Kinetic and Equilibrium Studies for Zn (II) and Cu (II) Metal Ions Removal Using Biomass (Rice Husk) Ash

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(Received on 19th April 2010, accepted in revised form 30th July 2010)

Summary: Heavy metal ions have the severe hazardous effects on human health even were present in traces in waste water. Conventional methods are not economical for the removal of low level concentration of these ions. The present research reports the adsorption of Cu and Zn ions from aqueous solutions at low concentration range (5-100 mg/L) in batch systems using Rice Husk Ash as an adsorbent, which is abundantly available as agricultural waste. The present study emphasizes on the experimental development of the optimum parameters such as equilibrium time, pH and initial concentration. Equilibrium data obtained have been fitted to the Langmuir, Freundlich, Tempkin and Dubinin - Radushekevich (DR) adsorption isotherms. Freundlich isotherm best fits the experimental results. Kinetic modeling of first order and pseudo-second order showed that the pseudo-second order equation was the most appropriate for the description of Zn (II) and Cu (II) adsorption by Rice Husk Ash.

Introduction

As a consequence of industrial development increased level of environmental contamination is posing a very serious threat to the global environment. Industrial processes for extracting metals or, more generally, all processes involving metals in their productive cycle create significant heavy metal cations [1]. Metal industries, refining, mine drainage, electroplating, dye and leather industries, landfill leachate, domestic effluents, and agricultural run off, all produce wastewater that contains heavy metal ions [2]. The presence of these heavy metals in the environment has created a number of environmental problems such as threats to public health and or affects the aesthetic quality of potable water. According to World Health Organization (WHO), the metals of most immediate concern are chromium, copper, zinc, iron, cadmium, and lead.

Due to their accumulation through food chain and persistence in nature, it is necessary to remove these toxic heavy metals from wastewater. Metals are non-biodegradable, toxic, and have great environmental, public health and economic impacts [3]. Zinc and copper are considered as essential element for life and act as micronutrient when present in trace amounts. These are reported to be toxic beyond permissible limits. Symptoms of zinc toxicity include muscular stiffness, loss of appetite, irritability and nausea. The metal is further reported to be bio-accumulated into flora and fauna creating ecological problems. Zinc is present in high concentration in wastewater of pharmaceutical, galvanizing, paint, pigment, insecticide, cosmetic industries [4]. Copper is found in diverse industrial activities such as electrical industry, alloys, algaecides, chemical catalysis and metal surface finishing that causes serious problem to the environment [5]. Its presence in humans can cause vascular injury and hemolytic anemia, resulting in severe kidney and liver damage [6]. EPA recommended level of zinc for the surface water discharge effluent is 2 mg/L and for copper this limit is 0.5 mg/L [7].

In order to solve the problems of heavy metal pollution in the ecosystem, it is important to find realistic solutions for the issue. There are several methods for treatment of metal-contaminated effluents such as precipitation, ion exchange, membrane processes and adsorption. Since the selection of wastewater treatment methods is based on the concentration of waste and the cost of treatment, adsorption is often the method of choice for removal of heavy metals from wastewater [8]. Furthermore, to enhance the cost effectiveness of the adsorption process for heavy metal treatment, various agricultural by-products have been developed as low cost sorbents. Utilization of one waste material to control pollution caused by another is of high significance in the remediation of environmental problems. Rice husk, an abundantly available agricultural waste, can be used as a low cost adsorbent for dyes [9] and metals like Lead, Mercury, Cadmium and Nickel [10-13].

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Possible utilization of Rice Husk Ash as an adsorbent for Zn (II) and Cu (II) ions from synthetically prepared aqueous solutions has been investigated in this study [14]. Focus of this paper is to find equilibrium time, optimum initial pH and effect of initial concentration of metal ion on the adsorption of Zn (II) and Cu (II) ions on Rice Husk Ash. The rate kinetics, adsorption isotherm models and their parameters were investigated to know the adsorption behavior.

Theoretical Fundamentals

Adsorption Kinetics

To predict the time to achieve the equilibrium state of sorption and to establish the mechanism, knowledge of the rate equations is required [14]. The rate kinetics of Zn (II) & Cu (II) on RHA was analyzed using two different kinetic models.

i) First - Order - Rate Kinetic Model

First order rate kinetic model proposed by Lagergren [15] is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t \qquad (1)$$

where q_e (mg/g) is the mass of solute adsorbed at equilibrium, q_t (mg/g) is mass of solute adsorbed at any time 't' and K_{ad} (min^{-1}) is the equilibrium rate constant of pseudo - first order adsorption. Values of K_{ad} and q_e are determined by slope and intercept of the plot of log (q_e - q_t) versus t.

ii) Pseudo Second - Order - Rate Kinetic Model

The pseudo-second order model leads to the following equation [14]:

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

where, k (g/mg.min) is the pseudo-second order rate constant. Value of q_e is determined by slope of the plot of t/q_t versus t.

Adsorption Isotherms

The isotherms are important and basic requirement for the analysis of adsorption systems, further more isotherms are used for design purposes [16]. A series of experiments were performed to evaluate the biosorption capacity of rice husk ash and further verified by using the Freundlich, Langmuir, Tempkin and Dubinin - Radushkevich (DR) isotherms.

i) Freundlich Isotherm

The Freundlich isotherm model is based on the assumptions that sorption takes place onto a heterogeneous surface, sorption sites are distributed exponentially with respect to heat of sorption. The Freundlich isotherm equation is given as [17]:

$$q_e = k_F C_e^{\frac{1}{n}} \qquad (3)$$

Equation (3) can be linearized as in equation (4):

$$\ln(q_e) = \ln(k_F) + \frac{1}{n}\ln(C_e) \qquad (4)$$

where, q_e (mg/g) equilibrium capacity of sorption, C_e (mg/L) equilibrium concentration of metal ions, k_F coefficient provides an indication of the sorption capacity and n coefficient related to intensity of sorption.

ii) Langmuir Isotherm

The Langmuir isotherm model is based on the assumptions that sorption takes place onto a homogeneous surface, all sites possess equal affinity for the sorbate. The Langmuir isotherm equation is given as [18]:

$$q_e = \frac{q_{max} C_e}{1 + b_L C_e} \qquad (5)$$

Equation (5) can be linearized as in equation (6):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b_L} + \frac{C_e}{q_{max}} \qquad (6)$$

where, q_e (mg/g) equilibrium capacity of sorption, C_e (mg/L) equilibrium concentration of metal ions, q_{max} (mg/g) maximum sorption capacity and b_L (L/mg) constant related to affinity and energy binding sites.

iii) Tempkin Isotherm

The Tempkin isotherm model is based on the assumption that heat of sorption decreases linearly with the coverage of sorbent due to sorbate -

sorbate interaction [19]. Tempkin isotherm equation is given as [20]:

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) \qquad (7)$$

Equation (7) can be linearized as in equation (8):

$$q_e = \frac{RT}{b_T}\ln(K_T) + \frac{RT}{b_T}\ln(C_e) \qquad (8)$$

where, q_e (mg/g) equilibrium capacity of sorption, C_e (mg/L) equilibrium concentration of metal ions, K_T (L/mg) equilibrium binding constant corresponding to maximum binding energy, R (8.134 x 10^{-3} kJ/mol K) universal gas constant, T (K) temperature and b_T (kJ/mol) constant related to heat of sorption.

iv) Dubinin - Radushkevich (DR) Isotherm

The Dubinin - Radushkevich (DR) isotherm model is based on the assumption that the characteristics of sorption curves relate to the sorbent. The Dubinin - Radushkevich (DR) isotherm equation is given as [21]:

$$q_e = q_D \exp(-B_D[RT\ln(1+\frac{1}{C_e})]^2) \qquad (9)$$

Equation (9) can be linearized as in equation (10):

$$\ln(q_e) = \ln(q_D) - 2B_D RT\ln(1+\frac{1}{C_e}) \qquad (10)$$

The mean energy of sorption, calculated by equation (11):

$$\mathrm{E} = \frac{1}{\sqrt{2\mathrm{B_D}}} \qquad (11)$$

where, q_e (mg/g) equilibrium capacity of sorption, C_e (mg/L) equilibrium concentration of metal ions, q_D (mg/g) sorption capacity, B_D (mol^2/kJ^2) constant related to the sorption energy, R (8.134 x 10^{-3} kJ/mol K) universal gas constant, T (K) temperature and E (kJ/mol) mean energy of sorption.

Results and Discussions

i) Effect of Initial pH

The removal efficiency for Zn (II) and Cu (II) ions as function of hydrogen ion concentration was examined over pH range 1.5 to7.5 and shown in Fig. 1. It is evident from the Fig. 1 that the adsorption of metal ions increases with an increase in pH. Up to pH 3, the adsorption increases gradually, which, however, at pH > 3 increases drastically. For Zn (II) maximum 73% removal was obtained at a pH value of 5.56. And for Cu (II) ions maximum 94% removal was achieved at pH 4.8. These values were actually the pH of metal ion salt solution alone, where no acid or base was added in it. These points were found to be the optimum values of initial pH of solution.

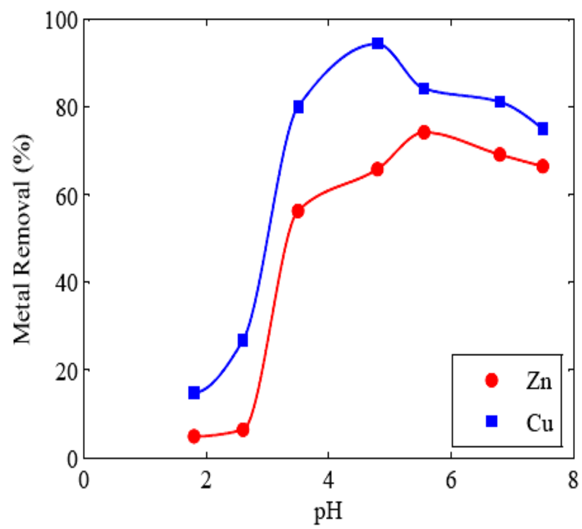

Fig. 1: Effect of initial pH of the solution on metal ions removal (%); Initial metal ion concentration = 100 mg/L, adsorbent dosage = 10g/L, contact time (Zn) = 100 min, contact time (Cu) = 60 min, temperature = 30 $^{\circ}$C.

The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, due to high positive charge density and due to protons on the surface sites, during uptake of metal ions electrostatic repulsion will be high, resulting in lower removal efficiency. Electrostatic repulsion decreases with increasing pH due to reduction of positive charge density on the sorption sites; thus an enhancement of metal adsorption is noted. Effect of pH on adsorption also has been reported by several earlier workers [22]. At higher pH values OH^- ions compete for Zn (II) with the active sites on the surface of the adsorbents [23].

ii) Effect of Initial Metal Ion Concentration

The adsorption uptake of Zn (II) and Cu (II) ions was examined for initial metal ion concentration range 5 to 100 mg/L and shown in Fig. 2. An increase in the initial concentration of Zn (II) and Cu (II) ions leads to increase in the adsorption capacity of these ions by RHA. The initial concentration provide the necessary driving force to overcome the resistance to mass transfer of adsorbent between aqueous and solid phases.

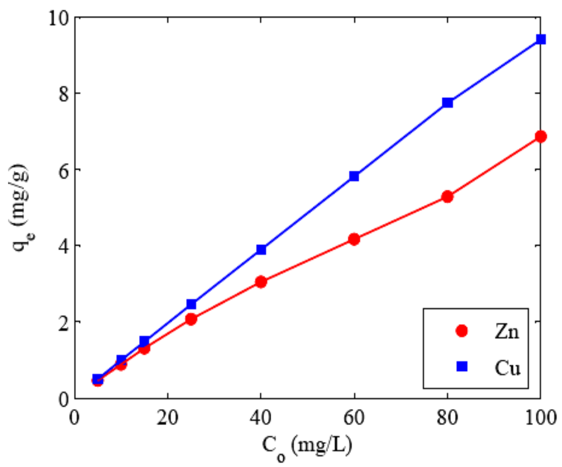

Fig. 2: Effect of Initial Metal Ion Concentration on Metal Uptake of Adsorbent; Adsorbent dosage=10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8, contact time (Zn) = 100 min, contact time (Cu) = 60 min.

iii) Effect of Contact Time

The uptake of Zn (II) and Cu (II) ions were studied over a time range 10 to 180 minutes and the effect of contact time on removal efficiency presented in Fig. 3.

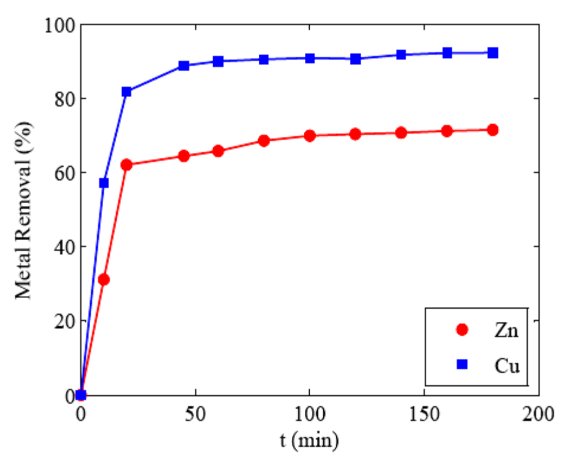

Fig. 3: Effect of contact time on removal of Zn (II) and Cu (II) ions by RHA; Initial metal ion concentration=100 mg/L, adsorbent dosage=10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8.

It was observed that almost 70% Zn (II) ions removed in first 100 minutes and concentration of filtrate remain constant with slight change of 1to2% more removal of Zn (II) ions for next 100 minutes. For the case of Cu (II) ions removal, 90 % ions were removed in first 60 minutes. So 100 minutes for Zn (II) ions and 60 minutes for Cu (II) ions is assumed to be sufficient to attain the equilibrium.

iv) Kinetics Study

Linear plots of the First-order, pseudo-second -order and intra -particle diffusion kinetic models for adsorption of Zn (II) and Cu (II) on RHA are shown in Fig. 4-6 and parameters of these models are given in Table-1.

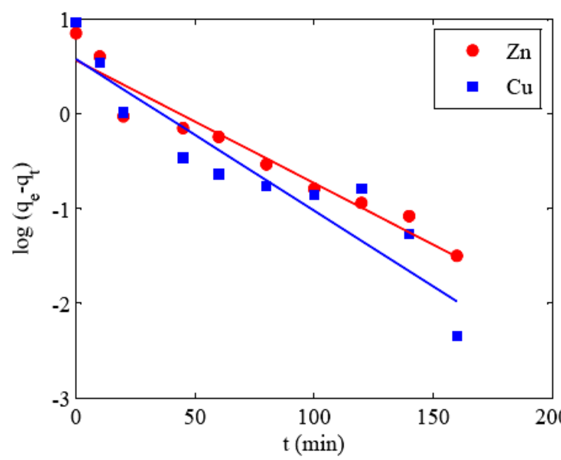

Fig. 4: 1st order rate Kinetics plot for adsorption of Zn (II) and Cu (II) by RHA Initial metal ion concentration=100 mg/L, adsorbent dosage=10g/L, pH of solution (Zn) =5.5, pH of solution (Cu) = 4.8.

Table-1: Adsorption rate constants by kinetic equation.

Kinetic Model	Zn (II)		Cu (II)	
First order	K_{ad}	R^2	K_{ad}	R^2
	0.0297	0.9438	0.0355	0.8638
Second order	k	R^2	k	R^2
	0.0156	0.9983	0.0271	0.9995

First - Order - Rate Kinetic Model

Fig. 4 shows the plot of t (min) versus log (q_e - q_t) for adsorption of Zn (II) and Cu (II) by RHA and its slope is used to evaluate the rate constant K_{ad} (Table-1). The non-linearity of plot and poor values of correlation coefficient indicates that 1st order mechanism is not followed in the process.

Pseudo Second - Order - Rate Kinetic Model

Linear plot of t versus t/q_t (Fig. 5) was used to determine the rate constants and correlation coefficients. For both Zn (II) and Cu (II) ions adsorption the values of correlation coefficients of all the examined data, were found very high (R^2>0.99). These values are given in Table-1. The rate constant k obtained from slope of plot of t versus t/q_t , for Cu (II) 0.0271 (mg/g min) > Zn (II) 0.0156 (mg/g min). This observation showed that Cu (II) ions adsorption takes place at higher rate than that for the Zn (II) ions.

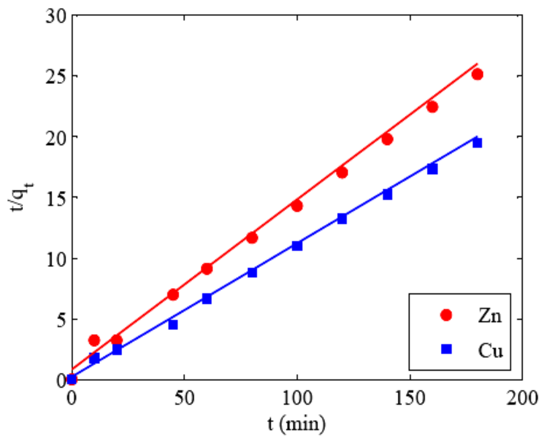

Fig. 5: Pseudo second - order plot for Zn (II) and Cu (II) ions adsorption by RHA Initial metal ion concentration = 100 mg/L, adsorbent dosage = 10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8.

The values of equilibrium uptake of metal ions q_e is obtained by intercept of plot, for Cu (II) it is 9.948 mg/g and for Zn (II) ions it is 7.528 mg/g, are similar to those obtained experimentally.The applicability of pseudo-second order kinetics model suggests that adsorption of Zn (II) and Cu (II) ions on RHA was based on chemisorption or metal complexation process [14]. Most favorable mechanism is the formation of complex by bonding of metal ion with the Silanol group present at the surface of silica [24].

$$M^{n+} + x(-SiOH) \Leftrightarrow M(-SiO)_x^{(n-x)+} + xH^+$$

v) Adsorption Isotherm

Linear plots of the Freundlich, Langmuir, Tempkin amd Dubinin - Radushkevich (DR) models for adsorption of Zn (II) and Cu (II) on Rice Husk Ash (RHA) are shown in Fig. 6 to 9 and parameters of these models are given in Table-2.

Freundlich Isotherm

The 1/n and k_F are slope and intercept of the plots ln (C_e) versus ln (q_e) (Fig. 6), the values of n_F and k_F are given in Table-2. The value of 1/n < 1, for both metal ions indicates favourable adsorption. For higher k_F value sorption intensity will be higher. Therefore, RHA is 4.7057 times good sorbent for Cu (II) with respect to Zn (II) as k_F for Cu (II) is 3.9843 and Zn (II) is 0.8467. The Freundlich isotherm best fitted for adsorption of Zn (II) and Cu (II) on RHA with corelation coefficient R^2 0.9941 and 0.9914, respectively.

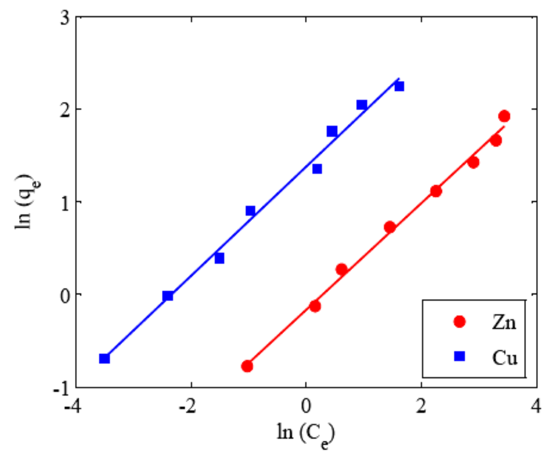

Fig. 6: Freundich plot for adsorption of Zn (II) and Cu (II) ions by RHA Adsorbent dosage = 10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8, contact time (Zn) = 100 min, contact time (Cu) = 60 min.

Table-2: Adsorption isotherms parameters and correlation coefficients.

Isotherms	Zn (II)			Cu (II)		
Freundlich	k_F	n	R^2	k_F	n	R^2
	0.8467	1.7341	0.9941	3.9843	1.6957	0.9914
Langmuir	q_{max}	b_L	R^2	q_{max}	b_L	R^2
	7.7221	0.0975	0.8995	11.5191	0.7433	0.9214
Tempkin	b_T	K_T	R^2	b_T	K_T	R^2
	1.9198	1.9268	0.8728	1.4292	18.9575	0.8730
Dubinin-Radushkevich (DR)	q_D	B_D	R^2	q_D	B_D	R^2
	4.2961	0.3836	0.8566	8.5197	0.1704	0.9592

Langmuir Isotherm

The plots of C_e versus C_e/q_e for Zn (II) and Cu (II) are shown in Fig. 7 and the linear isotherm parameters q_{max}, b_L and the correlation coefficient are given in Table-2. The maximum sorption capacity q_{max} of Cu (II) 11.5191 mg/g > Zn (II) 7.7221 mg/g showed that the RHA have greater ability to adsorb Cu (II).

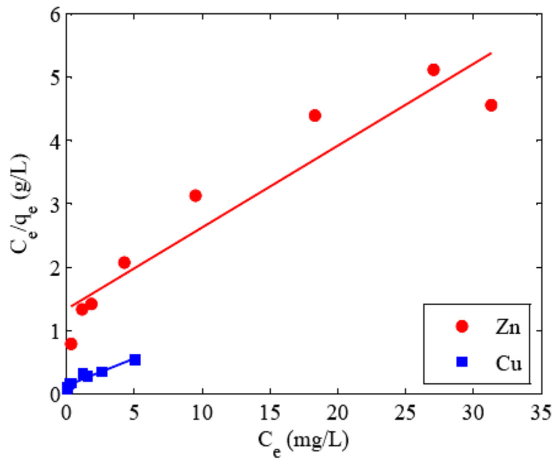

Fig. 7: Langmuir plot for adsorption of Zn (II) and Cu (II) ions by RHA Adsorbent dosage=10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8, contact time (Zn) = 100 min, contact time (Cu) = 60 min.

Tempkin Isotherm

The plots of ln (C_e) versus q_e for Zn (II) and Cu (II) are shown in Fig. 8 and the linear isotherm parameters b_T, K_T and the correlation coefficient are given in Table-2. The b_T constant related to heat of sorption for the Zn (II) is 1.9198 kJ/mol and Cu (II) is 1.4292 kJ/mol, therefore the K_T equilibrium binding constant of Cu (II) > Zn (II), indicating a lower biomass metal ion potential for Zn (II).

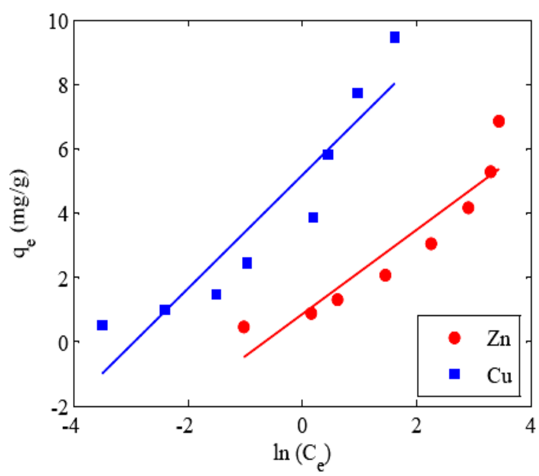

Fig. 8: Tempkin plot for adsorption of Zn (II) and Cu (II) ions by RHA Adsorbent dosage=10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8, contact time (Zn) = 100 min, contact time (Cu) = 60 min.

Dubinin - Radushkevich (DR) Isotherm

The plots of RT ln(1+1/C_e) versus ln(q_e) for Zn (II) and Cu (II) are shown in Fig. 9 and the linear isotherm parameters q_D, B_D and the correlation coefficient are given in Table-2. The sorption affinity of the RHA for Zn (II) and Cu (II) are 4.2961 mg/g and 8.5197 mg/g respectively, indicating that the RHA have a greater affinity for Cu (II). The constant related to heat of adsorption B_D for Zn (II) and Cu (II) is 0.3836 mol^2/kJ^2 and 0.1704 mol^2/kJ^2 respectively, further which gives mean energy 1.1417 kJ/mol and 1.7131 kJ/mol, respectively.

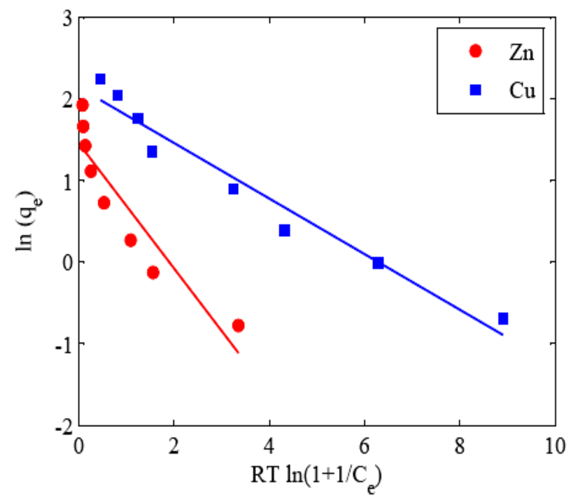

Fig. 9: Dubinin – Radushkevich (DR) plot for adsorption of Zn (II) and Cu (II) ions by RHA Adsorbent dosage=10g/L, pH of solution (Zn) = 5.5, pH of solution (Cu) = 4.8, contact time (Zn) = 100 min, contact time (Cu) = 60 min.

Experimental

Rice Husk Ash (RHA)

Rice Husk Ash samples for experimentation were collected with 90% silica content which was prepared by heating rice husk at 575 ˚C for 120 min in muffle furnace.

Reagents

All analytical grade chemical reagents, used in this study, were ZnSO4.7H2O (Merck), CuSO4.5H2O (Merck), 0.1N H2SO4 (95to98%, Merck), 0.1N NaOH (Merck), Cu (II) and Zn (II) atomic absorption spectrometry standard solution (1000mg/L) (Fluka Chemicals).

Batch Adsorption Studies

500 mL solution having 100 mg/L concentration of Zn (II) or Cu (II) ions was prepared and Initial pH of the solution was adjusted with the help of 0.1N HCl / 0.1N NaOH aqueous solution without any further adjustments during the experiments. 10 samples of 50 mL solution were taken in ten 250 mL flasks containing fixed adsorbent dose of 10g/L. These flasks were agitated at a constant rate of 200 rpm in a temperature controlled orbital shaker maintained at 30 ±1 ^{o}C temperatures. One of the sample flasks was withdrawn from orbital shaker after fixed time intervals (10, 20, 40, 60, 80, 100, 120, 140, 160, 180 min) and analyzed for remaining metal ions present in the adsorbate solution. RHA was separated from aqueous solution by filtration through Whatman No. 40 filter paper. The concentration of the Zn (II) and Cu (II) in solution samples were analyzed by using a "Shimadzu 6800 Atomic Absorption Spectrophotometer" equipped with an air - acetylene flame.

The metal removal (%) or removal efficiency of metal ion is evaluated by using the equation:

$$\text{Metal Removal (\%)} = \left(\frac{C_o - C_t}{C_o}\right)100 \qquad (12)$$

The amount of metal adsorbed q_t (mg/g) is calculated by the formula:

$$q_t = \frac{(C_o - C_t)V}{w} \qquad (13)$$

where, Co and C_t are initial ions concentration and concentration of ions at any time't', while V is volume of solution in litters and w is adsorbent dosage in g/L.

Effect of Initial pH

In order to establish the effect of pH on the adsorption of Zn (II) and Cu (II) ions onto RHA, batch equilibrium studies at different initial pH values of the solution were carried in the range 1.5 to 7.5 pH of the adsorbate solution was varied by the addition of 0.1N H_2SO_4 and 0.1N NaOH. Adsorbent dose of 10 g/L was contacted with 100 mg/L of metal ion solution at temperature 30±1 ^{o}C. The mixture was agitated on orbital shaker at 200 rpm for 100 min in case of Zn (II) solution and for 60 min for Cu (II) solution. 50mL solution volume was used.

Effect of Initial Metal Ion Concentration

The uptake of Zn (II) and Cu (II) ions by RHA was affected by the initial metal ion concentration. Concentration of metal ions were increased from 5 mg/L to 100 mg/L at constant pH 5.5 for Zn (II) and 4.8 for Cu (II), adsorbent dosage level was same for all experiments, i.e., 10 g/L and contact time was 100 min for Zn (II) and 60 min for Cu (II) removal.

Conclusion

The present study reports that Rice Husk Ash (RHA) was effective adsorbent for adsorption of Zn (II) and Cu (II) ions from aqueous solution. Adsorption was strongly affected by the parameters such as contact time, initial pH of the solution and initial metal ion concentration. Equilibrium time was 100 min for Zn (II) and 60 min for Cu (II) ions removal. Maximum removal was observed for solutions having initial pH 5.5 for Zn (II) and 4.8 for Cu (II). The adsorption isotherm could be well fitted by Freundlich equation. The kinetics of adsorption for both Zn (II) and Cu (II) was better described with second order kinetics.

Acknowledgement

Authors are thankful to the Department of Chemical Engineering, University of Engineering and Technology, Lahore - Pakistan for providing facilities for carrying out this research.

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