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Cadmium (Cd) Removal from Aqueous Solution Using Microwave Incinerated Rice Husk Ash (MIRHA)

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ABSTRACT

The presence of heavy metals in aquatic systems has become a serious problem. Heavy metals can have adverse effects on the environment as well as on human health. As a result, much attention has been given to new technologies for removal of heavy metal ions from contaminated waters. In this study, Microwave Incinerated Rice Husk Ash (MIRHA), a locally available agricultural waste, was used for the removal of Cd (as a representative heavy metal) from synthetic wastewater by batch adsorption process. The effects of pH, initial metal concentration, and contact time on Cd removal efficiency were studied. pH 4 was found to be the optimum. The removal efficiency was found to be correlated with the initial metal concentration and contact time between adsorbent and adsorbate. Cd adsorption kinetics followed the pseudo-second-order model and implied chemisorption. The adsorption equilibrium of Cd can be well described by the Freundlich isotherm model.

Keywords: Adsorption, Cadmium (Cd), kinetic, isotherm, microwave incinerated rice husk ash (MIRHA)

INTRODUCTION

Environmental contamination with heavy metals arises mainly as a result of industrial activities, although other sources, such as agriculture and waste disposal, are also contributors. These heavy metals are discharged into the atmosphere, water and land-based environments and may reach high concentrations, mainly near discharge sites. Metals can be distinguished from other toxic pollutants as they are non-biodegradable and cannot be converted to a simpler form than the elemental.

Various treatment techniques have been employed for the removal of heavy metals from water; these include precipitation,

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adsorption, ion exchange and reverse osmosis (Fu & Wang, 2011). However, most of the techniques were found to be less effective and possess many drawbacks when applied in the field. Moreover, it is very difficult to select an efficient method for heavy metals removal. Some are effective but economically not feasible and vice versa. Some are not user friendly, not technologically sound, are energy dependent, require post-treatment, need skill manpower, etc. Studies on the treatment of heavy metals bearing effluents have revealed adsorption to be a highly effective technique (Chand *et al*., 1994). Research in recent years has focused on the use of some natural biomaterials including agricultural products and by-products for heavy metals removal. This has been a result of the demand for low-cost treatment technology for heavy metal laden wastewaters. Some agricultural materials can be effectively used as low-cost adsorbents and can accumulate high concentration of heavy metals. Meanwhile, modification of agricultural by-products could enhance their natural capacity and improve their efficiency. Adsorbents generated from these biomass are cost effective and efficient (Kumar, 2006). Previous studies have reported successful removal of heavy metals with many agricultural by-products including oil palm fibre, rice husk, maize cobs, and sawdust (Isa *et al*., 2008; Ghani *et al*., 2007; Chuah *et al*., 2005).

Cadmium (Cd) is a toxic and potentially carcinogenic heavy metal from industry (e.g. battery, electroplating and paints). Exposure to its high concentrations can result in respiratory illness (Mugica *et al*., 2002). "Itai-Itai" is a disease that occurred in Japan due to cadmium toxicity. It affected the bones and joints of old women and resulted in a number of deaths. This study explored the possibility of using microwave incinerated rice husk ash (MIRHA) as an adsorbent for the removal of heavy metals such as Cd. Meanwhile, the influences of various factors, such as pH, contact time and initial Cd concentration on adsorption efficiency, were also studied. Adsorption kinetics and isotherm studies were also included.

MATERIALS AND METHODS

Adsorbent

Rice husk was obtained from BERNAS factory in Kg. Gajah. The husk was thoroughly washed with distilled water to remove dirt and dried at 105 °C for 2 hours until constant weight. Then, it was incinerated at 800 °C for 2 hour in a microwave furnace. Finally, the microwave incinerated rice husk ash (MIRHA) was powdered and stored in desiccators before use. The MIRHA components were determined by X-ray fluorescence (XRF) test. The results obtained are shown in Table 1. MIRHA was found to have high silicon oxide (SiO_2) content (75.8%).

Adsorbate

Cd stock solution of 1000 mg/L was prepared from cadmium chloride ($CdCl_2$). Suitable dilutions were made with distilled water to prepare solutions of pre-decided concentrations for the adsorption study. 1N Hydrochloric acid (HCl) and 1.5N sodium hydroxide (NaOH) solutions were used for pH adjustment.

Table 1: MIRHA characteristics

Item	Percentage	Item	Percentage
O	45.6		
Si	35.4	SiO2	75.8
P	0.849	P2O5	1.94
K	7.98	K2O	9.62
Ca	1.66	CaO	2.33
Fe	1.22	Fe2O3	1.75
Re	3.71	Re	3.71
Mg	-	MgO	-
Al	-	Al2O3	-
S	-	SO3	-
Cl	-	Cl	-
Mn	-	MnO	-
Compton	0.61	Compton	0.61
Rayleigh	1.07	Rayleigh	1.07
Norm.	100	Norm.	100

Experimental Procedures

Batch experiments were conducted by agitating MIRHA in 100 ml synthetic wastewater samples of desired strength and pH at room temperature (27 ± 1 °C) using an orbital shaker operating at 150 rpm. The samples were allowed to settle and filtered through 0.45 μm cellulose acetate membrane filters (Whatman filter) before Cd measurement using an atomic absorption spectrophotometer was carried out. The effect of pH was studied by adjusting the pH (1 to 5) of the test using HCl or NaOH solutions. Two hundred milligram of MIRHA was added into each flask. The flasks were agitated at 150 rpm for 60 minutes on an orbital shaker. The pH was measured using a pH meter. The effect of initial Cd concentration was determined by shaking 100 ml of synthetic wastewater samples of desired concentrations (5, 10, 22, 35, and 50 mg/L) with 200 mg MIRHA at 150 rpm. All samples were adjusted to the optimum pH prior to addition of the adsorbent. The samples were withdrawn from the shaker at pre-determined time intervals (20, 40, 60, 90, 120, 150, 180, 240, and 360 minutes) for analysis.

RESULTS AND DISCUSSION

Effect of Initial pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Nomanbhay & Palanisamy, 2005). Fig.1 shows the effect of pH on Cd removal. As pH rises, the percentage of Cd removed increases considerably from 30% at pH 1 to about 70% at initial pH 4 (optimum). Perez-Marin *et al*. (2007) also reported a similar pH effect on Cd removal using orange waste adsorbent, and found enhanced Cd removal at pH 4 to 6. According to Low *et al*. (1995), at low pH values, the surface of the adsorbent would be closely associated with hydronium ions
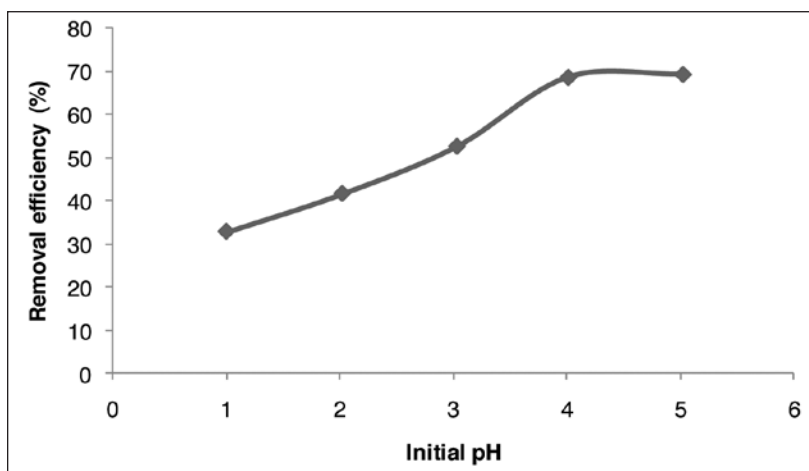
Fig.1: The effect of pH on Cd removal [Cd = 10 mg/L; volume, 100 ml; contact time, 1hr; mixing speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L]

(H_3O^+) which hinders the access of metal ions by repulsive forces to the surface functional groups, and this consequently decreases the percentage of metal removal.

Effects of Initial Cd Concentration and Contact Time

Fig.2 shows the effects of initial Cd concentration and agitation time on its removal at pH 4 (as determined above to be the optimum). Cd removal increased with the increase in agitation time due to greater contact between adsorbent and adsorbate; equilibrium was reached in about 4 hours for all the samples (note that lower initial concentrations reached equilibrium sooner).
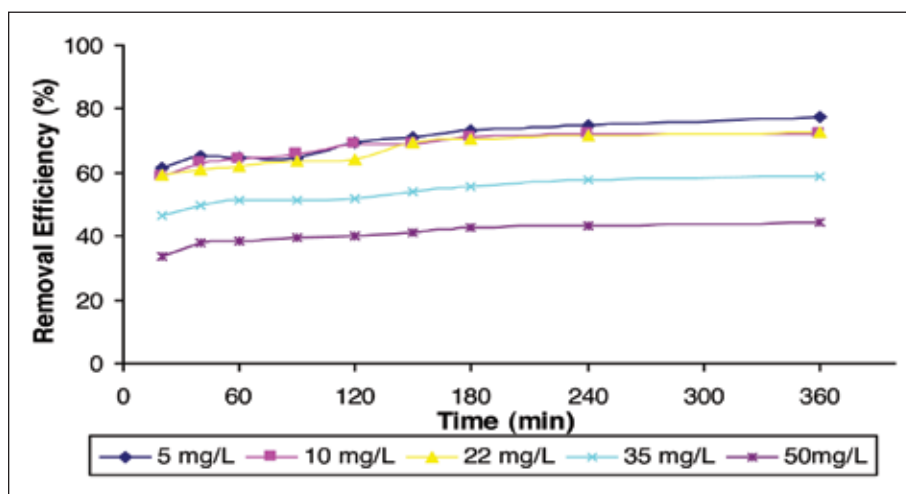

Fig.2: The effects of initial Cd concentration and contact time on Cd removal [pH 4, volume, 100 ml; mixing speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L]

This is quicker than the 6 to 7 hours of equilibrium time obtained by Izanloo and Nasseri (2005) using ground pine cone as an adsorbent for Cd removal. It is also seen that the higher the initial Cd concentration of the sample, the lower its percentage removal will be. A simple mass balance, however, shows that the actual amount of Cd removed increases with the increase in the initial Cd concentration. A higher Cd concentration resulted in a higher concentration gradient which accelerated the diffusion of the adsorbate from the solution into the adsorbent.

Adsorption Kinetics

Pseudo first- and pseudo second-order kinetic models were studied to determine the adsorption mechanism responsible for Cd removal. The models and their linear forms are as follows (Ho & McKay, 1998; Isa *et al.*, 2007):

Pseudo-first order kinetic model,

$$\frac{dq}{dt} = k_1'(q_e - q) \tag{1}$$

$$\log(q_e - q) = \log q_e - \frac{k_1'}{2.303}t \tag{2}$$

Pseudo second-order kinetic model,

$$\frac{dq}{dt} = k_2'(q_e - q)^2 \tag{3}$$

$$\frac{t}{q} = \frac{1}{k_2'q_e^2} + \frac{t}{q_e} \tag{4}$$

where,

q_e	=	the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g)
q	=	the amount of solute adsorbed at time t per unit weight of adsorbent (mg/g)
k_1' and k_2'	=	constants

Fig.3 and Fig.4 show the linear plots of the pseudo first- and pseudo second-order models, respectively. The values of the model constants calculated from these plots are shown in Tables 2 and 3. High the R^2 values (> 0.99) obtained show that Cd removal follows the pseudo second-order kinetic model; implying chemisorption between the adsorbent and adsorbate. Izanloo and Nasseri (2005) also found the pseudo second-order kinetic model to be suitable for describing Cd removal.

Adsorption Isotherms

Adsorption isotherms are important in the modelling procedure for the analysis and design of an adsorption system. Therefore, to correlate the isotherm with the adsorption of Cd, the sorption data were tested against the most commonly used isotherm models, namely, the Langmuir and Freundlich equations.

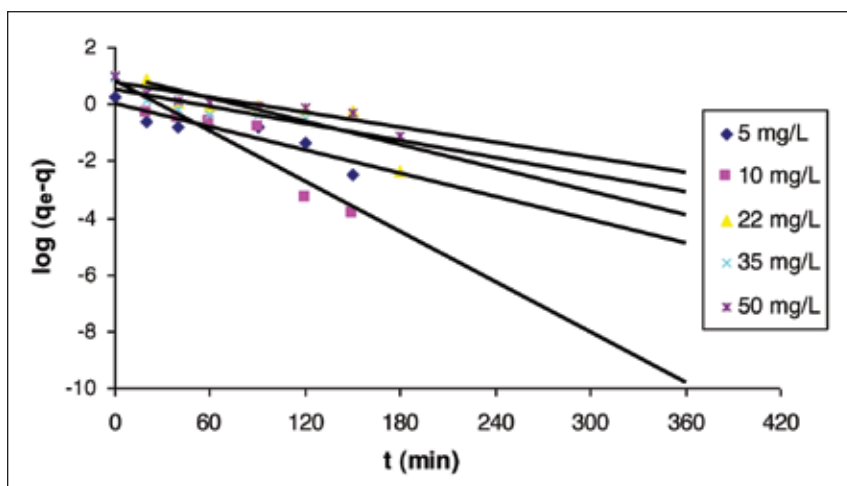The Langmuir equation, derived based on the equilibrium between condensation and

Fig.3: Pseudo first-order kinetic plot for Cd adsorption at different initial concentrations [pH 4; volume, 100 ml; mixing speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L]
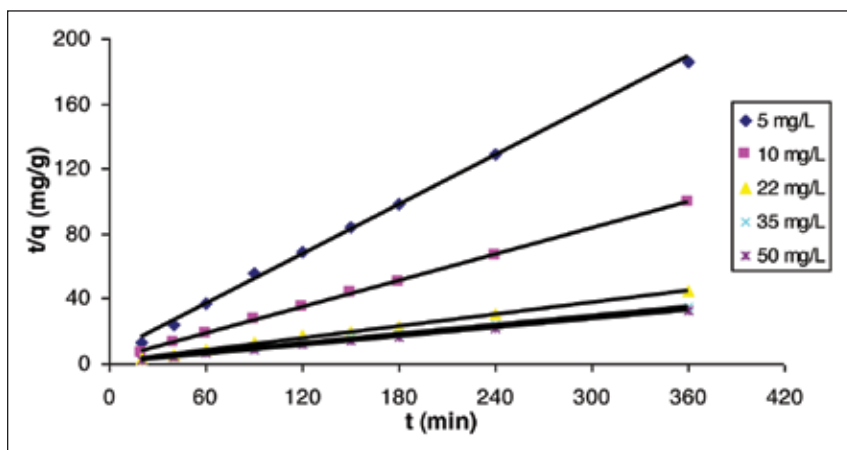

Fig.4: Pseudo second-order kinetic plot for Cd adsorption at different initial concentrations [pH 4; volume, 100 ml; mixing speed, 150 rpm; temperature 27±1 °C; adsorbent dosage, 2g/L]

Table 2: Pseudo first-order reaction rate constant for Cd adsorption

Cd Concentration (mg/L)	k'_1 (min^{-1})	R^2	Equation
5	0.0316	0.8242	$y = -0.0137x + 0.0008$
10	0.0656	0.88	$y = -0.0285x + 0.7032$
22	0.0318	0.6663	$y = -0.0138x + 1.0255$
35	0.0230	0.6925	$y = -0.01x + 0.5107$
50	0.0200	0.8356	$y = -0.0087x + 0.7281$

Table 3: Pseudo second-order reaction rate constant for Cd adsorption

Cd Concentration (mg/L)	$k'_2 \, (min^{-1})$	R^2	Equation
5	0.0389	0.9981	y = 0.5063x + 6.5858
10	0.0334	0.9997	y = 0.2704x + 2.1862
22	0.0109	0.9985	y = 0.122x + 1.3708
35	0.0075	0.9979	y = 0.0946x + 1.1969
50	0.0028	0.9958	y = 0.0896x + 2.9193

Table 4: Isotherm constants and correlation coefficients

Langmuir isotherm coefficients			Freundlich isotherm coefficients		
a	b	R^2	K_f	n	R^2
15.48	2.94	0.3267	1.08	1.29	0.7951

evaporation of adsorbed molecules, considers a monomolecular adsorption layer (Isa *et al.*, 2008) and is represented as:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \qquad (5)$$

where,
x/m = amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)
C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L)
n, a and b are constants

Equation 6 shows the straight line form of the Langmuir model.

$$\left(\frac{C_e}{x/m}\right) = \frac{1}{ab} + \frac{1}{a}C_e \qquad (6)$$

Meanwhile, Freundlich isotherm model and its straight line forms are given below:

$$\frac{x}{m} = K_f C_e^{1/n} \qquad (7)$$

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \qquad (8)$$

where K_f is a constant.

The Langmuir and Freundlich isotherm constants (obtained graphically) for Cd are shown in Table 4. A higher R^2 value obtained with Freundlich isotherm shows that the adsorption of Cd is better fitted with the Freundlich rather than Langmuir model. The maximum adsorption capacity for Cd was 15.48 mg/g. Mahvi *et al.* (2007) also obtained higher R^2 values for Freundlich isotherm when removing Cd.

CONCLUSIONS

The present study showed that MIRHA was capable of removing Cd from aqueous solution. The adsorption of Cd on MIRHA is pH dependent, and with the optimum pH being 4. Meanwhile, the equilibrium time was adopted as 4 h though it varied with the initial concentration of the adsorbate. The adsorption kinetics of Cd followed the pseudo second-order model and implied chemisorption. The adsorption equilibrium of Cd can be well described by Freundlich isotherm model.

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