

THERMODYNAMIC AND KINETIC STUDIES OF CADMIUM ADSORPTION FROM AQUEOUS SOLUTION ONTO RICE HUSK

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Abstract - The adsorption behavior of rice husk for cadmium ions from aqueous solutions has been investigated as a function of appropriate equilibrium time, adsorbent dose, temperature, adsorbate concentrations and pH in a batch system. Studies showed that the pH of aqueous solutions affected cadmium removal with the result that removal efficiency increased with increasing solution pH. The maximum adsorption was 98.65% at solution pH 6, contact time 60 min and initial concentration of 25 mg/L. The experimental data were analysed by the Langmuir, Freundlich and Temkin models of adsorption. The characteristic parameters for each isotherm and related correlation coefficients have been determined. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature. The kinetics of the sorption were analysed using the pseudo-first order and pseudo-second order kinetic models. Kinetic parameters, rate constants, equilibrium sorption capacities and related correlation coefficients for each kinetic model were calculated and discussed. It was shown that the adsorption of cadmium could be described by the pseudo-second order equation, suggesting that the adsorption process is presumably a chemisorption. The rice husk investigated in this study showed good potential for the removal of cadmium from aqueous solutions. The goal for this work is to develop inexpensive, highly available, effective metal ion adsorbents from natural waste as alternative to existing commercial adsorbents.

Keywords: Rice husk; Cadmium; Kinetics; Isotherms; Thermodynamics.

INTRODUCTION

The presence of heavy metals in the environment is a major concern due to their toxicity for many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products and accumulate in living organisms, causing various diseases and disorders (Bailey et al., 1999; Cheung et al., 2001). Therefore, the elimination of heavy metals from water and wastewater is important to protect public health.

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries. Some metals associated with these activities are cadmium, lead, chromium and mercury (Bailey et al., 1999).

Cadmium is widely used and extremely toxic in relatively low dosages, is one of the principal heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood Cells (Drush, 1993). The toxic elements discharged in the effluents will be absorbed and accumulated by microorganisms.

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Eventually, the toxic element will get transferred to humans via the food chain. Human beings have reported nausea and vomiting at a level of 15 mg/L of cadmium, with no adverse effects at 0.05 mg/L (Dezuane 1990). The treatment of cadmium contaminated water is similar to that of many metal contaminated effluents. There are several methods to treat the metal contaminated effluent such as precipitation, ion-exchange, adsorption etc., but the selection of the treatment method is based on the concentration of waste and the cost of treatment (Dezuane, 1990; Peternele et al., 1999; Cheung et al., 2001; Ajmal et al., 2003). In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metal from wastewater and water supplies (Allen and Brown, 1995; Gabaldon et al., 1996; Mahvi et al., 2004).

Activated carbon has been the most used adsorbent; nevertheless, it is relatively expensive (Lopez et al., 1995; Khalid et al., 2000; Mahvi et al., 2004). Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported and the expense of individual sorbents varies depending on the degree of processing required and local availability (Bailey et al., 1999). In general, a sorbent can be assumed to be low cost if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry (Bailey et al., 1999). Activated carbon from cheap and readily available sources such as coal, coke, peat, wood, or rice husk may be successfully employed for the removal of cadmium and other toxic heavy metals from aqueous solutions (Ajmal et al., 2003). Other adsorbents such as wood charcoal, red mud, fly ash, sunflower stalks and petiolar felt-sheath have also been used for the adsorption of cadmium (Namasivayam and Ranganathan, 1995; Marshall and Johns, 1996; Apak et al., 1998; Sun and Shi, 1998; Iqbal et al., 2002; Mahvi et al., 2004).

Plant materials are mainly comprised of cellulose materials that can adsorb heavy metal cations in aqueous medium (Sun and Shi, 1998). The utilization of agricultural waste materials is increasingly becoming a vital concern because these wastes represent unused resources and, in many cases, present serious disposal problems. The aim of this research is to develop inexpensive and effective metal ion adsorbents from plentiful sources of natural wastes (or byproducts) such as rice husk to offer these adsorbents as replacements for existing commercial materials. In the present paper, rice husks were examined for their sorption properties

towards cadmium cations. The influence of several operating parameters for adsorption of cadmium, such as contact time, pH, initial concentration, temperature and adsorbent dose were investigated in the batch mode. The kinetic data were fitted to pseudo-first and pseudo-second-order models and the isotherm equilibrium data were fitted to Langmuir, Freundlich and Temkin models.

EXPERIMENTAL

Adsorbent

The rice husk used was obtained from the village of Ilayangudi, Sivagangai District, Tamilnadu, India. The rice husk was crushed, sieved and stored in plastic bags by size. Then, husks were thoroughly washed with distilled water to remove all dirt and then were dried at 100°C. The dried husks were stored in a desiccator until used. Tables 1 and 2 show the typical composition and chemical analysis of the rice husk and reported values of its physical-chemical characteristics.

Table 1: Typical composition of rice husk

Composition	Percentage
Cellulose	31.12
Hemicellulose	22.48
Lignin	22.34
Mineral ash	13.87
Water	7.86
Extractives	2.33
Chemical analysis of mineral ash	
SiO ₂	93.19
K ₂ O	3.84
MgO	0.87
Al ₂ O ₃	0.78
CaO	0.74
Fe ₂ O ₃	0.58

Table 2: Physical-chemical characteristics of rice husk

Composition	Percentage
Bulk density (g/ml)	0.79
Solid density (g/ml)	1.48
Moisture content (%)	5.98
Ash content (%)	48.81
Particle size (mesh)	200-40
Surface area (m ² /g)	320.9
Surface acidity (meq/g)	0.15
Surface basicity (meq/g)	0.53

Adsorbate

Stock solution of cadmium (100 mg/L) was prepared by dissolving cadmium nitrate in double

distilled water. The concentration range of cadmium prepared from the stock solution varied between 20 to 100 mg/L. All the chemicals used were of analytical reagent grade.

Analysis

The concentrations of cadmium in the solutions before and after equilibrium were determined with a Perkin-Elmer 3100 Atomic absorption spectrometer. The pH of solution was measured with a Hanna pH meter using a combination glass electrode.

Adsorption Experiment

Adsorption experiments were conducted by varying pH, contact time, adsorbent dose, temperature, and adsorbate concentration. The experiments were carried out in 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 mL. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or HCl. The flasks were shaken for the required time period in a water bath shaker. The kinetics study was carried out by agitating 250 mL flasks containing 0.25 g of rice husk and 100 mL cadmium solutions in a water bath shaker. The mixture was agitated at 120 rpm at 25°C. The contact time was varied from 0 to 90 minutes. At predetermined times, the flasks were withdrawn from the shaker and the reaction mixtures were filtered through Whatman GF/A filter paper. For the thermodynamic study, the experiment was performed using 0.25 g rice husks added to 100 mL of cadmium solution in 250 mL flasks. The flasks were shaken at 120 rpm for 60 min at pH 6. The initial cadmium concentration used in this study was 50 mg/L. The isotherm study was performed using various concentrations of cadmium solutions (20 to 100 mg/L). A mixture of 0.25 g of rice husks with 100 mL cadmium solutions of various initial concentrations was shaken at 120 rpm for 60 min at 25°C. The initial pH of the solution was adjusted to 6. All experiments were performed in duplicate. The filtrate samples were analyzed by Atomic absorption spectrometry. The cadmium concentration retained in the adsorbent phase was calculated according to

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations (mg/L) of cadmium solution, respectively; V is the volume (L), and W is the weight (g) of the adsorbent.

RESULTS AND DISCUSSION

Effect of pH

The percentage removal of cadmium by rice husk increased as the pH of the solution increased and reached a maximum value at pH 6. There is also no significant variation in the adsorption capacity between pH 6 and 9, as shown in Fig. 1. Adsorption of cadmium on the adsorbent depends upon the nature of the adsorbent surface and the species distribution of the metal cation. Surface distribution mainly depends upon the pH of the system. The primary metal ion species in the pH range studied are Cd^{2+} and $CdOH^+$ (Elliott et al., 1982). The percent adsorption of metal ion decreased with the decrease in pH, because protons compete with metal ions for sorption sites on the adsorbent surface and because the contaminant decreases the negative charge of the same surface. At higher pH values, the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal removal process. This condition is often not desirable as the metal precipitation could lead to incorrect values of the adsorption capacity. In practice, metal precipitation generally does not produce a stabilized form of heavy metal. The precipitation can sometimes be very small in size and, upon the neutralization of the effluent from the wastewater treatment plant, the solubility of the metals increases, resulting in a re-contamination of the waste outlet stream. It has been reported that the precipitation of cadmium starts at pH 8.3. (Namasivayam et al., 1995; Ajmal et al., 2003).

Effect of Adsorbent Dose

The effect of the adsorbent dose was studied at room temperature (25°C) by varying the sorbent amounts from 0.5 to 3.0 g/L. For all these runs, the initial concentration of cadmium was fixed at 25 mg/L. Fig. 2 shows that the adsorption of cadmium increases rapidly with an increase in the amount of rice husk due to greater availability of the surface area at higher concentrations of the adsorbent. A significant increase in uptake was observed when the dose was increased from 0.5 to 2.5 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. From the results, it is revealed that, within a certain range of initial metal concentration, the percentage of metal adsorption on rice husk is determined by the sorption capacity of the rice husk (Namasivayam and

Ranganathan, 1995; Peternele et al., 1999; Cheung et al., 2001). The maximum removal of cadmium was obtained at the adsorbent dose of 2.5 g/L.

Effect of Contact Time

Adsorption of cadmium was measured at given contact times for the different initial cadmium concentrations from 20 to 100 mg/L. From Fig. 3, the plot reveals that the percent cadmium removal is higher at the beginning; this is probably due to a larger surface area of the rice husk being available at the beginning for the adsorption of cadmium. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. Most of the maximum percent cadmium removal was attained after about 90 min of shaking time at different concentrations. The increasing contact time increased the cadmium adsorption and it remained constant after equilibrium was reached in 60 min for different initial concentrations (Namasivayam and Ranganathan, 1995; Ajmal et al., 2003).

Effect of Initial Concentration

The effect of initial cadmium concentration in the range of 20 to 100 mg/L on adsorption was investigated and is shown in Fig. 4. It is evident from this figure that the percentage cadmium removal decreased with the increase in initial concentration of cadmium. The initial cadmium concentration provides the necessary driving force to overcome the resistances to the mass transfer of cadmium between the aqueous phase and the solid phase. The increase in initial cadmium concentration also enhances the interaction between cadmium and rice husk. Therefore, an increase in initial concentration of cadmium enhances the adsorption uptake of cadmium. This is due to the increase in the driving force of the concentration gradient produced by the increase in the initial cadmium concentration. This results in higher adsorption (Namasivayam and Ranganathan, 1995; Peternele et al., 1999; Mahvi et al., 2004). While the percentage cadmium removal was found to be 98.92% for a 20 mg/L initial concentration, this value was 68.72% for 100 mg/L.

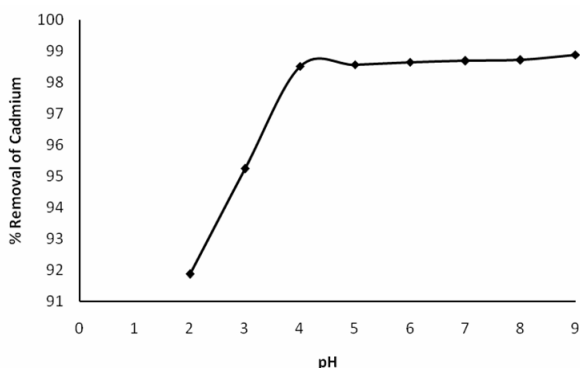


Figure 1: Effect of pH

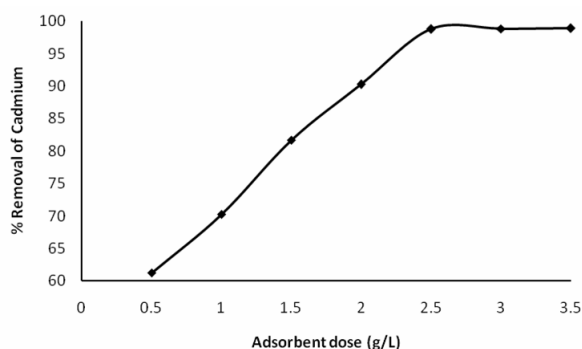


Figure 2: Effect of adsorbent dose

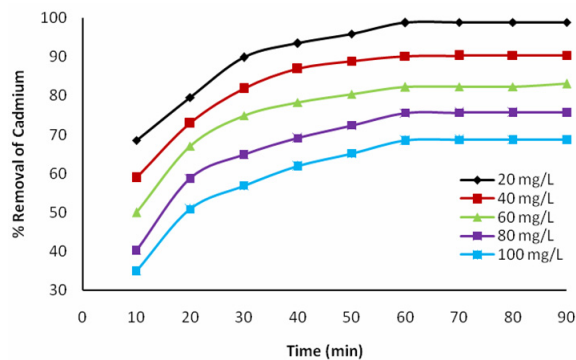


Figure 3: Effect of contact time

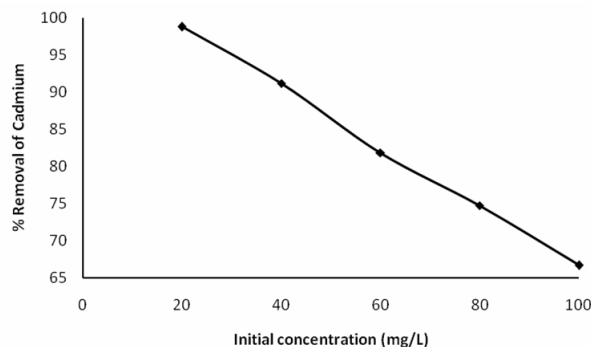


Figure 4: Effect of initial concentration

Effect of Temperature

The adsorption of cadmium on rice husk was investigated as a function of temperature and maximum uptake was obtained at 25°C. Experiments were performed at temperatures of 25, 35, 45 and 55°C for the initial cadmium concentration of 50 mg/L and at constant adsorbent dose of 2.5 g/L and pH of 6. The adsorption decreased from 86.87 to 76.25 % for the initial cadmium concentration of 50 mg/L with an increase in temperature from 25 to 55°C (Fig. 5). This is mainly due to the decreased surface activity, suggesting that adsorption between cadmium and rice husk is an exothermic process.

Thermodynamic Study

Thermodynamic parameters such as the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes during adsorption can be evaluated from the following Equations (2 and 3)

$$K_c = \frac{C_{Ae}}{C_e} \quad (2)$$

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (4)$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium

(mg/L). ΔG° , ΔH° and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH° and ΔS° were determined from the slope and the intercept of the plots of plots of $\log K_c$ versus $1/T$ (Fig. 6). The ΔG° values were calculated using Equation (3). Adsorption of cadmium on rice husk decreased when the temperature was increased from 298 to 328 K as shown in Fig. 5. The process was thus exothermic in nature. The plots were used to compute the values of the thermodynamic parameters (Table 3). The values of the enthalpy change (ΔH°) and the entropy change (ΔS°) found in this work were -20.12 kJ/mol and -51.95 J/mol/K, respectively, for a cadmium concentration of 50 mg/L. The negative ΔG° value indicates that the process is feasible and the adsorption spontaneous in nature. The negative ΔH° value indicates the exothermic nature of adsorption and the value of ΔS° the change in the randomness at the rice husk-solution interface during the sorption.

It has been reported that ΔG° values up to -20 kJ/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG° values more negative than -40 kJ/mol involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) (Horsfall et al., 2004). The ΔG° values obtained in this study for cadmium are <-5 kJ/mol, which indicates that physical adsorption is the predominant mechanism in the sorption process (Abdel Ghani and Elchaghaby, 2007).

Table 3: Thermodynamic parameters for the adsorption of cadmium onto rice husk

Initial Cadmium Concn. (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)			
			25°C	35°C	45°C	55°C
50	-20.12	-51.95	-4.681	-4.415	-3.443	-3.195

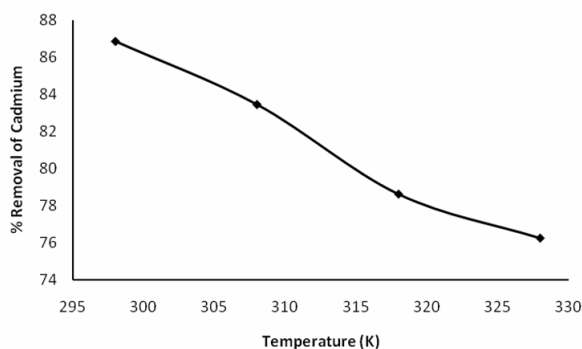


Figure 5: Effect of temperature

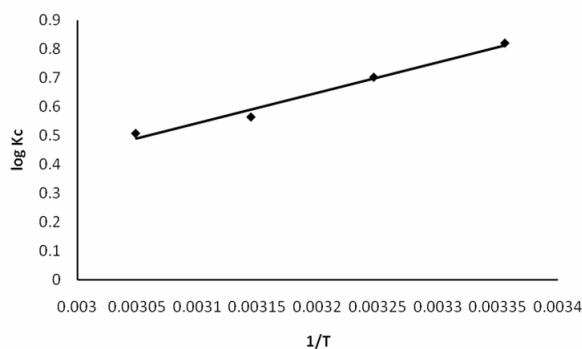


Figure 6: Thermodynamic study

Adsorption Isotherms

The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purpose. The adsorption capacity of this system was investigated with the Freundlich, Langmuir and Temkin adsorption isotherms.

The cadmium sorption isotherm followed the linearized Freundlich model, as shown in Fig. 7. The relation between the cadmium uptake capacity q_e (mg/g) of adsorbent and the residual cadmium concentration C_e (mg/L) at equilibrium is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where the intercept, $\log K_F$, is a measure of adsorbent capacity, and the slope $1/n$ is the sorption intensity. The isotherm data fit the Freundlich model well ($R^2=0.995$). The values of the constants K_F and $1/n$ were calculated to be 11.32 and 0.239, respectively. Since the value of $1/n$ is less than 1, it indicates a favorable adsorption. The Freundlich isotherm is more widely used, but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

The Langmuir equation relates the solid phase adsorbate concentration (q_e) or uptake to the equilibrium liquid concentration (C_e) as follows:

$$q_e = \frac{abC_e}{1 + bC_e} \quad (6)$$

where a and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant

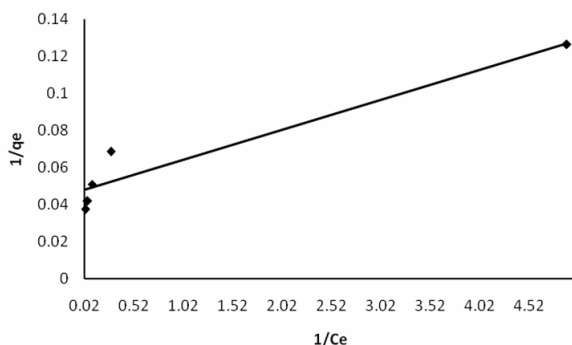


Figure 7: Langmuir adsorption isotherm

related to the heat of adsorption, respectively. It can be seen from Fig. 8 that the isotherm data fits the Langmuir equation more poorly ($R^2=0.919$) than the Freundlich and Temkin equations. The values of a and b were determined from Fig. 8 and were found to be 21.28 mg/g and 2.94 L/mg, respectively.

The Temkin isotherm has been used in the following form:

$$q_e = \frac{RT}{b_0} \ln(A C_e) \quad (7)$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b_0} \ln A + \frac{RT}{b_0} \ln C_e \quad (8)$$

$$q_e = B \ln A + B \ln C_e \quad (9)$$

$$\text{where } \frac{RT}{b_0} = B$$

The sorption data can be analyzed according to Eq. (9). Therefore, a plot of q_e versus $\ln C_e$ enables one to determine the constants A and B . The values of the Temkin constants A and B were determined from Fig. 9 and were found to be 31.33 L/g and 3.597, respectively. The correlation coefficient of 0.946 obtained showed that adsorption of cadmium also followed the Temkin model.

The Freundlich isotherm is obeyed better than the Langmuir and Temkin isotherms, as is evident from the values of the regression coefficients. The resultant values of the parameters K_F , n , a , b , A , B , R^2 for all the experiments in solutions with pH equal to 6.0 for maximum removal of cadmium are presented in Table 4.

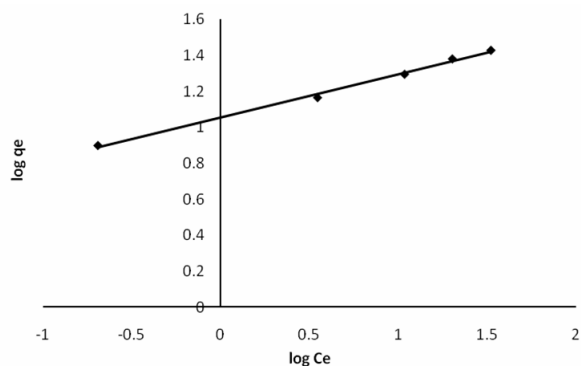


Figure 8: Freundlich adsorption isotherm

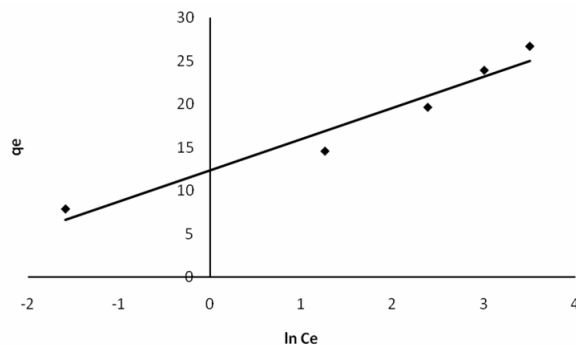


Figure 9: Temkin adsorption isotherm

Table 4: Isotherm models constants and correlation coefficients for adsorption of cadmium onto rice husk

Adsorbent	Langmuir isotherm			Freundlich isotherm			Temkin		
	a (mg/g)	b (L/mg)	R ²	K _f	n	R ²	A (L/g)	B	R ²
Rice Husk	21.28	2.94	0.919	11.32	4.184	0.995	31.33	3.597	0.946

Adsorption Kinetic Models

In order to investigate the controlling mechanism of the adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of cadmium adsorption onto rice husk.

Lagergren proposed a pseudo-first order kinetic model. The integral form of the model is

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \quad (10)$$

where q_t and q_e are the adsorption capacity at time t (mg/g) and at equilibrium respectively, and k_{ad} (min^{-1}) is the pseudo-first order rate constant of the adsorption. This equation was applied to the present study of cadmium adsorption. The rate constant k_{ad} and the correlation coefficients for cadmium adsorption at different concentrations were calculated from the linear plots of $\log(q_e - q_t)$ versus t (Fig. 10) and are listed in Table 5. The correlation coefficients for the pseudo-first-order kinetic model are low. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed, indicating a poor pseudo-first-order fit to the experimental data.

The adsorption kinetics can also be described by a pseudo-second order reaction. The linearized-integral form of the model is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (11)$$

where $h = kq_e^2$ ($\text{mg g}^{-1} \text{min}^{-1}$) can be regarded as the initial adsorption rate when $t \rightarrow 0$ and k is the rate constant for pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The plot of t/q_t versus t (Fig. 11) should give a straight line if pseudo-second-order kinetics are applicable and q_e , k and h can be determined from the slope and intercept of the plot, respectively. At all initial cadmium concentrations studied, straight lines with extremely high correlation coefficients (>0.998) were obtained. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetics. These suggest that the adsorption data are well represented by pseudo-second-order kinetics and supports the assumption that the rate-limiting step of cadmium adsorption on rice husk may be chemical sorption or chemisorption. In chemisorption, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface (Atkins, 1995). The pseudo-second-order kinetic analysis reveals that the values of the initial adsorption rates (h) increase with an increase in the initial cadmium concentration, but the rate constant (k) decreases with an increase in initial cadmium concentration. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites is high and, consequently, lower sorption rates are obtained (Wong et al., 2003). The equilibrium adsorption capacity (q_e), however, increased with an increase in initial cadmium concentration because a large number of cadmium ions are adsorbed at the available adsorption sites.

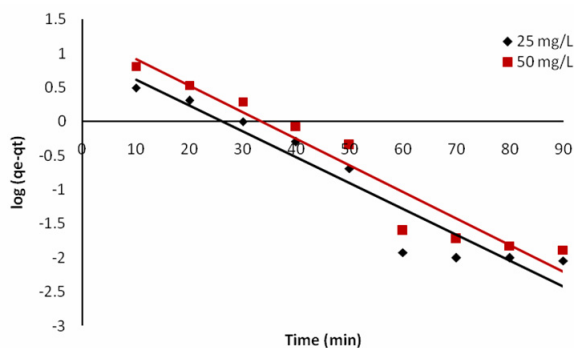


Figure 10: Pseudo-first-order reaction for cadmium adsorbed onto Rice Husk at different concentrations

Table 5: Comparison between the estimated adsorption rate constants, q_e , and correlation coefficients associated with the pseudo-first-order and the pseudo-second-order rate equations

Initial Cadmium Concn (mg/L)	pseudo-first-order rate equation			pseudo-second-order rate equations				
	k_{ad} (min^{-1})	q_e , cal (mg/g)	R^2	k ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e , cal (mg/g)	R^2	h ($\text{mg g}^{-1} \text{min}^{-1}$)	q_e , exp (mg/g)
25	0.085	9.66	0.914	0.018	9.93	0.999	1.808	9.88
50	0.090	20.04	0.930	0.009	18.16	0.999	2.941	17.40

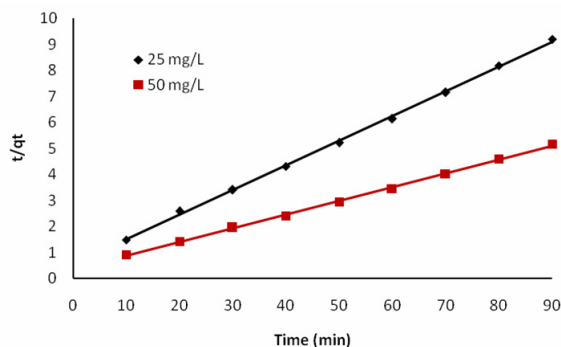


Figure 11: Pseudo-second-order reaction for cadmium adsorbed onto Rice Husk at different concentrations

CONCLUSION

A simple and cost effective treatment procedure was proposed for the removal of heavy metals through adsorption on rice husk. Adsorption is a strong choice for removal of heavy metals from wastewater. The adsorption process is exothermic and a pseudo-second-order kinetic equation is better obeyed than a pseudo-first-order one. The adsorption of cadmium on rice husk reached equilibrium in 60 minutes. The equilibrium sorption data fitted the Freundlich isotherm model better than the Langmuir and Temkin models. Rice husk showed high adsorption capacities and it can be successfully used for treatment of cadmium containing wastewater. Since this method involves less capital cost and is highly efficient, it is practicably feasible for

developing countries. The regeneration of rice husk is not essential because it is an easily available material. The results of this investigation will be useful for the removal of metals from industrial effluents.

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