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Biosorption Characteristics of Sawdust for the Removal of Cd(II) Ions: Mechanism and Thermodynamic Studies

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Surface reaction methodology was employed for the optimization of cadmium removal onto sawdust with respect to various physico-chemical parameters. FT-IR was principally employed for the assessment of the chemical structure of sawdust. The biosorption equilibrium data were best represented by Khan and Langmuir isotherms. The monolayer sorption capacity obtained from Langmuir model was found to be 41.21 mg/g. Biosorption showed pseudo second order rate kinetics at different initial concentration of Cd(II). The intraparticle diffusion study indicated that film diffusion may be involved in the current study. Thermodynamic parameters showed that the sorption process is exothermic and non-spontaneous.

1. Introduction

Awareness for environmental quality has resulted in the defining of strict limits on the permissible environmental levels of certain pollutants (Gupta and Rastogi, 2009). Heavy metals are necessary materials in many industrial processes, including: electroplating, aerospace, and metal industries. Cadmium is a heavy metal with a wide range of applications such as; metallurgical alloying, ceramics, photograph development, pigment works and pesticides. However, it is often discharged directly to the environment without any pre-treatment, causing serious ecological changes and severe public health problems (Benhima et al., 2008). Cadmium has been included in the "red list" of priority pollutants by the Department of Environment, UK (UK Red List Substances, 1991). Biosorption is relatively a new treatment method for removing heavy metal ions from dilute solutions and it is mainly based on the biomaterial–metal ion interaction. Biosorption has received considerable attention as it has the potential to become an efficient, clean and cheap technology for the treatment of wastewater. Biowastes are considered to be unused resources and in many cases present serious disposal problems. Sawdust is a waste by-product of the timber industry that is either used as cooking fuel or a packing material; however, it can be used as a low-cost adsorbent of heavy metals, principally due to its lignocellulosic composition. It is mainly composed of cellulose (45–50%) and lignin (23–30%), both with a capacity for binding metal cations due to hydroxyl, carboxylic and phenolic groups present in their structures. However, this work reports on the use of untreated wood sawdust as a low-cost natural solid waste biosorbent to remove Cd(II) from aqueous solutions.

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2. Experimental Materials and Methods

2.1 Experimental Methods

Sawdust used in this study was collected from the school of Civil Engineering at Queens University Belfast, which is a waste from the construction of model bridges (balsa wood). Sawdust was washed several times with hot deionised water to remove surface impurities and then dried in a conventional oven at 70 °C for 24 hours. $CdSO_4 \cdot 8/3H_2O$ (Sigma-Aldrich, 99.99% purity) was used to prepare the cadmium stock solution. Solutions of 1.0 M NaOH and HNO_3 were used for manually adjusted pH using a micro-pipette. Cadmium concentrations were determined using inductive couple plasma (ICP-OES, Optima 4300 DV, Perkin Elmer, USA) at wavelength 228 nm. Batch equilibrium studies were conducted at a room temperature of 20 °C in a mechanical shaker using 100 ml screw-cap conical flasks containing 50 ml of the Cd(II) solutions with the initial concentration ranging from 5 to 50 mg/L (adsorbent mass = 1 g/L; pH 8.0; time = 4 days). Kinetic experiments were undertaken at different initial concentrations (10, 30, 50 mg/L) and solution temperatures (20, 30, 40 and 60 °C). The samples were withdrawn at selected time intervals over 360 min using 2 ml syringes and prepared for ICP analysis. All the experiments were performed in a batch set up taking three replicates and average values were reported. Standard deviations were found to be within ± 3%.

2.2 Equations and Mathematical Modeling

The amount of Cd(II) adsorbed in (mg/g) was calculated using Eq. (1):

$$q_e = \frac{C_o - C_e}{m_s} \times V \tag{1}$$

where C_o and C_e are the initial and the equilibrium Cd(II) concentration in the aqueous solution respectively (mg/L). q_e is the Cd(II) uptake at equilibrium (mg/g), m_s is the mass of sawdust used (g) and V is the volume of the solution (L).

The isotherm models are based on the: Langmuir, Freundlich and Khan isotherm equations (Table 1). The best fit of each isotherm model was evaluated in terms of coefficient of determination (R^2), mean relative error (MRE) and standard error of estimate (SEE). The kinetics of Cd(II) biosorption on sawdust were analyzed by pseudo first order, pseudo second order and Intraparticle diffusion models. The Lagergren or pseudo first order equation can be expressed as followed:

$$q_t = q_e(1 - e^{-K_1 t}) \tag{2}$$

where and k_1 (1/min) is the adsorption rate constant of the pseudo first order equation.

The pseudo second order model is given as follows:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{3}$$

where k_2 (g/mg min) is the rate constant of second order adsorption.
The Intraparticle diffusion model was applied to the kinetic data with the pore diffusion factor described by Eq. (4):

$$q_t = K_{id} t^{\frac{1}{2}} + C_i \tag{4}$$

where K_{id} is the intra-particle diffusion rate constant (mg/g $min^{1/2}$) and C_i is associated to the boundary layer thickness.
The Eyring equation was applied to calculate the thermodynamic parameters such as enthalpy of activation ΔH°, entropy of activation ΔS° and Gibbs free energy of activation ΔG°. The Eyring equation is given as:

$$\ln\left(\frac{k}{T}\right) = \left[\ln\left(\frac{k_B}{h_P}\right) + \frac{\Delta S°}{R}\right] - \frac{\Delta H°}{R}\left(\frac{1}{T}\right) \tag{5}$$

And $\Delta G° = \Delta H° - T\Delta S°$

where k is the rate constant obtained from the pseudo second-order of Cd(II) biosorption, k_B is the Boltzmann constant (1.3807×10^{-23} J/K), h_P is Planck's constant (6.6261×10^{-34}) and R is the gas constant (8.314 J/mol K).
The Arrhenius equation was applied to evaluate the activation energy of biosorption (E_a) representing the minimum energy that reactants must have for the reaction to proceed:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{6}$$

where A is the frequency factor and E_a (kJ/mol) is the Arrhenius activation energy of biosorption.

3. Results and Discussion

3.1 Effect of solution pH and biosorption mechanisms

Preliminary equilibrium experiments showed that Cd(II) biosorption by the sawdust surface functional group was strongly dependent upon the pH of the solution. The maximum cadmium removal was found to be at pH 8. As pH of the solution increases the sawdust surface becomes more negative, which attracts the positive cadmium ions [M^{+2} and $M(OH)(n-1)^{+}$] (Semerjian, 2010). This increases the electrostatic forces between the sawdust surface and cadmium ions that leads to an increase in biosorption capacity and hence increases the amount of adsorbed Cd(II) on sawdust. The metal ion uptake properties of the sawdust can also be attributed to the carbonyl groups (C=O) or the hydroxyl groups (OH) of polyphenols. The oxygen of each carbonyl and hydroxyl group is considered to be a strong Lewis base because of the presence of its vacant doublet electrons (Taty-Costodes et al., 2003). At a pH higher than 8, cadmium removal

may take place through biosorption and by precipitation caused by OH^- ions forming complex with Cd(II). Therefore, all experiments were undertaken at pH values below the start of metal hydrolysis and precipitation (pH = 8). FTIR spectra analyses for the sawdust before and after biosorption of cadmium were undertaken and the results are illustrated in Figure 1. The FTIR spectra indicate that there is a shift of some functional group bands, which indicates changes in biosorbent functional groups and surface properties. This can be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, indicating that acidic groups, carboxyl and hydroxyl, are the main functional groups in the biosorption of cadmium ions, which is in a good agreement with the pH analysis results.

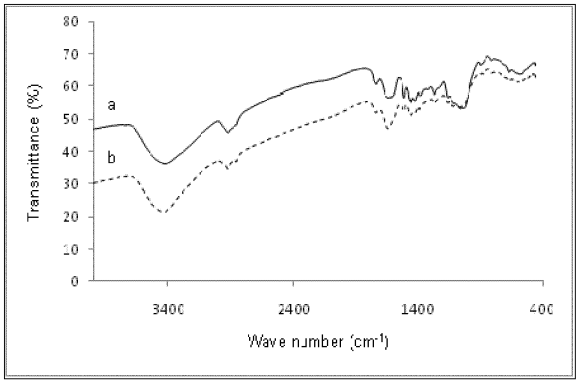

Figure 1: FTIR spectra of sawdust (a) before and (b) after the biosorption of cadmium.

3.2 Biosorption isotherm models

Table 1: Isotherm model coefficients, mean relative error and standard error of estimate for adsorption of Cd(II) on sawdust.

Model	*Parameters*	
Langmuir	q_{max} *(mg/g)*	41.2
	K_L *(L/mg)*	0.04
$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$	R^2	0.99
	MRE (%)	2.66
	SEE	0.34
Freundlich	K_F *(mg/g (L/mg)1/n)*	2.48
	1/n	0.66
$q_e = K_F C_e^{1/n}$	R^2	0.98
	MRE (%)	7.15
	SEE	0.76
Khan	q_s	*37.9*
	b_K	*0.04*
$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$	a_K	*0.95*
	R^2	*0.99*
	MRE (%)	*2.59*
	SEE	*0.38*

The model coefficients, with the corresponding coefficient (R^2), mean relative error (MRE) and standard error of estimate (SEE), values are shown in Table (1). Based on the average values of the statistical parameters for each model, it can be concluded that, the Langmuir and Khan isotherm models provide the best representation of the experimental equilibrium data. On the other hand, the least suitable isotherm model is the Freundlich isotherm model, with the highest MRE and SEE average values. Langmuir constant, q_{max}, which is a measure of monolayer biosorption capacity of sawdust was determined as 41.21 mg/g and Langmuir constant K_L referring to biosorption energy, was determined as 0.041. Also, the calculated constant values of Khan and Toth isotherm models are represented in Table (1), the q_s maximum uptake capacity calculated for Khan model is calculated as 37.92 mg/g.

3.3 Biosorption kinetic studies

The experimental kinetic data of Cd(II) uptake were fitted to Eq. (2) and (3) and the plots of q_t (mg/g) versus time, t are shown in Figures (2).

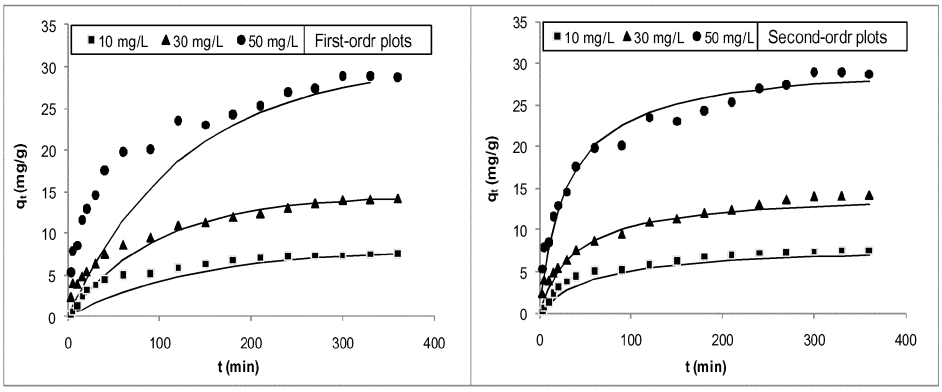

Figure 2: Pseudo first and second order kinetic plots for the biosorption of Cd(II) on sawdust for various initial concentrations at 20°C.

It can be seen in Fig. 2 that the pseudo second-order is able to describe the kinetic data better than the pseudo first-order and that the rate-limiting step may be chemisorption which involves valency forces through sharing or exchange of electrons between the sorbent and sorbate. The kinetic models constant are listed in Table 2.

Table 2: Pseudo first order and pseudo second order model constants for biosorption of Cd(II) onto sawdust at 20°C and pH 8.

Cd(II)	Pseudo first order kinetic model				Pseudo second order kinetic model		
(mg/L)	$q_{e,exp}$	$q_{e,cal}$	$k_1 \times 10^3$	R^2	$q_{e,cal}$	$k_2 \times 10^3$	R^2
10	7.56	7.53	7.60	0.96	6.92	2.09	0.98
30	14.2	14.1	10.5	0.97	13.0	1.78	0.99
50	28.7	28.4	8.00	0.96	27.8	1.11	0.99

where k_1 (1/min); k_2 (g/mg min) and q_e (mg/g)

The fact that k_2 declines with increasing initial concentration, indicates that it is faster for the biosorption system to reach a specific temporal equilibrium at lower initial concentration. The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. The plot of q_t versus $t^{1/2}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. Plots were not linear over the whole time range and did not pass through the origin, implying that the biosorption process proceeds by film diffusion and intraparticle diffusion.

3.4 Biosorption Thermodynamics

The calculated values of ΔH°, ΔS° and ΔG° of biosorption of Cd(II) on sawdust were calculated. The negative ΔH° (-4.08 kJ/mol) value obtained indicated that the biosorption process was exothermic in nature. The negative value of ΔS° (-0.315 kJ/mol K) obtained reflects the decreased randomness at the solid/liquid interface during the biosorption process. The positive values of ΔG° obtained at different temperatures (20, 30, 40 and 60 °C) were found to be 88.2, 91.4, 94.5 and 100.8 KJ/mol, respectively. This indicates the non-spontaneous nature of the biosorption process at the range of temperature being studied. The increase in the ΔG° values with temperature suggests that the process is not feasible at higher temperatures. A low value of the activation energy E_a (-1.58 kJ/mol) suggests that the biosorption process is controlled by film diffusion mechanism (Sismanoglu and Pura, 2001), which is in agreement with the results obtained in the previous section.

4. Conclusions

The batch studies conducted in the present work provide significant information regarding biosorption mechanism of cadmium on sawdust. The studies showed that readily available solid waste sawdust can be used as potential low-cost biosorbent for the removal of Cd(II) from aqueous solutions over a wide range of concentrations.

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