



Removal of Cadmium(II) from Aqueous Solution by Bicarbonate Modified Coconut Oilcake Residue Carbon

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The adsorption of Cd(II) on modified coconut oilcake residue carbon (bicarbonate treated coconut oilcake residue carbon-BCORC) was employed for the removal of Cd(II) from water and wastewater. The influence of various factors such as agitation time, pH and carbon dosage on the adsorption capacity has been studied. Adsorption isothermal data could be interpreted by Langmuir and Freundlich equations. In order to understand the reaction mechanism, kinetic data has been studied using reversible first order rate equation. Similar studies were carried out using (commercially available activated carbon-CAC), for comparison purposes. Column studies were also conducted to obtain breakthrough capacities of bicarbonate treated coconut oilcake residue carbon and commercially available activated carbon. Common anions and cations affecting the removal of Cd(II) on both the carbons were also studied. Experiments were also done with wastewater containing Cd(II), to assess the potential of these carbons.

Key Words: Cadmium(II) removal, Bicarbonate treated coconut oilcake residue carbon, Adsorption by batch and column studies.

INTRODUCTION

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentration. These toxic metals have become an eco toxicological hazard of prime interest and increasing significance owing to their tendency to accumulate in living organisms¹. Cadmium is attracting wide attention of environmentalists as one of the most toxic heavy metals. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining process². Cadmium has been recognized for its negative effects on the environment where it readily accumulates in living system. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung diseases, cancer in humans³. The maximum levels permitted in wastewater are 0.01mg/dm³ for cadmium⁴. Various techniques have been employed for the treatment of heavy metal waste, such as chemical precipitation, adsorption, electrolysis, ion exchange and reverse osmosis⁵. Due to increase in environmental awareness and government policies, there has been a push towards development of new environment friendly ways to clean metal contamination of water⁶. Adsorption appears to be one of the most promising techniques for the treatment of waste stream contaminated by metal ions⁷. According to Huang, activated carbons are capable of adsorbing metals include chromium, cadmium, mercury,

copper, iron, zinc, nickel vanadium, gold and silver⁸. Activated carbon is one of the most popular adsorbents for the removal of metal ions from aqueous solutions^{9,10}. However high cost of commercially available activated carbon limits its use in developing countries and there is growing need to prepare activated carbon from cheaper and readily available waste materials. A variety of low-cost adsorbent derived from agricultural waste such as almond shells, olive stones and peach stones¹¹, coconut coir¹², coconut coir pith¹³, cotton stalks¹⁴, date-pits¹⁵, sugarcane bagasse pith¹⁶, cocoa shells¹⁷ and ciewa pendandra hulls¹, for cadmium(II) removal have been reported.

The aim of this study is to investigate the application of activated carbon prepared from coconut oilcake residue for the removal of cadmium(II) by continuous adsorption method. This paper describes the investigation carried out with respect to the removal of Cd(II) ion from aqueous system on by bicarbonate treated coconut oilcake residue carbon (BCORC) and attempts were made to compare with commercial activated carbon (CAC). This present investigation deals with batch studies, kinetic studies, adsorption isotherms and column studies for the removal of cadmium(II) by both carbons in order to evaluate the potential of these carbons.

EXPERIMENTAL

Preparation of carbons: Coconut oilcake residue procured from oil industries was washed with distilled water, dried at

110 °C, cut into small pieces and sieved to 0.575 mm (20-50 ASTM) mesh size. Then it was treated with concentrated sulphuric acid in 1:1 weight ratio and kept in an air-oven at 150 ± 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 2 % sodium bicarbonate until effervescence ceased and further soaked in the same solution for 2 days to remove any residual acid. The material was then washed with distilled water, dried at 105 ± 5 °C and again sieved to 20-50 ASTM mesh size (BCORC). Preliminary studies were carried out with raw coconut oilcake residue, sulphuric acid treated coconut oilcake residue and bicarbonate treated coconut oilcake residue for the removal of Cd(II). Based upon their efficiency, BCORC was chosen for further studies. The commercially available activated carbon (CAC) (SD fine chemicals) was procured from the market and sieved to 20-50 ASTM mesh size and characteristics were also found out. The characteristics of BCORC and CAC are summarized in Table-1.

TABLE - 1
CHARACTERISTICS OF BCORC AND CAC CARBONS

Description	Results	
	BCORC	CAC
Bulk (or) apparent density (g mL ⁻¹)	0.54	0.66
Moisture (%)	6.78	13.4
Ash (%)	5.5	2.4
Matter soluble in water (%)	1.93	1.15
Matter soluble in acid (%)	6.44	19.86
pH	7.6	8.15
Decolourizing power (MBT) (mg/g)	6.75	4.5
Phenol number	20.78	12.25
Ion exchange capacity (m equiv g ⁻¹)	0.75	Nil
Surface area (sq m/g)	211	214
Iron (%)	0.73	1.29

Preparation of solutions: A stock solutions of Cd(II) ions 500 mg/L was prepared by dissolving CdSO₄·8H₂O in distilled water. The stock solution was diluted with distilled water to obtain working solutions of desired concentration. The pH of the solutions was adjusted to the required value by using 0.1 M NaOH or 0.1 M HNO₃ solutions.

All the chemicals used for this study were of analytical reagent grade obtained from E. Merck, Ranbaxy, SD Fine and BDH.

Batch experiments: A stock solution of 100 mg/L of Cd(II) was prepared. Batch experiments were conducted in polythene bottles of 300 mL capacity. 100 mL of the solution containing 10 mg/L of Cd(II) ions under investigation adjusted to desired pH were taken in bottles and equilibrated for specific periods of time in a rotary mechanical shaker. At the end of equilibration period, the solutions were filtered using a G-3 crucible and the concentrations of Cd(II) ions were established by atomic absorption spectrophotometer (Elico, Model - SL 163). Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Cd(II) by the modified carbon dosage at constant level. Cd(II) removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} \times 100$$

where, C_i and C_f are the initial and final Cd(II) concentrations, respectively.

Column experiments: The investigation of column studies was done with sufficient weight of BCORC packed in a cylindrical tube of 2.5 cm diameter fitted with a Teflon stopper through the column. Optimum weight of carbon under proper flow rate and bed height conditions was used for column studies. An optimum flow rate of 10 mL/min with the optimum bed height of 6.5 cm was employed to assess the potential of BCORC carbon. Similarly other column of same diameter containing commercially available activated carbon was packed under an optimum bed height of 5 cm and a flow rate of 6 mL/min was maintained. The initial concentrations of Cd(II) employed were in distilled water (200 mg/L) for BCORC and CAC. Percolation of Cd(II) solution was stopped as soon as Cd(II) concentration in the effluent exceeded the arbitrary value¹⁸ of 0.1 mg/100 mL (Breakpoint). 100 mL lot volumes were collected and analyzed for Cd(II) content by using atomic absorption spectrophotometer. Regeneration and recycling of BCORC was done by treating with dilute solution of 0.5 N hydrochloric acid (optimum concentration) followed by soaking in 2 % sodium bicarbonate. Commercial activated carbon was also generated with 0.5 N Hydrochloric acid (optimum concentration), thoroughly washed and reloaded in the column under wet conditions. Breakthrough studies pertaining to Cd(II) adsorption in the presence of common impurities such as bicarbonate, chloride, sulphate, calcium and magnesium were done under optimum bed height and flow rate condition for both carbons.

Regeneration studies: In order to find out the percentage of Cd(II) desorbed, a series of experiments was conducted with both BCORC and CAC, by equilibrating with 100 mL of 10 mg/L of Cd(II) solution containing 150 mg of BCORC and 600 mg of CAC carbon at an optimum pH of 6 and 5, respectively and these solutions were equilibrated for 24 h. At the end of equilibration period, the solution was centrifuged and analyzed for Cd(II) content. The carbons were then separated carefully, washed several times with distilled water to remove any unadsorbed Cd(II). To each of these solution 100 mL of hydrochloric acid over the range 0.05-1.0 N was added and shaken for a period of 24 h, in a mechanical shaker.

RESULTS AND DISCUSSION

Examination of carbon characteristics (Table-1) shows that BCORC has considerable bulk density and high ion-exchange capacity. The moisture content of BCORC suggests that the acid treatment has made the carbon porous in nature. Even though BCORC shows lower surface area when compared with CAC, it has shown considerable ion-exchange capacity, which responsible for Cd(II) removal.

Effect of agitation time: Fig. 1. shows the effect of agitation time on the removal of Cd(II) by BCORC and CAC. The removal increases with time and attains equilibrium in 4 h for both BCORC and CAC for an initial Cd(II) concentration of 10 mg/L and for a carbon dosage 100 mg/100 mL. In the case of BCORC and CAC 99.9 and 35.7 % Cd(II) removal was achieved respectively.

Effect of pH: Fig.2. presents the effect of pH on the removal of Cd(II) by BCORC and CAC. It is evident that Cd(II)

removal was 99.9 % over the pH range 4.0-9.0 for BCORC and 38 % at pH of 5.0 for CAC. It could be noticed that BCORC is two times more effective in the removal of Cd(II) at an optimum pH of 6 when compared with CAC under an optimum pH of 5. Moreover BCORC has a wide range of pH when compared with CAC.

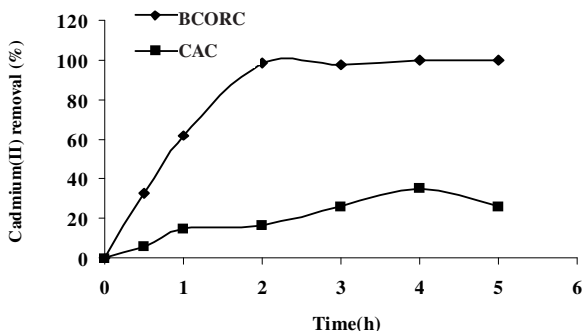


Fig. 1. Effect of contact time on the adsorption Cd(II)

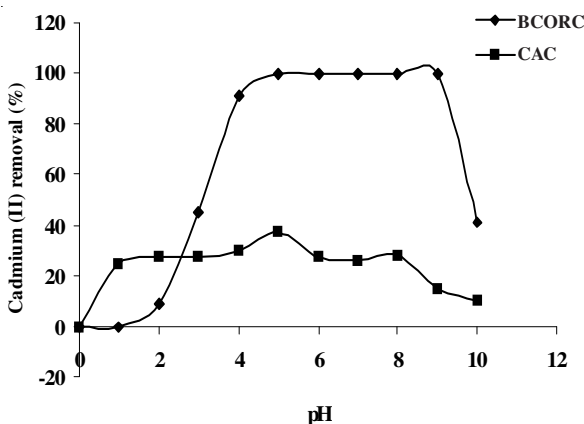
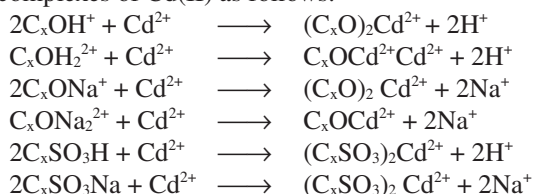


Fig. 2. Effect of pH on the adsorption Cd(II)

The influence of pH on Cd(II) removal may be explained as follows. A pure carbon surface is considered to be non-porous but in actual practice some carbon-oxygen complexes such as C_xO , CO_x and C_xO_2 are usually present which renders the surface slightly polar¹⁹. In the case of BCORC the following mechanism is suggested. Based upon the work of Frumkin²⁰, the surface oxide groups available on the surface of a carbon can undergo hydrolytic reaction with the result proton exchangeable sites such as $C_xOH_2^{2+}$, C_xOH^+ may be formed. Since BCORC was prepared upon treatment with sulphuric acid followed by sodium bicarbonate soaking, groups such as C_xONa^+ , $C_xONa_2^{2+}$ and C_xSO_3Na may also be present. Hence it is expected that Na^+ may be exchanging with Cd(II) and soluble complexes of Cd(II) as follows:



Effect of carbon dosage: Fig. 3 shows the removal of Cd(II) as a function of carbon dosage by both BCORC and CAC. It is evident that for 99.9 % removal of Cd(II) of 10 mg/L of Cd(II) in 100 mL, a minimum carbon dosage of 150 mg is

required in case of BCORC and 65 % of Cd(II) removal could be achieved with 500 mg of CAC. The data clearly indicated that BCORC is nearly 3 times more effective than CAC. This may be due to the moderate ion-exchange capacity of BCORC as compared to CAC.

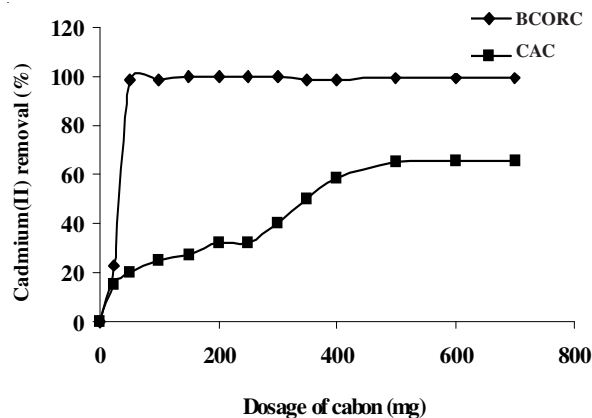


Fig. 3. Effect of carbon dosage on the adsorption of Cd(II)

Adsorption isotherms: The Langmuir equation was applied for adsorption equilibrium for both BCORC and CAC.

$$C_e/q_e = 1/Q_0b + C_e/Q_0$$

where, C_e is the equilibrium concentration mg/L. q_e is the amount adsorbed at equilibrium (mg/g) and Q_0 and b are Langmuir constant related to adsorption capacity and energy of adsorption, respectively. Linear plots C_e/q_e vs. C_e shows that the adsorption obeys the Langmuir model for both BCORC and CAC and it is shown in Fig. 4. Q_0 and b were determined from the Langmuir plots and found to be 2.1115 mg/g and 0.09286 mg/L respectively for BCORC and 2.564 mg/g and 0.1950 mg/L respectively for CAC. The ratio of Q_0 values of BCORC and CAC works out to be 0.82. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (or) equilibrium parameter R_L which is shown as $R_L = 1/(1+b C_0)$, where, b is Langmuir constant and C_0 be the initial concentration of Cd(II). R_L value shown in Table-2, indicate favourable adsorption of Cd(II) on both BCORC and CAC at the given concentration range at room temperature $30 \pm 1^\circ C$.

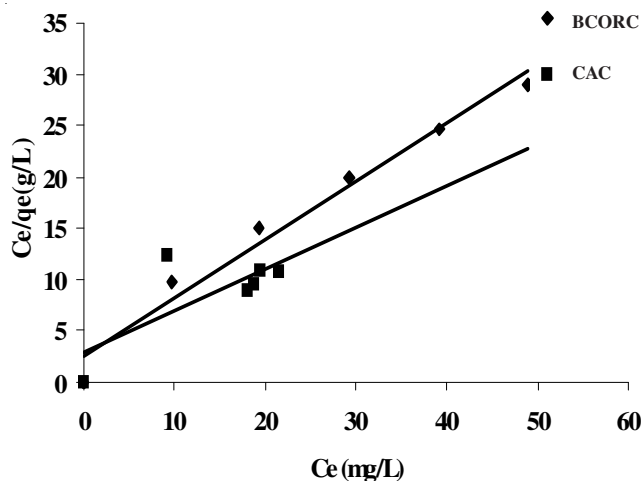


Fig. 4. Application of Langmuir model to the experimental data

Concentration in (mg/L)	R _L values	
	BCORC	CAC
10	0.0915	0.0836
20	0.0458	0.0418
30	0.0305	0.0278
40	0.0228	0.0209
50	0.0183	0.0167

Freundlich isotherm is represented by the equation²¹.

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

where, C_e is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit weight of BCORC (or) CAC (mg/g). Plots of $\log(x/m)$ vs. $\log C_e$ are linear for both BCORC and CAC. Fig. 5. shows the Freundlich adsorption isotherm for BCORC and CAC, in tap water and distilled water. The process followed was of Freundlich adsorption type. The 'K', 'n' and R^2 values for both the carbon were calculated from the intercepts and slopes, respectively and were shown in Table-3. The values of $1 < n < 10$ show favourable adsorption of Cd(II) on both BCORC and CAC²¹. The values of correlation coefficients (R^2) for Freundlich and Langmuir adsorption isotherm shows that R^2 value for Langmuir model are also very high when compared with Freundlich model. These results indicated that adsorption process could be more favourable for Langmuir isotherm model.

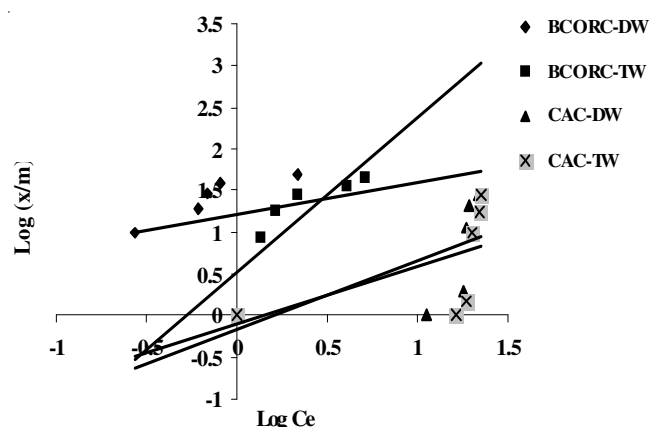


Fig. 5. Application of Freundlich model to the experimental data

Carbon	Freundlich model			Langmuir model		
	K(mg/g ⁻¹)	n(L mg ⁻¹)	R ²	q ₀ (mg/g ⁻¹)	b(L mg ⁻¹)	R ²
BCORC	26.3	1.399	0.846	2.11	0.0928	0.998
CAC	0.66	3.6	0.718	2.56	0.1950	0.980

Adsorption kinetics: The kinetics of Cd(II) adsorption on both BCORC and CAC follows the first order rate expression. The kinetic fits for both BCORC and CAC are shown in Figs. 6 and 7. The detailed mathematical derivations for calculating the reversible first order kinetics and the values of film and pore diffusion co-efficient are described elsewhere²². The kinetic data are furnished in Table-4. It is evident that the forward rate constant is much higher than the backward rate

constant, suggesting that the rate of adsorption is clearly dominant for BCORC and CAC. According to Michelsen¹⁹, for the adsorption of heavy metals on carbon surface, for film diffusion to be the rate determining process, the values of film diffusion co-efficient (D_f) should be between 10^{-6} - 10^{-8} cm²/sec. If pore diffusion (D_p) were to be rate determining, its value should be in the range of 10^{-11} - 10^{-13} cm²/sec. Using kinetic data, the values for film and pore diffusion constants were calculated (Table-5). It is evident that the removal of Cd(II) follows film diffusion process as outlined by Michelsen¹⁹, since the co-efficient values are very close to 10^{-8} cm²/sec (Table-5). Based on the regeneration studies, it could be seen from Table-6, about 98.00 and 65.0 % of Cd(II) could be recovered from BCORC and CAC, respectively with a minimum concentration of 0.5 M hydrochloric acid. Therefore it may be concluded that twice the amount of valuable Cd(II) could be recovered with BCORC.

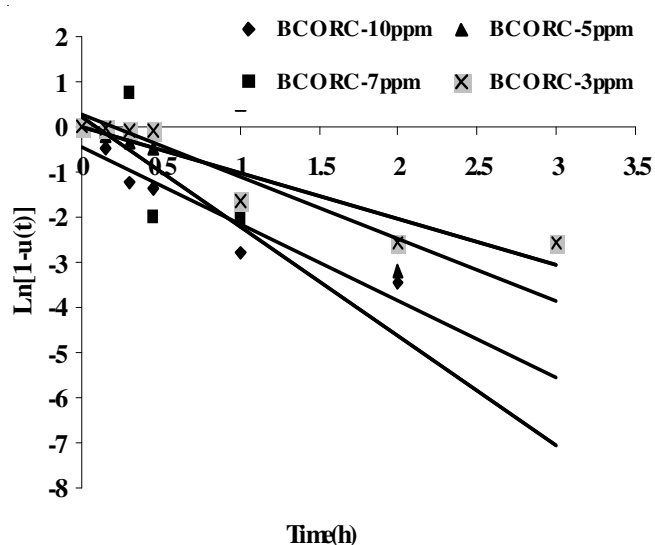


Fig. 6. Kinetic data for the adsorption of Cd(II) on BCORC

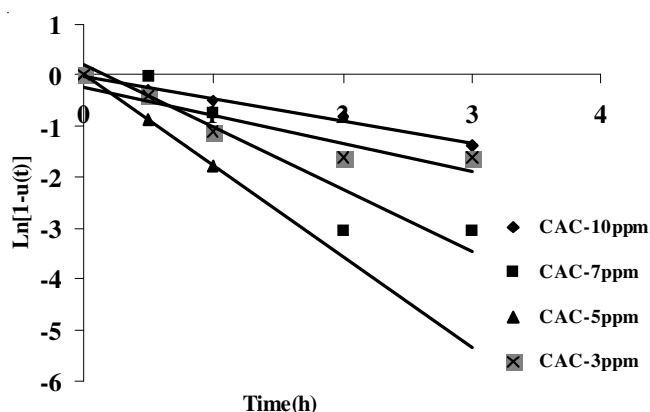


Fig. 7. Kinetic data for the adsorption of Cd(II) on CAC

Based upon column studies (Table-7) indicates the breakthrough capacities of carbon under optimum flow rate and bed height conditions of BCORC and CAC in distilled water from which it could be seen that BCORC is about 14 times superior to CAC.

Table-8 indicates the effects of common anions and cations may be in water on the removal of Cd(II) by BCORC and

TABLE – 4
RATE CONSTANTS FOR THE REMOVAL OF CADMIUM(II) BY BCORC AND CAC

Name of carbon	Concentration of Cd(II) (mg/L)	K overall rate constant (h ⁻¹)	k ₁ forward rate constant (h ⁻¹)	k ₂ backward rate constant (h ⁻¹)
BCORC	10	1.4000	1.3720	0.0280
	7	2.5000	2.3923	0.1077
	5	1.8660	1.6796	0.1864
	3	0.8590	0.7445	0.1145
CAC	10	0.3429	0.2749	0.0685
	7	1.0625	0.7438	0.3187
	5	0.7500	0.5700	0.1800
	3	0.8461	0.4231	0.4230

TABLE-5
DIFFUSION CO-EFFICIENT FOR THE REMOVAL OF Cd(II) BY BCORC AND CAC

Concentration of Cd(II) (mg/L)	Diffusion co-efficient (cm ² /s) BCORC		Diffusion co-efficient (cm ² /s) CAC	
	Pore diffusion (D _p)	Film diffusion (D _f)	Pore diffusion (D _p)	Film diffusion (D _f)
10	7.4214 × 10 ⁻¹¹	1.3915 × 10 ⁻⁸	7.2712 × 10 ⁻¹⁰	3.4083 × 10 ⁻⁹
7	1.9878 × 10 ⁻¹⁰	2.4848 × 10 ⁻⁸	1.3798 × 10 ⁻⁹	1.0560 × 10 ⁻⁸
5	2.4729 × 10 ⁻¹⁰	1.8547 × 10 ⁻⁸	7.5539 × 10 ⁻¹⁰	7.4543 × 10 ⁻⁹
3	9.1071 × 10 ⁻¹¹	8.5379 × 10 ⁻⁹	3.3639 × 10 ⁻¹⁰	8.4090 × 10 ⁻⁹

CAC. It could be seen that decrease in the capacities were noted in both BCORC and CAC. Bicarbonate and other anions and common cations such as calcium and magnesium ions affect the breakthrough capacity of CAC more than BCORC. The decrease in the removal of Cd(II) by both the carbons may be due to the formation of chloro and sulphate complexes of cadmium and competition for the ion exchange sites by calcium and magnesium in the case of BCORC.

in particle size because of its hardness. However CAC capacity was very much affected by the different cycles and showed nil value for I to V cycle of operation as shown in Table-9. Table-10 indicates the characteristics of synthetic wastewater used for experiments. It could be seen that BCORC showed the adsorption capacity to an extent of 159.92 mg/10 g whereas CAC showed nil adsorption capacity even after 10 times dilution of wastewater.

Conclusion

Activated carbon prepared from coconut oilcake waste, generated from oil industries after extracting oil, is capable of removing Cd(II) effectively from aqueous solution. The BCORC and CAC, conforms to Langmuir and Freundlich equation based on the formation of monolayer. The adsorption capacity of BCORC was found to be more and quantitative than CAC based upon its wider pH range for adsorption of Cd(II) and also on the carbon dosage. The adsorption of Cd(II), on both the carbons follows first order reversible kinetics with film diffusion and ion exchange process being the essential rate controlling step. The kinetic data could be useful for fabrication and designing of wastewater treatment plants. Based upon desorption studies of Cd(II), it could be concluded that BCORC was found to be more effective than CAC with respect to adsorption and recovery of the metal. Column studies also demonstrated that BCORC showed better removal of Cd(II) in the presence of common impurities in water and wastewater when compared with CAC.

TABLE-6
DESORPTION OF Cd(II) WITH HYDROCHLORIC ACID

Concentration of HCl (M)	Recovery of Cd(II) from BCORC (%)	Recovery of Cd(II) from CAC (%)
0.05	90.80	56.81
0.10	91.00	58.60
0.15	91.26	59.80
0.20	91.50	60.10
0.25	94.20	61.50
0.30	94.85	61.90
0.35	95.60	62.60
0.40	96.00	62.80
0.45	96.80	64.70
0.50	98.00	65.40
1.00	97.99	65.42
2.00	98.20	64.58

BCORC showed constant breakthrough capacity values in distilled water under different regeneration cycles indicating that carbon is effective in the removal of Cd(II) over the number of cycles and it was not undergoing any significant degradation

TABLE-7
BREAKTHROUGH CAPACITY OF CARBONS

CONDITION	Breakthrough capacity (mg/g)	
	BCORC	CAC
Room temperature	299.93	19.98

TABLE-8
EFFECT OF COMMON ANIONS AND CATIONS ON THE REMOVAL OF Cd(II)

Cd(II) concentration (BCORC)	: 200 mg/L	Cd(II) Concentration (CAC)	: 200 mg/L			
Flow rate (BCORC)	: 10 mL/min	Flow rate (CAC)	: 6 mL/min			
Weight of carbon (BCORC)	: 10 g	Weight of carbon (CAC)	: 10 g			
Bed height of carbon (BCORC)	: 6.5 cm	Bed height of carbon (CAC)	: 5 cm			
pH (BCORC)	: 6.0	pH (CAC)	: 5.0			
Break point (BCORC)	: 1.0 mg/L	Break point (CAC)	: 1.0 mg/L			
Cations and anions concentration	: 1000 mg/L separately added					
Carbon	None (mg/L)	HCO ₃ ²⁻ ions (1000mg/L)	Cl ⁻ ions (1000mg/L)	SO ₄ ²⁻ ions (1000mg/L)	Ca ²⁺ ions (1000mg/L)	Mg ²⁺ ions (1000mg/L)
BCORC	299.93	59.97	0	0	19.99	0
CAC	19.98	0	0	0	0	0

TABLE-9
REGENERATION STUDIES

Cd(II) concentration (BCORC)	: 200 mg/L	Cd(II) Concentration (CAC)	: 200 mg/L
Flow rate (BCORC)	: 10 mL/min	Flow rate (CAC)	: 6 mL/min
Weight of carbon (BCORC)	: 10 g	Weight of carbon (CAC)	: 10 g
Bed height of carbon (BCORC)	: 6.5 cm	Bed height of carbon (CAC)	: 5 cm
pH (BCORC)	: 6.0	pH (CAC)	: 5.0
Break point (BCORC)	: 1.0 mg/L	Break point (CAC)	: 1.0 mg/L
Cycle		BCORC	CAC
I		119.94	Nil
II		120.30	Nil
III		119.94	Nil
IV		119.90	Nil
V		119.90	Nil

TABLE-10
Cd(II) WASTEWATER CHARACTERISTICS

Cd(II) concentration (BCORC)	: 200 mg/L	Cd(II) Concentration (CAC)	: 200 mg/L
Flow rate (BCORC)	: 10 mL/min	Flow rate (CAC)	: 6 mL/min
Weight of carbon (BCORC)	: 10 g	Weight of carbon (CAC)	: 10 g
Bed height of carbon (BCORC)	: 6.5 cm	Bed height of carbon (CAC)	: 5 cm
pH (BCORC)	: 6.0	pH (CAC)	: 5.0
Break point (BCORC)	: 1.0 mg/L	Break point (CAC)	: 1.0 mg/L
Parameters	Amount (mg/L)	BCORC adsorption capacity (mg/g)	CAC adsorption capacity (mg/g)
Cadmium(II)	100.0	159.92 mg/10 g	Nil
Nickel(II)	10.75		
Copper(II)	7.500		
Chromium(III)	12.50		
Zinc(II)	10.00		

REFERENCES

- M.M. Rao, A. Ramesh, G.P.C. Rao and K. Seshiah, *J. Hazard. Mater.*, **129**, 123, (2006).
- M. Tsczos, *Hydrometallurgy*, **59**, 241, (2001).
- J. Yin and H.W. Blanch, *Biotech. Bioeng.*, **34**, 180 (1989).
- World Health Organization, Environmental Health Criteria 134, Cadmium International Programme on Chemical Safety (IPCS), Monograph (1992).
- A. Ucer, A. Uyanik and A.F. Aygun, *Sep. Purif. Technol.*, **47**, 113 (2006).
- J.E. Martins, R. Parto and R.A.R. Bonaventura, *Water Res.*, **38**, 693 (2004).
- G. McKay, Use of Adsorbents for the Removal of Pollutants from Wastewater, CRC Press, Boca Raton, FL (1995).
- C.P. Huang, In Carbon Adsorption Hand Book, Ann Arbor Science Publisher, pp. 281-329 (1978).
- M. Sekar, V. Sakthiand and S. Rengaraj, *J. Colloid., Interface Sci.*, **279**, 307 (2004).
- Y. Kikuchi, Q. Qian, M. Machida and H. Tasmoto, *Carbon*, **44**, 195 (2006).
- M.A. Ferro-Garcia, J. Rivera-Utrilla, J. Rodriguez-Gordillo and I. Bautista-Toledo, *Carbon*, **26**, 363 (1988).
- M. Chaudhuri, S. Rahman, M. Kutty and S.H. Yusuf, *Nat. Environ. Pollut. Technol.*, **9**, 25, (2010).
- K. Santhy and P. Selvapathy, *Sep. Sci. Technol.*, **39**, 3331, (2004).
- M. El Zayat and E. Smith, *Can. J. Environ. Constr. Civil Eng.*, **1**, 4, (2010).
- E. Banat, S.A. Ashes and L. Makhadmeh, *Adsorp. Sci. Technol.*, **21**, 245 (2003).
- K.A. Krishnan and T.S. Anirudhan, *Water SA*, **29**, 1520 (2003).
- N. Meunier, J. Laroulandie, J.F. Blais and R.D. Tyagi, *Bioresour. Technol.*, **90**, 255 (2003).
- N. Manivasakam, Industrial Effluents, Origin, Characteristics, Effects, Analysis and Treatment, First Reprint, Sakthi Publication, Coimbatore, India, pp. 498 (1997).
- L.D. Michelson, P.G. Gideon, E.G. Pace and L.H. Kutal, USDI, Office of Water Research and Technology, Bulletin No. **74**, 90 (1975).
- A. Frumkin, *Kolloidz.*, **51**, 123; *Chem. Abstr.*, **24**, 3, 412 (1930).
- S.S. Shukla, L. Yu, K.L. Doris and A. Shukla, *J. Hazard. Mater.*, **121**, 243 (2005).
- M.K.N. Yerkie and G.S. Natarajan, *Sep. Sci. Tech.*, **26**, 661 (1994).