ADSORPTION ISOTHERM MODELS AND KINETICS FOR PHOSPHATE ADSORPTION IN SEDIMENT

Askal Maimulyanti, Isna Nurhidayati, R. Wiwi Widarsih
Department of Analytical Chemistry, AKA Bogor Polytechnic, Indonesia

Corresponding Author: askal_m@yahoo.com

ABSTRACT
Phosphate ions in solution can be adsorbed using sediment. Phosphate adsorption by sediment was influenced by concentration, adsorbent dosage, and temperature. The research was carried out at pH 1 for 30 minutes. The optimum adsorption occurs at a concentration of 15 ppm with an adsorption capacity of 0.41 mg/g. The adsorbent dosage was used as 1 mg with a capacity of adsorption capacity of (0.6077 mg/g). The optimum temperature is obtained at 40°C with a capacity of adsorption (0.1250 mg/g). Adsorption isotherm follows the Langmuir and Freundlich model. The Langmuir parameters as $R^2$ (0.7270), $K_L$ (6.1750 L/mg), $q_m$ (0.3329 mg/g). Freundlich parameters were obtained as follows: $R^2$ (0.9741), $1/n$ (0.6059), and $K_F$ (0.5635 m/g (L/mg)${}^{1/n}$. Reaction kinetics based on pseudo-second-order kinetic with a value of $R^2 = 0.9717$, $K = 25.2554$ gmol$^{-1}$hour$^{-1}$.

Keywords: Sediment, Adsorption Isotherm, Adsorption Kinetic, Adsorption Capacity.

INTRODUCTION
Phosphates are found in waters as a result of human activities and biogeochemical processes. Excess phosphate in water causes eutrophication which results in a decrease in oxygen concentration in the water. This not only threatens the life of aquatic biota but also disrupts the food chain and causes a decrease in water quality. Effort to reduce phosphate levels in waters needs to be done so that the phosphate in the waters is safe for aquatic biota and does not damage water quality. Phosphates can be removed from the water by various methods, including chemical deposition, adsorption, and ion exchange. A chemical deposition is less environmentally friendly because it uses chemical reagents that can produce new waste. The use of the membrane process method is considered less economical because of high maintenance costs and the occurrence of membrane degradation. In the biological treatment method, usually, the phosphate that can be removed is not more than 30%, so another method is needed to remove the remaining phosphate. The adsorption method is the most widely used method because effective in reducing the phosphate concentration within the allowable limits compared to other methods. Sediment can be considered as a storage medium for phosphate. Its accumulation in sediment is due to use in households, agriculture, and industry. Several researchers have studied phosphate adsorption on various solids. The adsorption process of liquid on a solid surface can be studied through several isotherm models. The adsorption isotherm helps to evaluate the mechanism exhibited by the adsorption system. Commonly used isotherm models include the Freundlich and Langmuir isotherms. Langmuir isotherm occurs on a homogeneous side and only a kind of molecule occupies a monolayer. Freundlich's model explains that the heterogeneous surface of the adsorbent has adsorption sites with different bond energies. Adsorption kinetics is one aspect that is carried out to evaluate the characteristics of the adsorbent which is used to predict the adsorption rate. Research on phosphate ion adsorption has been widely discussed in previous studies. However, the use of sediment as a phosphate ion adsorbent has not been studied intensively. Phosphorus in the form of phosphate is very quickly absorbed by sediments, especially on the surface of oxygen-rich sediments. The absorption process also depends on the type of sediment, including the content of organic particles. Dissolved inorganic phosphate has a strong ability to bind to the surface of solids. The process of release and adsorption of phosphate by sediment is the cycle of phosphate in water. Phosphate is released through physical and biological processes and more than 90% of the total phosphorus in the waters is carried as suspension particles, then the material is deposited in the sediment. This study
EXPERIMENTAL

Preparation of Sediment
The marine sediments used in this study were taken from Jakarta Bay. The sediment was dried at $120^\circ$C for two days and mashed to a size of 100 mesh.

Adsorption Process
The adsorption process includes variations in concentration. The optimum concentration was determined by varying the concentration of phosphate to 2.5, 5, 7.5, 10, and 15 ppm carried out at pH 1, for 30 minutes, and stirring at 200 rpm. The adsorbent weight was varied from 1-6 grams at pH 1, and the stirring speed was 200 rpm for 30 minutes with an initial concentration of 15 ppm of phosphate. The variation of temperature of 25-45$^\circ$C, 30 minutes with 200 rpm, the concentration of 15 ppm, and a sediment weight of 6 grams.

Adsorption Isotherm
1 gram of adsorbent was added to 50 mL of phosphate solution with concentrations of 10, 20, 30, 40, and 50 ppm. The experiment was carried out at pH 1. The solution was shaken at 200 rpm for 30 minutes. The filtrate was measured with a UV-vis spectrophotometer. The absorption capacity was determined based on the following equation.\[ q_e = \frac{(C_0-C_e)V}{W} \] (1)

Langmuir adsorption model is based on the following equation:
\[ \frac{C_e}{q_e} = \frac{1}{q_{mon}K_L} + \frac{1}{q_{mon}}C_e \] (2)
\[ \ln q = k + \frac{1}{n}\ln C \] (3)

Freundlich adsorption model is based on the following equation:
\[ q_e = k_f C_e^{1/n} \] (4)
\[ \log q_e = \log k_f + \frac{1}{n}\log C_e \] (5)

Adsorption Kinetics
A total of 1 gram of adsorbent is added to 50 mL of 25 ppm phosphorus solution at pH = 1. The solution was stirred at 200 rpm. The interaction time was varied for 30, 60, 90, 120, and 150 minutes. The solution was filtered and analyzed. The first-order-kinetics equation model is based on the equation.\[ \log(q_0 - q_t) = \log q_e - \frac{k_1}{2.003}t \] (6)

The second-order adsorption kinetics model is as follows:
\[ \frac{t}{q_t} = \frac{1}{K_2q^2} + \frac{1}{q_e}t \] (7)

RESULTS AND DISCUSSION
Phosphate Adsorption with Different Concentration
The influence of the initial phosphate concentration by sediment can be seen in Fig.-1. The percentage of adsorption of phosphate decreased at the concentration from 2.5 ppm to 5 ppm, and then increased in the percentage of phosphate adsorption. Figure-1 indicated the sediment was saturated at low concentrations. When the total amount is considered, it can be observed that an increase in the concentration causes an increase in adsorption capacity. At higher concentrations, the driving force also increases and the mass transfer barrier between the solution and the solid surface can be overcome. This is due to the increasing number of active sites when the concentration is enlarged so it becomes easier for the molecules to adsorb.
to penetrate the adsorbent. Based on research that has been carried out, the optimum absorption occurs at a phosphate concentration of 15 ppm with a capacity of adsorption was 0.41 mg/g.

Effect of Adsorbent Weight
The dosage of adsorbent influenced the adsorption process. The effect of adsorbent weight can be seen in Fig.-2.

The results (Fig.-2) showed that the greater the adsorbent dose, the higher the absorption of phosphate in the solution. The adsorbent dose was varied in the adsorbent weight range of 1-6 grams with the amount of phosphate absorbed by 81.0767% -99.3360%. In addition, the adsorption capacity value decreased from 0.6077 mg/g to 0.1241 mg/g along with the increase in sediment weight, as shown in Fig.-2. A similar study was also conducted using Oued Boufekrane sediment.

Influence of Temperature
The temperature can influence the adsorption process and it can be seen in Fig.-3.
Figure-3 indicated an increase in phosphate adsorption at an increase in solution temperature. However, these results cannot reflect the actual conditions that occur in nature, because nature is heavily influenced by biological activity.\textsuperscript{24} High temperatures indicate that phosphate adsorption by sediments is an endothermic reaction. The increase in temperature causes an increase in the mobility of the phosphate ion so that the adsorption process also increases. The results of this experiment showed that the adsorption percentages from temperatures of 25ºC and 30ºC were 99.31% and 99.68%, respectively, and the adsorption capacity values were 0.12441 mg/g and 0.12446 mg/g. From these results, the optimum temperature for phosphate adsorption was 40 ºC with an adsorption capacity was 0.1250 mg/g.

**Adsorption Isotherm**

To study the phosphate ion adsorption isotherm model by marine sediments in Jakarta Bay, two types of modeling were used, it was the Freundlich and Langmuir models.\textsuperscript{25,26,27} The Langmuir isotherm assumes that the adsorption process only occurs in one layer (monolayer) on a homogeneous adsorbent surface.

Based on Table-1, it can be concluded that the phosphate adsorption by sediments is based on the Freundlich isotherm. This confirms that phosphate adsorption by marine sediments occurs through interactions between adsorbate molecules on heterogeneous surfaces to form a multilayer.\textsuperscript{28} The value of 1/n in the Freundlich constant indicates the validity of adsorption. If the value of 1/n lies between 0 and 1, then the adsorption capacity increases with increasing concentration and a new adsorption side appears which shows that this isotherm model is more suitable.\textsuperscript{29}

**Kinetics of Adsorption**

The experiment used the kinetic models based on pseudo-first-order and second-order. In the pseudo-first-order kinetic model it can be seen in Fig.-5 and Table-2.

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**Fig.-4:** Adsorption Isotherm (a) Langmuir (b) Freundlich

**Fig.-5:** Kinetic Models (A) Pseudo-Second-Order (B) Pseudo-Second-Order
The adsorption kinetics of phosphate ions by the sediment has the highest correlation coefficient ($R^2$) in the pseudo-second-order kinetics with $k$ (25.2554 g mmol$^{-1}$ hour$^{-1}$). It means 25.2554 grams of adsorbent was able to adsorb 1 mmol of adsorbate in 1 hour. Thus, the phosphate adsorption kinetics in this study can be explained by pseudo-second-order kinetics. Maximum adsorption is the formation of a monolayer surface in the sediment.

The first-order pseudo model constant can be determined by plotting ln ($q_e - q_t$) as a function of time ($t$). The pseudo-order kinetics model assumes that adsorption through two stages, were fast adsorption occurs on the active site and slow adsorption occurs on the lower energy side. This model shows a chemisorption process.

**CONCLUSION**

Sediments have the ability to adsorb phosphate. Based on the research, showed that phosphate adsorption by sediment was influenced by pH, contact time, and weight of the adsorbent. The optimum adsorption of phosphate by marine sediment from Jakarta Bay occurs at pH 1 with a contact time of 30 minutes with 200 rpm, a concentration of 15 ppm, and an adsorbent weight of 6 grams at a temperature of 40°C. The adsorption isotherm follows the Langmuir and Freundlich model. Reaction kinetics based on pseudo-second-order kinetic with a value of $R^2 = 0.9717$, $K = 25.2554$ g mol$^{-1}$ hour$^{-1}$.

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**REFERENCES**

10. J. Meng, Q. Yao and Z. Yu. *Ecological Engineering*, 70, 140(2014), [https://doi.org/10.1016/j.ecoleng.2014.05.007](https://doi.org/10.1016/j.ecoleng.2014.05.007)

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