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Phosphate Adsorption from Synthetic Aqueous Solutions by Waste Mussel Shell: Kinetics and Isotherms Studies

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ABSTRACT

The amount of phosphorus released to the wastewater from industry is alarming. One of the phosphorus effects to the environment is eutrophication that will cause algal blooms. Algal blooms will cover the water surface and cause the aquatic plants to not getting enough sun. Insufficient sunlight caused the plants to die thus limiting the oxygen supply to other aquatic life because photosynthesis cannot occur. This research focuses on reducing the amount of phosphorus in a synthetic aqueous solution by using waste mussel shell as absorbent and evaluate the data experiment using kinetic and isotherm models. A batch study was carried out using different adsorbent mass of waste mussel shell and different concentrations of synthetic solution. The absorption efficiency increased with the increasing mass of waste mussel shell but reached constant when the waste mussel shell reached the adsorption limit as equilibrium state. The adsorption was successfully achieved following the pseudo-second order, giving the R^2 as 0.9991. Isotherms model analysis showed that the Freundlich isotherms model was insufficient to explain the adsorption of phosphate onto waste mussel shell compared to Langmuir isotherm model (R^2=0.8505). The study advanced the understanding of the kinetic adsorption and isotherm study of waste mussel shell and proved that the waste mussel shell has the potential to reduce the amount of phosphorus released into the wastewater. The contribution of this study is alternative adsorbent from waste mussel shell to treat the wastewater in a prospective wastewater treatment facility setting.

Keywords: Adsorption, isotherm, phosphate, kinetic, waste mussel shell

1. INTRODUCTION

Phosphorus is an essential element that can harm human health and the environment. This element attaches to soil particles and flows into surface-water bodies following the water runoff. Phosphorus often move through groundwater currents because the groundwater discharged regularly through surface water; for example, by streams through rivers [1]. Concentrations of phosphorus in the groundwater could be a concern for water quality of a surface water. Overproduction of a lake or water source may contribute to an imbalance in the cycling process of nutrients and materials [2].

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Water is important for the environment because it can ensure the sustainability of the natural system. Untreated wastewater can affect human and aquatic life. The excessive amount of phosphate emitted from human activities and untreated wastewater may contribute to depletion of the receiving water quality, result in the eutrophication [3]. Eutrophication (from the Greek-meaning "fully nourished") is an enhanced primary crops activity contributing to the decrease in habitat stability [4].

The elimination of phosphorus (P) from household wastewater is specifically meant to mitigate the eutrophication risk in receiving waters [5]. Phosphorus removal from wastewater could be performed well using physio-chemical methods, biological treatment or combinations of both processes and many large-scale techniques which are well established [6]. From past studies, the phosphate removal capability was greatly influenced by treatment temperature and form of inert gas. When the temperature was increased, the phosphorus removal potential also increased [7]. Some methods have been suggested to protect and treat contaminated water to preserve human health and the environment from becoming more polluted [8]. The phosphate removal by adsorption method is an outstanding method due to the eco-environmental and simple operation [9].

In Kampung Pasir Putih, Johor Bahru, the villagers are facing problems with the piling up of the mussel shells. The used shells were just dumped into a landfill and left in abeyance. This cause the place to become smelly and dirty. Mussel shells, a by-product of aquaculture industry, contain an abundant residual source of calcium that could be utilized in a wastewater treatment. It is also a natural mesoporous mineralized biomass with the properties and characteristics of adsorption, dispersion, non-toxicity and mineralization [10].

After thermal treatment, mussel shell has high calcium oxide (CaO) content, which is an active component for the phosphate adsorption from wastewater [11]. Besides mussel shell, oyster shell and eggshell are also potential adsorbents that can be used to control pollution in water [12]. The calcium oxide (CaO) content of oyster shell under the thermal treatment is strong and has been an important ingredient for freshwater phosphate adsorption [13]. Meanwhile, the elemental composition of eggshell surfaces before adsorption contain no phosphorus, revealed that calcium carbonate-based eggshell was co-precipitated with calcium phosphate [14]. Nevertheless, the calcined mussel shell presented a higher retention capacity than oyster shell and eggshell, which can be attributed to the differences in its composition [15]. Waste mussel shells was chosen because the potential of this adsorbent as good adsorbent to treat the and remove the phosphorus elements from domestic wastewater [16].

The effects of different temperatures, contact times, and initial concentrations were examined to optimise the conditions used for phosphorus decontamination. Also, the understanding of adsorption kinetic and isotherms model is the importance due to verify the application of waste mussel shell is relevant as phosphate adsorbent. The objectives of this study were to evaluate the potential of waste mussel shells in removing phosphate from aqueous solution and to use adsorption kinetic and isotherm model as analysis model by performing batch experiments.

2. MATERIAL AND METHODS

Mussel shells were collected from a foreshore in Pasir Gudang, Johor (See Figure 1). The mussel shells are mostly dumped to landfill, causing the place to become smelly and dirty. Thus, it was chosen to be used as adsorbent for phosphate removal. Mussel shell is suitable for this project because it contains high amount of calcium that can reduce phosphate in wastewater [17] [18].

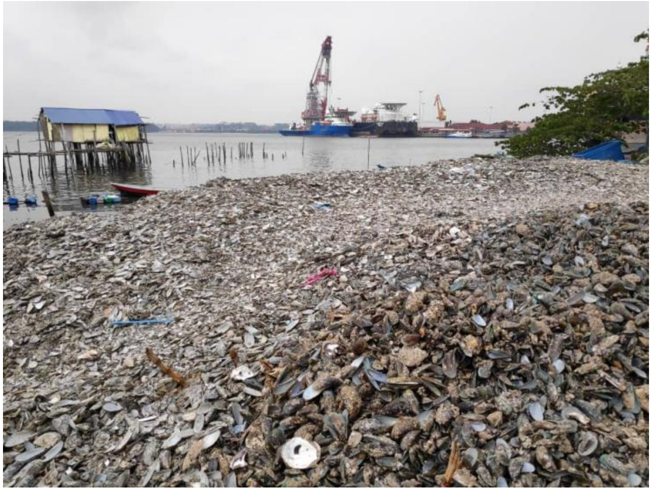


Figure 1. Sampling location.

The collected mussel shells were washed thoroughly with tap water. Then, the cleaned shells were rinsed and dried under the sunlight and completely dried in an oven at 30°C for 3 days, crushed and sieved through 0.6 mm, 1.18 mm, and 2.0 mm sieve proportion. The size range of 0.6 mm to 1.18 mm was chosen for this experiment. After obtaining the shell powder in the range of 0.6mm to 1.18mm, the mussel shells were packed into 2g, 4g, 6g, 8g of mass adsorbent. Figure 2 shows the preparation of mussel shells.

(a)

(b)

(c)

(d)

Figure 2. Preparation of the mussel shells adsorbent, (a) Cleaning of the raw materials, (b) Drying under sunlight, (c) Drying in oven (103°C to 105°C) and (d) Sieving.

Wastewater with concentration of 100 mg L^{-1} PO_4^{3-} was prepared by dissolving 0.1433 g of KH_2PO_4 (analytical grade) into 1 L of deionised water in a volumetric flask by using dilution method. The solution was diluted from 100 ppm KH_2PO_4 to 5, 10, 15, 20, and 25 mg/L as PO_4^{3-}. To prepare the 30 ppm aqueous solution; first, measured the stock solution was first measured in a measuring cylinder and poured into a volumetric flask. Then, distilled water was added into the volumetric flask until it reached 1 L. Figure 3 shows the preparation of the solution.

(a) (b) (c) (d)

Figure 3. Preparation of the synthetic aqueous solution, (a) Weighed the KH_2PO_4, (b) Dilution process (c) Phosphate, Reactive (Orthophoshate) Amino Acid Method, and (d) DR6000 UV Spectrometer.

All samples must be shaken well using orbital shaker at 170 rpm. HACH DR 6000 Spectrophotometer was then used to determine the concentration of the retained phosphate and each sample was analysed by measuring the intensity of light passing through the samples. The samples were tested by adding amino acid and molybdate. Data for the intensity of light passing was recorded. The analysis of data experiment is using in kinetic and isotherms model analysis to identify the best fitting equation for this adsorption process.

3. RESULTS AND DISCUSSION

3.1 Adsorption Kinetic

The rapidity of adsorption kinetics within the first few minutes can be defined by the mixing of adsorbent and aqueous solution at the beginning contact until equilibrium state at certain period of time [19]. The kinetics of solute adsorption on a solid in an aqueous solution is a complicated operation. Mathematical equations are commonly used to promote the interpretation of experimental results. The kinetic modelling of phosphorus adsorption on sediments was tested was based on two models: pseudo-first-order and pseudo-second-order.

The pseudo-first order kinetic model assumes that the occupation rate of sorption sites is proportional to the number of unoccupied sites. When plotted on a graph, the plot looks as in Figure 4. It can be observed that the best fitted line can be created to identify the linear relationship between the parameters.

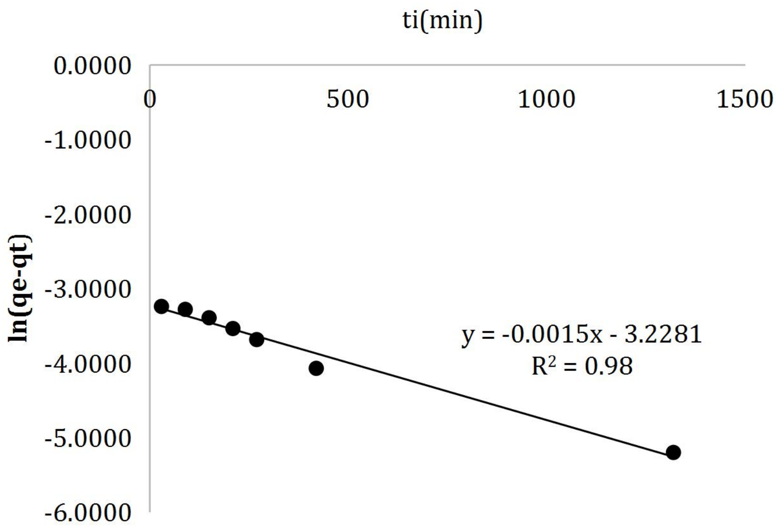


Figure 4. Pseudo First Order for ln(qe-qt) versus ti(min).

Pseudo first order linear equation (1) was used to identify the important parameters presented in Figure 4.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t_i \quad (1)$$

where q_e is the equilibrium amount of phosphate adsorbed (mg/g), q_t is the amount of phosphate adsorbed at adsorption time (mg/g), k_1 is a rate constant of pseudo-first-order equation (min^{-1}) and t_i is the adsorption time (min). The value of k_1 and $\ln(q_e)$ can be evaluated from the slope and intercept of plot $\ln(q_e-q_t)$ versus t_i, respectively. The adsorption kinetic follows a pseudo-first-order model when the plot of $\ln(q_e-q_t)$ versus t_i will give a straight line.

Table 1 Kinetic table of Pseudo First Order

C_i (mg/L)	q_e (mg/g)	k_1 (min^{-1})	R^2
5	0.052	-114.564	0.9800
10	0.069	-63.115	0.7709
15	0.180	-15.959	0.8491
20	0.268	-10.053	0.9456
25	0.229	-11.288	0.8557

According to the data that were obtained from the batch experiments of PFO as shown in Table 1, it can be seen that 5 mg/L of 2 g adsorbent mass gave R^2 of 0.9800. As for the 10 mg/L, the R^2 is 0.7709. And the value of R^2 are increase respectively for 15 mg/L, 20 mg/L and 25 mg/L that is 0.8491, 0.9456 and 0.8557, respectively. Pseudo second order kinetic model assumes that the adsorption rate of solute is proportional to the available sites on the adsorbent [20]. By using the Pseudo first order linear Equation (1), it is possible to identify the important parameters of R^2, while Pseudo second order linear in Equation (2), the best-fit line in Figure 5 can easily be derived by obeying the linear equation.

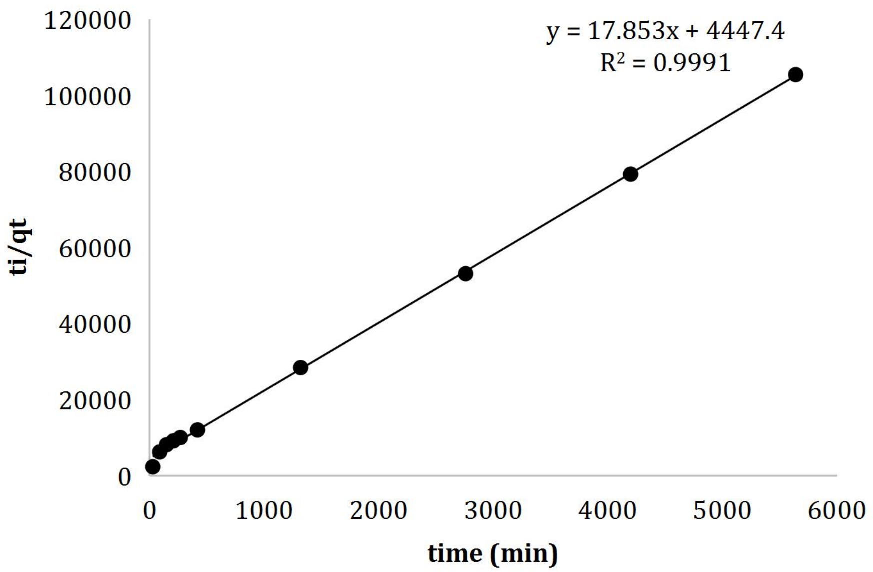


Figure 5. Pseudo Second Order for t_i/q_t versus t_i(min).

By referring to Figure 5, the linear state are coming from Pseudo Second Order linear equation as shown below,

$$\frac{t_i}{q_t} = \frac{1}{k_2 {q_e}2} + \frac{t_i}{q_e} \tag{2}$$

where, q_t (mg/g) is the amount of phosphate adsorbed at adsorption time, q_e is the amount of phosphate adsorbed at equilibrium time (mg/g), k_2 is a rate constant of pseudo second order model (min^{-1}) and t_i is the adsorption time (min). The value of k_2 and q_e can be evaluated from the intercept and slope of plot t_i/q_t versus t_i.

Table 2 Kinetic table of Pseudo Second Order

C_i (mg/L)	***q_e (mg/g)***	***k_1 (min^{-1})***	***R^2***
5	0.052	0.083	0.9991
10	0.069	0.137	0.9996
15	0.180	0.013	0.9939
20	0.268	0.003	0.8929
25	0.229	0.010	0.9921

Table 2 shows that 5 mg/L of 2 g adsorbent mass will get the value of R^2 which is 0.9991. Then for the 10 mg/L it gets 0.9996 for R^2. And the value of R^2 are increase drastically for 20 mg/L from 15 mg/L which is 0.9939 to 0.8929 and 25 mg/L is 0.9921. From the result of kinetic models, it shown that the pseudo second order model equation is the best fitting to describe the adsorption process occurs in active sites compared to pseudo first order from linear regression analysis, R^2.

3.2 Adsorption Isotherm

Isotherm model is one of the main relationships used to define the non-ideal adsorption which can be applied to the multilayer adsorption [21]. Freundlich adsorption isotherm shows the quantity of gas or liquid ingested per unit mass of adsorbent at constant pressure. The Langmuir isotherm model can be defined as a relationship between surface area and the adsorption capability, and can be used when assuming the homogeneous adsorbent layer of the system. One of the limitations of this model is that it is unable to be used for adsorption in high pressure that is a similar limitation with the Freundlich isotherm. The application of Langmuir isotherms model assumes that the adsorption occurs on a homogenous surface containing sites with the same adsorption and valid for complete monolayer of adsorption [22]. Meanwhile, the Freundlich model assumes that the adsorption occurs in surface layer with maximum distribution equal form bond. Freundlich equation is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where, q_e is the equilibrium amount of phosphate adsorbed (mg /g), K_F is the Freundlich constant (mg /g), n (dimensionless) is the heterogeneity factor should have a lower value for more heterogeneous surfaces and C_e is the equilibrium concentration (mg L^{-1}). The Langmuir equation is represented as:

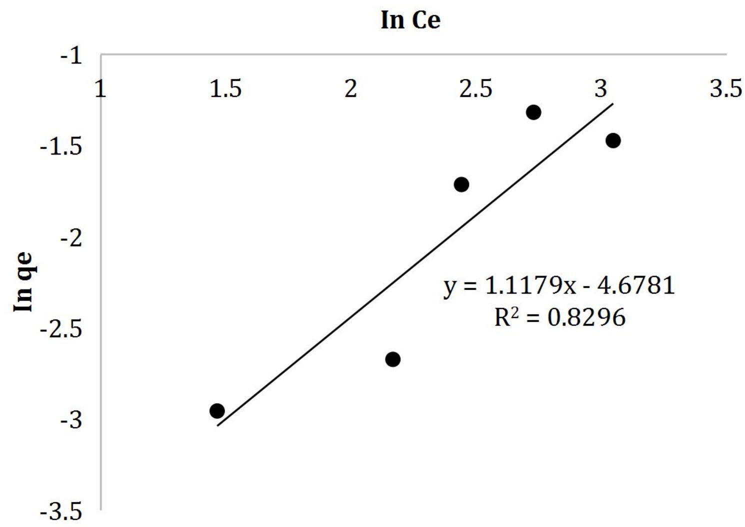
$$\frac{1}{q_e} = \frac{1}{K_L q_{\max} C_e} + \frac{1}{q_{\max}} \tag{4}$$

where q_e is the equilibrium amount of phosphate adsorbed (mg g^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}), K_L is the adsorption energy constant (L mg^{-1}) and C_e is the equilibrium concentration (mg/L). From the analysis of both isotherms model, Table 3 shows the important isotherms model for adsorption of phosphate.

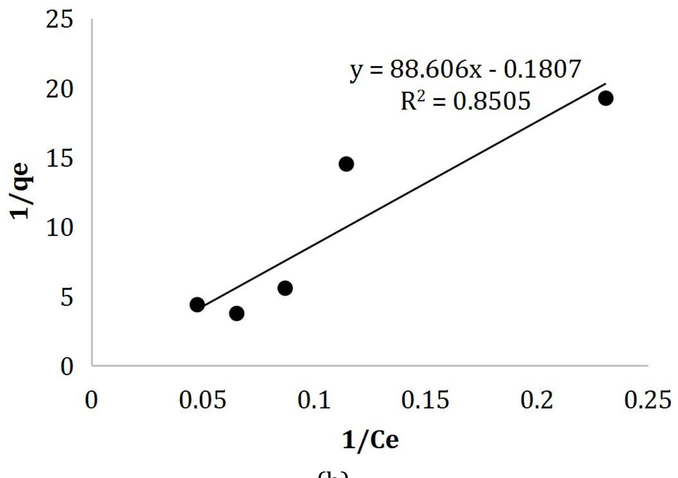
Table 3 Isotherm parameters for the adsorption of phosphate of WMS

Freundlich model				Langmuir model		
n	*1/n*	K_F *(mg/g)*	R^2	q_{max} *(mg/g)*	K_L *(L/mg)*	R^2
1.1179	0.895	4.687	0.830	5.534	0.00239	0.851

The Freundlich and Langmuir isotherms model were obtained into the Figure 6 (a) and (b), respectively. The linear regression analysis from experimental data (R^2= 0.8296) in Figure 6 (a) shows that the Freundlich isotherms model is less adequate to explain the adsorption of phosphate onto waste mussel shell compared to Langmuir isotherm model (R^2=0.8505).



(a)



(b)

Figure 6. Fits of the isotherms model, (a) Freundlich model, and (b) Langmuir model.

Based on both correlation of the models, the phosphate adsorption process for the study is best suited to the Langmuir isotherm model because the R^2 value for Langmuir is higher than the Freundlich model. The models verified the good fitting of this isotherm model with the experimental data.

4. CONCLUSION

In conclusion, waste mussel shells were successfully used as an adsorbent for the elimination of phosphate from wastewater. The study has shown the ability of mussel shells as an alternative for the reduction of phosphates and at the same time addressing the costly and troublesome problems of waste disposal. Reducing phosphates by adsorption is an enticing method because it is eco-friendly and fast. The results also demonstrated that the removal efficiency could be improved along with the decrease in the concentration of phosphate. This process can ensure the conservation of environment using this alternative adsorbent from waste mussel shell to treat the wastewater in a prospective wastewater treatment facility setting.

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