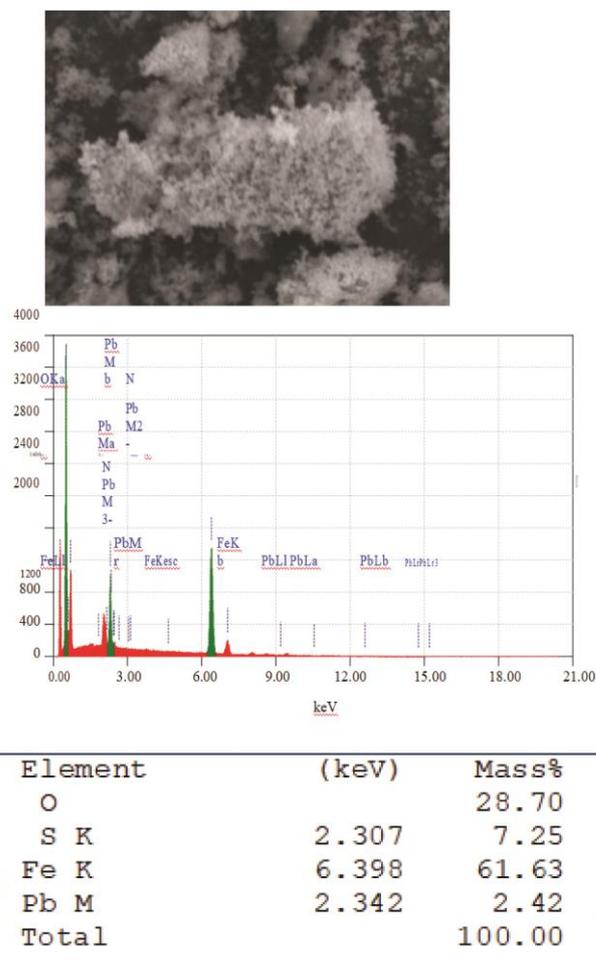


Figure 3. SEM-EDX data of the solid resulted from photo-Fenton process of Pb²⁺

3.2. The influence of the H₂O₂ concentration

H₂O₂ amount is also a critical variable in the photo-Fenton's process that needs to be studied and optimized (Kavitha and Palanivelu, 2005). From Figure 4. it is observed that the improvement of the effectiveness of the Pb(II) removal is resulted, when the concentration of H₂O₂ is increased (the concentration of Fe²⁺ 10 mmol/L, pH 3 and the reaction time 90 min, were maintained to be constant). Increasing H₂O₂ concentration produces more number of OH radicals, which enhances the oxidation process of Pb(II) ions.

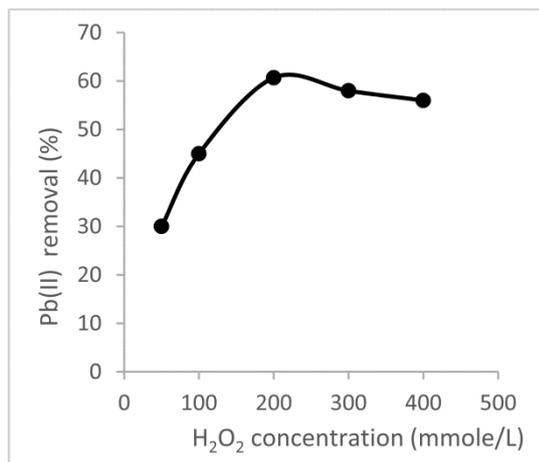
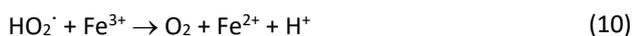


Figure 4. The influence of H₂O₂ concentration on the removal of Pb(II) in the solution

However the use of further larger concentration of H₂O₂ shows an opposite effect. The excess H₂O₂ can act as a scavenger of OH radicals. The reactions of the scavenging OH radical by the excessive H₂O₂ is presented as reaction (9) that reveals water and HO₂ radicals (Kavitha and Palanivelu, 2004; Zazouli *et al.*, 2012; Azhdarpoor *et al.*, 2015; Wahyuni *et al.*, 2016; Shaban *et al.*, 2017; Ali and Ameta, 2013)



Reaction (9) should deplete the amount of OH radicals, that must be followed by the less effective of the Pb(II) photooxidation.

3.3. The influence of reaction pH

pH is one of the major factors limiting the performance of the photo-Fenton process. The solution pH plays role in controlling the species of ferrous and the stability of hydrogen peroxide (Kavitha and Palanivelu, 2005). It is seen in the Figure 5 that alteration pH results in the various photooxidation efficiency.

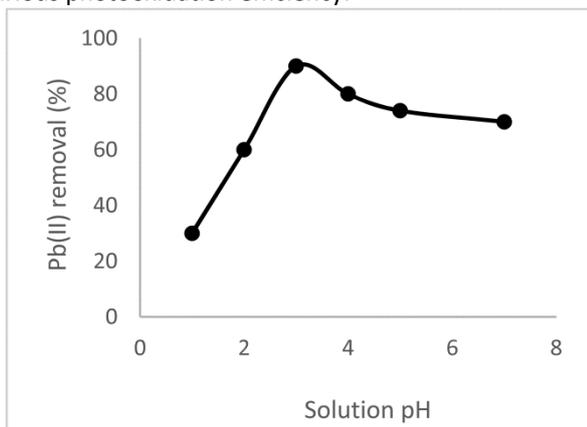


Figure 5. The influence of solution pH on the removal of Pb(II) in the solution

In more detail, increasing pH can enhance the photooxidation that reaches maximum level at pH 3, and the photooxidation slightly goes down with the increase of pH.

At low level of pH, Fe²⁺ forms a stable complex with H₂O₂, which neutralizes the iron catalyst and significantly reduces the Pb(II) oxidation (Wahyuni *et al.*, 2016). The other reason presented by Shaban *et al.* (Çiner, 2017), that is in the low pH, hydrogen ion (H⁺) are present in large amount, that can protonate of H₂O₂ to form protonated hydrogen peroxide or H₃O₂⁺. The protonated hydrogen peroxide inhibits the hydroxyl radical generation. This results in small number of OH radicals, that further leads to the lower photooxidation.

Increasing pH up to 3, the complex of Fe²⁺ with H₂O₂ should be decomposed allowing Fe²⁺ to catalyze H₂O₂ maximally, and much hydroxyl radicals can be provided. In addition, at higher pH the protonation of H₂O₂ should also decrease, that promote more hydroxyl radical formation. The more number of the radicals provided, should raise the photooxidation.

At pH higher than 3, the larger number of hydroxide ion (OH⁻) are available, facilitating Fe³⁺ ions resulted from Fe²⁺ ions, to deposit as Fe(OH)₃. As a consequence, the sufficient Fe²⁺ catalyst does not remain in the solution. This causes lower decomposition of H₂O₂ and reduces the efficiency of the Fenton's process. Also, studies have shown that oxidative potential of OH radicals decreases (Zazouli *et al.*, 2012; Shaban *et al.*, 2017; Çiner, 2017; Ali and Ameta, 2013) and hydrogen peroxide has less stability (Çiner, 2017) with increasing pH. All the previous conditions will result in decreasing the produced hydroxyl radicals, and hence the Pb²⁺ photooxidation.

It is clear that an essential characteristic of the Fenton's process is that pH in the acidic range strongly favors oxidation, that can avoid the Fe³⁺ from precipitation process. The finding optimum pH (= 3) agrees with several studies already carried out (Kavitha and Palanivelu, 2004, 2005; Huang *et al.*, 2010; Kusi *et al.*, 2006; Azhdarpoor *et al.*, 2015; Shaban *et al.*, 2017; Ali and Ameta, 2013). But the optimum pH values that were slightly lower (Wahyuni *et al.*, 2016) or higher than 3 (Çiner, 2017) in the range of 2.0 and 4.5 were also observed (Zazouli *et al.*, 2012).

3.4. The influence of the Pb²⁺ initial concentration

In order to find out the capacity of the photo-Fenton in oxidation of Pb²⁺, the initial concentration of Pb²⁺ was varied and the result is presented as Figure 6. The figure depicts that increasing initial Pb²⁺ concentration can enhance sharply the amount of Pb²⁺ oxidized, but further increase of the initial concentration, the slight increase is observed. The condition of low concentration of Pb²⁺ (5-10 mg/L) with a lot of OH radicals, promotes very effective oxidation, resulting in the complete oxidation (>90%). Increasing initial Pb²⁺ concentration can results in more effective collision between OH radicals with Pb²⁺ ions, that produce higher oxidation.

With very high concentration, much more Pb²⁺ ions are available for oxidation, that may start act as a filter for the incident light. This can inhibit the light intensity to reach at the reagents. As a result, a decrease in the rate of

oxidation of Pb^{2+} was attributed. In addition, with high Pb^{2+} that are oxidized, the OH radicals become depleted that leads to the slower oxidation. This finding is consistency with that of found by Shaban *et al.* (Çiner, 2017) for dye photodegradation.

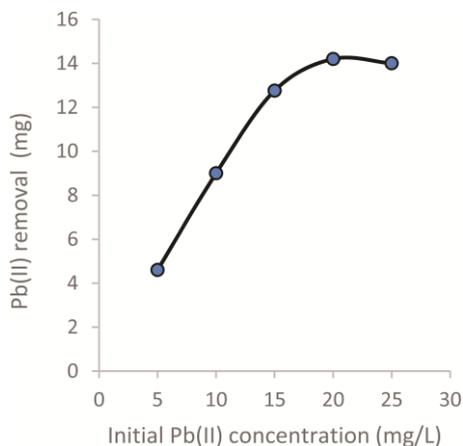


Figure 6. The effect of the initial Pb(II) concentration on the effectiveness of Pb^{2+} photo-oxidation

3.5. The Influence of reaction time

The reaction time also plays important role on the yields of the reaction, thereby it is important to be optimized. The influence of the reaction time is demonstrated by Figure 7. The expansion time up to 90 min can enhance of the photo-oxidation, but after 90 min, the photo-oxidation does not depend on the reaction time. With the amount of Fe^{2+} 10 mmole and H_2O_2 200 mmole, the longer of the reaction time can improve of the effectiveness of the interaction between Fe^{2+} and H_2O_2 and UV light with H_2O_2 that produces considerably amount of OH radicals (Babuponnusami and Muthukumar, 2014). The larger amount of OH radicals has promoted higher photo-oxidation of Pb^{2+} ions in the solution. The reaction time longer than 90 min, the large amount of PbO_2 solid has been produced that inhibit the light entering, accordingly the photo-oxidation does not change appreciably (Kavitha and Palanivelu, 2005; Tony and Bedri, 2014).

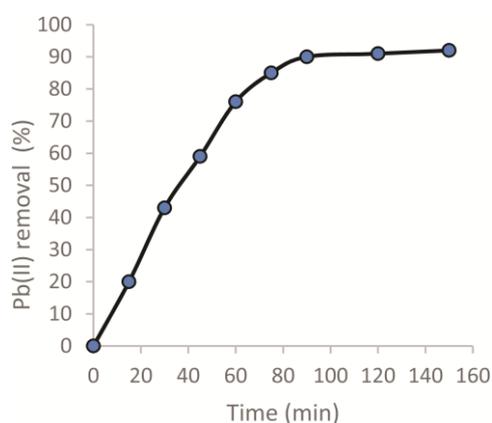


Figure 7. The influence of reaction time on the effectiveness of Pb^{2+} photo-oxidation

3.6. Kinetic study

The kinetic of photo-Fenton processes for oxidation of Pb^{2+} was studied to determine the reaction order and the constant of the reaction rate. In the process, the chemicals reacting were hydroxyl radicals formed from Fenton's agent assisted with UV light as oxidizing agent and Pb^{2+} as substrate in the solution. Consequently, the reaction rate should follow a second-order rate equation, that can be presented by equation (11):

$$d[Pb^{2+}]/dt = -k[Pb^{2+}][\cdot OH] \quad (11)$$

In the photo-Fenton reaction, the concentration of hydroxyl radicals is in excess, and during the reaction the concentration of the radicals may be constant (Kavitha and Palanivelu, 2005). Hence the equation of the reaction rate should be modeled as the pseudo first-order reaction following equation (12).

$$d[Pb^{2+}]/dt = -k'[Pb^{2+}] \quad (12)$$

The equation (12) can be derived into equation (13) as follow:

$$\ln[Pb^{2+}]_0/[Pb^{2+}]_t = -k'.t \quad (13)$$

With $[Pb^{2+}]_0$: initial concentration of Pb^{2+} in the solution, $[Pb^{2+}]_t$: concentration of Pb^{2+} left in the solution after t mins of the reaction, t : period of the reaction time, and k' : rate reaction constant of pseudo first-order reaction.

The experimental serial data is plotted into the equation (13) and the curve resulted is displayed as Figure 8. The figure demonstrates the linear curve with the correlation factor (r^2) is found about 0.98. It is obviously seen that the photo-oxidation of Pb^{2+} fits with the pseudo first-order reaction model. The same order of the photo-Fenton reaction has also been reported (Kavitha and Palanivelu, 2005; Tony and Bedri, 2014) for degradation of nitrophenols and phenol, respectively, by hydroxyl radicals formed by Fenton's agent. From the curve, the reaction rate constant (k') can also be calculated, that is as high as 0.07 min^{-1} .

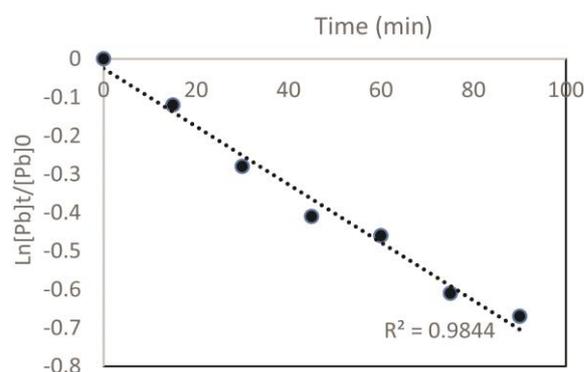


Figure 8. Pseudo first-order plot for Pb^{2+} oxidation by OH radicals

4. Conclusions

It can be concluded that by employing photo-Fenton process, the concentration of Pb^{2+} ions in the solution can be decreased due to the oxidation by hydroxyl radicals to

form PbO₂. The efficiency of Pb²⁺ photooxidation, in addition to be dependence on the concentrations of Fe²⁺ and H₂O₂ in the solution, and time, it is also controlled by the initial Pb²⁺ concentration and the reaction pH. The maximum decreasing Pb²⁺ concentration, that is about 80%, is obtained with the use of Fe²⁺/H₂O₂ mole ratio as 1/20 at pH 3 and 90 min of time, from 20 mg/L of the Pb²⁺ initial concentration in the solution. Furthermore, the oxidation of Pb²⁺ by OH radical generated by Fenton's agent is found to well fit with a pseudo-first order model with moderate rate.

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