Adsorption kinetics of ion of Pb$^{2+}$ using Tricalcium Phosphate particles

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Abstract. One of the heavy metals that can pollute water is Pb$^{2+}$. The concentration of ion Pb$^{2+}$ can be removed using the adsorption method. The purpose of this research is to determine the adsorption kinetics model of ions Pb$^{2+}$ using tricalcium phosphate (TCP) particles with variation of the temperature and adsorbent dosage. Five hundred milliliter Pb$^{2+}$ solution with of 3 mg/L were added 0.5 gr, 1 gr and 1.5 gr of TCP in a glass beaker and stirred with rate of 300 rpm at a temperature of 30 °C, 40 °C and 50 °C. Pb$^{2+}$ concentration in solution was analyzed by AAS (Atomic Adsorption Spectroscopy). The results showed that the rate of adsorption increased with the increasing of the temperature and adsorbent dosage. Minimum constant value of adsorption kinetic was 1,720 g/mg.min obtained at temperature of 30 °C and adsorbent dosage of 0.5 gr. The maximum value of adsorption kinetic constant was 9,755 g/mg.min obtained at temperature of 50 °C and adsorbent dosage of 1.5 gr. The appropriate model for adsorption kinetics followed the pseudo second order.

1. Introduction
Lead metal pollution becomes an environment problem. Lead metal can cause human health effects such as allergens, encephalopathy, anemia and carcinogens [1]. Currently, several method were used for removing the heavy metals from aqueous solution, such as ion exchange, carbon adsorption and neutralization. Adsorption have been considered high efficiency and low cost method, it can be used to remove the heavy metals concentration in solution[2]. Tricalcium phosphate (TCP) can be used to reduce the lead metals. TCP as adsorbent have also been considered amongst ideal low cost with smaller particle (nano and micrometer) so the surface area is larger, the highest stability and low density [3-4].

Yunizar (2013) has been studied the application of lead adsorption in water using tricalcium phosphate particle by determining the equilibrium of adsorption. The optimal TCP adsorption capacity at operating temperature of 30 °C with concentration 15 mg/L is 6,7880 mg/g with value of $\Delta H$ equal -8.8 kcal/mol.K and exothermic [5]. Kinetic study of lead in aqueous solution using tricalcium phosphate particle obtained the value of TCP optimal rate adsorption occured at concentration 14,619 mg/L with stirred 300 rpm is 3,129 g/mg.min [6].

This paper reported the effects of temperature and adsorbent dosage on the adsorption of lead using TCP. In addition, the kinetics of adsorption model with two orders kinetics adsorption of pseudo-first-order and pseudo-second-order are also reported to determine a suitable kinetic model for metal adsorption.
2. Materials and methods
The materials used in this study are Pb (NO\textsubscript{3})\textsubscript{2}, aquadest, and tricalcium phosphate Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} as adsorbent. Adsorption process was carried out by adding five hundred milliliter Pb\textsuperscript{2+} solution with 3 mg/L into 0.5 gr, 1 g and 1.5 gr of TCP in a glass beaker and stirred with rate of 300 rpm at a temperature of 30 °C, 40 °C and 50 °C. The solution was taken at intervals of 1 minute for 5 minutes as much as 10 mL, then separation by centrifuged. Pb\textsuperscript{2+} concentration in solution was analyzed using Atomic Adsorption Spectroscopy (AAS).

3. Results and discussion
3.1 Effect of time and temperature on Pb\textsuperscript{2+} concentration
The Pb\textsuperscript{2+} metal solution was prepared by dissolving Pb (NO\textsubscript{3})\textsubscript{2} into the aquades to obtain Pb\textsuperscript{2+} at the concentration of 3 ppm. The solution was added tricalcium phosphate as adsorbent. In Adsorption process the concentration of lead metal in solution will be decrease each time, it shown in Figure 1.

In five minute, Pb concentration was constant, so this time can be taken as equilibrium time. The smallest Pb concentration in solution at 5 minute with process condition at 30 °C, 0.5 gr adsorbent dosage and initial concentration (Co) 2.872 mg/L is 0.653 mg/L. Its due to the addition of adsorbent, PO\textsubscript{4}\textsuperscript{3-} adsorbent active site is increase, and the amount of lead metals was adsorbed is high. In the most cases, the increasing of the adsorbent amount causes the increasing of the adsorbent capacity. Due to the surface contact area of adsorben is increases with the more adsorbent dosage [7]. It also happen that the increasing of the activation time will increase adsorption ability, until become constant or decrease [8].

3.2 Adsorption kinetics
3.2.1. Pseudo first order
The lead (Pb) concentration againts time for pseudo first order equation with adsorbent dosage and temperatures variation are shown in Figure 2. The data shown adsorbent dosage for variation oftemperature i.e. 30°C, 40°C, 50°C. The first order model follows Equation 1 [9]:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

where \(q_e\) is adsorption equilibrium capacity (mg/g), \(q_t\) is amount of adsorbate adsorbed at time t (min) (mg/g), and \(k_1\) is adsorption rate constant.

Based on Figure 2, we get the result of \(q_e\) and \(R^2\) values for first order. Table 1 shown the k and \%SSE for first order kinetics. The concentration of lead metals was adsorbed in variation of adsorbent dosage are 0.5 gr, 1 gr, 1.5 gr at 30 °C for this study indicates a considerable correction range from...
18.747% to 53.987% at 40°C the range from 6.88% to 81.492%, and at 50°C the range from 14.652% to 29.403%.

![Figure 2](image)

Figure 2. Adsorption process follows pseudo first order kinetics model (a) 30°C gr, (b) 40°C, (c) 50°C.

Table 1. Parameter of kinetics adsorption pseudo first order model with temperature variation

| Temperature | 30°C | 40°C | 50°C |
|-------------|------|------|------|
| TCP Dosage  |      |      |      |
| (gr)        |      |      |      |
| 0.5         | -0.813 | 0.974 | 19.646 | -0.993 | 0.961 | 6.88 | -0.859 | 0.973 | 19.646 |
| 1           | -1.740 | 0.978 | 53.987 | -1.166 | 0.991 | 15.304 | -1.395 | 0.887 | 14.652 |
| 1.5         | -1.816 | 0.929 | 18.747 | -1.395 | 0.981 | 81.492 | -1.182 | 0.939 | 29.403 |

3.2.2 Pseudo second order

The lead (Pb) Concentration against time for pseudo second order equation with adsorbent dosage and temperatures variation are shown in Figure 3. The data shown for temperature variation 30°C, 40°C, 50°C and 1.5 gr adsorbent dosage. The second order model follows equation [10]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (2)

Based on Figure 3, we get the result of $q_e$ and $R^2$ values and comparison between experimental data for second order model. Where the value of $q_e$ is 0.762 mg/g and $R^2$ 0.997. Table 2 shown the $k$ and %SSE for second order kinetics. The concentration of lead metals was adsorbed in temperatures variation 30°C, 40°C, and 50°C and 0.5 gr adsorbent for this study indicates a considerable correction range from 3.23% to 3.578%, at 1 gr adsorbent the range from 2.897% to 3.28%, and at 1.5 gr adsorbent the range between 2.47% and 2.636%. The small value of correction indicates that the equation of second order can be used.
Figure 3. Adsorption process follows pseudo second order for 1.5 gr adsorbent at (a) 30 °C, (b) 40 °C and (c) 50 °C.

Table 2. Parameter of kinetics adsorption pseudo second order model with temperature variation

| Temperature | 30°C | 40°C | 50°C |
|-------------|------|------|------|
| TCP Dosage  |      |      |      |
| (gr)        |      |      |      |
| k₂ (g/mg.min) |      |      |      |
| R²          |      |      |      |
| %SSE        |      |      |      |
| k₂ (g/mg.min) |      |      |      |
| R²          |      |      |      |
| %SSE        |      |      |      |

| 0.5          | 1,720 | 0.991 | 3,578 | 1.982 | 0.992 | 3,281 | 2,022 | 0.992 | 3,230 |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1            | 4,117 | 0.994 | 3,217 | 4,330 | 0.994 | 3,280 | 4,996 | 0.995 | 2,897 |
| 1.5          | 8,479 | 0.995 | 2,636 | 9.6   | 0.996 | 2,605 | 9,755 | 0.997 | 2,470 |

From Table 2 we find a suitable kinetics model for adsorption of lead metal ions using TCP is pseudo second order. The highest linear regression (R²) parameter is 0.997 with the lowest %SSE value is 2,470. The kinetics adsorption constant of 9,755 g/mg at 50 °C and adsorbent dosage 1.5 gr. The value of adsorption velocity constant increases with the increasing of the temperature. Based on the theory that the adsorption rate increases with the highest temperature, where at high temperatures the activation of adsorbent surface side activates and give more kinetic energy of metals ion [11].

3.3 Effect of adsorbent dosage on constant value (k) adsorption rate

Kinetics adsorption process follows pseudo second order model to seen the effects of adsorbent dosage for adsorption of lead metal ions rate constant value. Data of adsorption lead metals ions is calculated using Equation (2).

Based on Figure 4, we get result of qₑ and R² values. The comparison between experimental data with second order model is increases with the addition of adsorbent. Where the highest of R² of 0.997
at temperature 50 °C and stirred at 300 rpm. From the figure we find $R^2$, and value of k and %SSE shown in Table 3.

![Graphs](image)

**Figure 4.** Adsorption process follows pseudo second order at 50 °C for adsorbent dosage (a) 0.5 gr, (b) 1 gr dan (c) 1.5 gr.

**Table 3.** Parameter of kinetics adsorption pseudo second order model with adsorbent dosage variation

| TCP Dosage | 0.5 gr | 1 gr | 1.5 gr |
|------------|--------|------|--------|
| Temperature (°C) | $k_2$ (g/mg.min) | $R^2$ | %SSE | $k_2$ (g/mg.min) | $R^2$ | %SSE | $k_2$ (g/mg.min) | $R^2$ | %SSE |
| 30         | 1.720  | 0.991 | 3,578 | 4,177  | 0.994 | 3,217 | 8,479  | 0.995 | 2,636 |
| 40         | 1.982  | 0.992 | 3,281 | 4,330  | 0.994 | 3,280 | 9,6   | 0.996 | 2,605 |
| 50         | 2.022  | 0.992 | 3,23  | 4,996  | 0.995 | 2,897 | 9,755  | 0.997 | 2,47  |

From Table 3 indicate that the increase of constant (k) adsorption rate was increased with addition of adsorbent dosage. The increase of constant (k) shown in Figure 5.
The addition of adsorbent dosage will increased the k value, caused the amount of adsorbent will activated the adsorbent active surface area, so the adsorption process progressively faster and increase the rate of adsorption (k) [12]. In this research, the results obtained for pseudo second order model with linear regression value $R^2$ is 0.997, %SSE 2.47 % and kinetics constant (k) 9,755 g/mg.min. The optimal condition were obtained at 50 °C with 1.5gr adsorbent dosage.

4. Conclusion
The adsorption process of lead metal ions in aqueous solution using tricalcium phosphate as adsorbent are influenced by temperature and adsorbent dosage. The higher temperature and amount of adsorbent dosage can causes the adsorption constant become larger. The highest lead metal ions adsorption constant (k) using tricalcium phosphate shown at optimal condition of 50 °C and adsorbant dosage 1.5 gr is 9,775 g/mg.min. The kinetics adsorption models to adsorb lead metal ions using tricalcium phosphate followed pseudo second order with k 9,775 g/mg.min.

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