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Utilization of *Filopaludina sumatrensis's* Shell as a Biosorbent for Removing of Pb^{2+} in Wastewater

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Abstract: *Filopaludina sumatrensis's* shell was used as a low-cost sorbent for removing of Pb^{2+} in synthetic wastewater. The shell was burnt in aerobic conditions at 400, 500 and 600°C using a furnace. The different burnt shells were then compared with an unburnt shell for the efficiency of Pb^{2+} removal at the 0.05 level of statistical significance. The results showed that there were not any significant differences between sorption efficiency of Pb^{2+} from the unburnt shell and burnt shells at any temperatures for initial Pb^{2+} concentration of 0.1 mM. Meanwhile, at an initial Pb^{2+} concentration of 1 mM, the burnt shell at 600°C has less Pb^{2+} sorption efficiency than that of the other conditions. The unburnt shell was selected for the further study of sorption kinetics and sorption isotherm. The pseudo second order kinetic model was suitable for the description of sorption kinetics. Although, it took 20 and 30 min to reach equilibrium for experiments at initial Pb^{2+} concentration of 1 and 0.1 mM, respectively. Biosorption isotherm data could be described with the Freundlich isotherm.

Key words: Biosorption, wastewater treatment, kinetics, isotherm, Pb^{2+}, Freundlich isotherm

INTRODUCTION

Lead (Pb) is one of the most widely used heavy metals in many industries such as battery factories, electrical appliances, etc. which created wastewater containing lead ion (Pb^{2+}). Contamination of lead ion in water body responses for adverse effects to ecosystems and human health, for example, reducing fertility in women, altering spermatogenesis for men, impairing kidney function. Thus, Pb^{2+} (and the other toxic substances) must be eliminated from the wastewater until it meets the regulation standard before discharging to the environment.

However, the treatment of this type of wastewater involves high-cost techniques such as ion exchange, evaporation, precipitation, membrane separation, etc. Unfortunately, these common techniques have been shown to be quite expensive for wastewater containing a low concentration of heavy metals but still does not compromise with water quality standard (Apiratikul *et al*., 2011). Biosorption, the adsorption process that uses sorbent derived from biomaterial has been introduced as an alternative method, for such treatment because it is inexpensive (Volesky, 2004).

Numerous researches have been studied about biosorption. The green macroalga *Caulerpa lentillifera* was used as a biosorbent for removing heavy metal ions in the aqueous phase (Apiratikul *et al*., 2011; Apiratikul and Pavasant, 2006, 2008; Apiratikul, 2017). The freshwater snails were found to be effective biosorbents for decreasing of heavy metal concentration from aqueous solution, e.g., *Melanoides tuberculata* (Hossain and Aditya, 2015), *Lymnaea luteola* (Hossain *et al*., 2015) and *Physa acuta* (Hossain and Aditya, 2013) for Cd^{2+} removal.

Filopaludina sumatrensis is a species of large freshwater snail with a gill and an operculum, an aquatic gastropod mollusk in the family Viviparidae. The snail was the most widely distributed snail for all 20 studied nursery ponds in the research (Madsen *et al*., 2015). There are many subspecies of this kind of snail, however, the subspecies of *Filopaludina sumatrensis* sumatrensis (Anonymous, 2019) are used in this study as it is widely found in South East Asia, especially, in Thailand. The snail is edible and widely seen as food along with the markets and restaurants. Nevertheless, its shell is an unwanted biomaterial as it is inedible. Hence, there is a need for the management of this overabundance of the shell. Furthermore, there is no unprecedented research about the application of this shell in the biosorption process and no research found to use freshwater snail's shell as a biosorbent for Pb^{2+} removal.

This research intends to exploit the discarded shell of *Filopaludina sumatrensis* as biosorbent in the removal of lead (II) ion from the wastewater for the first time. The effect of the shell's burning temperatures was investigated for the optimal condition of treatment. The effects of time and initial concentration of Pb^{2+} solution on the biosorption were also, studied in this research to elucidate the sorption kinetics and sorption equilibrium.

MATERIALS AND METHODS

Snail's shell collection and preparation: A large freshwater snail's shell, *Filopaludina sumatrensis* sumatrensis Anonymous (2019) was collected from Bueng Kra Jab households community, Vichianburi District, Petchaboon Province, Thailand. The shell was washed with deionized water and oven-dried at 105°C for 12 h. The shell was then, ground into a small particle using mortar and pestle and the ground particles were sieved through sieve mesh with the size of 75 μm. The product was then filled in the zip bag and store in a desiccator and defined it as an unburnt shell. Some of the products were burnt in aerobic condition at 400, 500 and 600°C for 1 h in a furnace for the studying of temperature modification's effect on sorption efficiency.

Biosorption of Pb^{2+}: The experiment was performed by adding a certain amount of 0.03 and 0.09 g of snail's shell to 30 mL of Pb^{2+} solutions to obtain the sorbent dose (X_o) of 1 and 3 g/L, respectively. Initial concentrations of Pb^{2+} solutions (C_o) varied from 0.1-3.0 mM. The mixtures were mixed slowly in a rotary shaker at an agitation rate of 150 rpm for a certain contact time varied from 5-120 min at room temperature (25±2°C). The pH was controlled at 5 using the CH_3COONH_4/CH_3COOH buffer system with the acetate concentration of 200 mM. The shell particle was then separated by filtration through the No. 93 filter paper. Pb^{2+}concentrations in the filtrates were measured by Atomic Absorption Spectrophotometer (AAS). The sorption efficiency was evaluated by two indicators, for instance, sorption capacity and removal percentage. The parameters could be described as in Eq. 1 and 2:

$$q=\left(\frac{C_o-C_t}{X_o}\right)\times 1000 \quad (1)$$

$$\text{Removal}(\%)=\left(\frac{C_o-C_t}{C_o}\right)\times 100 \quad (2)$$

Where:

q	= The sorption capacity (μmol/g)
C_o and C_t	= The initial Pb^{2+} concentration and concentration of Pb^{2+} at time t (mM)
X_o	= The sorbent dose (g/L)
Removal (%)	= The removal percentage (%)

Each experiment was triplicated to ensure that the obtained results were genuine. The results were reported as average values with an error bar of the statistical confidential interval of 95%.

Determining for optimal burning temperature: The comparison of Pb^{2+} biosorption efficiency between the unburnt shell and burnt shells at different temperatures was investigated for initial Pb^{2+} concentration of 0.1 and 1.0 mM. The sorbent dose was fixed at 1 g/L and contact time was fixed at 120 min to make sure that sorption reach equilibrium which yields the highest sorption capacity and removal percentage for each condition. The results were analyzed by ANOVA and t-test statistics to determine the difference of sorption efficiency between each group at the 0.05 level of statistical significance (alpha = 0.05). The optimum condition was then selected for further study.

The studies of sorption kinetics and equilibrium: The sorption kinetics was investigated for an initial Pb^{2+} concentration of 0.1 and 1.0 mM with the sorbent dose of 3.0 g/L. The contact time was varied in the range of 5-120 min. The time that required the sorption to reach equilibrium was elucidated from the experiments in this study. The sorption capacity at different times was analyzed using two well known kinetic models, i.e., pseudo first and second order kinetic models which were expressed by Eq. 3 and 4, respectively:

$$q_t=q_e\left(1-e^{-k_1 t}\right) \quad (3)$$

$$q_t=\frac{q_e^2 k_2 t}{1+q_e k_2 t} \quad (4)$$

Where:

q_t	= The sorption capacity at time t (μmol/g)
q_e	= The sorption capacity at equilibrium (μmol/g)
t	= The contact time (min)
k_1 and k_2	= The sorption rate constants for pseudo first order (min^{-1}) and pseudo second order (g μmolmin^{-1}) models

The experimental data of q_t at 120 min was assumed to q_e of the pseudo first order kinetic model and the rate constant (k_1) was determined by linearizing Eq. 3 to linearized form then uses statistical linear regression to obtain k_1. In the case of pseudo second order kinetic model, linearization of Eq. 3 was performed to evaluate both q_e and k_2 by statistical linear regression.

The set of an experiment for sorption equilibrium was carried out at the sorbent dose of 3.0 g/L. The contact time was fixed at 120 min to ensure that the sorption reaches equilibrium. Initial Pb^{2+} concentration was varied from 0.1-3.0 mM. The sorption capacity was calculated using Eq. 1 and denoted as q_e (μmol/g) which is Pb^{2+} equilibrium concentration in the solid phase. The remaining Pb^{2+} concentration in the solution at a contact time of 120 min was assumed as equilibrium concentration in the liquid phase which is denoted as C_e(mM). The relationship between q_e and C_e was plotted on rectangular coordinate as sorption isotherm and was then analyzed by Freundlich and Langmuir isotherm models as shown by Eq. 5 and 6, respectively:

$$q_e = k_f C_e^{1/n} \quad (5)$$

$$q_e = \frac{q_{max} b C_e}{1+bC_e} \quad (6)$$

Where:

k_f = The Freundlich constant ($\mu mol^{1-1/n} L^{1/n}/g$)
1/n = The Freundlich exponent (no unit)
q_{max} = The maximum amount of Pb^{2+} adsorbed per unit mass of sorbent (μmol/g)
b = The Langmuir sorption affinity constant (L/mmol)

These constants could be achieved by linearizing Eq. 5 and 6 then, applied a statistical linear regression technique.

RESULTS AND DISCUSSION

Effect of shell's burning temperature on sorption efficiency: The sorption capacity and removal percentage of different types of shell's modification was shown in Fig. 1.

Figure 1 revealed the similar patterns for sorption capacity and the removal percentage along with the various types of sorbent's pretreatment. For example, the highest average values (in sample scale) of both sorption efficiency indicators for initial Pb^{2+} concentration of 1.0 mM were found with shell pretreatment at 500°C while the lowest values of the indicators were found at 600°C of shell pretreatment.

In the case of initial Pb^{2+} concentration of 0.1 mM, ANOVA analysis gave a p-value of 0.089 which is greater than the significant level of 0.05 ($p>0.05$). This could be interpreted as there were not any significant differences between sorption efficiency indicators and types of shell's pretreatment (sorption efficiency indicators and types of shell's pretreatment were independent to each other). This might because the initial Pb^{2+} concentration is so, quite low that it was unable to discriminate the sorption efficiency indicators between each type of sorbent's pretreatment.

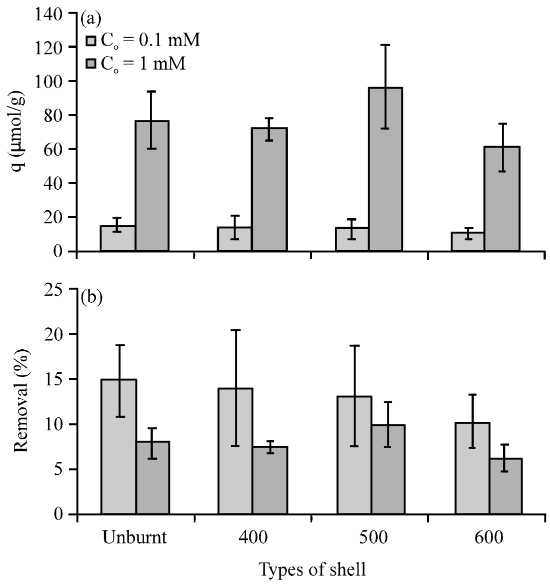

Fig. 1: a) Sorption capacity and b) Removal percentage of sorption efficiency of various types of sorbent's pretreatment

However, at the higher initial Pb^{2+} concentration, the results from ANOVA analyses show that sorption efficiency indicators depend on shell pretreatment with a p-value of 0.001 ($p<0.05$) for initial Pb^{2+} concentration of 1.0 mM. Hence, the t-test was then used to elucidate the difference of sorption efficiency indicators between each type of shell pretreatment for this case. The results of the t-test show that the burnt shells at 600°C have less Pb^{2+} sorption efficiency indicators than those of the other pretreatment conditions ($p<0.05$). Meanwhile, the unburnt shell was found to has the same mean values in population scale of Pb^{2+} sorption efficiency indicators like those of 400°C and 500°C of shell pretreatment ($p>0.025$). The reason for this could be due to the fact that the structure of the snail's shell does not change much after burning the shell at the temperature of 500°C and below 500°C while the structure is changed at the temperature of 600°C.

Hence, the unburnt shell was selected for further study as it did not have any significant differences in sorption efficiency indicators when compared to 400°C and 500°C of shell pretreatment. Furthermore, the sorption efficiency indicators of unburnt shell were significantly higher than those of 600°C of shell pretreatment.

Biosorption kinetics: Figure 2 illustrated the variation in the sorption capacity (q_t) and removal percentage (Removal) as a function of time.

The sorption capacity and removal percentage were increased with increasing contact time at an earlier state because the sorption system had not reached equilibrium.

Table 1: Sorption kinetic model constants

	Pseudo first order model			Pseudo second order model		
C_o (mM)	q_e (µmol/g)	k_1 (min^{-1})	R^2	q_e (µmol/g)	k_2 (g µmol/min)	R^2
0.1	4.54	0.0291	0.7839	5.05	0.0120	0.9908
1.0	29.8	0.0340	0.7470	29.3	0.0181	0.9982

Table 2: Constants of sorption isotherm models for the sorption of Pb^{2+}

Parameters	Values
Freundlich model	
k_f ($\mu mol^{1-1/n}$ $L^{1/n}$/g)	30.5000
1/n (no unit)	0.8150
R^2	0.9801
Langmuir model	
q_{max} (µmol/g)	138.6000
b (L/mmol)	0.3150
R^2	0.5931

At the longer contact time, increasing contact time did not affect the two sorption efficiency indicators as the system reached equilibrium. The sorption of Pb^{2+} occurred rapidly as the system reaching equilibrium within 30 and 20 min for initial Pb^{2+} concentration of 0.1 and 1.0 mM, respectively. This finding also, supports the assumption that the contact time of 120 min could represent the equilibrium state of the sorption.

The experimental data were tested with the sorption kinetic models and the model constants were summarized in Table 1.

Table 1 revealed that the correlation coefficient (R^2) of the Pseudo first order always lower than that of Pseudo second order Model. This could be interpreted as the experimental data could be better described with the Pseudo second order Model than the other model. The plots of kinetic models with the experimental data in Fig. 2 also confirmed the conformity between experimental data (represented as points) and the prediction by the Pseudo second order Model (represented as solid lines).

Both sorption rate constants (k_1 and k_2) were directly affected by the initial concentration of Pb^{2+}. This means the sorption with initial Pb^{2+} concentration of 0.1 mM reached equilibrium slower than the sorption with higher initial Pb^{2+} concentration, i.e., 1.0 mM.

The data from Table 1 demonstrated that the equilibrium sorption capacity (q_e) of Pb^{2+} increased with an increase in the initial Pb^{2+} concentration from 0.1-1.0 mM. This is because the initial concentration of 1.0 mM has a higher amount of Pb^{2+} in the system than the lower initial Pb^{2+} concentration. So, the higher amount of Pb^{2+} could attach more on the available binding site of the biosorbent.

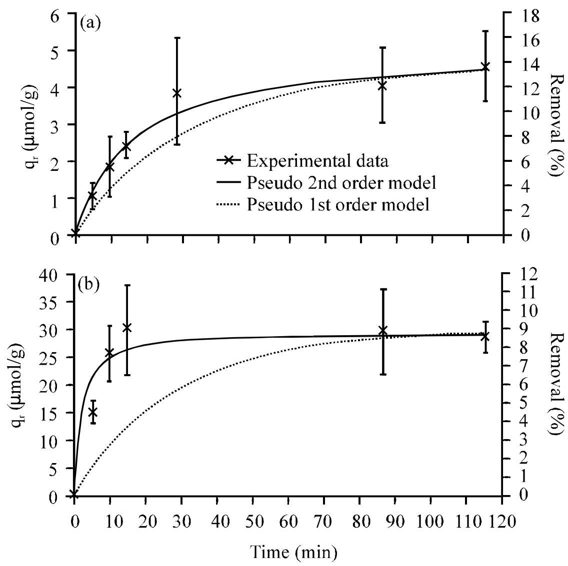

Fig. 2: Relationship between contact time and sorption efficiency for initial Pb^{2+} concentration (mM): a) 0.1 and b) 1.0 (mM)

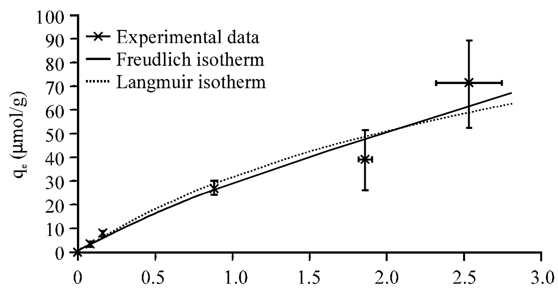

Fig. 3: Isotherm plot and curves for Pb^{2+} sorption by *Filopaludina sumatrensis*'s shell

Sorption equilibrium and isotherm: The experimental data at the sorption equilibrium state were plotted as isotherm and the results were shown as points in Fig. 3. The data were consequently, investigated with Langmuir and Freundlich isotherm models and the constants of the models were summarized as Table 2. The predictions from both models were calculated using the constants of each model. The results were subsequently compared to the experimental data by plotting the predicted results from both models as lines in Fig. 3.

The experimental data of biosorption at equilibrium fitted better to Freundlich than Langmuir isotherms as R^2 of the Freundlich isotherm is greater than that of Langmuir isotherm. This is because the initial Pb^{2+} concentration range employed in this research is not high enough to achieve saturation of the sorbent. Thus, the equilibrium Pb^{2+} concentration at the solid phase of sorbent (q_e) would still increase with an increase of equilibrium Pb^{2+} concentration in aqueous solution which. In the contrary, the solid phase equilibrium Pb^{2+}concentration of the saturated sorbent would not change significantly with an increase of equilibrium metal concentration in aqueous solution which would be better described by the Langmuir isotherm model.

CONCLUSION

The biosorption of Pb^{2+} by ground *Filopaludina sumatrensis*'*s* shell was studied here. The effects of various burnt temperature for the shell's pretreatment was examined and compared to unburnt shell. The finding from this research is the usage of an unburnt shell seemed to be the best choice among other conditions. The sorption system rapidly reached the equilibrium within 30 min and could be well described using the pseudo second order kinetic model. The sorption isotherms followed the Freundlich model as the sorbent had not reached its saturation within the initial Pb^{2+} concentration range in this study. This resaerch illustrated an alternative solution for the management of the unwanted biological materials where *Filopaludina sumatrensis sumatrensis* (Anonymous, 2019) one of the garbage from the restaurant and seafood industry could be utilized as a biosorbent for the removal of Pb^{2+} from the heavy metal contaminated wastewater.

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