

Removal of Cadmium from Aqueous Solutions by Adsorption onto Sugarcane Bagasse

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Abstract: The ability of sugarcane bagasse to adsorb Cd²⁺ from aqueous solutions has been investigated through batch experiments. The highest Cd²⁺ adsorption was achieved at agitation rate of 150 rpm. The adsorption process was relatively fast and equilibrium was achieved after about 90 min of contact. The optimum adsorption of cadmium occurred at pH range 5-7. The kinetic process of Cd²⁺ adsorption onto sugarcane bagasse was tested by applying pseudo-first order, pseudo-second-order and intraparticle diffusion rate equations. The equilibrium data fitted the Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm was found to be 6.79 mg g⁻¹ at 30°C.

Key words: Adsorption • sugarcane bagasse • cadmium • kinetic • isotherm • pH

INTRODUCTION

The presence of heavy metals in the environment poses a serious and complex pollution problem that has been and still is, a focus of attention all over the world. Heavy metals are among the main pollutants of surface and groundwater. The environmental impact due to their toxicity has led to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscapes and water bodies. Cadmium is one of the heavy metals, which is highly toxic to humans, plant and animals. The metal is of special concern because it is non-degradable and therefore persistent. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1]. Most conventional waste water-treatment techniques such as filtration, flocculation, activated carbon, reverse osmosis, chemical precipitation or coagulation, ion-exchange, ultrafiltration and electrochemical deposition require high capital and operating costs and may produce large volumes of wastes [2, 3]. Therefore the aforementioned techniques are not economically feasible for small and medium industries. Adsorption processes using agricultural waste products or biosorption are becoming the new alternative for waste water treatment. According to Kargi and Cikla [4], biosorption process is much superior to chemical and physical methods due to the following factors:

- Excess sludge generated from waste water treatment plants can be used as biosorbent
- Biosorbents are cheap, free availability and possible reuse of the biosorbent
- Selective adsorption of metal ions can be achieved using biosorbents
- High adsorption capacity
- Biosorption process can be operated over broad range of environmental conditions such as pH, ionic strength and temperature.

In this present work, the effectiveness of adsorption of cadmium ion by sugarcane bagasse was studied by determining the maximum adsorption capacity of cadmium by batch mode process. The kinetic or rate of adsorption based on pseudo-first order, pseudo-second order and intraparticle diffusion rate equations were also studied.

MATERIALS AND METHODS

Preparation of synthetic waste water: Analytical reagent grade of cadmium solution, Cd(NO₃)₂ · 4H₂O (1000 mg l⁻¹) supplied by Merck was used as synthetic waste water. The synthetic waste water was first prepared by diluting the stock solution of Cd²⁺ with distilled water to desired concentrations. The pH of the waste water was then adjusted to 4 by addition of drops of 0.1 M NaOH or 0.1 M HNO₃ solution.

Preparation of adsorbent: Sugarcane bagasse was extensively washed with distilled water and soaked in methanol for 24 h. This was carried out in order to clean sugarcane bagasse from impurities that may interfere with the adsorption result and to remove colour. Then, sugarcane bagasse was dried in oven at 100°C for 24 h. After drying, it was ground and sieved to get the average adsorbent size of 850 µm.

Adsorption experiments: The effect of agitation rate of Cd²⁺ on adsorption was studied by agitating 0.1 g of adsorbent in 50 ml cadmium solutions (1 mg l⁻¹) at various speeds, 50-200 rpm. Kinetic studies were carried out in a series of Erlenmeyer flasks of 250 ml capacity by agitating 0.1 g of the adsorbent in 100 ml of the aqueous Cd²⁺ solutions at constant temperature (30°C), in a water bath shaker (Memmert, Germany). Adsorption process was performed at a pre-determined time interval and at a constant agitation rate of 150 rpm. The effect of pH on cadmium adsorption was conducted over pH range 2-7 at a constant initial cadmium concentration of 5 mg l⁻¹, adsorbent dose 1 g l⁻¹ solution, agitation rate of 150 rpm and agitation period of 90 min. Adsorption isotherm tests were carried out by mixing 0.1 g of adsorbent in 100 ml of Cd²⁺ solution with varying cadmium concentrations (1-100 mg l⁻¹) at constant temperature (30°C). After adsorption, the mixture was filtered through Whatman filter paper (No. 40). The concentrations of cadmium in the solutions before and after equilibrium were determined by atomic absorption spectrophotometer (Hitachi Model Z-8100 Polarized Zeeman) using air acetylene flame. All experiments were carried out in duplicates and results are reported as average.

Metal uptake: The amount of Cd²⁺ adsorbed, q (mg g⁻¹) was computed by using the following expression:

$$q = \frac{C_0 - C_t}{m} V \quad (1)$$

Where, C₀ and C_t are Cd²⁺ concentrations in mg l⁻¹ before and after adsorption at time t, V is the volume of adsorbate in liter and m (g) is the weight of the adsorbent.

RESULTS AND DISCUSSION

Effect of agitation rate: As can be seen from Fig. 1, cadmium adsorption generally increased with increasing agitation rate. Adsorption of cadmium increased from 0.193 to 0.372 mg g⁻¹ when agitation rate increased from 50 to 150 rpm. According to Nomanbhay and

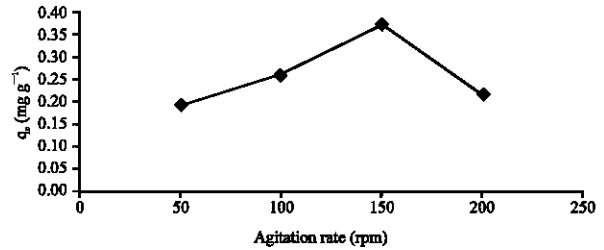


Fig. 1: Effect of agitation time on cadmium adsorption by sugarcane bagasse

Palanisamy [5], the increase in agitation rate improves the diffusion of metal ions towards the adsorbent surface. The diffusion rate of cadmium ions from the bulk liquid to the liquid boundary layer surrounding particles becomes higher when the agitation rate is increased due to enhancement of turbulence and a decrease in the thickness of the liquid boundary layer. Thus, the external diffusion resistance can be neglected. The decreased value of Cd²⁺ adsorbed by sugarcane bagasse at 200 rpm in comparison to the value at 150 rpm was about 42.7%. Therefore, a too vigorous agitation rate (200 rpm) would result in more Cd²⁺ desorbed from the adsorption sites.

Effect of pH: pH is one of the most important controlling parameters in all adsorption processes. The effect of pH on cadmium adsorption is shown in Fig. 2. Cadmium adsorption was found to increase with increasing pH of the solution. Adsorption was only 1.20 mg g⁻¹ at pH 2 but increased to 2.03 mg g⁻¹ at pH 7. According to Namasivayam and Ranganathan [6], precipitation of cadmium starts at pH 8.2. Therefore, in this study the effect of pH on cadmium adsorption was performed at pH range 2-7. At low pH, Cd²⁺ ions had to compete with H⁺ ions for adsorption sites on the adsorbent surface. As the pH increased, this competition weakens and more Cd²⁺ ions were able to replace H⁺ ions bound to the adsorbent surface. A similar trend of dependency of Cd²⁺ on pH was reported by Taty-Costodes *et al.* [7].

Adsorption kinetic: Adsorption kinetics, which describes the solute adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. The adsorption data (at pH 4) for initial Cd²⁺ concentration of 1 mg l⁻¹ is shown in Fig. 3. The plot shows that kinetic of adsorption of Cd²⁺ consisted of two phases; an initial rapid phase where adsorption was fast and a second slower phase where equilibrium uptake was achieved. The first phase is related to external surface adsorption and adsorption occurs instantaneously. The second phase is the gradual

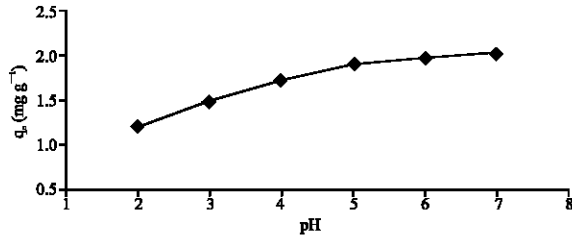


Fig. 2: Effect of pH on cadmium adsorption by sugarcane bagasse

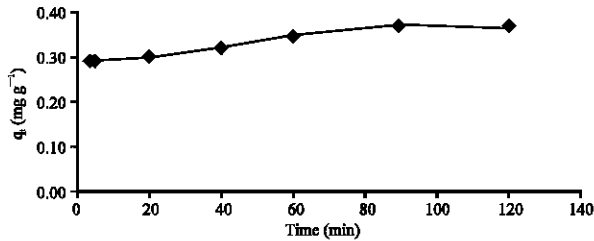


Fig. 3: Effect of contact time on cadmium adsorption by sugarcane bagasse

adsorption stage before the metal uptake reaches equilibrium. The time to reach equilibrium is 90 min and the maximum amount of Cd²⁺ adsorbed is 0.372 mg g⁻¹. According to Bhattacharyya and Gupta [8], the initial high rate of metal uptake may be attributed to the existence of the bare surface. The number of available adsorption sites decreased as the number of Cd²⁺ ions adsorbed increases. The enhanced adsorption of metal ion with increase in agitation time may also be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ions [9]. By increasing the agitation time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution. Based on the data obtained from this kinetic study, the contact time was maintained for 90 min for isotherm experiment to ensure that equilibrium was really achieved. Identifying the slowest step or rate determining step is also crucial in any adsorption study. Therefore, three kinetics models were applied mainly pseudo-first order, pseudo-second order and intraparticle diffusion rate equations.

The pseudo-first order rate equation [10] is expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

Where, q_e and q_t are the amount of metal adsorbed (mg g⁻¹) at equilibrium and at any time t, respectively and

k₁ is the pseudo-first order rate constant (min⁻¹). The integrated rate law, after applying the initial condition of q_t = 0 at t = 0, is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

In this equation, the rate of adsorption is assumed to be proportional to the difference between the adsorption capacity (q_e) at equilibrium and the capacity at any time t. A straight line plot of log (q_e-q_t) versus t was used to determine the rate constant, k₁ and correlation coefficient, R² as shown in Fig. 4. The values of k₁ (min⁻¹) and q_e (mg g⁻¹) predicted from this plot are 1.73×10⁻² and 9.26×10⁻¹, respectively. The pseudo-first order rate equation did not adequately describe the adsorption result since the correlation coefficient value, R² is low. The predicted cadmium capacity was also found to be lower than the experimental value (0.372 mg g⁻¹). According to Sağ and Aktay [11], if the experimental results do not follow equations 3, they differ in two important aspects: (i) k₁ (q_e-q_t) does not represent the number of available adsorption sites and (ii) log q_e is not equal to the intercept of the plot of log (q_e-q_t) against t. This was mainly due to a boundary layer or external resistance controlling at the beginning of the adsorption.

The pseudo-second order rate equation is expressed as [12]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (4)$$

Where, h = kq_e² (mg g⁻¹ min⁻¹) is the initial adsorption rate can be regarded as the initial adsorption rate as t → 0 and k is the rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹). The plot t/q_t versus t should give a straight line if pseudo-second-order kinetics is applicable and q_e, k and h can be determined from the slope and intercept of the plot, respectively. The plot of the linearized form of the pseudo-second-order reaction is shown in Fig. 5.

The plot of t/q_t versus t for pseudo-second order rate equation yields a good straight line (R²>0.99) as compared to the plot of pseudo-first order. The pseudo-second order rate constant and initial adsorption rate were reported as 7.86×10⁻¹ g mg⁻¹ min⁻¹ and 1.12×10⁻¹ mg g⁻¹ min⁻¹, respectively. The theoretical value of q_e (0.377 mg g⁻¹) predicted from pseudo-second order plot also agrees well with the experimental one (0.372 mg g⁻¹). This suggests that the adsorption of Cd²⁺ ions by sugarcane bagasse follows pseudo-second order model, which relies on the assumption that chemisorption

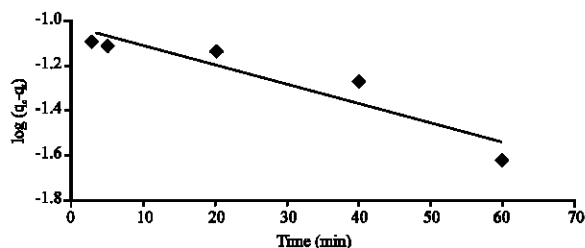


Fig. 4: Pseudo-first order plot for cadmium adsorption by sugarcane bagasse

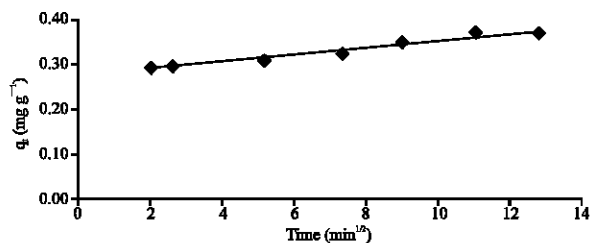


Fig. 6: Intraparticle diffusion plot for cadmium adsorption by sugarcane bagasse

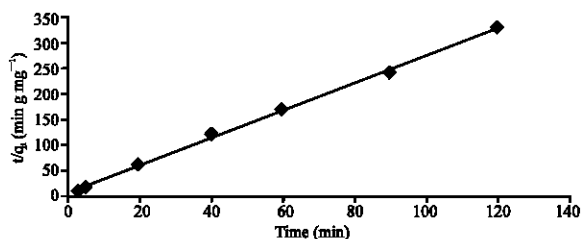


Fig. 5: Pseudo-second order plot for cadmium adsorption by sugarcane bagasse

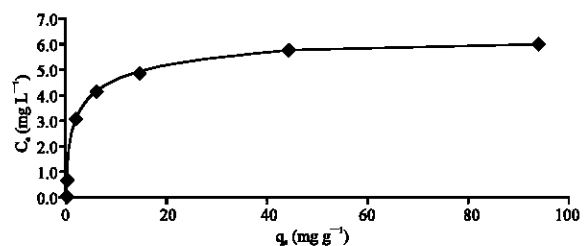


Fig. 7: Adsorption isotherm plot for cadmium adsorption by sugarcane bagasse

or chemical adsorption is the rate-limiting step. Chemisorption involves valency forces through sharing or exchange of electron between adsorbent and adsorbate. The pseudo-second order kinetic for adsorption reactions is also reported in some studies such as the adsorption of Cr (VI) and Cu (II) by chitin, chitosan and *Rhizopus arrhizus*, adsorption of thiocyanate onto ZnCl₂ activated carbon [11] and adsorption of Cd²⁺ onto rubber leaf powder [13].

According to Poots *et al.* [14], during batch mode of operation, there was a possibility of intraparticle pore diffusion of cadmium, which is often the rate-limiting step. The intraparticle diffusion varies with square root of time and is introduced by Weber and Morris [15] as:

$$q_t = k_{id} t^{1/2} \quad (5)$$

Where, q_t is the amount adsorbed (mg g^{-1}) at time t (min) and k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the rate constant of intraparticle diffusion. If the rate-limiting step is intraparticle diffusion, a plot of solute adsorbed against the square root of the contact time should yield a straight line passing through the origin. The intraparticle diffusion values can be calculated from the slope of the straight-line portion of the respective plot. If the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intraparticle diffusion is not the only rate-limiting step. The intraparticle diffusion plot

is shown in Fig. 6. The value of k_{id} determined from the plot of q_t versus $t^{1/2}$ is $9.40 \times 10^{-3} \text{ mg g}^{-1} \text{ min}^{-1/2}$. The intercept does not pass through the origin, which indicates that pore diffusion is not the only rate-limiting step [16].

Adsorption isotherms: The maximum adsorption capacity of sugarcane bagasse for cadmium was investigated over a range of cadmium concentrations. Figure 7 shows the plot of the adsorption capacity, q_e (mg g^{-1}) versus the equilibrium concentration of cadmium ions in the solution, C_e (mg l^{-1}). The amount of cadmium adsorbed was found to increase with increasing cadmium concentration until the maximum adsorption capacity was achieved. Langmuir and Freundlich adsorption models can be used to describe the equilibrium between adsorbed cadmium ions and cadmium ions in solution. The Langmuir model assumes monolayer coverage of adsorbent surface and no interaction of adsorbate in the plane of the adsorbent surface. The linear form of Langmuir isotherm is given by the following equation [17]:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0 C_e} \quad (6)$$

Where, q_e is the amount adsorbed (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg l^{-1}), Q_0 and b are Langmuir constants related to maximum adsorption capacity (mg g^{-1}) and energy of

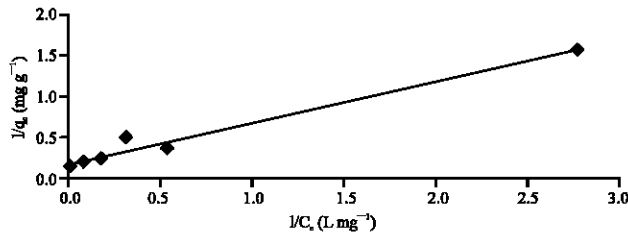


Fig. 8: Langmuir adsorption isotherm for cadmium adsorption by sugarcane bagasse

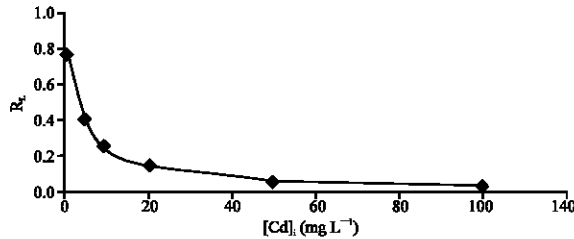


Fig. 9: Separation factor for cadmium adsorption by sugarcane bagasse

adsorption (mg l^{-1}), respectively. The values of Q_0 and b can be obtained from the intercept and the slope of the plot $1/q_e$ versus $1/C_0$, respectively as shown in Fig. 8.

The magnitude of the Langmuir constant b is small (0.293 mg l^{-1}) and the maximum adsorption capacity was determined as 6.79 mg g^{-1} . The essential feature of the Langmuir isotherm can be expressed by means of R_L , a dimensionless constant referred to as a separation factor or equilibrium parameter. R_L is calculated using the following equation [18]:

$$R_L = \frac{1}{(1 + bC_0)} \quad (7)$$

Where, C_0 is the initial Cd^{2+} concentration (mg l^{-1}) and b is obtained from Langmuir plot. The parameter R_L indicates the shape of the isotherm accordingly, as explained in Table 1. The calculated values of R_L at different initial Cd^{2+} concentration are shown in Fig. 9. The values of R_L in the range of 0 to 1 at all initial cadmium concentrations confirm the favorable uptake of cadmium process.

The Freundlich equation can be described by the linearized form [19]:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (8)$$

Where, K_F (mg g^{-1}) and n are the Freundlich constants of the system, indicating the adsorption

Table 1: Separation factor

Values of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

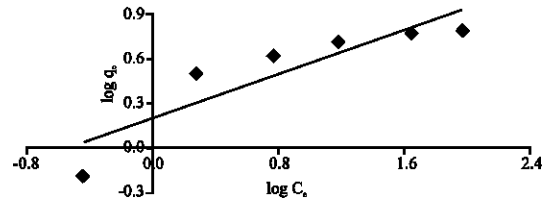


Fig. 10: Freundlich adsorption isotherm for cadmium adsorption by sugarcane bagasse

capacity and adsorption intensity, respectively. The values of n and K_F can be calculated from the slope and intercept of the plot, respectively. The Freundlich equation assumes a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. Figure 10 shows Freundlich adsorption isotherm obtained by plotting $\log q_e$ versus $\log C_e$. The values of n and K_F determined from Freundlich plot are 2.71 and 1.55 mg g^{-1} , respectively. However, the higher correlation coefficient obtained from Langmuir plot ($R^2 > 0.99$) compared to Freundlich plot ($R^2 = 0.81$) suggests monolayer coverage of the adsorbent by cadmium ions.

CONCLUSIONS

This study indicates that sugarcane bagasse has rapid adsorption rate and good adsorption capacity for cadmium. The Cd^{2+} adsorption was found to be dependent on agitation rate, pH and contact time. The adsorption of cadmium was found to be fitted the Langmuir isotherm model, which suggests monolayer coverage of adsorbent surface. Kinetic study however obeyed pseudo-second order model, which indicates chemisorption as the rate limiting step in adsorption process. This work showed that sugarcane bagasse could be used as a good adsorbent material for Cd^{2+} removal from dilute aqueous solution.

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