International Journal of Modern Agriculture
ISSN: 2305-7246
Volume 9 Issue 3, 2020

Experimental Investigation on Biosorption of Copper from Dilute Solutions by using Protonated Marine Algae - Kinetic and Isotherm Studies

R. Ramsenthil, B.Sivaprakash
Department of Chemical Engineering Annamalai University
Annamalainagar - 608002
Email: shiv_bhaskar@yahoo.com

Abstract

Water pollution is a key outcome of industrial growth that is needed for urbanization. Heavy metals forms a class of pollutants and they are relatively present in lesser quantities than the other pollutants. The trace amounts are themselves found to be very hazardous. Hence the researches on heavy metal removal has attracted wide interest among the people working in environmental discipline. The present report is on the modelling of biosorption of copper metal from synthetic effluent using the dead marine algae *Sargassum tennerrimmum*. Sorption kinetic studies using the three kinetic models, Lagargren First order kinetics, Pseudo Second order kinetics and Fractional order showed that the third model gave the best fit. The isotherm parameters of Langmuir model, Freundlich model and Redlich Peterson models were computed and reported. The algae was able to adsorb metal ions with an efficiency of 92% recovery.

Introduction:

Environmental pollution is a consequence of industrial revolution. The risks of this issue on the habitats of all the living things in land, air and water is a major concern which will have adverse effects on the ecosystem. (Aulakh et al., 2009; Nassef and Taweel, 2015). Water is the basic need and hence a precious resource gifted by nature. Owing to the pollution, problems pertaining to quantity and quality of water is of more threat (Schwarzenbach et al., 2010). Rapid industrialization and urbanization have increased the scarcity of usable water and burden all the water resources like rivers, lakes, ponds, etc. (Sivaprakash et al., 2010). The left over chemicals and undesirable by products from small and large scale industries are discharged into the water resources without following the stipulations of the pollution control agencies. This makes the aquatic environment highly toxic and dearth of essential oxygen for the organisms living in it (Shandra et al., 2008).

Toxic heavy metals are a class of water contaminants which can enter the human organs and cause severe health problems (Feitoza et al., 2014). Also they are heavy threats to plants, animals and organisms that are not tolerant to undesirable levels of these metals (Ayawei et al., 2015; Nassef and Taweel, 2015). Lead, Chromium, Arsenic, Copper, Iron, Cobalt, etc. from mining operations, refineries, ore processing units and production of fertilizers, batteries, pulp and paper, etc. are few instances of heavy metal discharges into the environment (Sivaprakash et al., 2010). Improper treatment of effluents before discharge to the ecosystem will have chronic adverse impact which cannot be reversed. Hence reducing the level of these metals to the permissible limit is mandatory (Pavan et al., 2006). A major problem with heavy metals is that they are non-biodegradable unlike other pollutants and hence they sustain in living organisms (Ayawei et al., 2015; Sadeek et al., 2015).

Third important transition metal in human bodies is copper (Cu(II)) ions and lead a pivotal role in many of the essential physiological process of living organisms. Cytochrome oxidase, super- oxide dismutase and tyrosinase are few mettaloenzymes that are based on copper metal (Awual and Hasan, 2015). Blood streams and few pigments are rich in copper in human body (Hasanur et al., 2009). However, beyond certain level of concentration, it is very dangerous (Ayawei et al., 2015).

Copper is often encountered in the manufacture of circuit boards, metal and alloy production, electroplating, polishing, larger scale production of paints, wood preservatives, etc. (Nassef and Taweel, 2015). The permissible level of Cu(II) in potable water is 1.5 mgl^{-1} (Aman et al., 2008). The acceptance concentration of Cu ions for release onto land and surface waters is 3.0 mg/L (Huang and Su, 2010). Excessive consumption of copper by human causes physiological problems like head ache, loss of hair, hypoglycemia, elevated level of heart rate, nausea, kidney and liver damage. Pychological problems like anxiety, brain disorder and schizophrenia are also the ill health effects of excess copper levels (Aman et al., 2008). Therefore, it is essential to find a technology that helps to treat the effluents containing copper ions (Awual and Hasan, 2015).

Conventional methods of treatment of wastewater like ion exchange, precipitation using chemicals, reverse osmosis and electrodialysis suffer from limitations like high cost, poor efficiency, inadequate removal, intensive operation and higher level of energy requirements (Saha et al., 2010). Hence comes the need of cost-effective technologies to recover or remove heavy metals from the concept of mass transfer. This motivated the researchers to work on exploring the adsorption based method to bind the metal ions using various low cost and harmless materials (Saha et al.2010). Low cost, simplicity of design, easy operation, low residue generation, easy metal recovery and reusability of the adsorbent are the advantages of adsorption process (Feitoza et al., 2014). The choice of adsorbents are usually based on its cost and availability (Pavan et al., 2006). Numerous sorbents based on natural and synthetic origin to remove heavy metals have been reported by many researchers (Huang and Su, 2010; Saha et al., 2010). These sorbents were selected on the basis of the easiness of processing, recycling, regeneration that can be an alternative to the conventional materials used as sorbents (Pavan et al., 2006). Essential characteristics of sorbents are affinity to the metal ions and enhanced capacity of loading of the sorbates onto the sorbent surfaces (Ayawei et al., 2015). Binding of metals to the sorbents are facilitated by the functional groups that posses anions to capture the metallic cations (Pavan et al., 2006).

Biosorption uses biological substances as sorbents to remove pollutants (Pehlivan et al., 2012) and a variety of enormous materials from biological origin were investigated to treat effluents containing heavy metals (Chen et al., 2010). By-products or waste materials from industry or agricultural field are broadly recognised as biosorbents (Lu and Gibb, 2008). The process of biosorption takes place fundamentally on the cell surface and may involve vander waals forces or chemisorption phenomenon in recovering metal ions (Jacinto et al., 2009). Biosorption has the advantages of easier and abundant availability, cheaper and simpler operation, zero or minimum level of sludge production volume and regeneration of sorbents and recovery of metals from the biosorbents (Pehlivan et al., 2012).

Materials and methods:

Copper nitrate of analytical grade was purchased from Ganesh Scientifics, India and used for preparing the synthetic solutions using double distilled water in the concentration range of 25 - 100 mg/L. The dead algae samples collected from Portnovo, Tamilnadu, India were initially subjected to water wash and drying at room temperature (> 30°C). After powdered they were sieved and the size range of 100- 150 microns were used for the study after treating with 0.1 N hydrochloric acid for protonation. The acid treated biomass were again water washed, dried and used for the experimentations. 2 g of sorbent was added for one litre of the synthetic solutions. All the batch experiments were conducted in 250 ml conical flasks. To carry out the kinetic experiments, initial metal ion concentrations in the range 25, 50, 75 and 100 mg/L were added with sorbents and agitated at a speed of 200 rpm. The samples were analyzed in regular time intervals. The concentrations of metal solutions before and after adsorption were measured using Atomic Adsorption Spectrophotometer (AAS SL176 - Elico Limited India). The amount of metal uptake is calculated by the Eqn. 1.

$$q_e = \frac{V(C_0 - C_e)}{M} \qquad (1)$$

q_e equilibrium metal uptake (mg g^{-1}) ; V- sample volume (L) ; M - mass of the adsorbent (g) C_e and C_o - equilibrium and initial metal ion concentrations (mg L^{-1}) respectively.

Kinetic Studies:

In the present investigation Lagergran First order kinetics, Pseudo second order kinetics and Fractional order kinetics have been taken for modelling of the Cu uptake. The equations are given below.

Lagergran First order kinetics (LFOK):

$$q_t = q_1\left(1 - e^{-k_1 t}\right) \qquad (2)$$

Pseudo -Second order kinetics (PSOK):

$$q_t = \frac{t k_2 q_e^2}{(1 + t k_2 q_e)} \qquad (3)$$

Fractional order kinetics (FOK):

$$q_t = k_{int}\, t^n \qquad (4)$$

q_t (mg g^{-1}) - metal uptake at time, t, k_1(min^{-1}) and k_2 (g (mg min) $^{-1}$) are the equilibrium rate constants for Lagergran First order and Pseudo second order kinetics respectively, k_{int} (mg g min^{-n}) and n are the Fractional order kinetics parameters.

Isotherm Studies:

Adsorption isotherms aids in predicting the characteristics or nature of the metal uptake by adsorption technique. The adsorption experimental data were modelled using the simple adsorption models given below:

Langmuir isotherm: $q = q_{max} bC_f / (1+bC_f)$ (5)

Freundlich isotherm: $q = K(C_f^{(1/n)})$ (6)

Redlich - Petersoon isotherm: $q = k_{RP} C_f / ((1+(a_{RP} C_f^{\beta}))$ (7)

where C_f is the final concentration (mg/L), q_{max} is the maximum copper uptake (mg/g), b the Langmuir equilibrium constant (L/mg), K $(l/mg)^{1/n}$ and n are the Freundlich constants, K_{RP} (l/g) , a_{RP} $(l/mg)^{\beta}$ and β are Redlich Peterson constants.

Results and Discussions:

The theoretical metal uptakes for the various initial metal ion concentrations were computed for the three models mentioned above. The fitness of these models for the experimental data was checked using the MATLAB software using the cftool kit. This also yielded the parameters of the models along with the regression coefficients. The modelling results reveal that the PSOK model was able to fit the experimental uptakes with greater accuracy than the other two models. This is shown in Fig.1. The parameters estimated for all the models are presented in Table 1.

Table 1. Kinetic model parameters of Cu uptake using protonated *Sargassum tennerrimmum* for initial concentrations of 25 - 100 mg/l

Kinetic model	Parameters	Initial metal concentration(mg/L)			
		25	50	75	100
Lagergran first order	k_1				
kinetics	q_1	0.005105	0.005685	0.0058	0.0073
	R^2	10.99	32.12	24.83	53.28
		0.9721	0.9528	0.9421	0.9980
Pseudo second order	k_2	0.00009	0.0002	0.00009	0.0001
kinetics	q_2	17.45	55.67	38.78	39.17
	R^2	0.9781	0.9853	0.9628	0.9573
Fractional order	k_{int}	0.1684	0.1610	0.4711	0.7549
kinetics	n	0.7036	0.8216	0.6744	0.6185
	R^2	0.9945	0.9975	0.9906	0.9914

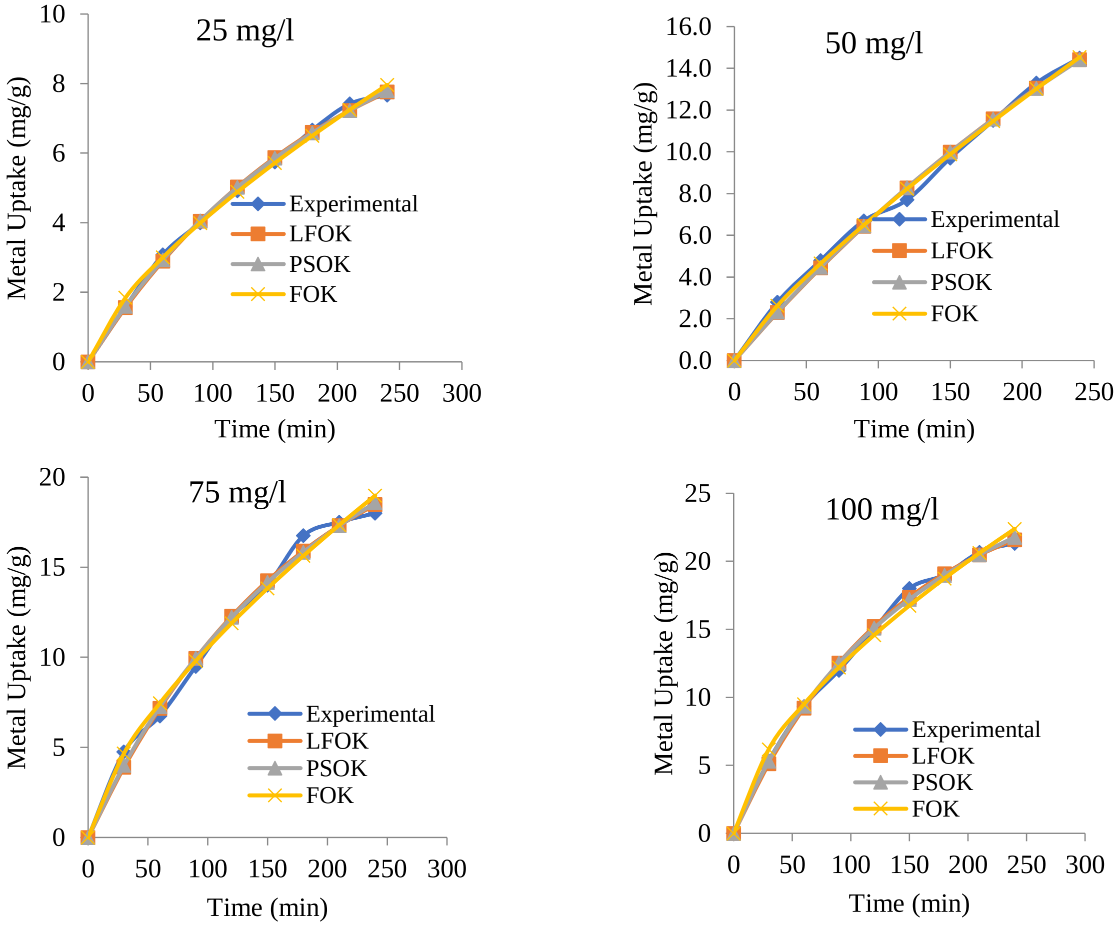

Fig. 1 Comparison between experimental and model predicted kinetics for Co (II) biosorption using *Sargassum tennerrimmum*

The isotherm modelling was also performed using the same procedure adopted for kinetic modelling. The experimental and model predicted equilibrium uptake values of the Cu ions against the equilibrium concentration were computed for the three isotherm models. The values of the adsorption isotherm parameters for the models along with the respective regression coefficients are shown in Table 2. The results of the sorption isotherm study show that the adsorption of copper by the treated algae follows the Langmuir isotherm model with highest accuracy than the Freundlich and RP models. Hence it can be concluded that the sorption pertains to monolayer level and also the sorbent surface is homogeneous. However the values of Freundlich constant (Table 2) confirms the easier separation of copper ions from dilute solutions by adsorption. The Redlich Peterson isotherm constant β approaches unity (0.9083) is an indication that the RP tends towards the Langmuir isotherm for the Co (II) recovery using the marine algae *Sargassum tennerrimmum*.

Table 2. Adsorption Isotherm model parameters for Cu ions recovery using protonated *Sargassum tennerrimmum*

Isotherm model	Constants	R^2
Langmuir	$q_{max} = 22.730$; $b = 0.2547$	0.9921
Freundlich	$K = 7.274$; $n = 3.302$	0.9547
Redlich - Peterson	$K_{RP} = 7.441$;$a_{RP} = 0.4574$ $\beta = 0.9083$	0.9838

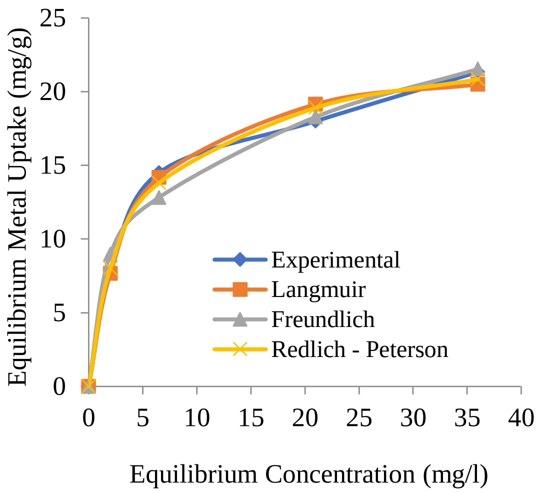

Fig. 2 Comparison between experimental and Isotherm models for equilibrium uptake of Cu using *Sargassum tennerrimmum*

Conclusion:

Biosorption of copper metal ions using the marine algae *Sargassum tennerrimmum* is found to be a potential method to remove the heavy metal from synthetic waste. The kinetic studies show that the sorption follows the FOK model with the regression coefficients approaching unity. Also it was seen that the Redlich Peterson model fits the adsoprtion isotherm better than the Langmuir model and Freundlich models. The maximum metal uptake obtained was 21.33 mg/g. It can be concluded that the dead mass of the marine algae chosen can be used as an effective sorbent to recover copper ions in a very economical and simpler way.

References

1. Aman, T., Kazi, A. A., Sabri, M. U., & Bano, Q. (2008). Potato peels as solid waste for the removal of heavy metal copper (II) from waste water/industrial effluent. *Colloids and Surfaces B:*

Biointerfaces, *63*(1), 116-121.
2. Aulakh, M. S., Khurana, M. P. S., & Singh, D. (2009). Water pollution related to agricultural, industrial, and urban activities, and its effects on the food chain: Case studies from Punjab. *Journal of New Seeds*, *10*(2), 112-137.
3. Awual, M. R., & Hasan, M. M. (2015). Colorimetric detection and removal of copper (II) ions from wastewater samples using tailor-made composite adsorbent. *Sensors and Actuators B: Chemical*, *206*, 692-700.
4. Ayawei, N., Ekubo, A. T., Wankasi, D., & Dikio, E. D. (2015). Synthesis and Application of Layered Double Hydroxide for the removal of Copper in Wastewater. *International Journal of Chemistry*, *7*(1), 122-132.
5. Chen, H., Dai, G., Zhao, J., Zhong, A., Wu, J., & Yan, H. (2010). Removal of copper (II) ions by a biosorbent—Cinnamomum camphora leaves powder. *Journal of Hazardous Materials*, *177*(1-3), 228-236.
6. Feitoza, N. C., Goncalves, T. D., Mesquita, J. J., Menegucci, J. S., Santos, M. K. M., Chaker, J. A., & Sousa, M. H. (2014). Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater. *Journal of hazardous materials*, *264*, 153-160.
7. Hasanur, J., Debarati, C., & Papita, S. (2009). A study of the thermodynamics and kinetics of copper adsorption using chemically modified rice husk. *Clean-Soil, Air, Water*, *37*(9), 704-711.
8. Huang, C. C., & Su, Y. J. (2010). Removal of copper ions from wastewater by adsorption/electrosorption on modified activated carbon cloths. *Journal of Hazardous Materials*, *175*(1-3), 477-483.
9. Jacinto, M. L. J., David, C. P. C., Perez, T. R., & De Jesus, B. R. (2009). Comparative efficiency of algal biofilters in the removal of chromium and copper from wastewater. *Ecological Engineering*, *35*(5), 856-860. Jacinto, M. L. J., David, C. P. C., Perez, T. R., & De Jesus, B. R. (2009). Comparative efficiency of algal biofilters in the removal of chromium and copper from wastewater. *Ecological Engineering*, *35*(5), 856-860.
10. Lu, S., & Gibb, S. W. (2008). Copper removal from wastewater using spent-grain as biosorbent. *Bioresource Technology*, *99*(6), 1509-1517.
11. Nassef, E., & El-Taweel, Y. A. (2015). Removal of copper from wastewater by cementation from simulated leach liquors. *Journal of Chemical Engineering & Process Technology*, *6*(1),1.
12. Pavan, F. A., Lima, I. S., Lima, E. C., Airoldi, C., & Gushikem, Y. (2006). Use of Ponkan mandarin peels as biosorbent for toxic metals uptake from aqueous solutions. *Journal of hazardous materials*, *137*(1), 527-533.
13. Pehlivan, E., Altun, T., & Parlayici, Ş. (2012). Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. *Food chemistry*, *135*(4), 2229-2234.
14. Sadeek, S. A., Negm, N. A., Hefni, H. H., & Wahab, M. M. A. (2015). Metal adsorption by agricultural biosorbents: Adsorption isotherm, kinetic and biosorbents chemical structures. *International journal of biological macromolecules*, *81*, 400-409.
15. Saha, P., Datta, S., & Sanyal, S. K. (2010). Application of natural clayey soil as adsorbent for the removal of copper from wastewater. *Journal of Environmental Engineering*, *136*(12), 1409-1417.
16. Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., Von Gunten, U., & Wehrli, B. (2010). Global water pollution and human health. *Annual review of environment and resources*, *35*, 109-136.
17. Shandra, J. M., Shor, E., & London, B. (2008). Debt, structural adjustment, and organic water

pollution: A cross-national analysis. *Organization & Environment*, *21*(1), 38-55.

18. Sivaprakash. B, N.Rajamohan and A. Mohamed Sadhik, (2010). Batch and column sorption of heavy metal from aqueous solution using a marine alga *Sargassum tenerrimum*, *International Journal of ChemTech Research*, 2(1),155-162
19. Sivaprakash, B and N. Rajamohan (2011). Equilibrium and Kinetics Studies on the Biosorption of As (III) and As (V) by the Marine Algae Turbinaria conoides, *Research Journal of Environmental Sciences*, Science Alert, 5 (10), 20, 779-789