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Biosorption and Desorption of Lead (Pb+2) from Simulated Waste Water Using Freshwater Snail Shells, *Melanoides tuberculata* Muller (Family Thiaridae)

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Abstract. In view of the increasing rate of environmental pollution resulting from lead containing industrial effluents, this study aimed to investigate the biosorption and desorption capacity of pretreated freshwater snail, *Melanoides tuberculata* Muller (Family Thiaridae), shells as a biosorbent for the removal of lead (Pb^{+2}) from simulated wastewater and its ability to be regenerated after the process. The biosorption was carried out as a function of contact time and initial Pb^{+2}concentration at pH 5.5. Desorption of Pb^{+2} from the biosorbent was done using 0.1M HCl at various contact time. The cycle of the biosorption and desorption was performed until the biosorbent was exhausted, at a temperature range of 27°-30°C. The Pb+2concentration before and after each process were measured through Flame Atomic Absorption Spectrophotometer (FAAS). The results of the study showed that estimated optimum contact time for the biosorption and desorption of Pb^{+2} was seen at 80 and 60 min, respectively, based on the mean percent efficiency. Linearity for the two adsorption isotherm models was low thus the results cannot be described by either of the Langmuir and Freundlich isotherms. The biosorption using snail shells followed a pseudo second-order rate of reaction having a R2 value of ≥0.99, though for desorption the data was not conclusive of which order of reaction it follows. Based on the data and results obtained, pretreated freshwater snail shells are potential biosorbents for Pb+2 contaminated waste water and can be regenerated after 2 cycles of adsorption.

Keywords: Lead, Biosorption, Desorption, Regeneration, Freshwater snails, Flame atomic absorption spectroscopy, Adsorption isotherms, Pseudo first-order kinetics, Pseudo second-order kinetics

1. Introduction

Heavy metal pollution is a global burden that affects all forms of living and non-living organisms. One of the most toxic metals is lead, which is a cumulative toxicant that affects multiple body systems including the neurologic, hematologic, gastrointestinal, cardiovascular, and renal systems.[14]

Several methods such as reverse osmosis, ion exchange resin, solvent extraction, electrolytic and precipitation processes, electrodialysis, and membrane technology have been used to remove heavy metals from industrial effluents. However, one of the best methods was the use of adsorbents since it outperforms other techniques due to its low cost, high efficiency, simplicity, and insensitivity to toxic substances.[11] Several studies were made about the ability of different organic wastes such as grains, banana peel, coconut husk, peanut shells, tea wastes, oysters and periwinkles, pomelo peels, saw dust, and snail shells to adsorb lead. [5] [7] [8] [11] [12] [13] However, the use of snail shells were limited to biosorption studies using different modified samples such as *Archachatina marginata* Swainson (Fam. Achatinidae) or African giant land snail.

Freshwater snail, *Melanoides tuberculata* Muller (Fam. Thiaridae) belongs to the phylum Mollusca and to the class Gastropoda.[7] They are abundant in nature and used as food, but the shell is not consumed hence it litters and eventually pollutes the environment. However, it can be converted to wealth as a water treatment technique among many other applications or uses. [7]

Generally, the study aimed to evaluate the biosorption and desorption capacity of freshwater snail shells.Specifically, to determine the biosorption and desorption capacity of the pretreated freshwater snail shells, optimum contact time for maximum biosorption and desorption, amount of Pb uptake upon reuse of the biosorbents, and to study the biosorption mechanism of the pretreated biomass using different adsorption isotherm and kinetic models.This study mainly investigated the ability of pre-treated snail shells to reduce lead ions level from waste water by biosorption and the capability of the biosorbent to be regenerated after desorption at predetermined pH and amount of biosorbent, varying contact times between biosorbent and simulated waste water of different concentrations.

Based on a study conducted by the Environmental Management Bureau in 2006, exceedingly high levels of lead, cadmium, chromium, copper, zinc, mercury and cyanide are polluting the different rivers in the Philippines.[4] Given this alarming situation of water bodies, this research will promote the use of wastes like snail shells as possible cost-effective means of treating industrial effluents. The use of biosorbent can also address high cost problems of the conventional water treatments and in some cases, their inadequacy to remove heavy metals.[9] The heavy metals can also be recovered from the biosorbent in which according to the U.S. EPA, the regenerated ones can still be used by a number of different industries such as jewelry, plating, electronics, automotive, and art foundries.

2. Materials and Methods

2.1. Materials

Freshwater snail shells, *Melanoides tuberculata* Muller (Family Thiaridae) were purchased from Balintawak market, Quezon City, Philippines. The shells were thoroughly washed with distilled water, air-dried, crushed and soaked in 0.1M HCl for 4 hours to remove all the calcium carbonate present.[2] The treated biomass was washed with distilled water, dried at 70˚C for 2 hours, further crushed and sieved to the desired size (0.25mm). The stock solution (1g/L) of lead (Pb^{+2}) was prepared in distilled water using lead acetate and all working solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods

Five grams of the pretreated biosorbent, and 100mL of each lead spiked solution (1.2 (A), 1.4 (B), 1.6 (C), 1.8 (D), and 2.0 (E) mg/L) and 0.1M HCl were acid-digested using concentrated HNO_3, filtered and then transferred to different PET bottles for the subsequent analysis using FAAS, in which the results served as the baseline lead value for each.

The biosorption studies were carried out as a function of contact time (20-120 min at 20 min interval) and initial Pb^{2+} concentration at pH 5.5 using 0.5g of pretreated biosorbent. The pH of the solutions was adjusted with 0.1M of NaOH and HNO_3.[11] [16] All mixtures were agitated using Burell Wrist Action Shaker to ensure equilibrium. The biomass underwent vacuum filtration using Whatman filter paper (40 µm), dried at 70˚C for 2 hours, cooled to room temperature for 10 minutes, and weighed. The dried biomass was used in desorption studies while the filtrates were prepared for FAAS analysis.

The batch desorption studies were done using 100mL of 0.1M HCl following the same conditions as the biosorption studies except for the pH. The pretreated biosorbents made in contact with the spiked solution containing 1.6 ppm were subjected to another biosorption and desorption cycle until exhausted. Kinetic studies were employed to the first biosorption and desorption cycle to determine the optimum contact time.

3. Results and Discussion

The biosorption capacity, biosorption and desorption efficiency, adsorption isotherms and kinetics were used to describe the adsorption process. The biosorption capacity of the biosorbent was computed using Eq. 1, where qe is the biosorption capacity (mg/g), *V* is the volume of the solution (mL), and *m* is the mass of the biosorbent (g). The biosorption efficiency was calculated based on Eq. 2 where C_o and C_e are the initial and equilibrium lead concentration (mg/L) and *%E* is the biosorption efficiency.[2] The desorption efficiency was determined using Eq. 3 where *%D* is the desorption efficiency and C_d is the eluted lead concentration (mg/L).[15]

$$q^e = \frac{v(c_o - c_e)}{m} \text{ (Eq. 1)} \qquad \%E = \frac{c_o - c_e}{c_o} \times 100 \text{ (Eq. 2)} \qquad \%D = \frac{cdxv}{10xq^e xm} \text{ (Eq. 3)}$$

Figure 1 showed the biosorption and desorption efficiency of the biosorbent. The highest biosorption was seen in solution E at 80 min with 95.32%, and the lowest in solution A at 20 min with 75%. However, the estimated optimum contact time was seen at 80 min based on the average *%E* per time. This graph also showed that at 20 min, an average of 80% of Pb^{+2} in the solution was already adsorbed and further increase in time after 80 min did not increase the Pb^{+2}adsorbed on the surface of the biosorbent. In general, solutions C, D and E, exhibited the highest *%D* at 120 min with values seen in Figure 1, but for solutions A and B, this was observed at 20 and 100 min, respectively. However, the mean values estimated that 60 min is the optimum contact time to achieve maximum desorption.

The biosorption and desorption was repeated to investigate the ability of the biosorbent regarding Pb^{+2} adsorption and regeneration after 1 cycle. Figure 2 showed the efficiency of the 2 adsorption cycles done using concentration C (1.6ppm). Based on the plot, the biosorption I values were higher than biosorption II values indicating that adsorbed Pb^{+2} decreased at the second process due to the decreased amount of biomass in the solution and number of available sites for adsorption. The desorption efficiency, on the other hand, was higher on the second process, which may show that some Pb^{2+} were retained on the shell surface and desorbed during the second desorption. The results differ from the study of Zhe Lynn in 2011, which conducted three cycles of adsorption and desorption studies of lead on palm shell activated carbon surface using HCl and HNO_3, showed that the first desorption efficiency was highest among the three cycles and that the desorption efficiency decreases as the number of cycles increases.

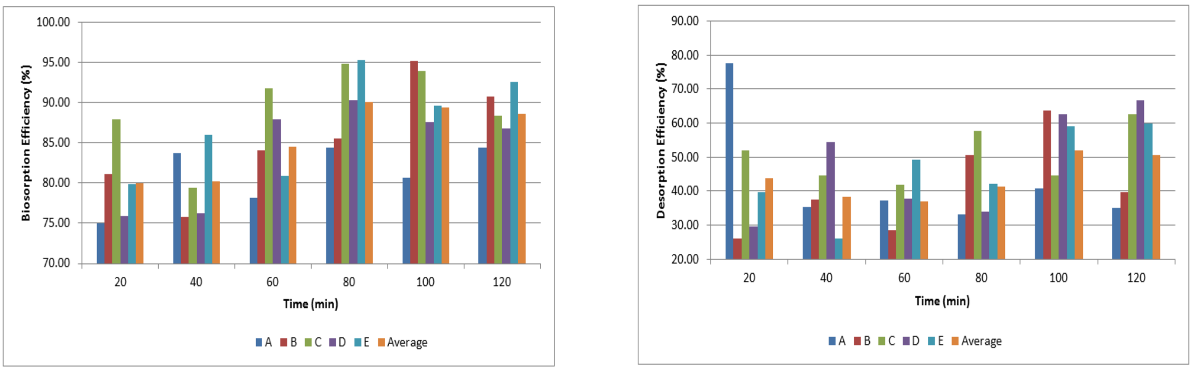

Fig. 1: Biosorption and Desorption Efficiency(%) of pretreated biosorbent for lead(Pb^{+2}) against time(min).

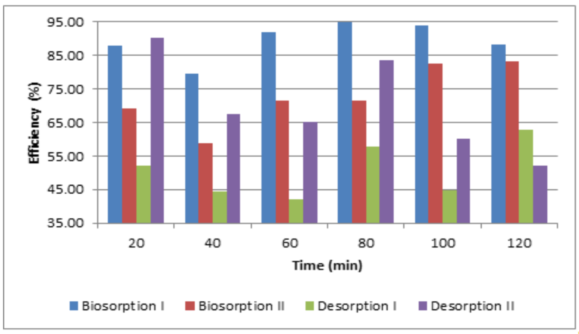

Fig. 2: Comparison of the Biosorption and Desorption Efficiency (%) of lead (Pb+2) from pretreated biosorbent against time (min) using the data from Concentration C for the two cycles of Adsorption.

3.1. Adsorption Isotherms

An adsorption isotherm describes the relationship between the amount of metal adsorbed and the metal ion concentration remaining in the solution at fixed temperature at equilibrium. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases and is described by Eq. 4, where *Ce* is the equilibrium concentration (mg/L) and *qe* is the amount adsorbed at equilibrium (mg/g).

The Langmuir constants are *qm* (mg/g) that represents the maximum biosorption capacity, and *b* (L/mg) which is the ratio of the biosorption and desorption rate. The Freundlich isotherm estimates the adsorption intensity of the adsorbent towards the adsorbate and is represented by Eq. 5, where *Kf* indicates the Freundlich adsorption constant and *n* represents an empirical parameter related to the intensity of adsorption.[6]

$$\frac{1}{q_e} = (\frac{1}{q_m b})(\frac{1}{c_e}) + (\frac{1}{q_m}) \qquad \text{(Eq. 4)}$$

$$\log\, q_e = \log \mathrm{K}_f + (\frac{1}{n}) \log C \qquad \text{(Eq. 5)}$$

$$RMSE = \sqrt{\frac{\sum_1^p (q - q_m)^2}{2}} \qquad \text{(Eq. 6)}$$

The root mean squared error (RMSE) was calculated to determine the model fit. The squared difference between the experimental metal uptake (*q*) and the corresponding model predictions for the uptake of (q_m) was summed up and divided by the number of data points (*p*) for each data set to calculate the mean square error (MSE). The RMSE may be considered as the average deviation between the predicted and actual uptake of the metal ion and was obtained by taking the square root of MSE.[1] A study of Igwe and Abia in 2007, used Langmuir and Freundlich isotherms to demonstrate that maize cob which is an environmental pollutant could be used to adsorb heavy metals (Cd, Pb and Zn) and achieve cleanliness.

Theoretically, the plot of q_e versus C_e shows a characteristic plateau, however, for this study, it was not obtained (not shown) because equilibrium was not met. As seen in Table 1, the regression coefficient of the Langmuir isotherm model was very low signifying that the data did not fit well to the model. The coefficient *b* in Langmuir equation is a measure of the stability of the complex formed between metal ions and biomass under specified experimental conditions.[2] The values for *b* in this study were low except for 120 min,however there was no reference value to compare the data.

Freundlich isotherm is commonly used to describe adsorption characteristics for heterogeneous surface. According to Igwe and Abia in 2007 *n* values between 1 and 10 represents beneficial adsorption, and the higher the K_f value, the greater the adsorption intensity. The *n* values were within the said range only for 20 and 40 min, other time points have negative or values greater than 10, which may signify unfavorable adsorption for the other time points and K_f values were consistently low.

The comparison of the experimental data and the theoretical data for the adsorption capacity of Pb by the pretreated biomass revealed that the experimental data points gave a good fit with the theoretical data points considering the calculated RMSE of less than 0.1 for the majority of the data points.

Table 1: Adsorption isotherm constants for the biosorption (I) of lead (Pb) by the pretreated biosorbent

Biosorption								
Time (min)	**Langmuir Isotherm**				**Freundlich Isotherm**			
	q_m	**B**	**R^2**	**RMSE**	**K_f**	**N**	**R^2**	**RMSE**
20	0.4100	13.7041	0.0321	0.0773	0.4355	4.2751	0.0914	0.0733
40	0.5974	3.4433	0.3780	0.0780	0.4894	2.7205	0.2286	0.0783
60	0.3476	-58.1970	0.0871	0.0871	0.4027	18.7696	0.0060	0.0840
80	0.2786	-18.4022	0.3317	0.0854	0.2028	-2.3200	0.3740	0.0801
100	0.3665	-90.1438	0.0146	0.2195	0.3855	-36.2172	0.0030	0.0921
120	0.3927	261.6114	0.0001	0.1876	0.4122	39.4088	0.0004	0.0933

3.2. Adsorption Kinetics

In many cases, the adsorption kinetics based on the overall adsorption rate is described by one site kinetic models, which were used in this study. To investigate the mechanism of biosorption and desorption and the potential rate controlling steps, the pseudo first and second-order kinetic models were used.

According to the study of Zawani et al. in 2009, the pseudo first-order rate and pseudo second-order rate expression can be expressed using Eq. 7 and 8, respectively. Linear plot of $log\ (q_e - q_t)$ versus t indicates the applicability of the pseudo first-order model, while linear relationship of t/q_t and t indicates the applicability of the other model.

$$\log\,(q_e - q_t) = \log q_e - (\frac{k_1}{2{,}303})t \qquad \text{(Eq. 7)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q^e})t \qquad \text{(Eq.8)}$$

The q_e, which is necessary for the pseudo first-order rate kinetics computation, was not obtained due to the absence of saturation point (plateau) thus pseudo second-order rate kinetics was calculated instead. This represented the data on biosorption appropriately since the regression coefficients obtained in each time points ranged from 0.99 and above indicating linearity. The applicability of this model suggested that biosorption of Pb by the pretreated biosorbent was based on adsorption interaction between the metals and active sites on the freshwater snail shells. In a study conducted by Kelesoglu in 2007, a better correlation was also obtained using the pseudo second order model for the biosorption of Pb^{2+} in chitin and chitosan biopolymers. However for the desorption process, the pseudo second-order kinetics can only be applied to solution A having a correlation of 0.9705.

Table 2: Pseudo Second-Order Rate constants and regression coefficients for the biosorption and desorption of lead (Pb) by the pretreated biosorbent.

Sample	**Biosorption**		**Desorption**	
	k_2	R^2	k_2	R^2
A	1.5831	0.9958	-0.4563	0.9705
B	0.2997	0.9899	0.0251	0.5723
C	1.0840	0.9895	0.0465	0.8458
D	0.5644	0.9943	0.0094	0.5452
E	0.3007	0.9909	0.0062	0.6500

4. Conclusion and Recommendations

Based on the results, the pretreated powdered snail shells are potential biosorbents for lead contaminated waste water and can be regenerated up to 2 cycles of adsorption. The estimated optimum contact time for the biosorption of lead using the pretreated biosorbent was 80 min, after which, decreased biosorption capacity in general was observed. The estimated optimum contact time to obtain maximum desorption capacity was at 60 min. The experimental data did not fit the Langmuir and Freundlich isotherms. Nevertheless, RMSE values for both models demonstrated a good fit. Pseudo first-order kinetics for both biosorption and desorption was not computed but based on the data from the pseudo second-order model, the rate of biosorption is proportional to the square of the number remaining free surface sites of snail shells. The desorption results were not conclusive of which order of reaction it follows.

Further studies to assess the applicability of freshwater snail shells in actual waste water remediation are highly recommended since the results obtained for both biosorption and desorption processes were not accurately conclusive. Inductive Coupled Plasma- Mass Spectrophotometer (ICP-MS) that can detect up to parts per billion may be used on biosorption and desorption analyses. Also, drying to constant weight must be considered since the weight variation may affect the result. Other desorbing reagents like EDTA, NaOH and HNO_3 could be evaluated, to determine which medium could regenerate higher Pb amount from thebiosorbent. Lastly, Fourier Transform Infrared Spectroscopy may be performed on the biosorbent to further assess its characteristics with regards to biosorption and regeneration of heavy metals.

5. References

[1] K. Andres, J. Bawalan, and N. Galang. Use of *Citrus grandis* (L.) Osbeck (Fam. Rutaceae) Peels Waste as a Biosorbent for Lead-Contaminated Water. *International Journal of Chemical and Environmental Engineering*. 2012, 3(2).

[2] N.A. Babarinde, J.O. Babalola, and K.A. Adegboye. Kinetic, Isotherm and Thermodynamic Studies of the Biosorption of Cadmium (II) by Snail *(Lymnaearufescens*) Shell. *Journal of Applied Sciences Research*. 2008, 4(11): 1420-1427.

[3] J.O. Duruibe, M.O.C. Ogwuegbu, and J.N. Egwurugwu. Heavy metal pollution and human biotoxic effects.*International Journal of Physical*. 2007, 2(5): 112-118.

[4] Greenpeace. *The State of Water Sources in the Philippines*. Quezon City, Philippines: Greenpeace Southeast Asia. 2007, pp. 16-17.

[5] E.U. Ikhuoria and C. Uyammadu. Adsorption of Heavy Metals on Modified Snail (*Archachatinamarginata*) Shell.*Ghana Journal of Science*. 2001, 41: 29-33.

[6] J.C. Igwe and A.A. Abia. Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *Ecletica Quimica*. 2007, 32(1): 33-42.

[7] E.O. Jatto, I.O. Asia, E.E. Egbon, J.O. Otutu, M.E. Chukwuedo, and C.J. Ewansiha. Treatment of Waste Water from Food Industry Using Snail Shell. *Academic Arena*. 2010, 2(1): 32-36.

[8] A. Jideowno, J.M. Okuo, and P.O. Okolo. Sorption of Some Heavy Metal Ions by Chitosan and Chemically Modified Chitosan. *Trends in Applied Sciences Research*. 2007, 2(3): 211-217.

[9] T.A. Johnson, N. Jain, H.C. Joshi, and S. Prasa. Agricultural and agro-processing wastes as low cost adsorbents for metal removal from wastewater: A review. *Journal of Scientific & Industrial Research*. 2007, 67: 647-658.

[10] S. Kelesoglu. Comparative Adsorption Studies of Heavy Metal Ions on Chitin and Chitosan Biopolymers. [Graduate Thesis] *Graduate School of Engineering and Science of Izmir Institute of Technology.* 2007, pp.83.

[11] Q. Li, L. Chai, J. Zhao, Z. Yang, and Q. Wang. Lead desorption from modified spent grain. *Transactions of Nonferrous Metal Society of China*. 2009, 19:1371-1376.

[12] S.A. Odoemelam and N.O. Eddy. Studies on the Use of Oyster, Snail and Periwinkle Shells as Adsorbents for the Removal of Pb2+ from Aqueous Solution. *E-Journal of Chemistry.* 2009, 6(1): 213-222.

[13] B.O. Opeolu, O. Bamgbose, T.A. Arowolo, and M.T. Adetunji. Utilization of biomaterials as adsorbents for heavy metals' removal from aqueous matrices. *Scientific Research and Essays*. 2010, 5(14): 1780-1787.

[14] P.P. Sood and R. Prakash, ed. *Heavy Metal Pollution, Toxication and Chelation*. New Delhi: M. D. Publications, 1998.

[15] E. Wambu, G. Muthakia, P. Shiundu, and K. Thiongo. Kinetics of Copper Desorption from Regenerated Spent Bleaching Earth. *American-Eurasian Journal of Scientific Research*. 2009, 4(4): 317-323.

[16] D. Wankasi, M. Horsfall, Jnr., and A.I. Spiff. Desorption of Pb^{2+} and Cu^{2+} from Nipa Palm (*Nipafruticans*Wurmb) biomass. *African Journal of Biotechnology*. 2005, 4(9): 923-927.

[17] A.L. Zhe Lynn. Determination of Kinetics and Optimal Conditions for the Desorption of Lead ions of the Palm Shell Activated Carbon Surface. *Faculty of Engineering and Science, Universiti Tunku Abdul Rahman.* 2011, pp. 29-34.