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Adsorption of Heavy Metal Ions on Rice Husk: Isotherm Modeling and Error Analysis

N PRIYANTHA, A N NAVARATNE AND T P K KULASOORIYA

Department of Chemistry, Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

Email: namal.priyantha@yahoo.com, namalpriantha@pdn.ac.lk

Abstract: Rice husk, a readily available industrial waste, offers strong adsorption characteristics for heavy metal ions, namely, Cd(II), Cr(III), Cu(II), Pb(II), Ni(II) and Zn(II), which are present in effluents of metal finishing industries. Presence of these heavy metals would pose environmental and human threat owing to their highly toxic nature. Adsorption studies conducted using individual metal ion solutions by varying one experimental parameter at a time, while keeping others unchanged, lead to optimum values of 10 min shaking time, 10 min settling time, 4.0-5.0 solution pH and 100 °C firing temperature. Surface titrations carried out suggest variations of the surface charge with solution pH, while thermogravimetric analysis shows the increase in thermal energy after a firing temperature of 100 °C as a result of combustion of organic constituents present in rice husk. Among the six adsorption isotherms investigated; Langmuir, Freundlich, Temkin, Dubnin-Redushkevich, Redlich-Peterson and Sips; the Langmuir isotherm fits the best with a regression coefficient close to unity together with small errors.

Keywords: Rice husk, Heavy metal ions, Adsorption isotherms, Static conditions.

1. Introduction

Industrial expansion is a requirement to fulfill the demand of ever increasing population. Many industries, such as metal finishing, leather tanning, synthetic dye production, mining and metallurgy, electroplating, paint and photography, release considerable amounts of heavy metal ions to the surrounding through their effluents. Treatment of industrial effluents has thus become a necessity to safeguard the ecosystem [1, 2].

Biosorption, among many treatment methods in practice, is one of the best methods to remove heavy metals from effluents released from industries. To minimize the risk of using synthetic chemicals to treat waste water, environmentally friendly substances are nowadays introduced. Natural substances, such as agricultural waste, brick clay, fruit peel waste, tea leaf, saw dust and peat have been used to remove heavy metal ions from wastewater [3-7]. Phosphoric acid modified rice husk was also reported as an effective adsorbent to remove Zn(II) from solution [8].

The study reported is on rice husk, a readily available waste material in Sri Lanka. Much of the husk produced from processing of rice is either burnt or dumped as waste. On the other hand, rice husk is used as a raw material for production of organic substances, such as xylitol, furfural, ethanol and acetic acid, and used as a cleaning or polishing agent in metal/machine industry [9]. Use of rice husk as an adsorbent is a main

advantage for remediation of environmental pollution problems. For such investigation, the study of adsorption isotherms is much important because it leads to equilibrium concentrations of adsorbate after completion of adsorption. Further, they provide information to determine process parameters which lead to maximum extent of adsorption. The shape of isotherm curves also predicts the type of adsorption. Among many adsorption isotherms available, Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Redlich-Peterson and Sips are of significance for characterization of adsorbent-adsorbate interactions with regard to environmental pollution.

The main objective of this study is to investigate the removal efficiency of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) from aqueous solution using heat-treated rice husk. Effect of firing temperature, shaking time, settling time and solution pH on the extent of metal ion removal was studied to determine the optimum conditions, which were subsequently used for isotherm studies.

2. Materials and Methods

2.1. Materials

Standard solutions of Cd(II), Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) were prepared using Cd(NO₃)₂, Cr(NO₃)₃, CuSO₄, NiSO₄, Pb(NO₃)₂ and ZnSO₄, respectively. All the experiments were conducted under static conditions using individual metal ion solutions. Rice husk samples were obtained from a rice mill in the

District of Kandy, Sri Lanka. They were thoroughly rinsed with water and used in its natural form.

2.2. Instrumentation

Samples of rice husk were fired using Carbolite CTF 12/100/900 tube furnace, while spectro-electronic M series atomic absorption spectrophotometer (AAS) was used to measure the total metal concentration of all solutions. Mass changes of rice husk and heat flow at different firing temperatures were studied using thermal gravimetric analyzer (TGA) (Model STA-N-650).

2.3. Research Design

2.3.1. Effect of firing temperature

Rice husk is a natural substance having a variable composition. Therefore, representative samples of rice husk were prepared by mixing large portions of its samples, and fired at predetermined temperatures for 4.0 h followed by cooling down to room temperature through natural convection. All experiments were performed under static conditions using metal ion solutions of 10.0 ppm. In each experiment, 50.0 cm³ of each metal ion solution was shaken with 2.50 g of rice husk, fired at various temperatures, the system was allowed to reach equilibrium and the extent of removal of metal ion by rice husk was determined as a percentage removal using the relationship,

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

Where C_i is the initial concentration of metal ion and C_f is the final concentration of metal ion after treatment with rice husk. All experiments were conducted at a rotation speed of 150 rpm.

2.3.2. Effect of contact time

The effect of contact time on adsorption was observed by varying shaking time and settling time, separately by keeping all other variables constant, and determining the percentage removal.

2.3.3. Effect of pH

Heavy metal ion solutions of 10.0 ppm having pH ranging from 2-10 were prepared using HNO₃ and NaOH solutions. Solutions of higher pH were not prepared as precipitation problems were encountered for certain metal ion solutions. Each solution was then treated with rice husk for optimum shaking and settling time periods, and the extent of removal was determined using Equation (1).

2.3.4. Adsorption isotherms

The amount of heavy metal ions adsorbed on rice husk fired at the optimized firing temperature of 100 °C for previously optimized contact time was studied using

solutions of concentration varying from 2-1000 ppm. After each solution was filtered, atomic absorption measurements were recorded. These data were fitted to different adsorption isotherm models, namely Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Redlich-Peterson and Sips [10].

3. Results and Discussion

3.1. Effect of Firing Temperature on Removal of Heavy Metal ions from Aqueous Solutions

Figure 1 shows the percentage removal of heavy metal ions determined using pre-fired rice husk with different metal ion solutions.

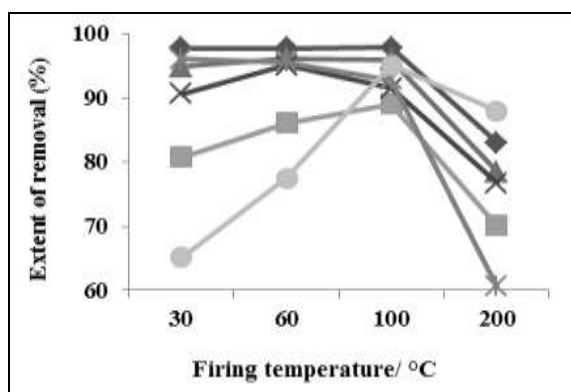


Figure 1. Extent of removal of heavy metal ions by rice husk fired at different temperatures: Cd(II) (♦), Cu(II) (■), Zn(II) (▲), Cr(III) (×), Ni(II) (*) and Pb(II) (●). [2.50 g rice husk, 50.0 cm³ 10.0 ppm metal ion solution, 60 min shaking, 60 min settling]

The extent of removal of Cd(II), Zn(II), Cu(II) and Pb(II) is increased with firing temperature up to 100 °C and then decreased up to 200 °C. However the extent of removal of Cr(III) and Ni(II) remains constant up to 100 °C, followed by a decrease by rice husk fired at higher temperatures. Therefore, 100 °C can be taken as the optimum firing temperature of rice husk for the removal of all metal ions investigated.

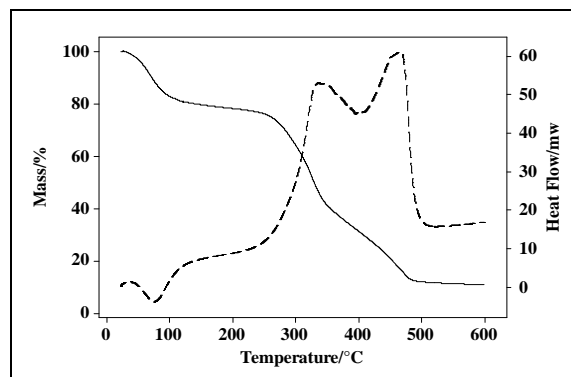


Figure 2. Variation of mass of rice husk (—) and heat flow (----) when firing at different temperatures

Variations of mass reduction and heat flow during the firing process are shown in Figure 2, which indicates a significant decrease in mass reduction, beyond the firing temperature of 100 °C, probably due to the combustion of organic matter. The exothermic nature of combustion is evident by observing positive energy release values at firing temperatures beyond 100 °C.

3.2. Surface Titrations

The surface charge of the bio-sorbent was determined to be highly dependent on the pH of the medium as clearly observed from the plots of the surface charge versus pH of the medium for different ionic strengths (Figure 3). NaNO_3 is commonly used for surface titrations because its constituent ions do not specifically bind to the bio-sorbent surface. Hence it is assumed that no ion other than protons in the medium binds to the bio-sorbent during surface titrations [11].

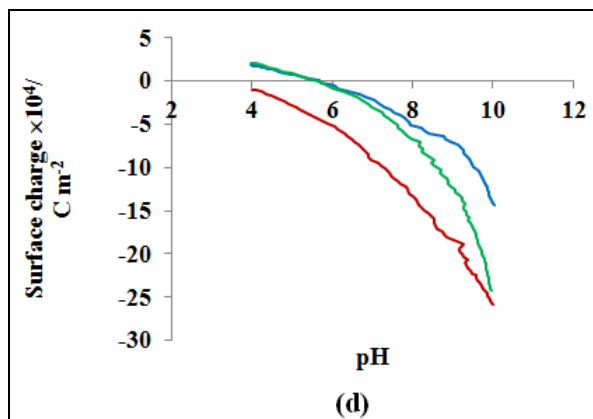
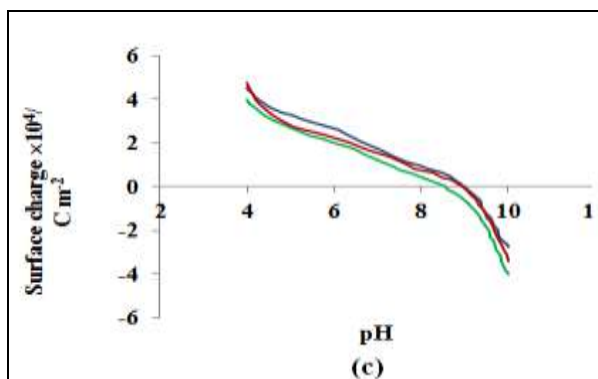
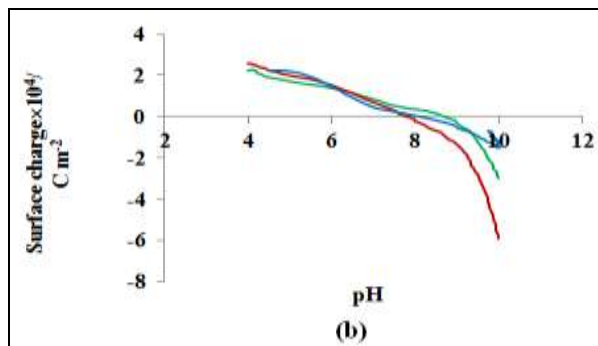
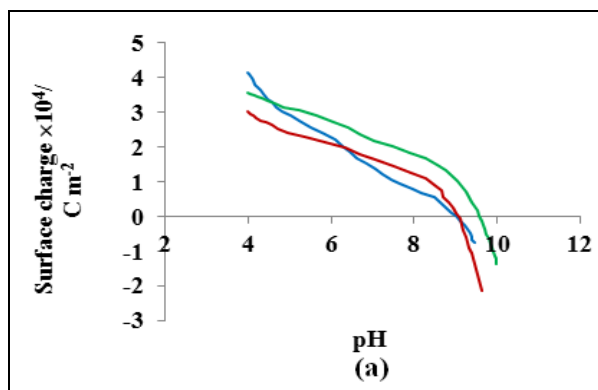
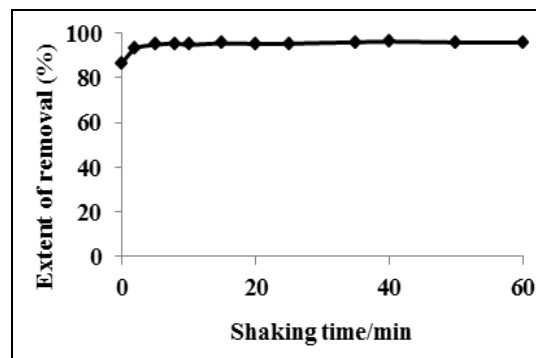


Figure 3. Surface titration curves of rice husk suspensions, plotted as variation of surface charge with pH controlled by different additions of NaOH for rice husk fired at different temperatures. (a) unfired (b) heated in to 60 °C (c) heated in to 100 °C (d) heated in to 200 °C. Ionic strengths are 0.1 M (—), 0.01 M (—) and 0.001 M (—)

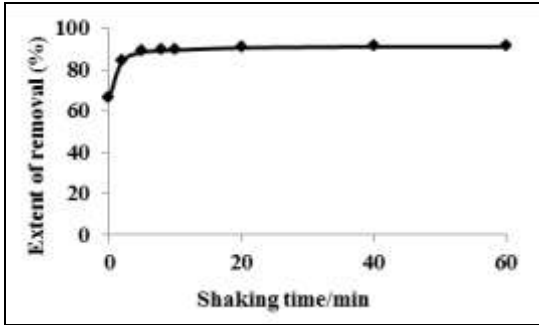
For all rice husk samples, the curves obtained at three ionic strengths do not intersect at a common point, and the curves obtained for 0.1 M and 0.01 M ionic strengths are almost parallel to each other indicating that the pH independent surface charge of rice husk is more predominant compared to the pH dependent charge [12]. The point of zero charge can however be estimated by considering two curves obtained for two lower concentrations at pH of 4.6, 6.0, 4.0 and 5.2 for unfired, 60 °C, 100 °C and 200 °C, respectively.

3.3. Optimization of contact time

The relationship between the extents of removal of heavy metal ions with contact time, as shown in Figure 4, indicates that the rice husk-metal ion solution system reaches equilibrium quickly. For both Cd(II) and Ni(II), percentage removal reaches the maximum and retains at the maximum after 10 min shaking time. Therefore, it is a reasonable assumption that the optimum shaking time for all metal ions used in this study, to be taken as 10 min.



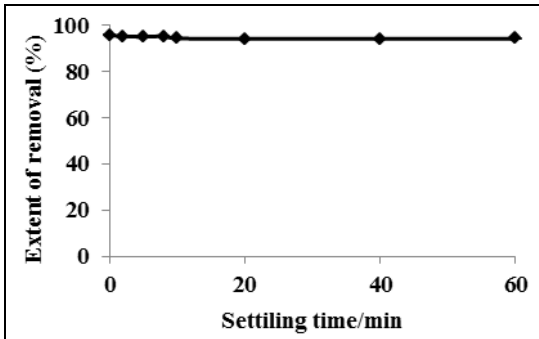
(a)



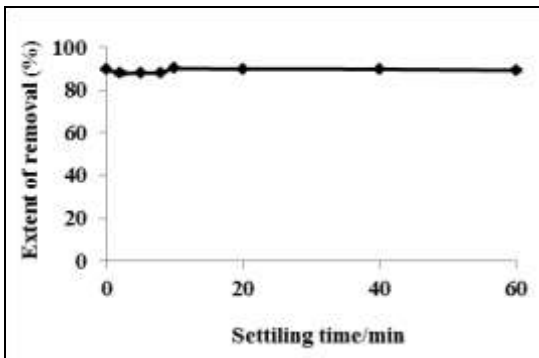
(b)

Figure 4. Variation of extent of removal with shaking time for heavy metal ions: (a) Cd(II) (b) Ni(II)

Further, there is no change in the extent of removal of Cd(II) and Ni(II) with the settling time as observed in Figure 5. However, a time period of 10 min was selected as the optimum settling time to assure that the establishment of equilibrium is complete.



(a)



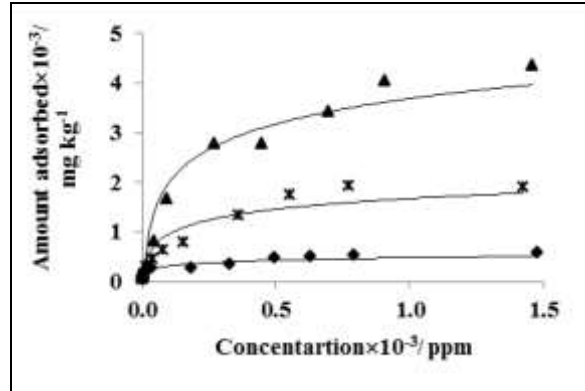
(b)

Figure 5. Variation of extent of removal with settling time for heavy metal ions: (a) Cd(II) (b) Ni(II)

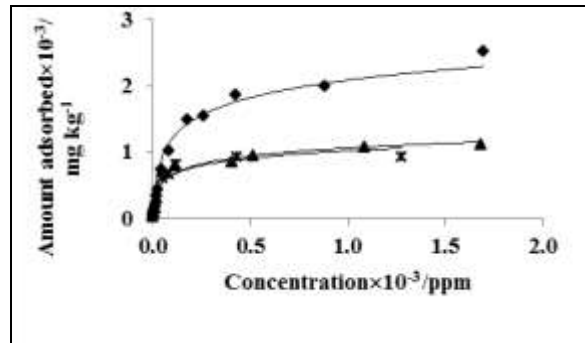
3.4. Isotherm Studies

The amount adsorbed plotted against the initial concentration provides clear indication that the adsorption of all metal ions investigated qualify Type I isotherm according to IUPAC isotherm classification (Figure 6) [13]. This overall behavior suggests that rice

husk shows microporous characteristics for adsorption of these metals. However the extent of removal depends on the type of the metal ion [13, 14].



(a)



(b)

Figure 6 Amount of heavy metal ions adsorbed on rice husk. (a) - Cr(III) (♦), Ni(II) (*), Pb(II) (▲) and (b) - Cd(II) (♦), Cu(II) (▲), Zn(II) (*)

Six isotherm models; Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Redlich-Peterson and Sips, were attempted to fit for all metal ion adsorption systems. The standard equations of the six isotherm models are given in Table 1.

Table 1: Standard equations of the six isotherm models

Isotherm Model	Standard equations
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \cdot K_L} \cdot \frac{1}{C_e}$
Freundlich	$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$
Temkin	$q_e = B \ln K_T + B \ln C_e$
Dubnin-Radushkevich	$\ln q_e = \ln q_s - \frac{B \epsilon^2}{1 + \frac{1}{C_e}}$ $\epsilon = RT \ln [1 + \frac{1}{C_e}]$
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{b_R}}$
Sips (Langmuir - Freundlich Isotherm)	$q_e = \frac{K_S C_e^{1/b_S}}{1 + \alpha_S C_e^{1/b_S}}$

In Table 1, q_m and q_e are maximum adsorption capacity and equilibrium adsorption capacity; C_e is the equilibrium concentration of metal ion; K_L , K_F , K_T , K_R , K_S are Langmuir, Freundlich, Temkin, Redlich-petersom and Sips isotherm constants, respectively; n , B , a_R , b_R , a_S , b_S are constants.

Among the six isotherms, constants for Langmuir and Freundlich isotherms, the most widely used models, are given in Table 2 and Table 3, respectively. Langmuir isotherm model assumes monolayer adsorption which occurs on specific sites and is independent on the amount of material adsorbed. On the other hand, Freundlich isotherm model is applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. This is derived by assuming an exponentially decaying sorption site energy distribution [7]. It is clear from values in Table 2 and Table 3 that the Langmuir adsorption isotherm model, having regression coefficients (R^2) close to unity for all six metal ion systems, is better suited to explain adsorption characteristics of metal ions on rice husk fired at 100 °C.

Table 2: Isotherm constants and regression coefficients (R^2) for Langmuir adsorption isotherm model

Metal ion	$K_L \times 10^2 / \text{L mg}^{-1}$	$q_m / \text{mg kg}^{-1}$	R^2
Cd(II)	22.2	2500	0.988
Cu(II)	13.9	1000	0.990
Ni(II)	15.3	909	0.985
Pb(II)	3.30	5000	0.986
Zn(II)	37.5	833	0.964
Cr(III)	3.00	769	0.983

According to Table 2, the adsorption capacity varies in the order of Pb(II) > Cd(II) > Cu(II) > Ni(II) > Zn(II) > Cr(III). The highest adsorption capacity towards Pb can be attributed to the lowest hydrated radius of Pb(II), which changes in the order of Cu(II) > Cd(II) > Pb(II), being able to be trapped easily in the pores of the adsorbent [15].

Table 3: Isotherm constants and regression coefficients (R^2) for Freundlich adsorption isotherm model

Metal ion	n	K_F	R^2
Cd(II)	2.73	239	0.895
Cu(II)	2.77	111	0.812
Ni(II)	2.19	97	0.958
Pb(II)	2.12	214	0.915
Zn(II)	2.86	147	0.879
Cr(III)	5.32	130	0.904

Isotherm constants for the adsorption models, Temkin, Sips, Redlich-Peterson (R-P) and Dubnin-Radushkevich (D-R), are given in Table 4.

Table 4: Isotherm constants and respective regression coefficient (R^2) for Temkin, D-R, Sips and R-P isotherm model for considered heavy metal ions

Temkin Isotherm				
Metal ion	B	K_T	R^2	
Cd(II)	231	7.74	0.963	
Cu(II)	130	3.57	0.968	
Ni(II)	228	1.38	0.874	
Pb(II)	516	2.03	0.962	
Zn(II)	114	9.17	0.990	
Cr(III)	58.9	3.21	0.885	
Dubnin-Reduskevich (D-R) Isotherm (for higher concentrations)				
Metal ion	$B \times 10^3$	q_s	R^2	
Cd(II)	0.10	1894	0.698	
Cu(II)	5.6	1106	0.998	
Ni(II)	1.9	1798	0.927	
Pb(II)	7.1	4298	0.934	
Zn(II)	0.20	968.9	0.925	
Cr(III)	4.1	518.3	0.940	
Sips Isotherm				
Metal ion	K_S	$a_S \times 10^2$	b_S	R^2
Cd(II)	394	9.60	1.69	0.987
Cu(II)	167	16.5	1.20	0.970
Ni(II)	68.9	2.40	1.57	0.975
Pb(II)	451	7.60	2.08	0.967
Zn(II)	264	26.6	1.69	0.987
Cr(III)	76.0	-43.3	2.97	0.947
Redlich-Peterson (R-P) Isotherm				
Metal ion	$K_R \times 10^{-2}$	a_R	b_R	R^2
Cd(II)	12.5	2.3	0.79	0.994
Cu(II)	1.92	0.30	0.93	0.984
Ni(II)	0.195	0.020	0.89	0.966
Pb(II)	4.67	0.40	0.82	0.978
Zn(II)	4.46	0.95	0.88	0.993
Cr(III)	-2.51	-2.9	0.74	0.936

Regression coefficients for all six systems listed in Table 5 shows that the best fitted model for the removal of all six heavy metal ions under investigation using rice husk is the Langmuir isotherm model. Redlich-Peterson isotherm and Sips isotherm also were fitted to a certain extent with high R^2 values. Freundlich, Temkin and D-R isotherms do not explain the adsorption behavior of these metal ions.

Table 5: Regression coefficients of adsorption isotherm models for all heavy metal ions under investigation

Metal ion	Langmuir isotherm	Freundlich isotherm	Temkin isotherm	D-R isotherm Higher concentrations (>100 ppm)	R-P isotherm	Sips isotherm
Cd(II)	0.988	0.895	0.963	0.698	0.994	0.987
Cu(II)	0.990	0.812	0.968	0.998	0.984	0.970
Ni(II)	0.985	0.958	0.874	0.927	0.966	0.975
Pb(II)	0.986	0.915	0.962	0.934	0.978	0.967
Zn(II)	0.964	0.879	0.990	0.925	0.993	0.987
Cr(III)	0.983	0.904	0.885	0.940	0.936	0.947

As the D-R model, tested only for high concentrations, did not show any trend with respect to heavy metal ions investigated, it was not considered for error analysis, which was conducted for further clarification of the validity of adsorption results. The results of error analysis, namely, average relative error (ARE), Sum square error (SSE), Hybrid fractional error function (HYBRID), nonlinear chi-square test and Sum of absolute error (EABS) are shown in Table 6 [3]. The error terms obtained for various isotherm studies vary

without any trend. However, the Langmuir isotherm shows smallest error values in general, and hence, the selection of the Langmuir isotherm as the best fitted model is further convinced. The validity of other isotherm models by considering all types of error analyses can be given in the order of Langmuir > R-P > Sips > Temkin > Freundlich for heavy metal ions Cd(II), Cu(II) and Pb(II). However, this order is slightly different for Ni(II), Zn(II) and Cr(III).

Table 6: Values of different error analyses for isotherm models

	Metal ion	ARE	SSE	HYBRID	Non-linear chi-square test	EABS
Langmuir isotherm	Cd(II)	25.82	0.000	0.024	0.002	0.007
	Cu(II)	6.590	0.000	0.001	0.000	0.001
	Ni(II)	50.47	0.000	0.034	0.003	0.005
	Pb(II)	19.20	0.000	0.004	0.000	0.002
	Zn(II)	9.457	0.000	0.004	0.000	0.002
	Cr(III)	2.127	0.000	0.000	0.000	0.000
Freundlich isotherm	Cd(II)	6.217	2.220	4.410	0.485	4.210
	Cu(II)	8.294	2.736	7.431	0.594	4.201
	Ni(II)	3.971	0.852	2.196	0.198	2.116
	Pb(II)	5.818	2.154	3.680	0.331	4.025
	Zn(II)	6.002	1.457	3.819	0.306	3.064
	Cr(III)	1.578	0.196	0.387	0.035	0.995
Temkin isotherm	Cd(II)	High	High	High	High	High
	Cu(II)	198.1	High	High	High	High
	Ni(II)	184.2	High	High	High	High
	Pb(II)	High	High	High	High	High
	Zn(II)	High	High	High	High	High
	Cr(III)	41.76	High	High	High	High
R-P isotherm	Cd(II)	16.17	High	High	94.50	High
	Cu(II)	25.63	High	High	114.1	High
	Ni(II)	38.02	High	High	High	High
	Pb(II)	32.63	High	High	High	High
	Zn(II)	10.91	High	High	43.77	High
	Cr(III)	28.31	High	High	153.3	High
Sips isotherm	Cd(II)	41.33	High	High	High	High
	Cu(II)	28.85	High	High	146.5	High
	Ni(II)	18.14	High	High	196.4	High
	Pb(II)	66.66	High	High	High	High
	Zn(II)	19.06	High	High	69.94	298.7
	Cr(III)	26.87	High	High	143.9	High

4. Conclusions

Rice husk shows microporous characteristics toward adsorption. Among the six isotherms tested for the validity of six heavy metal ions, namely Cd(II), Cr(III), Cu(II), Pb(II), Ni(II) and Zn(II), for adsorption behavior, the best fitted model is the Langmuir isotherm, followed by Redlich-Peterson, Sips, Temkin and Freundlich based on regression analysis. The error analysis based on average relative error (ARE), Sum square error (SSE), Hybrid fractional error function (HYBRID), nonlinear chi-square test and Sum of absolute error (EABS) further supports the validity of the Langmuir isotherm as compared to others. The adsorption capacity of the six metal ions follows order of Pb(II) > Cd(II) > Cu(II) > Ni(II) > Zn(II) > Cr(III) according to the Langmuir isotherm having 5000 mg kg⁻¹ for Pb(II) under the optimized conditions employed.

References

- [1] J.O. Nriagu, "A History of global metal pollution", *Science*, 272., 223-224., 1996.
- [2] W. Saikaew and P. Kaewsam, "Cadmium ion removal using biosorbents derived from fruit peel wastes", *Songklanakarin Journal of Science and Technology*, 31(5)., 547-554., 2009.
- [3] R.S.D. Castro, L. Caetano, G. Ferreira, P.M. Padilha, M.J. Saeki, L.F. Zara, M.A.U. Martines and G.R. Castro, "Banana peel applied to the solid phase extraction of copper and lead from river water: Pre concentration of metal ions with a fruit waste", *Industrial Engineering Chemistry Research*, 50., 3446-3451., 2011.
- [4] C.V.R Murthy, P. Ramesh and A. Ramesh, "Study of biosorption of Cu(II) from aqueous solutions by coconut shell powder", *Chemical Sciences Journal*, 3., CSJ 17., 2012.
- [5] K. Gopalakrishnan, V. Manivannan and T. Jayadoss, "Comparative study on biosorption of Zn(II), Cu(II) and Cr(VI) from textile dye effluent using sawdust and neem leaves powder", *E-Journal of Chemistry*, 7., S504-S510., 2010.
- [6] A. Yoshita, J.L. Lu, J.H. Ye and Y.R. Liang, "Sorption of lead from aqueous solutions by spent tea leaf", *African Journal of Biotechnology*, 8(10)., 2212-2217., 2009.
- [7] Y.S. Ho, J.F. Porter and G. Mckay, "Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component system", *Water, Air and Soil Pollution*, 141., 1-33., 2002.
- [8] A.O. Dada, A.P. Olalekan, A.M. Olatunya and O. DADA, "Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk", *Journal of Applied Chemistry*, 3., 38-45., 2012.
- [9] A. Kumar, K. Mohanta, D. Kumar and O. Parkash, "Properties and industrial applications of rice husk: A review", *International Journal of Emerging Technology and Advanced Engineering*, 2., 86-90., 2012.
- [10] H.I. Chieng, L.B.L. Lim, N. Priyantha and D.T.B. Tennakoon, "Sorption characteristics of peat of Brunei Darussalam III: Equilibrium and kinetics studies on adsorption of crystal violet (CV)", *International Journal of Earth Science and Engineering*, 6., 791-801., 2013.
- [11] L.S. Chan, W.H. Cheung, S.J. Allen and G. McKay, "Error Analysis of adsorption isotherm models for acid dyes onto bamboo derived activated carbon", *Chinese Journal of Chemical Engineering*, 20., 535-542., 2012.
- [12] H. Matt, "Synthesis and modification of micro and mesoporous materials as CO₂ adsorbents", *Universiti Teknologi Malaysia*, 2006.
- [13] S. Lowell and J.E. Shields, "Adsorption isotherms", *Powder Surface Area and Porosity*, 11-13., 1984.
- [14] L.T. Arenas, E.C. Lima, A.A.D.Santos. J.C.P. Vaghetti, T.M.H. Costa and E. V. Benvenuto, "Use of statistical design of experiments to evaluate the sorption capacity of 1,4-diazoniabicyclo[2.2.2]octane/silica chloride for Cr(VI) adsorption", *Colloids and Surfaces*, 297., 240-248., 2007.
- [15] YanLiang-HSAB-SSA2011poster.pdf, [Online]. Available: <http://img.docstoccdn.com/thumb/orig/111069073.png>.