

Study of Modified Banana Fiber as Adsorbent for Cadmium(II) Ions from Aqueous Solution

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Raw banana fiber (RBF), acid treated banana fiber (ATBF) from banana stem was evaluated as adsorbent for the elimination Cd^{2+} from solution. The Cd^{2+} solution of 1000 mg/L concentration was prepared from $\text{Cd}(\text{NO}_3)_2$ and different concentrations were prepared by dilution of stock solution. Effects of adsorbent dose, contact time, temperature, initial metal concentration and pH study were evaluated. Langmuir and Freundlich isotherms were employed to describe adsorption capacity. The maximum amounts of cadmium(II) adsorbed (q_m), which was evaluated by Langmuir isotherm, were 0.469 mg/g and 5.230 mg/g, and highest R^2 (0.9968, 0.9815,) for raw banana fiber and acid treated banana fiber, respectively. Pseudo-second order kinetics best fitted with $R^2 = (0.9457), (0.9571)$ for raw banana fiber and acid treated banana fiber, respectively. Thermodynamic parameters obtained were ΔG° (-8.268) $\text{kJ mol}^{-1} \text{K}^{-1}$, ΔH° (-9.874), $\text{kJ mol}^{-1} \text{K}^{-1}$ and ΔS° (-5.152) kJ mol^{-1} for acid treated banana fiber and spontaneity decreases with increase in temperature in case of raw banana fiber and acid treated banana fiber. This indicates that the system is exothermic. Banana stems possess feasible characteristics for making an adsorbent and acid treated banana fiber is more efficient for removal of Cd^{2+} ion from its aqueous solution.

Keywords: Adsorption isotherms, Banana stem, Kinetics, Thermodynamics, Cadmium.

INTRODUCTION

At present time, it is been observed that the rapid growth of industrialization has turned out to be a curse for the environment owing to the uncontrolled discharging of the industrial effluents and wastewater in aqueous bodies contaminated with heavy metal ions such as Cu(II), Cd(II), Zn(II), Fe(II), etc. The different studies conducted indicate that the cadmium is the one of the most hazardous and toxic metal which is discharged in water through various industries such as melting, plating, metal mining, batteries, oil paint, pigments, pesticides and alloys [1,2]. Cadmium affects the physio-chemical behaviour and since it has propensity to act as biological catalyst [3]. Due to the hazardous and toxic property of the heavy metals, different techniques have been put to use for the extirpating of heavy metal, methods viz. chemical precipitation [4], reduction-oxidation [5], ion-exchange [6] and biological process [7]. Various studies illustrate that among the different methods of extirpating of heavy metals, adsorption technique is more promising owing to its economical and easy operation. Several studies have been devoted on this method [8,9]. For efficient extirpating of heavy metal ions, it is necessary that adsorbent should have properties like surface area should be high and must possess high adsorption capacity, appropriate pore size and volume, mechanical stability, compatibility, ease of

regeneration, easy accessibility, cost effectiveness and environment friendliness [10]. Different agricultural wastes and non-conventional material have been focused and utilized by researchers as to remove heavy metal ions from water bodies are canola residue [11], melon seed husk [12]; cassava waste [13], groundnut husk [14], maize cob [15], orange waste [16], Manihotsculentacranz waste [17,18], rape straw [19], feather, palm fruit fibre [20,21] and rice husk [22]. Among all these adsorbents banana plant has also demonstrated the tendency to remove heavy metals from aqueous solution. Primarily banana is cultivated for fruit, fibre production and sometimes as an ornamental plant. It is normally tall and sturdy, in some species 8 m of height can be reached.

In this study the removal of cadmium ion from aqueous solution by utilizing banana fiber as well as sulfuric acid treated banana fiber was evaluated as an adsorbent. Adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of adsorbent were evaluated by adsorption kinetics, thermodynamics studies and Langmuir, Freundlich isotherms, respectively.

EXPERIMENTAL

Adsorbent preparation: Banana stem was obtained locally from Allahabad. It was chopped into small chunks of

small size 2.5 cm × 2.5 cm. The banana stem chunks were then boiled for about 1 h and later dried at 70 °C in a hot air oven. After drying, the pieces were grounded using high speed blender and passed through different sieves and the size 500-250 μm of banana fiber was collected for the experiment. This material obtained was utilized as an adsorbent, called raw banana fiber (RBF). Further, the sulfuric acid treatment of RBF was done with an intention to increase its adsorption capacity by increasing its surface [23]. Sulfuric acid (13 M) about 100 mL was added to RBF the temperature of the blend was raised to 175-180 °C and maintained for 20 min. After this it was cooled to room temperature and then the resulting mixture was filtered with a Bucher funnel under vacuum. To separate the acid from the material washing with deionized water was done and was repeated till a neutral pH was observed and then the adsorbent was dried. The material obtained was termed as acid treated banana fiber (ATBF) which was further stored and utilized as an adsorbent for further adsorption studies.

Preparation of cadmium solution: The stock solution of Cd²⁺ was prepared by dissolving analytical grade Cd(NO₃)₂ in deionized water (1000 mg/L). Several solutions with different concentrations of cadmium ranging from 1 to 10 mg/L were prepared by successive dilutions of the stock solution. The resulting solutions were then used to determine the uptake capacity of the adsorbent at a constant temperature. The pH of the solutions was adjusted using HNO₃ (0.1 M) and NaOH (0.1 M) solution.

Atomic absorption spectrometer (AAS) of Perkin-Elmer 100, working with an air acetylene flame was used to analyze the concentration of Cd²⁺. Three standard solutions of concentration of Cd²⁺ ion in the linear range of the instrument was used to construct the calibration curve. All estimations were repeated three times which resulted in normal derivation ± 0.1 mg/L (which was not mentioned). The pH of the solution was maintained using the controlled pH analyzer (LAB INDIA). Two buffers solutions of pH 4 and 7 were used for the standardization of pH meter. For the adsorption study Macro scientific thermostatic shaker was used.

Batch adsorption experiments: In this experiment batch studies were made. The Cd²⁺ solutions of diverse dilutions were prepared (1 to 10 mg/L). For the kinetic experiments in a 250 mL Erlenmeyer flask 0.5g of adsorbent (RBF and ATBF) in 100 mL solution of 5 mg/L of cadmium solution were added. After this the resulting mixture was agitated on a thermostatic shaker at 25 °C at 180 rpm and the filtration was done using Whatman No. 42 filter paper. The suspension of adsorbent was separated after the completion of equilibration process. The pH of solution was adjusted using 0.1 N HNO₃ and 0.1 N NaOH. After 480 min of agitation the metal concentration left in filtrates was determined with atomic absorption spectrophotometer. The amount of Cd²⁺ adsorbed by RBF and ATBF was evaluated by adsorption efficiency and capacity by using following equation:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where, Q_e is the adsorption capacity of metal ion (mg g⁻¹), C_o is the initial metal ion concentration (mgL⁻¹), C_e is the final equilibrium concentration of test solution (mg L⁻¹) V is the volume of the metal ion solution (L) and W is the adsorbent weight.

RESULTS AND DISCUSSION

Effect of contact time: Contact time is one of the important parameters which affects the adsorption of cadmium from aqueous solution by RBF and ATBF. In the experiments, an optimum pH value 7, Cd concentration of 5 mg/L, adsorbent dose 0.5 g, contact time from 60 to 480 min at 180 rpm at 25 °C. Fig. 1 indicates that with the increase of time the adsorption capacity increased, the maximum capacity observed was 0.641 mg/g and 0.868 mg/g for RBF and ATBF, respectively. However after 360 min, no significant increase was observed in adsorption capacity.

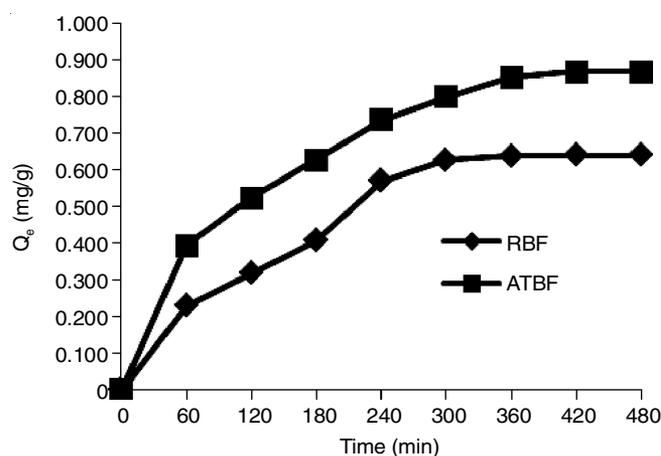


Fig. 1. Effect of contact time for the adsorption of Cd²⁺ ions onto RBF and ATBF

Effect of adsorbent dosages: The effect of the RBF and ATBF dose on the adsorption of cadmium was studied at different dosages in the ranges of 0.1 to 1.5 g, cadmium solution of 5 mg/L at optimized conditions, respectively. The results are reflected in Fig. 2. The figure shows that the dose of adsorbent significantly makes change in the adsorption of heavy metal

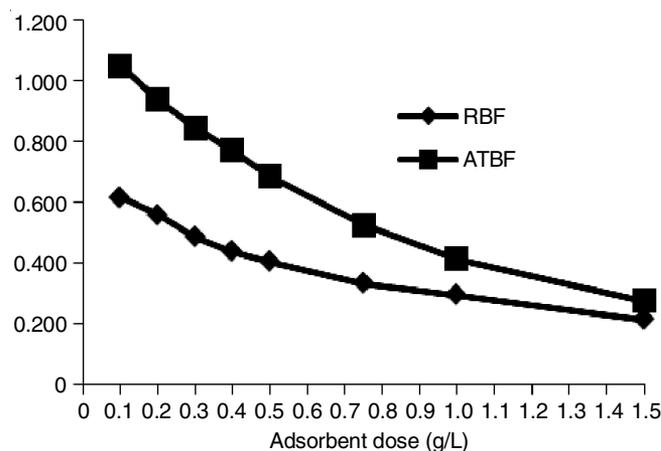


Fig. 2. Effect of adsorbent dose for the adsorption of Cd²⁺ ions onto RBF and ATBF

ions from water. It was seen that the adsorption capacity of RBF and ATBF decreased from 0.614 to 0.213 mg/g; and from 1.048 to 0.274 mg/g, respectively.

Effect of pH: pH of the solution prominently affects the adsorption process in many ways. Initially it affects the surface charge of the adsorbent, the nature of adsorbate and the degree of ionization is also dependent on pH of the medium. Thus the adsorption capacity of RBF and ATBF in the Cd^{2+} solution was studied at different pH range from 2 to 10 (Fig. 3). It was apparent that the hydrogen ion concentration of the medium controls the H^+ ion concentration when the protons concentration increases in solution they compete with the metal ions for active sites on the adsorbent surface [24]. At a lower pH, when the H^+ ion concentration is more there is more competition of H^+ ion and metal ions for the available adsorption sites. However, as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [25]. The maximum adsorption capacity was observed at 0.636 mg/g and 0.736 mg/g for RBF and ATBF at pH 7 and after pH 7 it started to decrease.

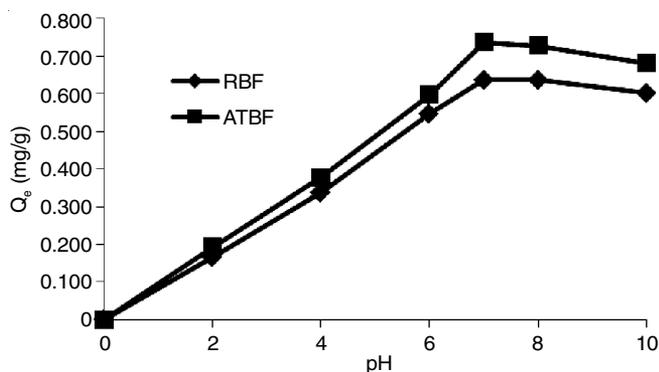


Fig. 3. Effect of pH for the adsorption of Cd^{2+} ions onto RBF and ATBF

Effect of initial concentration: The cadmium solutions with initial concentrations of 1-10 mg/L were prepared. All the parameters such as contact time, adsorbent dose, agitation speed and temperature were kept constant; the solution pH was maintained to 7. The effect of initial Cd^{2+} concentration on the adsorption of Cd^{2+} is shown in Fig. 4 which illustrate that the amount of Cd^{2+} adsorbed onto RBF (0.132 to 0.601) mg/g

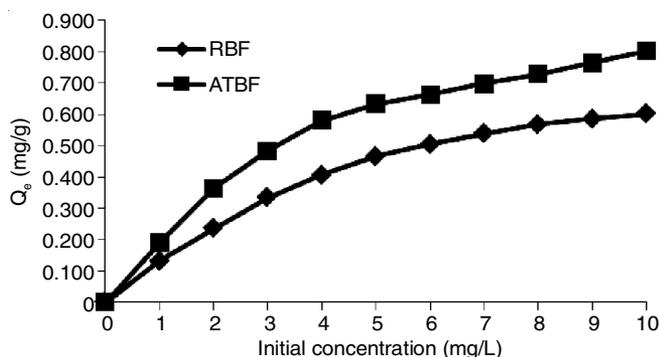


Fig. 4. Effect of Initial concentration for the adsorption of Cd^{2+} ions onto RBF and ATBF

and ATBF (0.152 to 0.802) (mg/g), respectively increased as the initial Cd^{2+} concentration increased. This may be ascribed to higher driving force of mass transfer [26].

Thermodynamic studies: For the study of thermodynamic factors, the temperature range was taken from 293-323 K. The thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and Gibbs free energy change (ΔG°) were estimated using the following equation [27]:

$$K_c = \frac{C_s}{C_e} \quad (3)$$

where, K_c is the equilibrium constant, C_s is the solid phase concentration at equilibrium (mg L^{-1}) and C_e is the equilibrium concentration in solution (mg L^{-1}).

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (5)$$

van't Hoff equation was applied to determine ΔH° and ΔS° . The values of ΔH° and ΔS° were obtained from the slope and the intercept of the plot of $\log K_c$ vs. $1/T$ (Fig. 5) and presented in Table-1. In case of RBF and ATBF, it was seen that the value of ΔG° is negative and decreasing with increase in temperature confirming spontaneity. Study demonstrates that the adsorption of Cd^{2+} ion onto RBF and ATBF is spontaneous. The negative value of ΔH° and ΔS° indicate the exothermic nature and the randomness at solid/liquid solution interface during the adsorption of ion onto RBF and ATBF.

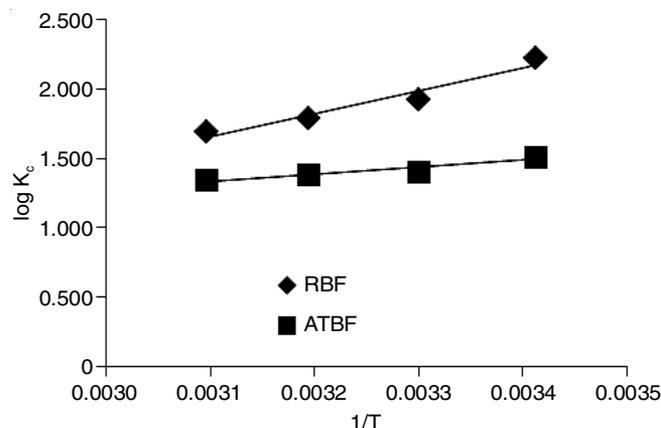


Fig. 5. Thermodynamic studies for the adsorption of Cd^{2+} ions onto RBF and ATBF

TABLE-1 THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF Cd^{2+} ION ON RBF AND ATBF				
Temp. (K)	ΔG° ($\text{kJ mol}^{-1} \text{K}^{-1}$)	ΔH° ($\text{kJ mol}^{-1} \text{K}^{-1}$)	ΔS° (kJ mol^{-1})	R^2
RBF				
293	-12.448	-31.278	-0.065	0.9405
303	-11.112			
313	-10.718			
323	-10.451			
ATBF				
293	-8.467	-9.874	-5.152	0.9188
303	-8.139			
313	-8.279			
323	-8.268			

Adsorption kinetics: The mechanism of adsorption and the kinetics was studied by different models of kinetics like pseudo-first order; pseudo-second order plots, intraparticle diffusion and Elovich equation were tested to investigate the experimental data. The pseudo-first-order reaction equation of Lagergren was widely used for the adsorption of liquid/solid system on the basis of solid capacity [28]. The following equation pseudo-first-order kinetics equation was analyzed.

The linearized form of equation is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are adsorbed heavy metal amount at time t and equilibrium, k_1 is the rate constants (min^{-1}). Through the linear plot of $\log(q_e - q_t)$ vs. t the values of k_1 , R^2 and q_e (cal.) were calculated as shown in Table-2. The results reveal that the calculated adsorption capacity ($q_{e, \text{cal}}$) values are not similar to the experimental q_e ($q_{e, \text{exp}}$) value and regression coefficient (R^2) value is also low, so it does not follow pseudo 1st order kinetics. Therefore, the kinetic data were analyzed again by using pseudo-second-order kinetics equation, based on the equilibrium adsorption which is used for the determination of the rate constant [29]. The linearized form of equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2} q_e^{-2} + \frac{1}{q_e} \quad (7)$$

where, k_2 is the pseudo second-order rate constant ($\text{g mg}^{-1} \text{min}$), q_t is the amount of metal ion adsorbed (mg g^{-1}) at given time t (min), q_e is the amount of metal ion adsorbed at equilibrium (mg g^{-1}). A plot of t/q_t versus t is shown in Fig. 6. The comparison of results was done using the correlation coefficient (R^2) as given in Table-2. The R^2 value for pseudo second order kinetics is high in contrast to first order kinetics. The q_e (exp) value of second order was also found in agreement with the q_e (cal) as compared to first-order kinetics. Therefore, the data propose that the adsorption followed the pseudo second-order kinetics.

Intraparticle diffusion model: In batch adsorption process the intraparticle diffusion model assumes that the adsorbate diffuse into the interior of the adsorbent and this process is

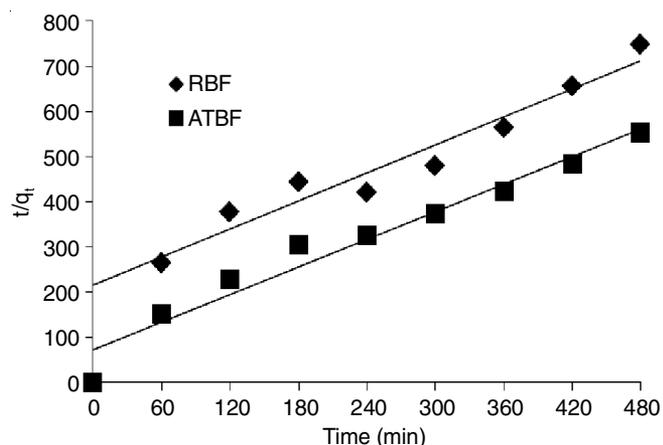


Fig. 6. Pseudo 2nd order Kinetics for the adsorption of Cd^{2+} ions onto RBF and ATBF

TABLE-2
KINETICS PARAMETERS FOR THE
ADSORPTION OF Cd^{2+} ION ONTO RBF AND ATBF

Parameters	RBF	ATBF	
Pseudo-first-order	q_e (exp) (mg g^{-1})	0.641	0.868
	q_e (cal) (mg g^{-1})	2.332	1.329
	k_1	0.017	0.010
	R^2	0.9088	0.905
Pseudo-second-order	q_e (exp) (mg g^{-1})	0.641	0.868
	q_e (cal) (mg g^{-1})	0.967	0.983
	k_2	4.983	0.014
	R^2	0.9457	0.9571
Intraparticle diffusion	K_{id}	0.0514	0.0459
	C	-0.254	0.0059
	R^2	0.9709	0.9634
Elovich equation	A	-0.7357	-0.6654
	B	0.2296	0.2527
	R^2	0.9363	0.9687

dependent on the square root of time ($t^{1/2}$) rather than time (t), where the intercept (C) is related to the boundary layer [30,31]. The equation is as follows:

$$q_t = k_{id} t^{1/2} + C \quad (8)$$

where, q_t = amount of Cd^{2+} adsorbed at time 't' (mg g^{-1}); k_{id} = intraparticle diffusion constant ($\text{mg g}^{-1} \text{min}^{-1/2}$); C = constant related to the thickness of the boundary layer. Larger the intercept; higher is the boundary layer effect [32]. The value of k_{id} , C and R^2 were determined from the slope of plot q_t versus $t^{1/2}$ as given in Table-2. It was observed from the Fig. 7 that the value of intercept is not zero but high and it increases with increases in concentration of Cd^{2+} onto adsorption of RBF and ATBF.

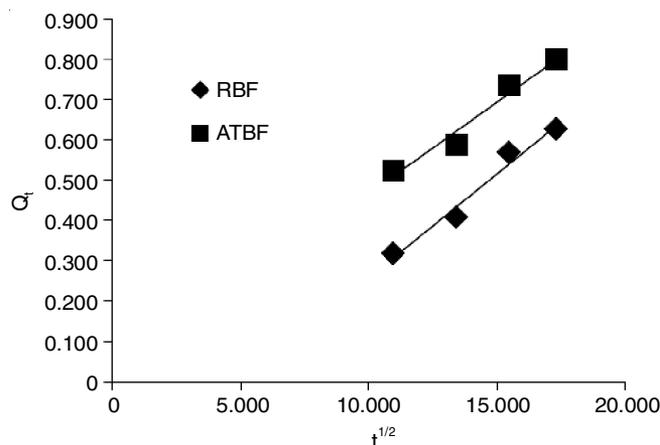


Fig. 7. Intraparticle diffusion for RBF and ATBF

The adsorption data was further tested with the Elovich equation which is given as [33]:

$$q_t = A + B \ln t \quad (9)$$

where A and B are Elovich constant. The values of A, B and R^2 are calculated and given in the Table-2, which tells that the process is physisorption process. It is evident that the experimental data is best followed by pseudo-second-order kinetics.

Adsorption isotherm: Several isotherms equations were tested for the equilibrium modeling of adsorption systems. Among these, the commonly used isotherms are the Langmuir

and Freundlich isotherm equations. The Langmuir equation assumes that (i) the solid surface presents a finite number of identical sites which have uniform energy; (ii) there is no interaction between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption; (iii) a monolayer is formed when the solid surface reaches saturation [34]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{b \cdot q_m} + \frac{1}{q_m} \frac{1}{C_e} \tag{10}$$

where, q_e is the equilibrium capacity of Cd^{2+} on adsorbent ($mg\ g^{-1}$), C_e is the equilibrium concentration of cadmium solution ($mg\ L^{-1}$), q_m is the monolayer adsorption capacity of adsorbent ($mg\ g^{-1}$), b is the Langmuir constant ($L\ mg^{-1}$) which is related to free energy of adsorption. A plot of $1/q_e$ versus $1/C_e$ is plotted (Fig. 8) and the values obtained are given in Table-3.

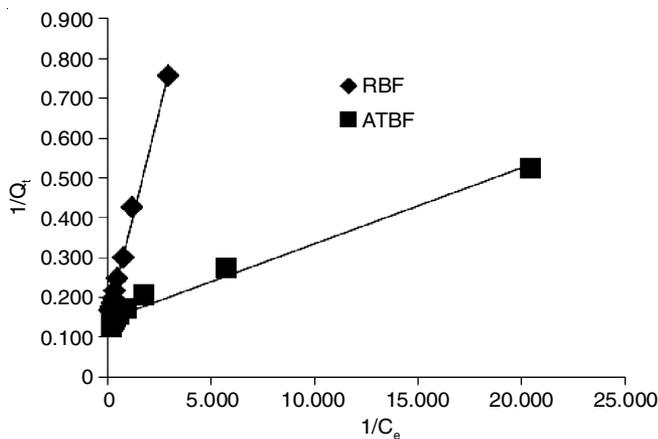


Fig. 8. Langmuir Isotherm for the adsorption of Cd^{2+} ions onto RBF and ATBF

Parameters		RBF	ATBF
Langmuir isotherm	q_{max} ($mg\ g^{-1}$)	0.4690	5.2300
	b (mg^{-1})	1.5360	0.1320
	R^2	0.9968	0.9815
Freundlich isotherm	$1/n$	0.4940	0.2717
	K_f	0.2590	0.5130
	R^2	0.9632	0.9576

The Freundlich model is an empirical equation based on adsorption on a heterogenous surface. It is also assumed that as the heat of adsorption increases the number of adsorption sites increase exponentially [35]. The linear form of Freundlich equation is given as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{11}$$

where, q_e is the adsorption capacity of metal ion at concentration ($mg\ g^{-1}$), K_f [$(mg\ g^{-1})(L\ mg^{-1})(1/n)$] and $1/n$ are Freundlich constant which is related to adsorption capacity and adsorption intensity, respectively. The plot of $\log q_e$ versus $\log C_e$ with different adsorbents (RBF and ATBF) is shown in Fig. 9 and the values of the constant and R^2 are given in Table-3. The value

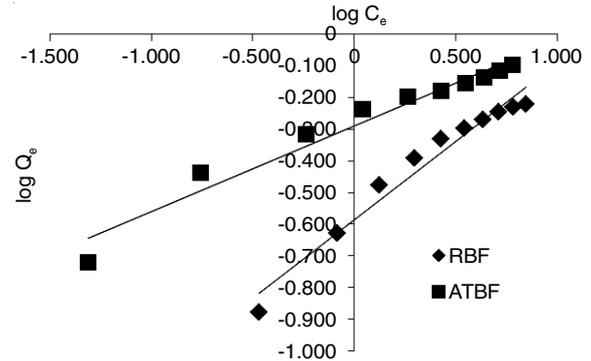


Fig. 9. Freundlich Isotherm for the adsorption of Cd^{2+} ions onto RBF and ATBF

of $1/n$ and correlation coefficient (R^2) which favour adsorption isotherm predicts the feasibility.

Conclusion

The present study reveal that banana fiber treated with H_2SO_4 is highly favourable and can be used as an alternative adsorbent for the removal of Cd^{2+} from aqueous solution. The Cd^{2+} adsorption on banana fiber was pH dependent. The adsorption process followed a pseudo-second-order kinetic model and best fitted by Langmuir isotherm in case of RBF and ATBF. The monolayer adsorption capacity of RBF is $0.469\ mg\ g^{-1}$ and for ATBF is $5.230\ mg\ g^{-1}$. The negative value of ΔH° (-9.874) $kJ\ mol^{-1}\ K^{-1}$ and ΔS° (-5.152) $kJ\ mol^{-1}\ K^{-1}$ indicate the exothermic nature and the randomness at solid/liquid solution interface during the adsorption of ion on RBF and ATBF which show the process is exothermic, with decrease in spontaneity with increase in temperature. An attempt has been made to compare the present results with some of the reported agriculture waste adsorbents for cadmium(II) ions (Table-4). A comparison of various low-cost adsorbents derived from different agricultural wastes for the removal of cadmium(II) ions is summarized in Table-4. However, a right cost evaluation is related to the application scale and, although many studies about non-conventional low-cost adsorbents are available in the literature, they are limited to laboratory scale only.

Adsorbents	q_{max} (mg/g)	Ref.
Hickory modified biochar (HMB)	0.9800	[36]
Exhausted coffee	1.4800	[37]
Banana peel	4.7500	[38]
Walnut sawdust	4.5100	[39]
Coconut copra meal	4.9900	[40]
Rice husk	4.0000	[41]
Palm kernel shell charcoal	0.4689	[42]
Palygorskite	4.5400	[43]
Corn cob	5.0900	[44]
Hazelnut shell	5.4200	[45]
Wheat bran	0.7000	[46]
Tea wastes	2.5900	[47]
Charcoal	2.9000	[48]
Rice bran	1.1000	[49]
Mangosteen shell	3.1500	[50]
Raw banana fiber	0.4690	Present study
H_2SO_4 treated banana fiber	5.2300	Present study

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