Nature Environment and Pollution Technology *An International Quarterly Scientific Journal*	Vol. 7	No. 4	pp. 763-768	2008

Original Research Paper

Adsorptive Removal of Copper from Aqueous Solution onto Raw Rice Husk: Kinetics and Isotherms

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Key Words:
Heavy metals
Copper
Adsorption
Raw Rice Husk
Langmuir isotherm
Freundlich isotherm

ABSTRACT

The pollution of water with heavy metals has been of great concern due to their toxic nature and other adverse effects. All heavy metals, including those required in small amount for the physiological machinery of living organisms, are extremely toxic at high concentrations. Therefore, heavy metal burden of industrial wastewaters need to be substantially reduced before discharging them into water bodies. Dissatisfaction with conventional methods of metal removal from wastewaters has led to a surge in efforts aimed at finding out suitable alternatives. This work presents the results of study on heavy metals removal from wastewater by adsorption using low cost adsorbents which could be used as an alternative approach to remove heavy metals from wastewater. A series of batch studies were conducted using raw rice husk (RRH) of particle size 300-150 μm mixed with synthetic heavy metal solutions to see the removal of copper metal.

INTRODUCTION

Wastewater discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have a negative effect on the water environment. Electroplating industries are one of the oldest industries concentrating on surface finishing and metal deposition. However, these processes produce metal-contaminated wastewaters. Among these contaminants, copper is an important metal of industrial use and its ingestion beyond the permissible level causes various types of acute and chronic disorders in Man. The industrial sources of copper in the wastewater include pulp and paper mills, fertilizers, petroleum refineries, basic steel work foundries, non-ferrous metal works, motor vehicles, aircraft plating and finishing (Kadirvelu et al. 2001, Chuah et al. 2005). The most widely used method for removing Cu (II) is precipitation as insoluble hydroxide at alkaline pH (7–10) or as sulphides. However, major problem with this precipitation is the disposal of the precipitated cupric hydroxide (Nomanbhay & Palanisamy 2005). Ion-exchange treatment which is the second most widely used method for copper removal does not present a sludge disposal problem and has the advantage of reclamation of Cu (II). However, ion-exchange treatment does not appear to be economical. The adsorption phenomenon has been found economically appealing for the removal of toxic metals from wastewaters. Several adsorbents have been used earlier for the treatment of Cu-rich effluents at the solid-solution interface (Ajmal et al. 2000). Adsorption, using commercial activated carbon (CAC) is an effective purification and separation technique used in industry, especially in water and wastewater treatments that can remove heavy metals from wastewater (Gun et al. 2005). Activated carbon surfaces have a pore size that determine its adsorption capacity, a chemical structure that influences its interaction with polar and non-polar adsorbates, and active sites which determine the type of chemical reactions with other molecules (Ahmedna et al. 2004). However, CAC remains an expensive material for heavy metal removal.

Rice husk is an important agricultural crop residue generated as a by-product during dehusking at rice mills. For every ton of rice processed, rice husk production is estimated to be about 0.23 tons. A large amount of rice husk is burnt *in situ*, generating CO_2 and other forms of pollution. Thus, the use of rice husk not only would provide a less costly sorbent to activated carbon or synthetic ion-exchanger as it is cheap and easily available, but will also save the environment from this pollution. Rice husk contains lots of silica. The organic compounds are mainly cellulose, hemicellulose and lignin. It was reported to be a good sorbent for a variety of metal cations (Kumar & Bandopadhyay 2006). Due to their low cost, after these materials have been expended, they can be disposed off without expensive regeneration.

MATERIALS AND METHODS

Materials: Raw rice husk is obtained from a rice mill in Kattur at Tiruchirappalli. All chemicals used in this study were of analytical reagent grade. The synthetic solutions were prepared using copper sulphate ($CuSO_4.5H_2O$).

Preparation of adsorbents: Raw rice husk used was first washed, dried and then ground to pass through 0.150 mm sieve and retained at 0.075mm (Fig. 1 and Fig. 2).

Methodology: The adsorbent samples were collected from the local rice mills and ground to 150 µm size so that they can be used as a good adsorbent. As the particle size of the adsorbent decrease the specific surface area of the adsorbent increases, which gives up more sites for adsorption. Then the sample was characterized by knowing the physical properties like moisture content, specific gravity, loss due to ignition (ash content), etc. This sample is later mixed with the metal ion solution and the study was done by varying the dosage and contact time.

Batch study: Adsorption studies were carried out by batch process. The mixture of 4 g/L rice husk and copper solution (10mg/L) was mixed well in an orbital shaker at a rate of 150 rpm at 30°C. The final concentration of the mixture was determined by using atomic absorption spectrophotometer. The amount of metal ion removed was calculated by subtracting final concentration and the initial concentration of the solution.

Optimization of contact time: The series of samples was taken with constant adsorbent dosage and kept in the shaker. The samples of the mixture were taken for analysis at various time intervals, i.e, 2, 5, 10, 15, 20, 30, 45, 90, 60, 120, 180, 240 and 300 minutes. The difference between the initial and final concentration gives the amount of metal ions removed. A graph between time and removal efficiency was plotted and the optimum contact time was found. Based on this the kinetics study has been carried out.

Optimization of dosage: The sample was taken with varying dosage and kept in the shaker for constant time period (optimum contact time). Then the sample was taken and analysed for the final concentration of the metal ions and isotherm plots were made.

RESULTS AND DISCUSSION

Physical characteristics: The physical characteristics of the adsorbent like specific gravity, moisture content, loss on ignition was performed and the results are given in Table 1.

Analysis of adsorbate: The synthetic sample prepared was mixed with the adsorbent and kept in shaker at an agitation speed of 150 rpm at a temperature of 30°C. The particle size of the adsorbent used is between 300µm to 150 µm. As discussed earlier, the study was carried out in two stages namely kinetic study (optimization of contact time) and isotherm study (optimization of dosage of the adsorbent).

In order to measure the concentration of copper ion in the solution, a calibration curve was drawn by measuring the absorbance of known concentration of the heavy metal ion solution. By interpreting this curve, the copper concentration of the unknown solution can be found out by measuring the absorbance of the solution. The calibration curve obtained is shown in Fig. 3.

Effect of contact time: The sample was analysed for various time intervals for a total period of 4 hours (Fig. 4). It was found that reaction rate was faster for the first 20 min and as the time progressed the reaction has started to slow down and at 90 min, removal efficiency was 72 %, which remained constant thereafter as the time increased. The optimum removal was obtained at duration of 90 min.

Effect of adsorbent dosage: Effect of dosage of the rice husk on removal of copper is shown in Fig. 5. The initial concentration of copper was kept at 10 mg/L. The amount of adsorbent dose was varied from 0.5 to 22 g/L. Results show that with the increase in adsorbent dosage, the percentage removal of copper also increases up to a certain level and beyond that it is more or less constant. Copper removal of 74% was observed with rice husk at 5 g/L of adsorbent dose at 30°C, and thereafter the percentage reduction was very less.

Kinetic study: Kinetic adsorption experiments were carried out to establish the effect of time on the adsorption process and to determine the rate of adsorption for Cu removal. It was observed that uptake of metal-ion occurred in two stages, i.e., an initial rapid uptake within 15-20 min followed by subsequent slow uptake from 20 to 240 min. Various sorption kinetic models have been used to describe the uptake of metals. The pseudo first-order rate equation by Lagergren and pseudo second-order kinetic models have been used widely.

The pseudo first order rate equation can be written as (Ho 2004):

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

Table 1: Physical characteristic of the adsorbent.

Properties/Adsorbent	Specific Gravity	Moisture Content	Loss of Ignition
Raw Rice Husk	1.47	1.36%	11.1%

Table 2: Adsorption kinetics constants.

Adsorbent	Pseudo First Order			Pseudo Second Order		
	R^2	$Q_e$mg/g	Kg/mg.min	R^2	$Q_e$mg/g	Kg/mg.min
Raw Rice Husk	0.811	0.212	0.053	0.999	0.701	1.205

Table 3: Adsorption Isotherm constants.

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	R^2	$Q_m$mg/g	Kal/mg	R^2	1/n	$K_f$mg/g
Raw Rice Husk	0.943	1.528	0.199	0.954	3.215	0.071

Fig. 1: Raw rice husk from the rice mill.

Fig. 2: Prepared rice husk as adsorbent (300-150µm)

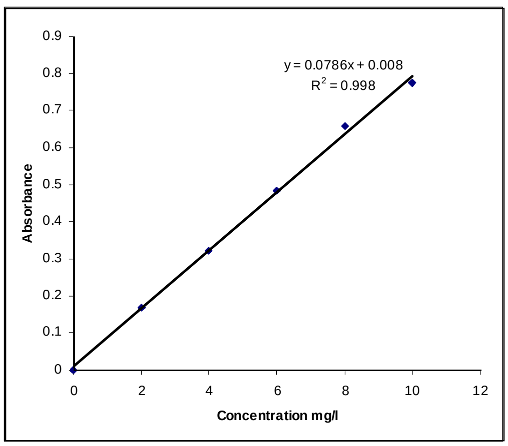

Fig. 3: Calibration curve for copper.

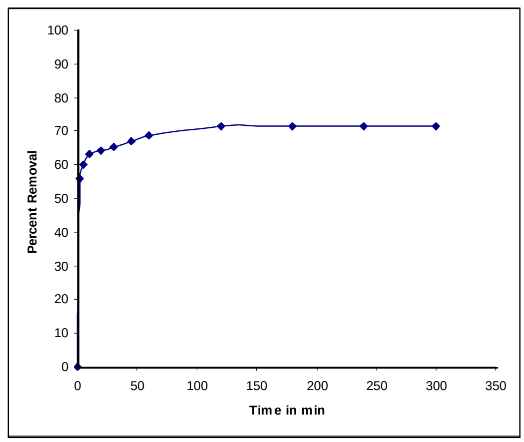

Fig.4: Effect of contact time on the removal of copper by RRH.

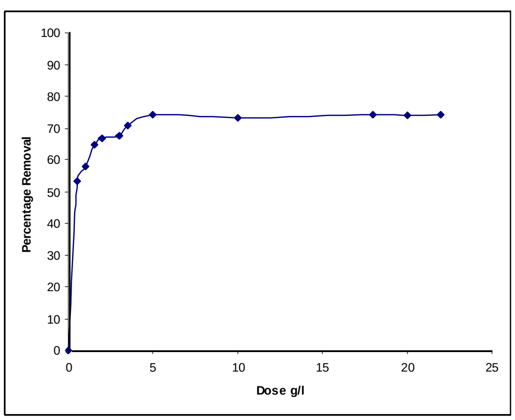

Fig. 5: Effect of dosage on the removal of copper by RRH.

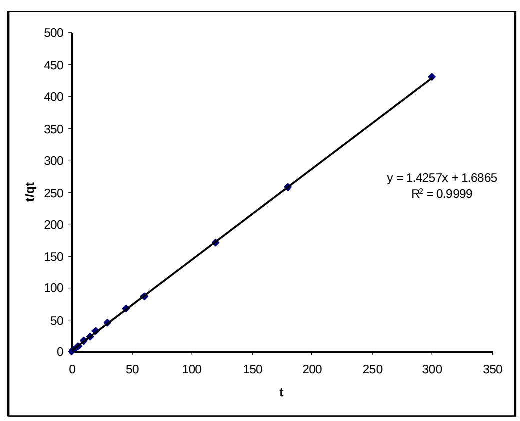

Fig. 6: Pseudo second order sorption kinetics of copper onto RRH.

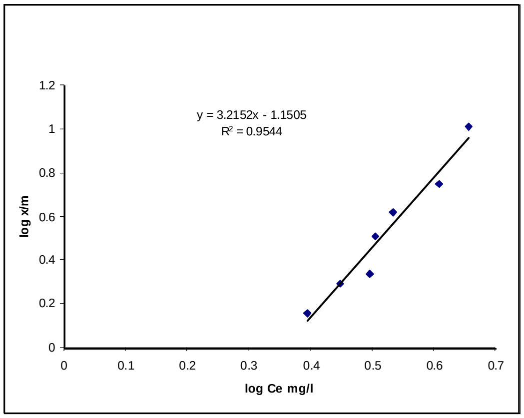

Fig .7: Freundlich isotherm for sorption of copper onto RRH.

Where q_e is the amount of metal ions adsorbed at equilibrium, q the amount of metal ions adsorbed (both in mg/L) at time t (min) and K_{ad} is the rate constant (min^{-1}).

The pseudo second order equation can be written as (Ho 2004):

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

$h_0 = kq_e^2$

Where t is the contact time (min), q and q_e are the quantities of sorbate, sorbed at time t and at equilibrium (mg/g), k is the rate constant (g/mg min) and h_0 is the initial sorption rate (mg/g min).

The results obtained for adsorption of copper onto RRH were fitted in eqs. (1) and (2). It was found that the pseudo second order model fitted better than pseudo first order model for the adsorption of copper on rice husk. The correlation coefficient value of pseudo second order was closer to unity and higher than pseudo first order reaction for RRH. The plot of t/q versus t for the linear second order model is shown in Fig 6. The kinetic parameters calculated are given in Table 2.

Isotherm study: The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm (Feng et al. 2004). The Langmuir and Freundlich isotherms are the equations most frequently used to represent the adsorption from the solution.

The Linear form of Langmuir isotherm can be written as:

$$\frac{1}{q_e} = \frac{1}{K_a Q_m C_e} + \frac{1}{Q_m} \qquad ...(3)$$

Where q_e is the equilibrium sorption capacity (mg/g), C_e is the equilibrium liquid phase concentration (mg/L), Q_m adsorption maximum (mg/g) and the K_a is the sorption equilibrium constant (mg/L).

Freundlich isotherm, which is the earliest known relationship describing the sorption isotherm, can be used in sorption from dilute solutions. Its sorption isotherm can be expressed by following equation:

$$Q_e = K_f C_e^{1/n} \quad ...(4)$$

Where Q_e is the equilibrium sorption capacity (mg/g), C_e is the equilibrium liquid phase concentration (mg/L), K_f is the adsorption capacity (mg/g) and 1/n is the adsorption intensity.

The experimental values are fitted in the eqs. (3) and (4) and a curve is obtained. Based on the correlation coefficient values, it was found that the Freundlich isotherm model fitted better than the Langmuir isotherm model for RRH. The plot of log Ce versus log(x/m) is shown in Fig 7. The correlation coefficient value of 0.954 for RRH is obtained. The values of Q_m, Ka, 1/n and K_f for RRH are given in Table 3.

CONCLUSION

- In this study tests were performed to evaluate the use of RRH as an adsorbent for copper removal and it was found that the optimum contact time for the rice husk was 90 min with the maximum removal efficiency of 72%.
- In the study of adsorption kinetics the pseudo second order model provides a better fit for RRH than pseudo first order model with a regression coefficient of 0.999 respectively.
- In the isotherm study the Freundlich isotherm gives a better fit than Langmuir isotherm for RRH with an adsorption intensity of 3.215 and adsorption capacity of 0.071 mg/g respectively.

ACKNOWLEDGEMENT

The authors thank the Department of Civil Engineering of National Institute of Technology, Tiruchirappalli for providing the facilities to carry out this work.

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