Sorption of Cadmium(II) from Aqueous System by Using Bicarbonate Impregnated Sulphuric Acid Treated *Pongamia pinnata* Seedpod Carbon

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The adsorption of Cd(II) on modified bicarbonate impregnated sulphuric acid treated *Pongamia pinnata* activated carbon (BSPAC) prepared from its seedpods was investigated. The maximum adsorption was observed as a function of solution pH, contact time, carbon dosage and initial metal ion concentration. The adsorption capacity of adsorbent for cadmium was obtained by using Freundlich, Langmuir and Temkin isotherms. Kinetic studies were made with pseudo-first-order, pseudo-second-order and reversible-first-order kinetic equations. The results were compared with commercially available activated carbon (CAC) of 20-50 ASTM mesh size.

Key Words: Cadmium removal, Isotherm, Kinetics, *Pongamia pinnata* seedpod activated carbon.

INTRODUCTION

Cadmium has been considered as the most inorganic toxic pollutant present in water due to increasing industrialization and population[1,2]. Researchers published numerous articles for the removal of cadmium from aqueous system by using different carbon adsorbents prepared from various organic waste materials[3-7]. In the present work activated carbon prepared from *Pongamia pinnata* seedpods by sulphuric acid treatment followed by bicarbonate impregnation was used for the removal of cadmium(II) from aqueous solution by batch adsorption techniques.

EXPERIMENTAL

Pongamia pinnata seedpods, available largely as a waste material, were collected from in and around of Salem, Tamilnadu, India. The material was washed with distilled water and dried at 105 ± 5 °C. Then it was cut into small pieces and sieved to 20-50 ASTM mesh size. The sieved material was treated with concentrated sulphuric acid in the weight ratio 1:1 and kept in an air oven at 160 ± 5 °C for 24 h. The carbonized material was washed with distilled water to remove the free acid and dried at 105 ± 5 °C. Then it was repeatedly soaked in 1 % sodium bicarbonate solution until effervescence ceased and further soaked in the same solution for 2 days.

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The material was then washed with distilled water to remove the residual bicarbonate, dried at 105 ± 5 °C and again sieved to 20-50 ASTM mesh size (BSPAC). The commercial activated carbon procured from SD Fine chemicals was also ground and sieved to the same 20-50 ASTM mesh size and comparative studies were simultaneously carried out. The characteristics of bicarbonate impregnated sulphuric acid treated *Pongamia pinnata* activated carbon (BSPAC) and commercially available activated carbon (CAC) were determined using standard procedures.

All the chemicals used for the analysis were of analytical reagent grade from E-Merck and SD Fine. Working standards were prepared in distilled water by progressive dilution of stock cadmium solution (1000 mg/L). The pH of the solutions was adjusted using 0.1 M HNO_3 and 0.1 M NaOH solutions.

Batch adsorption experiments: Adsorption studies were carried out using 100 mL of Cd(II) solution of desired concentration taken in 300 mL capacity polythene bottles. The pH was adjusted to a desired value by using dilute sulfuric acid and sodium hydroxide solutions. Known amounts of BSPAC or CAC were added and the solutions were agitated for a predetermined period at 30 ± 1 °C in a horizontal mechanical shaker. Then the carbons were separated by centrifugation and the filtrate was analyzed by using atomic absorbance spectrophotometer (Elico SL 161 Model). Adsorption isotherm and kinetic studies were carried out with different initial concentration of Cd(II) with optimum carbon dose. In order to correct for any adsorption of Cd(II) onto the containers, control experiments were carried out without adsorbent. It was found that there was no significant adsorption on the container walls.

Desorption studies: Desorption studies help in recycling the adsorbent and recovery of cadmium. After equilibrium, adsorbent saturated with cadmium was removed from solution and washed with distilled water to eliminate unadsorbed metal ions. The adsorbent, after washing, was treated with 100 mL of optimum concentration HCl solution and the bottles were shaken for optimum period at 30 ± 1 °C using a horizontal mechanical shaker. The solutions were then centrifuged and analyzed for cadmium ion concentration.

RESULTS AND DISCUSSION

Characteristics of both BSPAC and CAC were summarized in Table-1. BSPAC possesses higher surface area and ion exchange capacity than CAC. The high surface area of BSPAC suggests the availability of more sites on the activated carbon and the high ion exchange capacity is the mechanism for the adsorption of Cd(II). The high moisture content of BSPAC than CAC is due to the acid treatment that made the carbon more porous.

Effect of agitation time: The effect of agitation time at pH 5.00 ± 0.02 on the removal of Cd(II) present in the 100 mL solutions of 10 mg/L concentration with 100 mg of BSPAC and 500 mg of CAC was shown in Fig. 1. The maximum per cent removal of 99.5 was achieved at 3 h for BSPAC but in the case of CAC the maximum

TABLE-1
CARBON CHARACTERISTICS

Parameter	BSPAC	CAC
Bulk density (g/mL)	0.57	0.69
Moisture (%)	18.72	11.03
Ash (%)	9.82	4.72
Solubility in water (%)	1.04	0.91
Solubility in acid (%)	6.07	3.09
pH	7.12	7.68
Decolourizing power (%)	1.90	1.21
Ion exchange capacity (meq/g)	0.49	Nil
Surface area (m^2/g)	496	314
Iron (%)	0.23	0.58
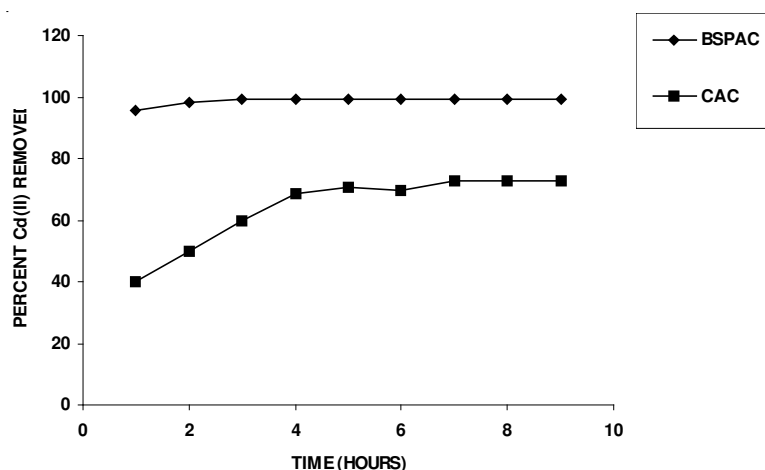
Fig. 1.   Effect of agitation time on the removal of Cd(II) from 10 mg/L at pH 5;
BSPAC-100 mg/100 mL and CAC-500 mg/100 mL

per cent removal was found to have 70.6 even after 5 h of agitation. This shows that the optimum time required by BSPAC would be approximately 1.6 times lesser than that required by CAC.

Effect of carbon dosage: The removal of Cd(II) as a function of carbon dosage by both BSPAC and CAC was shown in Fig. 2. It could be seen that for the quantitative removal of Cd(II) from an initial concentration of 10 mg/L, a given minimum carbon dosage of 25 and 500 mg/100 mL were required for BSPAC and CAC, respectively. However an optimum dose of 50 mg/100 mL was used in subsequent experiments in the case of BSPAC. The data clearly indicates that BSPAC is almost 20 times more effective than CAC. This may be due to the higher surface area and ion exchange groups present on the surface of BSPAC than CAC.

Effect of pH: The influence of pH for the removal of Cd (II) was shown in Fig. 3 for both BSPAC and CAC. It clearly shows that BSPAC was effective for the

quantitative removal of Cd(II) over the wide range of pH from 4.0 - 10.0 ± 0.02. However for further experiments an optimum pH of 6.00 ± 0.02 was taken for BSPAC. On the other hand CAC showed a narrow pH range of 6.0 - 8.0 ± 0.02 and an optimum pH of 7.0 ± 0.2 was considered for further experiments. At lower pH values, the removal of Cd(II) decreases which is due to the electrostatic repulsive forces acting between the dominant H_3O^+ ions and Cd(II) ions. Above optimum pH value, the metal ions start precipitating as $Cd(OH)_2$ causing a decrease in the removal.
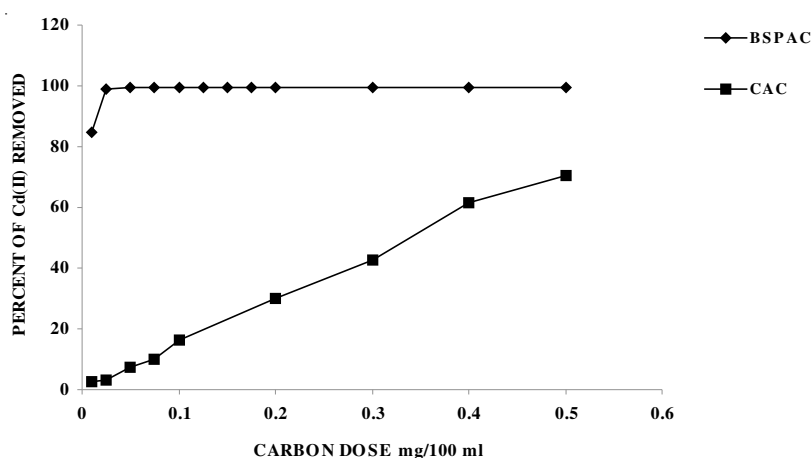
Fig. 2.   Effect of carbon dose on the adsorption of Cd(II) from 100 mL of 10 mg/L at pH 5; BSPAC: agitation time 3 h, CAC: agitation time 5 h
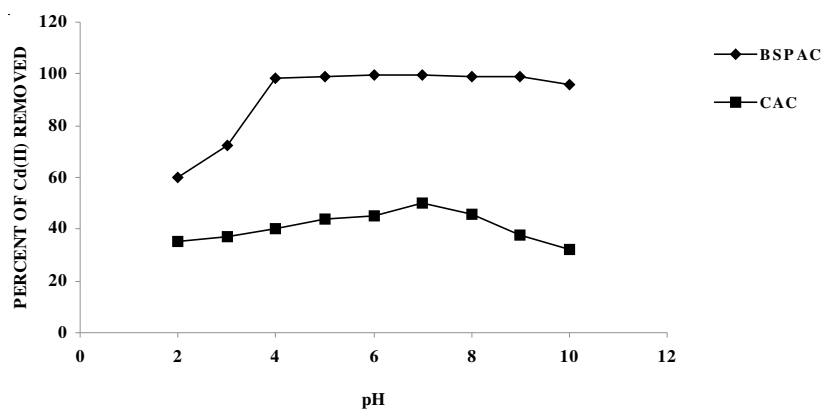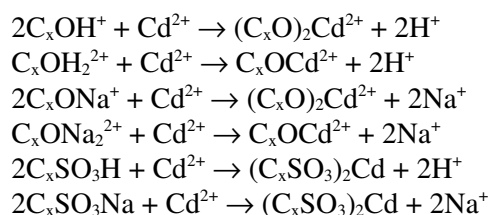
Fig. 3.   Effect of pH on the removal Cd(II) from 100 mL of 10 mg/L BSPAC: dosage, 50 mg; CAC: dosage, 500 mg

The following reaction mechanism may be suggested for the adsorption of Cd(II) on the BSPAC surface. Based on the work of Frumkin[8], the surface oxide groups present on carbon may undergo hydrolytic reactions with the result of proton

exchangeable sites such as $C_xOH_2^{2+}$, C_xOH^+ *etc.* Since BSPAC was prepared upon treatment with sulphuric acid followed by sodium bi-carbonate solution soaking, groups such as C_xONa^+, $C_xONa_2^{2+}$, C_xSO_3H and C_xSO_3Na may be present[9]. Hence it is expected that these Na^+ ions got exchanged with Cd(II) and soluble complexes of Cd(II). The Na^+ groups may be playing a significant role in removing cadmium ions as follows:

$$2C_xOH^+ + Cd^{2+} \rightarrow (C_xO)_2Cd^{2+} + 2H^+$$
$$C_xOH_2^{2+} + Cd^{2+} \rightarrow C_xOCd^{2+} + 2H^+$$
$$2C_xONa^+ + Cd^{2+} \rightarrow (C_xO)_2Cd^{2+} + 2Na^+$$
$$C_xONa_2^{2+} + Cd^{2+} \rightarrow C_xOCd^{2+} + 2Na^+$$
$$2C_xSO_3H + Cd^{2+} \rightarrow (C_xSO_3)_2Cd + 2H^+$$
$$2C_xSO_3Na + Cd^{2+} \rightarrow (C_xSO_3)_2Cd + 2Na^+$$

It may be stated that the presence of -OH groups on the surface of carbons is also indicated by FT-IR spectrum of BSPAC (at 3387 cm^{-1}) as shown in Fig. 13.

Desorption studies: To make the adsorption process more economical, it is important to desorb cadmium and to reuse the spent adsorbents. Desorption studies were carried out by batch process using hydrochloric acid of different concentrations ranging from 0.02-0.10 M. In highly acidic medium solutions, the protons (H$^+$ ions) displace the Cd(II) ions by ion exchange process. The per cent recoveries of Cd(II) from BSPAC were found to be 80.8, 90.0, 97.9, 97.8 and 97.9 by 0.02, 0.04, 0.06, 0.08 and 0.10 M hydrochloric acid, respectively and 0.04 M was taken as optimum concentration of HCl solution for subsequent desorption studies. The adsorption capacity of BSPAC was tested by performing five cycles of consecutive adsorption-desorption studies. The results show that the removal capacity of BSPAC for Cd(II) was maintained in the range 96-98 % even up to five cycles of operation.

Adsorption kinetics: Kinetic models[10,11] of pseudo-first-order, pseudo-second-order and reversible first-order equations were used for the purpose of investigating the sorption mechanism of cadmium on BSPAC and CAC.

The Lagergren pseudo-first-order kinetic model is expressed as

$$\ln (q_e - q_t) = -k_1 t + \ln q_e$$

where q_e and q_t are the amount of metal adsorbed (mg/g) at equilibrium at time t, respectively and k_1 = pseudo first order equilibrium rate constant (min^{-1}). The plots of $\ln (q_e - q_t)$ *versus* t gave straight lines (Figs. 4 and 5) for all different initial concentrations of Cd(II) indicating the applicability of the pseudo first order equation for both BSPAC and CAC. However, the correlation coefficient values (R^2) were low and the experimental q_e values did not coincide with the calculated ones. This shows that the sorption of Cd(II) onto BSPAC and CAC did not follow the pseudo first order mechanism.

The pseudo-second-order adsorption rate equation of Ho and Mckay[11a] can be written as
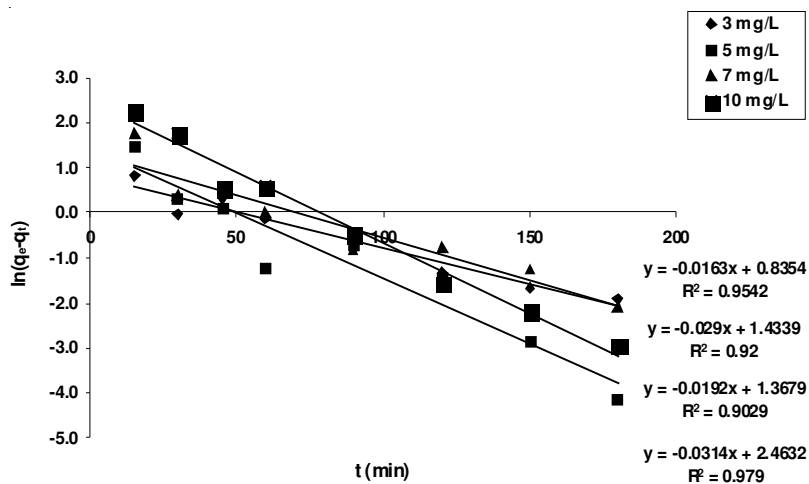
$$dq_t/dt = k_2 (q_e - q_t)^2$$

y = -0.0163x + 0.8354
R² = 0.9542

y = -0.029x + 1.4339
R² = 0.92

y = -0.0192x + 1.3679
R² = 0.9029

y = -0.0314x + 2.4632
R² = 0.979

Fig. 4. Kinetic fits for pseudo first order-BSPAC

y = -0.0195x - 2.3979
R² = 0.9137

y = -0.0185x - 1.0585
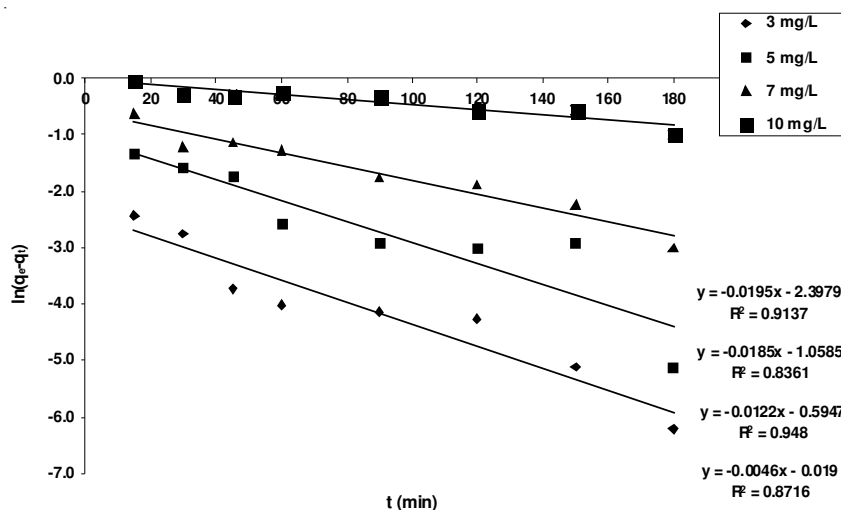R² = 0.8361

y = -0.0122x - 0.5947
R² = 0.948

y = -0.0046x - 0.019
R² = 0.8716

Fig. 5. Kinetic fits of pseudo first order-CAC

The integrated form of the above equation becomes:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e$$

where k_2 = pseudo-second-order adsorption rate constant (g mg^{-1} min^{-1}). The plots of t/q_t *versus* t produced straight lines (Figs. 6 and 7) for different initial concentrations of Cd(II) which indicated the applicability of pseudo-second-order model. The correlation coefficient values (R^2) were also high and the experimental q_e values were consistent with the calculated values for both BSPAC and CAC. This shows that the adsorption system could be explained well by pseudo second order kinetic model for all time intervals.
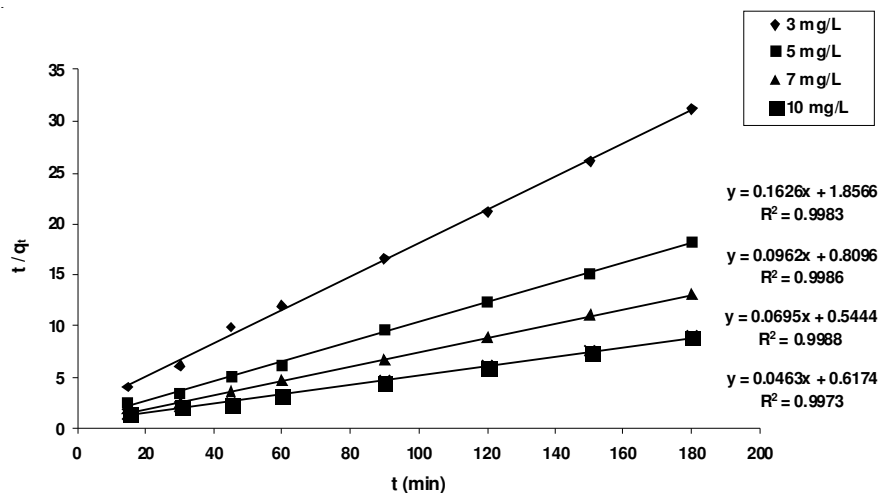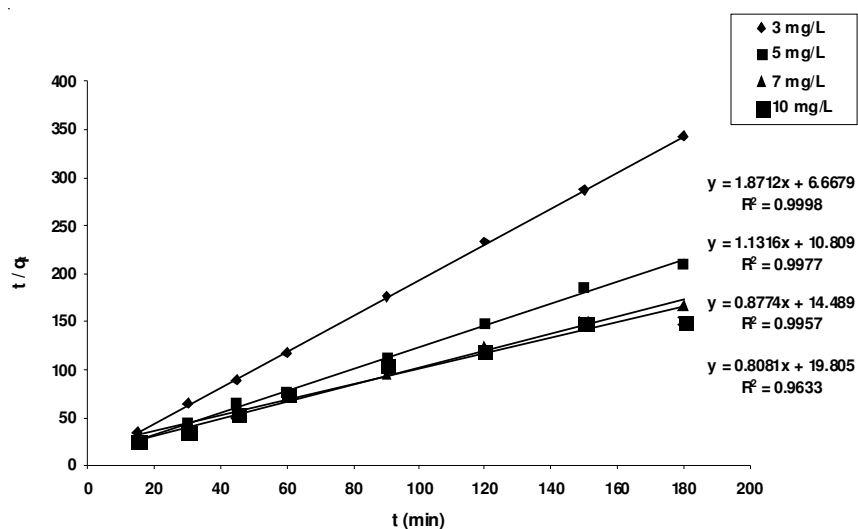
Fig. 6. Kinetic fits of pseudo second order-BSPAC

Fig. 7. Kinetic fits of pseudo second order-CAC

The reversible first-order rate equation for the sorption of metal ion from liquid phase to solid is expressed as:

$$\ln (1 - U_t) = - kt$$

where $U_t = (C_0 - C_t)/(C_0 - C_e)$.

The C_0, C_t and C_e are the concentrations of Cd(II) in mg/L initially, at time t and at equilibrium, respectively. k = overall rate constant (min⁻¹) of the reversible reaction. The plots of ln (1 - U_t) *versus* t gave straight lines (Figs. 8 and 9). The forward rate constants (k_f) and backward rate constants (k_b) were calculated using the following equations.
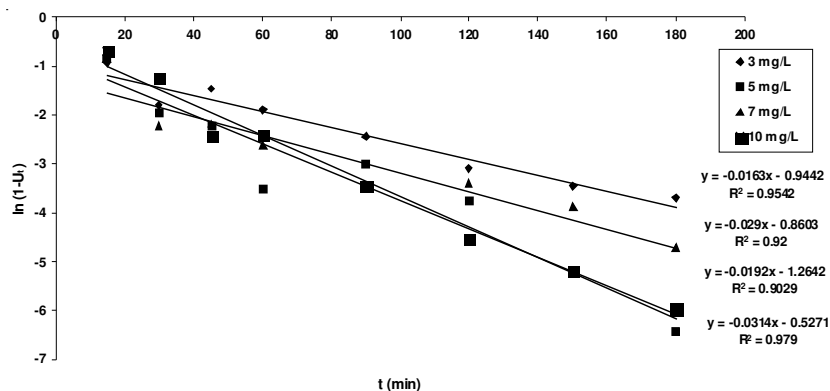
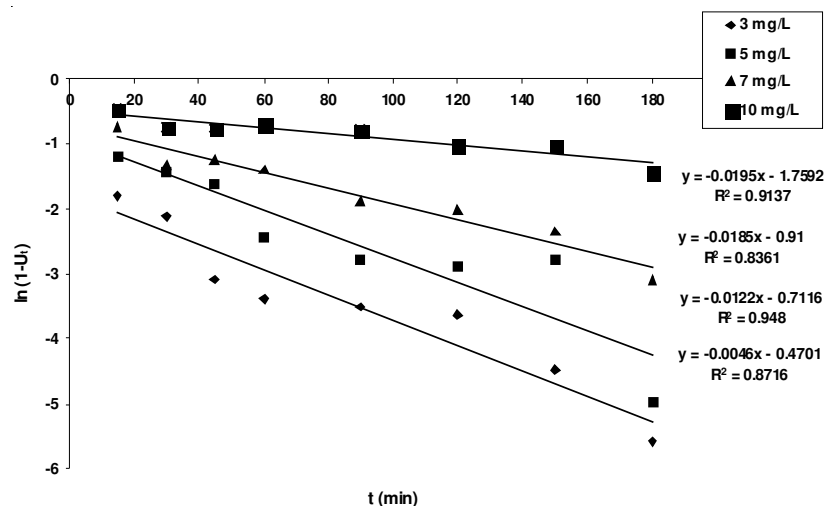Fig. 8. Kinetic fits of reversible first order-BSPAC

Fig. 9. Kinetic fits of reversible first order-CAC

$$k = k_f + k_b$$
$$K_C = k_f/k_b$$
$$k = k_f [1 + (1/K_C)]$$

where K_C = equilibrium constant. The kinetic data for the sorption of cadmium on activated carbons are presented in Table-2. It could be seen that the forward rate constants were found to be higher than backward rate constants, suggesting the rate of adsorption is clearly dominant for both BSPAC and CAC.

Adsorption isotherm: The adsorption of cadmium(II) on BSPAC and CAC was described as a function of different initial metal ion concentrations at optimum pH conditions as shown in the Figs. 10-12. The Freundlich, Langmuir and Temkin isotherm models were applied to explain the sorption capacity of cadmium(II) by BSPAC and CAC.

TABLE-2
ADSORPTION KINETICS DATA FOR CADMIUM(II) REMOVAL

Adsorbent	Conc. of Cd(II) (mg/L)	q_e (exp) (mg/g)	Pseudo-first order			Pseudo-second order			Reversible-first order			
			k_1 (min^{-1})	R^2	q_e (theo) (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2	q_e (theo) (mg/g)	k	k_f	k_b	R^2
BSPAC	3	5.93	0.016	0.954	2.31	0.014	0.998	6.15	0.0163	0.0161	0.0002	0.954
	5	9.92	0.029	0.920	4.20	0.011	0.999	10.40	0.0290	0.0288	0.0002	0.920
	7	13.9	0.019	0.903	3.93	0.009	0.999	14.39	0.0192	0.0191	0.0001	0.903
	10	19.9	0.031	0.979	11.74	0.004	0.997	21.60	0.0314	0.0312	0.0002	0.979
CAC	3	0.53	0.020	0.914	0.09	0.534	0.999	0.53	0.0195	0.0172	0.0023	0.914
	5	0.86	0.019	0.836	0.35	0.120	0.998	0.88	0.0185	0.0159	0.0026	0.838
	7	1.12	0.012	0.948	0.55	0.053	0.996	1.14	0.0122	0.0098	0.0024	0.948
	10	1.57	0.005	0.872	0.98	0.033	0.963	1.24	0.0046	0.0036	0.0010	0.872

$y = 0.7722x + 2.3701$
$R^2 = 0.9242$

$y = 0.6162x - 0.006$
$R^2 = 0.9951$

Fig. 10. Freundlich isotherm model

$y = 0.0023x + 0.0012$
$R^2 = 0.9878$

$y = 0.4338x + 0.3989$
$R^2 = 0.9392$
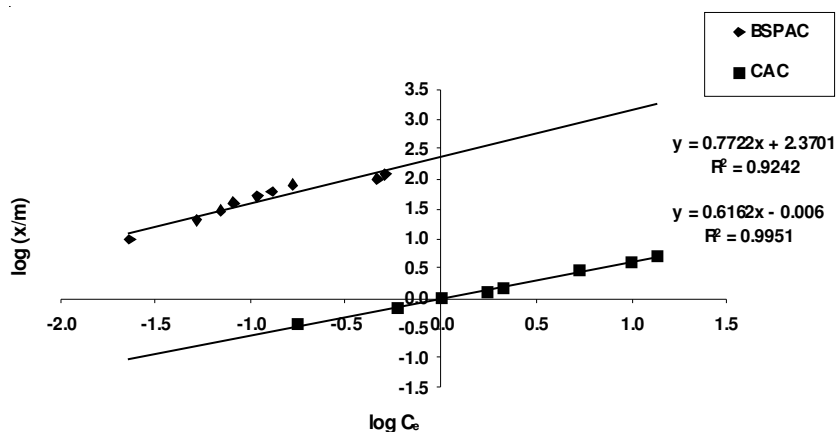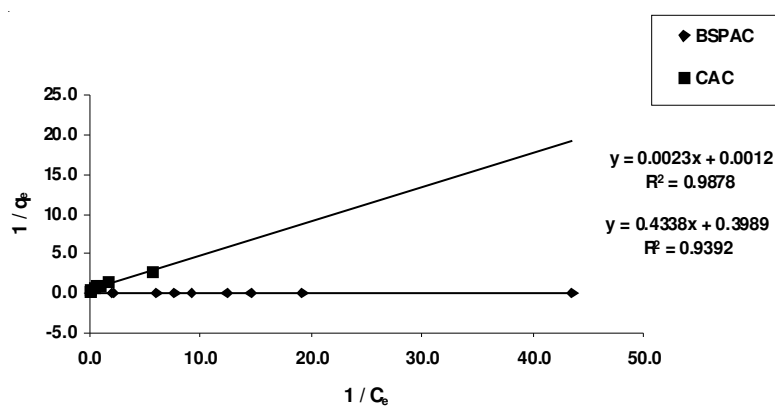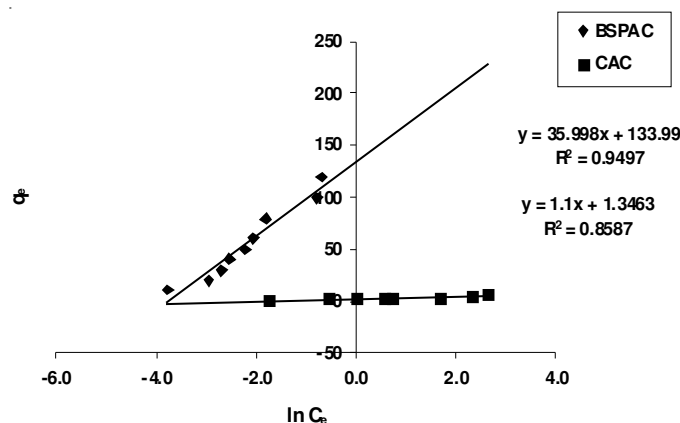
Fig. 11. Langmuir isotherm model

Fig. 12. Temkin isotherm model

The relationship between the metal uptake capacity [log (x/m)] of adsorbent and the residual metal ion concentration (C_e) at equilibrium conditions is given by Freundlich[12] as:

$$\log (x/m) = \log K_F + 1/n \log C_e$$

where x/m = amount of metal ions adsorbed per unit mass of BSPAC or CAC (mg/g) and C_e = equilibrium metal ion concentration (mg/L). The intercept log K_F is the measure of adsorbent capacity and the slope n is the sorption intensity. The plots of log (x/m) *versus* log C_e were linear (Fig. 10) for both BSPAC and CAC. The values of the constants K_F and n for both activated carbons were calculated from the plots and given in Table-3. The values of n were found to be 1 to 10, *i.e.*, 1 < n < 10, indicating the favourable adsorption of Cd(II) on both BSPAC and CAC.

TABLE-3
ADSORPTION ISOTHERM DATA FOR CADMIUM(II) REMOVAL

Adsorbent	Freundlich isotherm			Langmuir isotherm			Temkin isotherm		
	K_F	n	R^2	a	b	R^2	K_t	B	R^2
BSPAC	234.48	1.30	0.924	833.3	0.522	0.988	41.35	35.99	0.950
CAC	0.986	1.62	0.995	2.507	0.920	0.939	3.40	1.1	0.859

The Langmuir isotherm is based on the assumption of monolayer adsorption onto an adsorbent containing finite number of adsorption sites with uniform energies of adsorption and with no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir equation[13-15] is described as:

$$1/q_e = 1/a + (1/ab) (1/C_e)$$

where C_e = equilibrium metal ion concentration (mg/L) and q_e = amount of Cd(II) adsorbed at equilibrium (mg/g). a and b are Langmuir constants representing measure of adsorption capacity and measure of energy of adsorption, respectively. The linear

nature of the plots of $1/C_e$ *versus* $1/q_e$ shows that the adsorption follows the Langmuir model for both BSPAC and CAC (Fig. 11).

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is given as:

$$R_L = 1/(1 + bC_o)$$

where b and C_0 are the Langmuir constant representing the nature of adsorption and the initial Cd(II) ion concentration (mg/L), respectively. Table-4 gives the relationship between the R_L values and the isotherm shapes. The calculated R_L values as shown in the Table-5 were between 0 to 1 for both BSPAC and CAC suggesting favourable adsorption of Cd(II) on BSPAC and CAC.

TABLE-4
R_L VALUES AND ISOTHERMS

R_L Value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

TABLE-5
EQUILIBRIUM PARAMETER, R_L

Initial Cd(II) concentration (mg/L)	BSPAC	Initial Cd(II) concentration (mg/L)	CAC
5	0.277	2	0.352
10	0.161	4	0.214
15	0.113	6	0.153
20	0.087	8	0.120
25	0.071	10	0.098
30	0.060	20	0.052
40	0.046	30	0.035
50	0.037	40	0.026
60	0.031	–	–

Temkin equation assumes that the heat of adsorption falls with increasing surface coverage due to sorbate-sorbent interactions and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The general form of Temkin equation[16] is given as:

$$q_e = B \ln K_t + B \ln C_e$$

where B and K_t are the constants representing the equilibrium binding constant corresponding to maximum binding energy and the heat of sorption, respectively. From the plots of $\ln C_e$ *versus* q_e (Fig. 12), the values of isotherm constants K_t and B were calculated.

The correlation coefficient (R^2) values were calculated for all the above isotherm models and the values of constants were summarized in Table-3. From the values of R^2, it has been found that Langmuir isotherm model fit well for BSPAC while Freundlich model for CAC.

FT-IR and SEM studies: The functional groups which are responsible for Cd(II) metal uptake in BSPAC and CAC were examined by using solid state FT-IR (Shimaduz, FTIR 8400S) spectral analysis. FT-IR spectra for both BSPAC and CAC, before and after adsorption processes were recorded and adsorption peaks were interpreted. Spectra displays a number of absorption peaks, indicating the complex nature of the material examined. The broad peaks at 3387 and 1037 cm^{-1} of BSPAC indicated the presence of O-H and S=O groups, respectively which shows that the material was prepared by sulphuric acid treatment. It could also be observed that all the peaks in the figures (Figs. 13-16) are responsible for cadmium adsorption, since they are shifted to lower absorbance value after the adsorption process. The scanning electron microscope (SEM-Joel JSM 6360) images of BSPAC and CAC were recorded. The SEM images of BSPAC and CAC presented in Figs. 17 and 18, show the presence of minute pores on the carbon surface which is responsible for the adsorptive capacity of both the activated carbons.
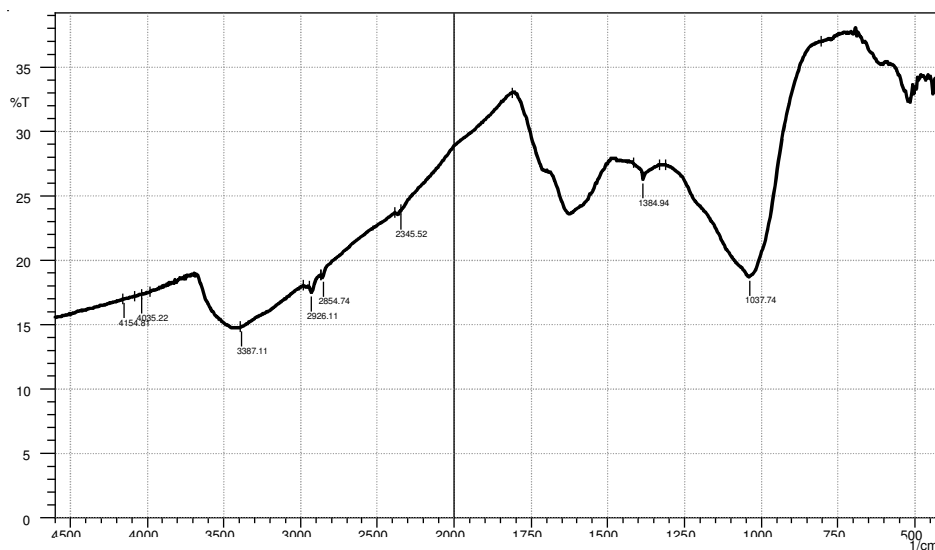

Fig. 13. FT-IR spectrum of BSPAC-before adsorption

Conclusion

The removal of cadmium(II) from aqueous solution is possible by using abundantly available low cost carbon adsorbents prepared from *Pongamia pinnata* seedpods. Detailed experimental investigations have been carried out for Cd(II) using a concentration of 10 mg/L under various pH conditions and different carbon dosages which
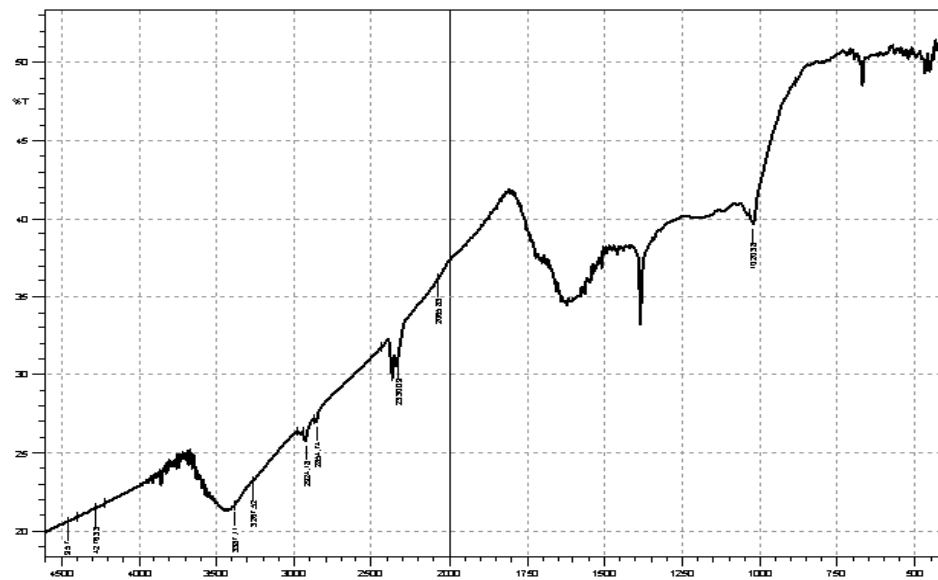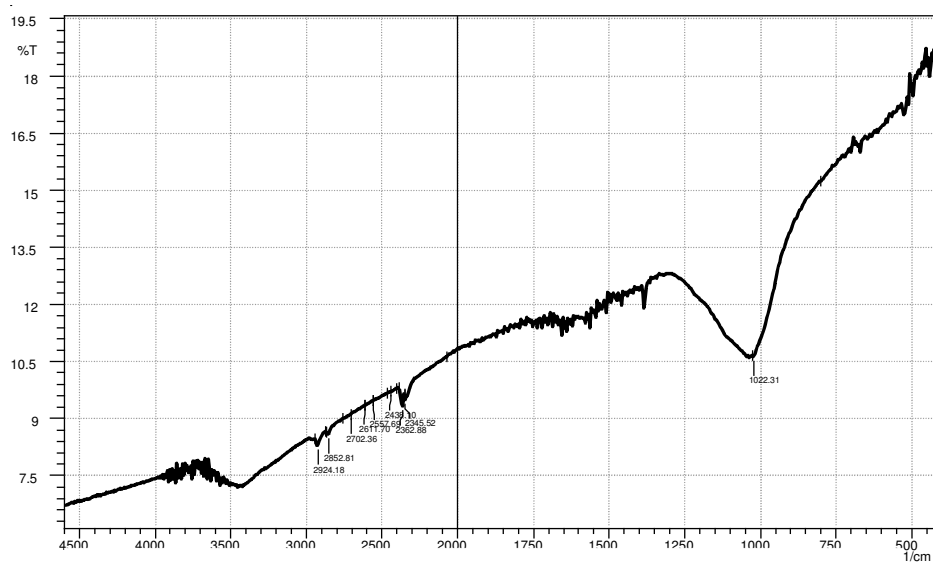
Fig. 14. FT-IR spectrum of BSPAC-after adsorption

Fig. 15. FT-IR spectrum of CAC-before adsorption

indicated that BSPAC showed 20 times greater adsorption capacity over a wider range of pH than CAC. The high R^2 values and the coinciding theoretical and experimental q_e values suggest that the adsorption of Cd(II) on BSPAC and CAC follow pseudo-second-order kinetic equation. The bicarbonate impregnated sulphuric acid treated *Pongamia pinnata* activated carbon (BSPAC) prepared from its seedpods
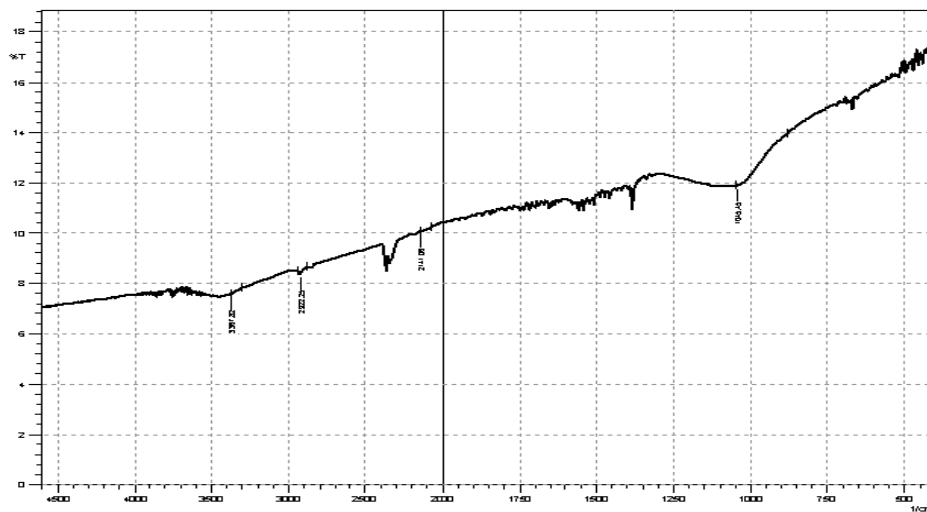
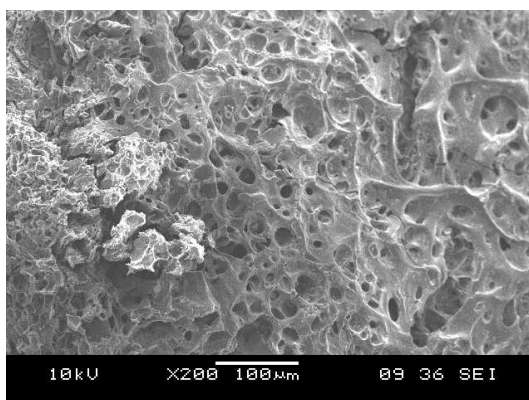Fig. 16. FT-IR spectrum of CAC-after adsorption

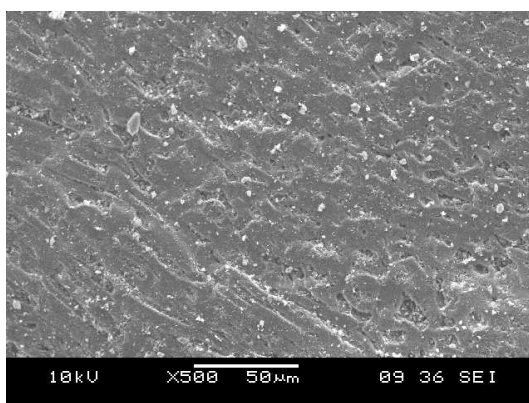Fig. 17. SEM image of BSPAC

Fig. 18. SEM image of CAC

has followed the Langmuir isotherm equation while commercial activated carbon is conformed to Freundlich isotherm equation based on their regression coefficient (R^2) values. The adsorption capacity of BSPAC is found to be more and quantitative than commercial activated carbon based up on its isotherm constants and wider pH range for Cd(II) sorption. The reported data may be useful in developing a cheap and waste material for the process involving stirred tank flow reactors in the removal and recovery of Cd(II) from cadmium containing water from chemical and allied process industries.

REFERENCES

1. P.N. Cheremisinoff, Hand Book of Water and Wastewater Treatment Technology, New York, Marcel Dekker Inc. (1995).
2. M.R. Spivey Fox, *J. Food Sci.*, **39**, 321 (2006).
3. A. Arulanantham, N. Balasubramaniam and T.V. Ramakrishna, *Metal Finish.*, **87**, 51 (1989).
4. H.A. Jamali, A.H. Mahvi and S. Nazmara, *World App. Sci. J.*, **5**, 16 (2009).
5. K. Periyasamy and C. Namasivayam, *Ind. Eng. Chem. Res.*, **33**, 317 (1994).
6. A.B. Perez-Marin, V.M. Zapata, J.F. Ortuño, M. Aguilar, J. Sáez and M. Lloréns, *J. Hazard. Mater.*, **139**, 122 (2007).
7. E.I. El-Shafey, *J. Hazard. Mater.*, **147**, 546 (2007).
8. A. Frumkin, *Kolloidz*, **51**, 123 (1930).
9. A. Ramadevi and K. Srinivasan, *Ind. J. Chem. Tech.*, **12**, 407 (2005).
10. V.B.H. Dang, H.D. Doan, T. Dang-Vu and A. Lohi, *Bioresour. Tech.*, **100**, 211 (2009).
11. A. Sharma and G.K. Bhattacharyya, *J. Hazard. Mater.*, **125B**, 102 (2005).
11a. Y.S. Ho and G. McKay, *Water Res.*, **34**, 735 (2000).
12. H. Freundlich and W.J. Helle, *J. Am. Chem. Soc.*, **61**, 2 (1939).
13. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
14. A. Meena and C. Rajagopal, *Ind. J. Chem. Tech.*, **10**, 72 (2003).
15. C. Namasivayam and D. Sangeetha, *Ind. J. Chem. Tech.*, **12**, 513 (2005).
16. M.J. Tempkin and V. Pyzhev, *Acta Physiochim. URSS*, **12**, 217 (1940).