Journal of Faculty of Engineering & Technology

journal homepage: www.pu.edu.pk/journals/index.php/jfet/index

LINEAR AND NON-LINEAR REGRESSION ANALYSIS ON THE BIOSORPTION OF Cu(II) BY RICE STRAW

A. Anwer[1], K. Shahzad[2], S. Hussain[3], Z.A. Khan*[4], Z. Idrees[5], M. Kazmi[6]
[*1]Department of Basic Sciences and Humanities, University of Engineering and Technology, KSK Campus, GT Road, Lahore, Pakistan.
[2]Center for Clean Coal Technology, University of Punjab
[3]Chemical Engineering Department, NFC IET Multan
[4,5,6] Department of Chemical Engineering, University of Engineering and Technology, KSK Campus, GT Road, Lahore, Pakistan

Abstract

This study elucidates equilibrium and kinetic modelling for the removal of Cu(II) ion on rice straw(RS). The Adsorption isotherms are empirical relations between equilibrium uptake in solid phase and residual concentration in the liquid phase. A variety of adsorption isotherms are available in the literature which are mainly characterized as 2 and 3 three parameters adsorption isotherm models. In this study various 2 parameters adsorption isotherms are used to elucidate the equilibrium behaviour of Cu(II) removal by rice straw at an average pH = 5, by using linear and non-linear regression analysis. Similarly, Pseudo 1st and 2nd kinetic models are fitted on the experimental data. R^2, SSE, MSE, RMSE, ARE and SAE were used as the criteria of the best fit of a model in its linear or non-linear form. On the basis of R^2, temkin adsorption isotherm described best behaviour of the Cu(II) removal by rice straw indicating highest value of 0.9664 both for linear and non-linear regressions. Kinetic modelling showed pseudo 2nd order kinetic model both in linear and non-linear form best represented the experimental data of Cu(II) ion removal on rice straw(RS).

Keywords: Biosorption, Equillibrium Modelling, Kinetics, Rice Straw, Isotherms

1. INTRODUCTION

In general waste may be in form of solid or liquid. Both forms may be toxic and hazardous. Liquid waste could be classified into two types, organic and inorganic waste. The waste effluent from industries contain various toxic heavy metals and organic substances which are produced during different industrial processes [1].

Wastewater effluents of mining, electroplating, paint, fertilizer, textile industries and tanneries are main sources of heavy metals like Cd, As, Hg, Cr, Pb, Cu, Mg and Zn etc [2,3]. Heavy metals are extremely toxic elements, because they are non-biodegradable which can seriously affect plants and animals and have been involved in causing a large number of sicknesses [4]. The level of heavy metals in drinking and waste water must be according to

* Corresponding Author: a.anwar@uet.edu.pk

World Health Organization's (WHO) permissible level. For Cu (II) The maximum acceptable concentration of Cu (II) in drinking water is 1.5 mg/L and 0.5 mg/L for Cu (II) for safe discharge [5]. The common methods used for the removal of heavy metals are ion exchange [6], reverse osmosis [7], electrolysis [8], precipitation [9], evaporation [10], Carbon adsorption [11] and ultrafiltration [12]. Reverse Osmosis is a technique used for the purification of water using semipermeable membranes. In reverse osmosis a high applied pressure is applied across the osmotic pressure of waste water caused due to dissolved solids. The disadvantage of this method is high cost of power and recovered water is less than the feed water. Evaporation is a slow process and uses a large amount of heat. Ultrafiltration is a water purification technique which uses variety of membranes driven by pressure and concentration gradient. In this process a large amount of sludge is produced. Ion exchange is comparatively a better technique than previous described techniques but is expensive [6].

Due to the production of toxic sludge, low recovery, high power consumption, expensive chemical treatment and incomplete metal removal emphasized to establish a new methodology named as biosorption. Biosorption is the capability of various biological materials to remove heavy metals from waste water metabolically. For biosorption a low cost sorbent is employed for the removal of metals. Sorbants are naturally abundant materials mainly obtained from dairy products, beverage and pharmaceutical industries, agricultural and livestock products [14]. Various algae, nonpathogenic deceased fungi, bacteria and yeast [15] are also employed for biosorption. Agriculture by products like rice husk [16], maize husk [17], corncobs [18], peanut shells [19], wheat bran [20] and coconut meal [21] etc. contains lignin, hemicellulose and cellulose which contain polar functional groups like alcohols aldehydes, ketones, phenols and ethers [22]. They tend to bind heavy metals by replacing hydrogen atom with heavy metal ions or by the donation of electron to form a metal complex [23]. Biosorption generally takes place in three different ways adsorption of metal ions, intracellular uptake and chemical transformation of metals by microorganisms. Low cost, high efficiency, regeneration of biosorbent, minimum production of chemical and biological sludge makes biosorption an effective method [24].

The objective of this present work is to analyse different 2 parameters adsorption isotherms on the removal of Cu(II) by rice straw using linear and non-linear regression analysis.

2. Materials and Methods

Analytical grade $Cu(NO_3)_2.5H_2O$, $MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$ were used to prepare stock solutions Cu(II), Mg(II) and Zn(II). The concentrations of stock solutions were 1000 ppm from which further known dilutions were prepared. For batch experiments an orbital shaker with water bath was used.

For Kinetic study of Cu(II) the initial concentration was 100 ppm the flasks were shaked at 120 rpm and 30±2 °C for a time limit of 1, 2, 3, 5, 6, 8, and 15 minutes. Equilibrium Studies were carried out at 2, 3, 5, 10, 15, 30, 45, 60, 85 and 100 ppm as initial concentration and pH was measured with a digital pH meter. All investigations were performed in triplicate and 100ml adsorbate was used. Biosorbent was separated simply by filtration. The unknown concentrations of Cu (II) were measured by Atomic Absorption Spectrophotometer (Shimadzu 6800) using air-acetylene flame.

3. Result and Discussion

3.1 Langmuir Isotherm

The adsorption of metal using rice straw (RS) demonstrated best fitting of Langmuir Model. The results of linear Langmuir model are not as satisfactory as in the case of non-linear model due to the alteration of error distribution on converting model to linear form. As non-linear showed a best correspondence with experimental data, so this indicates the monolayer adsorption of metal onto the surface of RS. The parameters q_{max} and K_L of the Langmuir equation predicted by non-linear and linear regression are 57.46 (mg/g), 0.1814 (L/mg) and 69.37 (mg/g), 0.0637 (L/mg). The K_L expresses the energy of adsorption and q_{max} predicts the monolayer capacity.

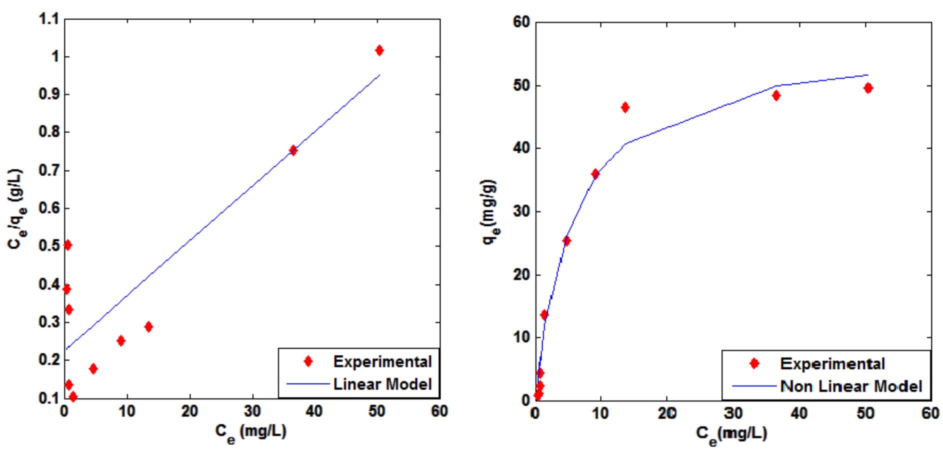

Figure 1: Linear and Non-linear plots of Langmuir Isotherm Model

3.2 Freundlich Isotherm

Both linear and non-linear form of Freundlich model showed almost similar behaviour towards the experimental data of metal adsorption using RS. The values of Freundlich exponent *n* and constant K_F were 3.926 (L/g) and 1.222 in the case of linear analysis and 11.66 (L/g) and 2.473 for non linear analysis. The reciprocal of exponent *n* explains the adsorption intensity ranges from 0 to 1 as shown in table 1. These values of *n* indicate the heterogeneous nature of adsorbent predicting chemisorptions process.

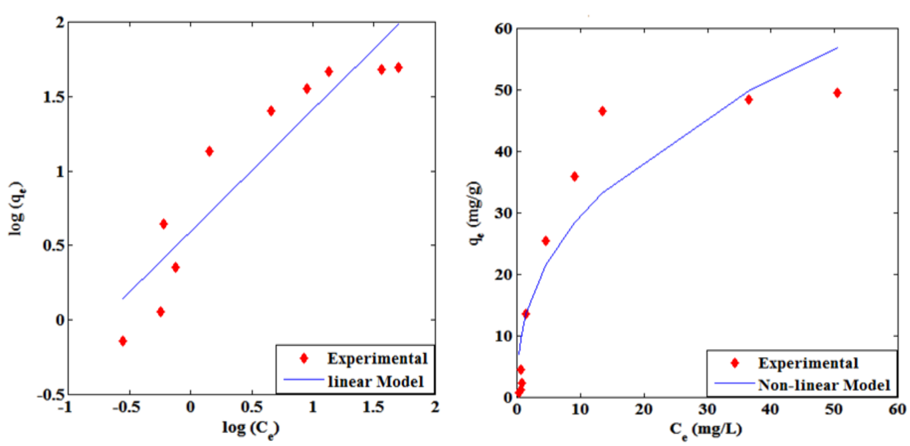

Figure 2: Linear and Non-Linear plots of Freundlich Isotherm Model.

3.3 Temkin Isotherm

Temkin isotherm model presented a good correlation of its Linear and non-linear forms with experimental data. As R^2 is 96% in both cases but it is slightly less than the value obtained by using the non-linear form of the Langmuir isotherm model. The parameter b_T represents the heat of adsorption and its value obtained is below 8 kJ/mol showing the physiosorption process.

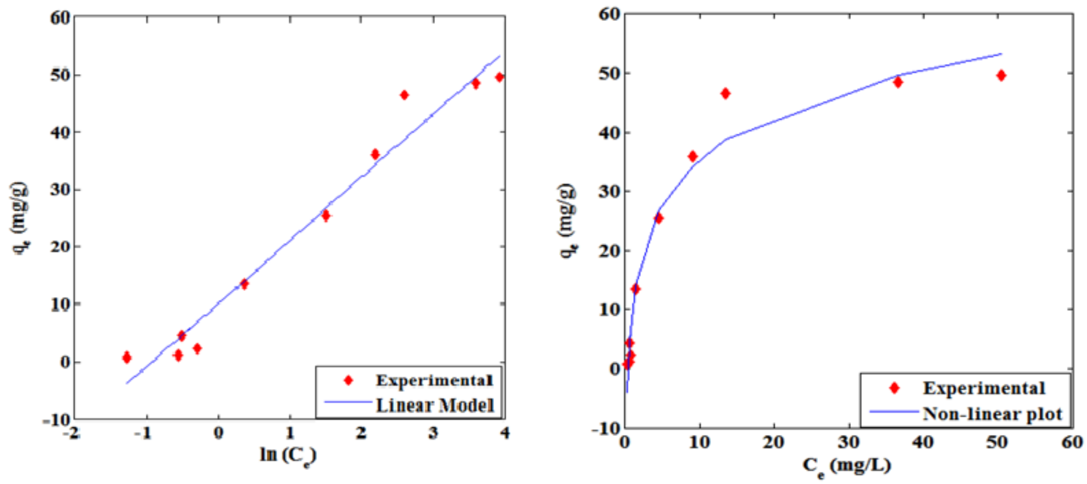

Figure 3: Linear and Non-Linear plots of Temkin Isotherm Model.

3.4 Dubinin - Radushkevich Isotherm

Dubinin-Radushkevich (D-R) provides information regarding the nature of biosorption by estimated the value of mean free energy *E*. The values of constant k_d (0.3216 and 1.1630 (mol^2/kJ^2)) are obtained by plotting linear and non-linear model is less than 8kJ/mol shows the physical adsorption on the surface of RS. The metal uptake of 45.240 (mg/g) estimated in the case of non-linear model of D-R is less than the value obtained in non-linear Langmuir model. This indicates the lower efficiency of adsorption process.

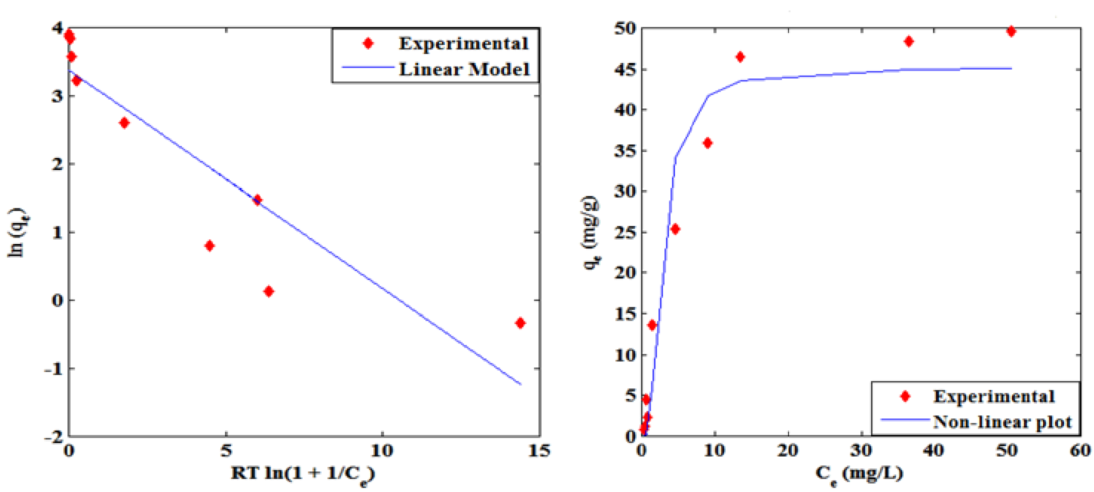

Figure 4: Linear and Non-Linear plots of Dubinin - Radushkevich Isotherm Model

Table 1: Comparison of Two Parameter Models.

Isotherms	Parameters		Values of the Different Error Functions					
Langmuir	q_m (mg/g)	K_L (L/g)	**SSE**	**MSE**	**RMSE**	**ARE**	**SAE**	R^2
Linear	69.37	0.0637	0.1821	0.0182	0.1349	48.63	1.1786	0.7602
Non-Linear	57.46	0.1814	89.05	8.905	2.9842	93.21	24.258	0.9748
Freundlich	N	K_F (L/g)	**SSE**	**MSE**	**RMSE**	**ARE**	**SAE**	R^2
Linear	1.222	3.926	0.6888	0.0689	0.2624	62.484	2.4895	0.8515
Non-Linear	2.473	11.66	499.95	49.995	7.0708	215.01	61.211	0.8522
Temkin	b_T (kJ/mol)	A_T (L/g)	**SSE**	**MSE**	**RMSE**	**ARE**	**SAE**	R^2
Linear	0.2264	2.4970	132.068	13.206	3.6341	114.027	28.3733	0.9664
Non-Linear	0.2264	2.4970	132.068	13.206	3.6341	114.027	28.3733	0.9664
Dubinin-Radushkevic	q_{DR} (mg/g)	k_d (mol^2/kJ^2)	**SSE**	**MSE**	**RMSE**	**ARE**	**SAE**	R^2
Linear	29.520	0.3216	4.4145	0.4415	0.6644	90.945	5.2636	0.8206
Non-Linear	45.240	1.1630	231.356	23.135	4.810	51.424	41.101	0.9483

3.5 Kinetic Modelling

There are many kinetic models that are available to evaluate the nature of biosorbent. In order to investigate the Cu(II) biosorption on rice straw(RS) two most common kinetic models i.e. Pseudo 1st and 2nd order modelling was performed. The results of kinetic modelling are shown in both linear and non-linear form as follows.

Pseudo 1st Order Kinetic Model

The non-linear model of Cu(II) biosorption on RS was shown by plotting graph between metal uptake (q_t) vs time (t). The plot directly showed that most of the metal uptake took place within 2 min time interval. After that no significant biosorption was noticed and biosorption process was assumed to be in equilibrium after 2 min time interval. The maximum metal uptake at equilibrium was 47 mg/g. The non-linear model is shown in figure 5 while values of different error functions are represented in table 2.

The Pseudo 1st order model was fitted on experimental results to check its feasibility. Its Lagergan form is represented as follows.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

By putting the boundary conditions i.e. t=0, t=t and q_t=0, qt=q_t and integrating the equation we obtain linear expression for pseudo 1st order system as follows.

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t \qquad (2)$$

Where q_e, q_t, represents equilibrium and instantaneous Cu(II) uptake respectively while k_1 and t represents rate constant and time respectively. The values of equilibrium uptake(q_t) and rate constant(k_1) were calculated by slope and intercept on linear graph respectively in figure 5. The values of different error functions are represented in table 2. It is clear from the results that calculated and experimental metal uptake has large difference, therefore, pseudo 1st order kinetic model is not suitable to represent the kinetics of metal biosorption process on RS.

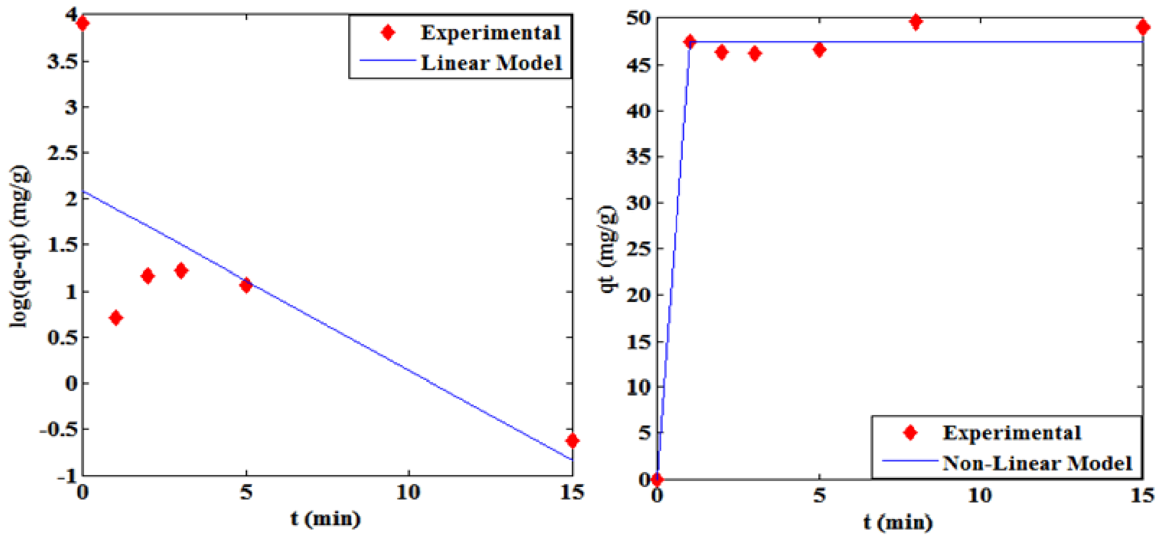

Figure 5: Linear and Non-Linear plots of Pseudo 1st Order Kinetic Model.

Pseudo 2nd Order Kinetic Model

The non-linear Pseudo 2nd order model was represented by plotting graph between Cu(II) uptake (q_t) vs time (t). The model clearly indicated that most of the metal uptake took place within first 2 min time interval and after this time interval no significant biosorption was observed. The non-linear behaviour plot is shown in figure 6 and results of different error functions are shown in table 2.

The pseudo 2nd order equation can be expressed by following equation.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

By putting boundary condition and integrating we get linear form of pseudo 2nd order model which is represented as follows.

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

Also, we can define the initial sorption rate through following equation.

$$b = k_2 {q_e}^2 \quad (5)$$

Where q_t and q_e represents instantaneous and equilibrium Cu(II) uptake in mg/g respectively while k_2 and t represents rate constant and time respectively. The values of k_2 and q_e were determined by finding slope and intercepts of plot between t/q_t vs t. The calculated and experimental values of Cu(II) uptake was quite close to each other which ensured that pseudo 2nd order model best represents kinetic behavior of metal uptake on RS. The values of different error functions also showed that percentage deviation from experimental results was also minimum for pseudo 2nd order model. For example, the correlation coefficient R^2 value for pseudo 2nd order system was 0.9992. This value clearly indicates that experimental results best fits in this model. On the other hand, R^2 value for Pseudo 1st order system was only 0.5502 indicating less compliance with experimental findings. The nonlinear form also produced the same results and are shown in table 2.

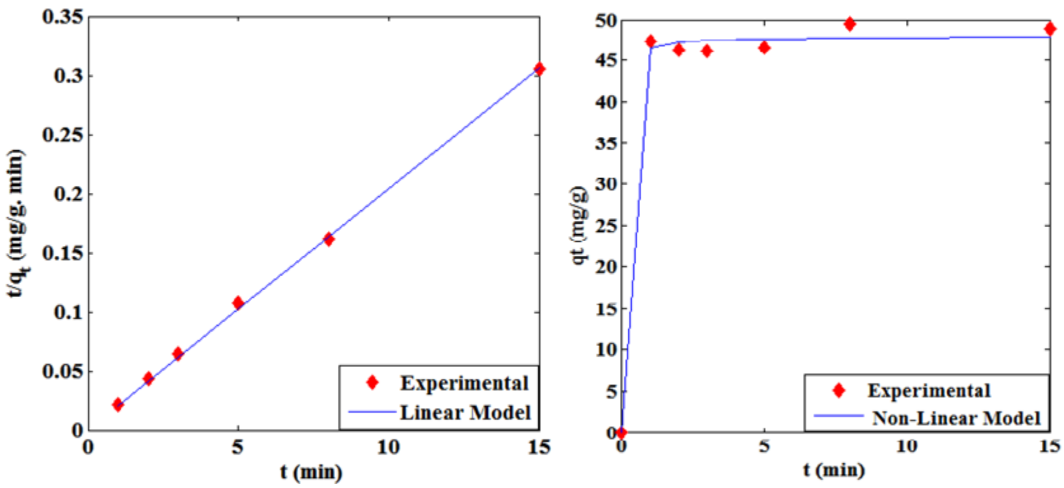

Figure 6: Linear and Non-Linear plots of Pseudo 2nd Order Kinetic Model.

Table 2: Comparison of Kinetic models

Models	**Parameters**		**Values of Different Error Functions**					
Pseudo 1St Order	**k_1** (1/min)	**qe_1** (mg/g)	**SSE**	**MSE**	**RMSE**	**ARE**	**SAE**	**R^2**
Linear	0.1956	8.0910	5.0945	0.8491	0.9216	....	Inf	0.5502
Non-Linear	7.4300	47.590	10.445	1.4922	1.2216	2.436	6.9931	0.9946
Pseudo 2nd Order	**k_2** (g/mg.min)	**qe_2** (mg/g)	**SSE**	**MSE**	**RMSE**	**ARE**	**SAE**	**R^2**
Linear	1.9430	48.910	4.5e-5	7.5e-6	0.0027	2.9814	0.0141	0.9992
Non-Linear	0.6089	48.18	9.009	1.2866	1.1343	2.5170	7.1918	0.9954

4. Conclusion

On the overall, linear regression showed better fit for the data of Cu(II) removal by rice straw than the non-linear regression. However, no specific symmetry was observed in the results for the declaration of the best fit. For example, on the basis of R^2, temkin adsorption isotherm described best the behaviour of the Cu(II) removal by rice straw as shown by the highest value of 0.9664 both for linear and non-linear regressions. Kinetic modelling showed pseudo 2nd order kinetic model both in linear and non-linear form best represented the experimental data of Cu(II) ion removal on rice straw(RS).

References

[1] F. Hammaini, A. Gonza, M.L. Ballester, J.A. Bla zquez, Biosorption of heavy metals by activated sludge and their desorption characteristics, Journal of Environmental Management 84 (2007) 419–426.

[2] T.G. Kazi, A.R. Memon, H.I. Afridi, M.K. Jamali, M.B. Arain, N. Jalbani, R.A. Sarfrz, Determination of cadmium in whole blood and scalp hair samples of Pakistani male lung cancer patients by electro thermal atomic absorption spectrometer, Sci. Total Environ. 389 (2008) 270–276.

[3] A. Özer, D. Özer, Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats, Journal of Hazardous Materials B100 (2003) 219–229.

[4] V.C. Srivastava, I.D. Mall, and I.M. Mishra, "Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA," Journal of Hazardous Materials, vol. 134, no. 1–3, pp. 257–267, 2006.

[5] N.D. Tumin, A.L. Chuah, Z. Zawani, and S.A. Rashid, "Adsorption of copper from aqueous solution by Elais Guineensis kernel activated carbon," Journal of Engineering Science and Technology Review, vol. 3, pp. 180–189, 2008.

[6] J.A.S. Tenório, D.C.R. Espinosa, "Treatment of chromium plating process effluents with ion exchange resins," Waste Management, vol. 21, no. 7, pp. 637–642, 2001.

[7] N. Ahalya, T.V. Ramachandra, R.D. Kanamadi, Biosorption of Heavy Metals *Research Journal of Chemistry and Environment,* Vol.7 (4) Dec. (2003).

[8] R.S. Juang, R.C. Shiau, "Metal removal from aqueous solutions using chitosan-enhanced membrane filtration," Journal of Membrane Science, vol. 165, no. 2, pp. 159–167, 2000.

[9] J.O. Esalah, M.E. Weber, J.H. Vera, "Removal of lead, Cadmium and Zinc from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate," The Canadian Journal of Chemical Engineering, vol. 78, no. 5, pp. 948–954, 2000.

[10] J.A. Scott, A.M. Karanjkar, Repeated cadmium biosorption by regenerated *Enterobacter aerogenes* biofilm attached to activated carbon. *Biotechnol. Left,* 14**,** 8:737-740 (1992).

[11] N.T. Abdel-Ghani, M. Hefny, G.A.F. El-Chaghaby, "Removal of lead from aqueous solution using low cost abundantly available adsorbents," International Journal of Environmental Science and Technology, vol. 4, no. 1, pp. 67–73, 2007.

[12] D. Kalderis, S. Bethanis, P. Paraskeva, E. Diamadopoulos, "Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times," Bioresource Technology, vol. 99, no. 15, pp. 6809–6816, 2008.

[13] K.S. Low, C.K. Lee, S.C. Liew, Process Biochem. 36 (2000) 59–64.

[14] M.C. Palmieri, O. Garcia, P. Melnikov, Process Biochem. 36 (2000) 441–444.

[15] K. Wilson, H. Yang, C.W. Seo, W.E. Marshall, "Select metal adsorption by activated carbon made from peanut shells," Bioresource Technology, vol. 97, no. 18, pp. 2266–2270, 2006.

[16] R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodriguez, "Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob," Separation and Purification Technology, vol. 45, no. 1, pp. 41–49, 2005

[17] Y. Bulut, Z. Baysal, "Removal of Pb(II) from wastewater using wheat bran," Journal of Environmental Management, vol. 78, no. 2, pp. 107–113, 2006.

[18] A.E. Ofomaja, Y.S. Ho, Effect of pH on cadmium biosorption by coconut copra meal, Journal of Hazardous Materials B139 (2007) 356–362.

[19] G. Uslu, M. Tanyol, *J. Hazard. Mater.*, B135, 87 (2006).

[20] M.G. Lee, J.H. Lim and S.K. Kam, *Korean J. Chem. Eng.*, 19(2), 277 (2002)

[21] Y. Zhang, R. Zheng, J. Zhao, F.M.Y. Zhang, Q. Meng, Characterization of -Treated Rice Husk Adsorbent and Adsorption of Copper(II) from Aqueous Solution, BioMed Research International, Volume 2014 (2014), Article ID 496878, 8 pages.

[22] P.A. Terry, W. Stone, "Biosorption of cadmium and copper contaminated water by Scenedesmus abundans," Chemosphere, vol. 47, no. 3, pp. 249–255, 2002.

[23] N. Feroze, M. Kazmi, N. Ramzan, Dead immobilized Rhizopus Arrhizus as a potential biosorbent for copper removal, *Korean J. Chem. Eng*, DOI: 10.1007/s11814-012-0088-y.

[24] M.G.A. Vieira, A.F. de Almeida Neto M.G.C. da Silva, C.N. Carneiro, A.A. Melo FilhoAdsorption of lead and copper ions from aqueous effluents on rice husk ash in a dynamic system, Braz. J. Chem. Eng. vol.31 no.2 São Paulo Apr./June 2014.