



Removal of Lead(II) Ions by Adsorption onto Bamboo Dust and Commercial Activated Carbons -A Comparative Study

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Abstract: Studies on the removal of lead(II) ions by adsorption onto indigenously prepared bamboo dust carbon (BDC) and commercial activated carbon (CAC) have been carried out with an aim to obtain data for treating effluents from metal processing and metal finishing industries. Effect of various process parameters has been investigated by following the batch adsorption technique at $30 \pm 1^\circ\text{C}$. Percentage removal of lead(II) ions increased with the decrease in initial concentration and increased with increase in contact time and dose of adsorbent. Amount of lead(II) ions adsorbed increases with the decrease in particle size of the adsorbent. As initial pH of the slurry increased, the percentage removal increased, reached a maximum and the final solution pH after adsorption decreases. Adsorption data were modeled with the Freundlich and Langmuir isotherms, the first order kinetic equations proposed by Natarajan – Khalaf, Lagergren and Bhattacharya and Venkobachar and intra- particle diffusion model and the models were found to be applicable. Kinetics of adsorption is observed to be first order with intra-particle diffusion as one of the rate determining steps. Removal of lead(II) ions by bamboo dust carbon (BDC) is found to be favourable and hence BDC could be employed as an alternative adsorbent to commercial activated carbon (CAC) for effluent treatment, especially for the removal of lead(II) ions.

Keywords: Removal of lead(II) ions, Bamboo dust carbon (BDC) and commercial activated carbon (CAC), Adsorption isotherms, Kinetic equations, Intra-particle diffusion model.

Introduction

In developing countries like India, the development of indigenous low – cost materials for the water and wastewater treatment is essentially needed, because the commercially available commercial activated carbon (CAC) is highly costly and the difficulty exists in its procurement in developing countries like India. Heavy metal ions, especially lead(II) ions are highly toxic to the living beings, especially to the aquatic plants and animals, and therefore to be necessarily removed from water and wastewater¹.

India is basically an agricultural country with plenty of agricultural wastes. At present there is an urgent need to develop new cheaper indigenously prepared activated carbons (IPACs) from the abundant agricultural wastes². Agricultural by-products and some industrial wastes contain high carbon content and hence they could be used as starting/raw materials for the preparation of IPACs.

Although some attempts have already been made to economize the activated carbon (AC), the scope for minimizing its cost and development of alternative adsorbent materials to CAC by preparing IPACs from agricultural wastes is still open. Several attempts have been made to prepare carbons from unconventional raw materials like saw dust³, cow dung⁴, rice husk⁵, waste tea leaves⁶, wood charcoal⁷, and rice hull were prepared by activation with and without $ZnCl_2$ at different temperatures⁸. Activated ground nut husk carbon⁹, AC prepared from *Strecculia feetida* L (Seema Badam) fruit shell¹⁰, IPACs prepared from kapok fruit coat, cashew nut shells and coconut shells¹¹ and chemically prepared ACs prepared from straw, and dates nut¹² and coconut shell and dates nut¹³ were also used for the removal of metal ions like Hg^{2+} , Pb^{2+} , Ca^{2+} and Cu^{2+} ions. The reported results revealed that carbons prepared from agricultural wastes exhibit a high adsorption capacity, obeyed Langmuir and Freundlich isotherms, first order kinetic equations and found to be pH sensitive towards the removal of metal ions. Carbons prepared from these agricultural wastes are found to be porous in nature with high surface area and hence suitable for the removal of metal ions. Based on this idea, the present work is an attempt to indigenously prepare activated carbon from the locally available agricultural wastes *viz.*, bamboo dust, to study the suitability of bamboo dust carbon (BDC) for the removal of lead(II) ions by determining the effect of various process parameters like initial concentration, contact time, dose, particle size and initial pH on the extent of removal of lead(II) ions and to model the adsorption data with various isotherms and first order kinetic equations and to compare the data with that of CAC.

Experimental

Reagents

CAC was procured commercially from BDH, India. Raw material for the preparation of BDC *viz.*, bamboo dust was collected locally, cleaned, dried and cut into small pieces before carbonization. All the chemicals used were of analytical grade reagent obtained from both SD fine chemicals and Fischer, India. Double distilled (DD) water¹⁴ was used throughout the experiments. Lead(II) nitrate (BDH, AR) was used as a source of lead(II) ions.

Adsorbent

The raw material, *viz.*, bamboo dust (BD), was carbonized with sodium bicarbonate at 300-400°C and kept at 600°C in a muffle furnace (Neolab, India) to get carbon. The carbon was sieved (CAC=90 micron and BDC=45-250 micron); activated by digesting it with 4 N nitric acid solution for 2 h at 80°C and finally activated in an air - oven for 5 h at 120°C. BDC was stored in an airtight wide mouth reagent bottles and used for adsorption studies. CAC was also acid digested and stored.

Adsorption experiments

Adsorption experiments were carried out at room temperature ($30 \pm 1^\circ\text{C}$) under batch mode^{15,16}. Stock solution of lead(II) nitrate was prepared suitably diluted with DD water and estimated by EDTA method using xylenol orange, as indicator. Exactly 50 mL of lead(II) ion solution of known initial concentration was shaken with a required dose of adsorbent (CAC=4-22 g/L and BDC=10-28 g/L) of a fixed particle size (CAC=90 micron and BDC=45-250 micron) in a thermostatic orbit incubator shaker (Neolab, India) at 200 rpm after noting down the initial pH of the solution (pH = 7.2). The initial pH was adjusted to the required pH value (range: 2-8) by adding either 1 M HCl or 1 M NaOH solution. After equilibration, the final concentrations (C_e) were also measured complexometrically. The value of percentage removal and amount adsorbed (q in mg/g) were calculated using the following relationships:

$$\text{Percentage removal} = 100 (C_i - C_e) / C_i \quad (1)$$

$$\text{Amount adsorbed (q)} = (C_i - C_e) / m \quad (2)$$

where, C_i and C_e are initial and equilibrium (final) concentration of lead(II) ions (ppm), respectively and m is the mass of adsorbent, in g/L.

The adsorption isotherms were specified at pH 7.2 for BDC and CAC. Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of isotherms and kinetic equations, respectively.

Results and Discussion

Effect of Initial concentration

The adsorption experiments were carried out under batch mode at different experimental conditions (Table 1) and the results obtained are discussed below. The results on the extent of removal (% removal) of lead(II) ions under various experimental conditions are given in Table 1. The effect of initial concentration is shown in Figure 1.

The percentage removal decreased with the increase in initial concentration of lead(II) ions. This may probably be due to the limited number of available active sites on the surface of CAC and BDC to accommodate higher concentration of lead(II) ions. The optimum initial concentration of lead(II) ions is fixed as 600 ppm for both BDC and CAC.

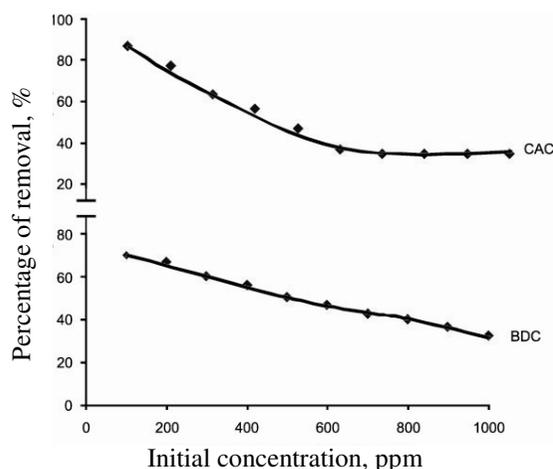


Figure 1. Effect of Initial concentration on the removal of lead(II) ions by BDC and CAC.

Table 1. Effect of initial concentration for the extent of removal of lead(II) ions by CAC and BDC at 30°C

Process parameter	Range	Percentage of Removal	
		CAC	BDC
Initial conc, ppm	100 -1000	86.9-34.5	70.06-31.80
Contact time, min.	5-55	59.4-84.4	17.94-62.29
Dose of adsorbent, g/L	4-22 (CAC); 10-28 (BDC)	28.5-87.7	31.24-71.17
Initial pH	2.0-8.0	32.0-92.15	13.51-66.64
Particle size, μ	45-250	-	49.12-17.94

Adsorption Isotherms

Adsorption data were modeled with the help of Freundlich and Langmuir isotherms¹⁷. The adsorption data were fitted with these isotherms (a) by plotting the values of $\log q_e$ vs $\log C_e$ and (C_e/q_e) vs C_e and (b) by carrying out correlation analysis between the values of (i) $\log q_e$ and $\log C_e$ and (ii) (C_e/q_e) and C_e (Table 2).

$$\text{Freundlich isotherm: } \log q = \log K + (1/n) \log C_e \quad (3)$$

$$\text{Langmuir isotherm: } (C_e/q) = (1/Q_0b) + (C_e/Q_0) \quad (4)$$

where, K and $1/n$ are the measures of adsorption capacity and intensity of adsorption, respectively; q is the amount adsorbed per unit mass of adsorbent (in mg/g); Q_0 and b are Langmuir constants, which are the measures of monolayer adsorption capacity (in mg/g) and surface energy (L/mg), respectively. The results of correlation analysis along with the isotherm parameters are given in Table 2. The observed linear relationships are statistically significant as evidenced from the correlation coefficients (r -values) close to unity, which indicate the applicability of these two adsorption isotherms and the monolayer coverage of lead species on the carbon surface. The monolayer adsorption capacity, Q_0 value (Table 2) indicates that BDC is a better adsorbent for lead(II) ions.

Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor, R_L , which is defined by the following equation¹⁸⁻²⁰.

$$R_L = 1 / (1 + bCi) \quad (5)$$

Table 2. Adsorption isotherm data for removal of lead(II) ions by CAC and BDC at 30°C

S.No.	Parameters	CAC	BDC
1.	Freundlich isotherm		
	Slope (1/n)	0.810	0.298
	Intercept (log K)	0.590	3.302
	Correlation coefficient (r)	0.997	0.992
2.	Langmuir isotherm		
	Slope (1/Q ₀)	0.168	0.465
	Intercept (1/Q ₀ b)	0.126	0.265
	Correlation coefficient (r)	0.992	0.997
	b, L/mg	1.330	0.569
	Q ₀ , mg/g	5.950	2.151
	RL	0.746	0.997

The separation factor, R_L , indicate the shape of the isotherm and the nature of the adsorption process as given below:

R_L value	Nature of the process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L < 0$	Irreversible

In the present study, the computed values of R_L (Table 2) are found to be fraction in the range of 0-1, indicating that the adsorption process is favorable for these adsorbents for the removal of lead(II) ions.

Effect of contact time

The percentage removal increased with increase in contact time and reached a constant value. This may be due to the attainment of equilibrium condition at 35 min of contact time for CAC and 45 min of contact time for BDC, which are fixed as the optimum contact time.

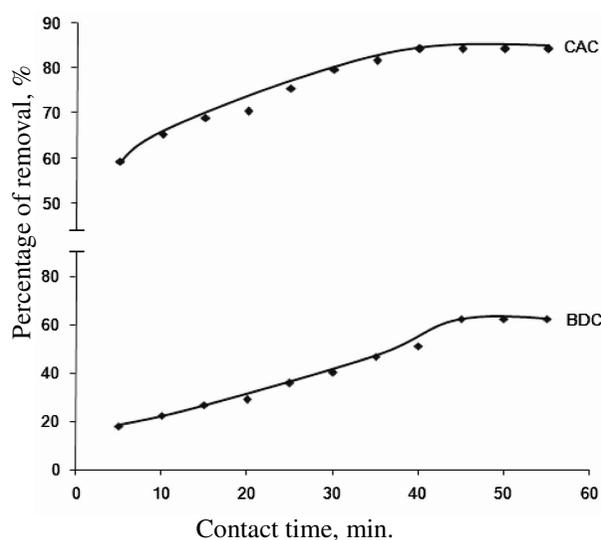


Figure 2. Effect of contact time on the removal of lead(II) ions by BDC and CAC

The effect of contact time is shown in Figure 2. At the initial stage, the rate of removal of lead(II) ions was higher, due to the availability of more than required number of active sites on the surface of carbons and became slower at the later stages of contact time, due to the decreased or lesser number of active sites²¹. Similar results have been reported in literature for the removal of dyes²², organic acids²³ and metal ions²⁴ by various adsorbents.

Kinetics of Adsorption

The kinetics of adsorption of lead(II) ions by BDC and CAC has been studied by testing the applicability of various first order kinetic equations proposed by Natarajan and Khalaf, Lagergren as cited by Pandey, *et al.*,²⁵ and Bhattacharya and Venkobachar²⁶.

Natarajan and Khalaf eqn:

$$\log (C_i/C_t) = (k/2.303) t \quad (6)$$

Lagergren eqn:

$$\log (q_e - q_t) = \log q_e - (k/2.303)t \quad (7)$$

Bhattacharya & Venkobachar eqn:

$$\log (1-U(T)) = - (k/2.303) t \quad (8)$$

where, $U(T) = [(C_i - C_t) / (C_i - C_e)]$; C_i , C_t and C_e are the concentration of lead(II) ions (in mg/L) at time zero, time, t , and at equilibrium time; q_e and q_t are the amount adsorbed per unit mass of adsorbent (in mg/g) and at time t , respectively; and k is the first order rate constant (in/min) for adsorption of lead(II) ions. The values of first order rate constants are given in Table 3. All linear correlations are found to be statistically significant as evidenced by r - values close to unity. The results indicate the first order nature of adsorption process and applicability of these kinetic equations. The k values calculated from Bhattacharya and Venkobachar equation are noted to be close to that of the k values computed from Lagergren equation, for any given adsorbent. This conclude that, in future any one of these two kinetic equations can be employed to calculated the k values in adsorption process of metal ions, in general and lead(II) ions, in particular.

Table 3. Kinetics of adsorption for removal of lead(II) ions by CAC and BDC at 30°C

S.No	Parameter	CAC	BDC
1.	Natarajan – Khalaf eqn.		
	Correlation coefficient (r)	0.994	0.990
	$10^3 k$, /min.	27.11	0.007
2.	Lagergren equation		
	Correlation coefficient (r)	0.965	0.991
	$10^2 k$, /min	7.26	0.001
3.	Bhattacharya & Venkobachar eqn.		
	Correlation coefficient (r)	0.966	0.990
	$10^2 k$, /min.	7.25	0.017
4.	Intra – particle diffusion model		
	Correlation coefficient (r)	0.993	0.953
	$10^2 k_p$, mg/g/min. ^{1/2}	1.29	9.387
	Intercept	0.31	8.152
	log (% removal) vs log (time)		
5.	Correlation coefficient (r)	0.984	0.987
	Slope (m)	0.169	1.181

Adsorbate (lead) species are most probably transported from the bulk of the solution to the solid phase through intra- particle diffusion / transport process, which is often the rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor²⁷.

Intra-particle diffusion model

The possibility of the presence of intra- particle diffusion as the rate limiting step was explored by using the intra- particle diffusion model²⁸⁻²⁹.

$$q_t = k_p t^{1/2} + c \quad (9)$$

where, q_t = amount adsorbed in time t , c = intercept and k_p = intra- particle diffusion rate constant (in mg/gm/min.^{0.5}). The values of q_t are found to be linearly correlated with values of $t^{1/2}$. The k_p values are calculated and given in Table 3. The values of intercept (c) give an idea about the boundary layer thickness, *i.e.*, the larger the intercept greater is the boundary layer effect. BDC is more porous than CAC.

The correlations of the values of \log (% removal) and \log (time) also resulted in linear relationships, as evidenced by r -values close to unity (CAC=0.984 and BDC=0.987). The divergence in the value of slope from 0.5 (slope : CAC=0.169 and BDC=1.181) indicates the presence of intra-particle diffusion as one of the rate limiting steps³⁰, besides many other processes controlling the rate of adsorption, all of which may be operating simultaneously.

The results of the present study conclude that, BDC could be used as an adsorbent alternative to CAC in cost – effective effluent treatment, especially for the removal of metal / lead(II) ions. The results will be highly useful in designing low- cost effluent treatment plant. Thus, results of this study will be useful in the development of strategy for the production of low cost adsorbent (BDC), which is indigenously prepared from the locally available agricultural wastes / by – product is BD.

Effect of dose

The effect of dose of adsorbent on the percentage removal of Pb^{2+} ions was studied. The percentage removal increased with increase in dose of adsorbent (Table 1 and Figure 3). This may be due to the rapid increase in surface area and number of available active sites for the adsorption of lead(II) ions, or due to conglomeration of carbons at higher doses³². The relative increase in the percentage removal of Pb^{2+} ions is found to be insignificant after a dose of 20 g/L of BDC and 10 g/L of CAC, which is fixed as the optimum dose. The values of \log (% removal) are also found to be linearly correlated with \log (dose) values. The values of $\log q$ are found to be linearly correlated to \log (dose) with correlation coefficients, which are almost unity (r -values: CAC = 0.988; BDC = 0.998). This is in accordance with the fractional power term of the dose as:

$$q = [\text{dose}]^n + c \quad (9)$$

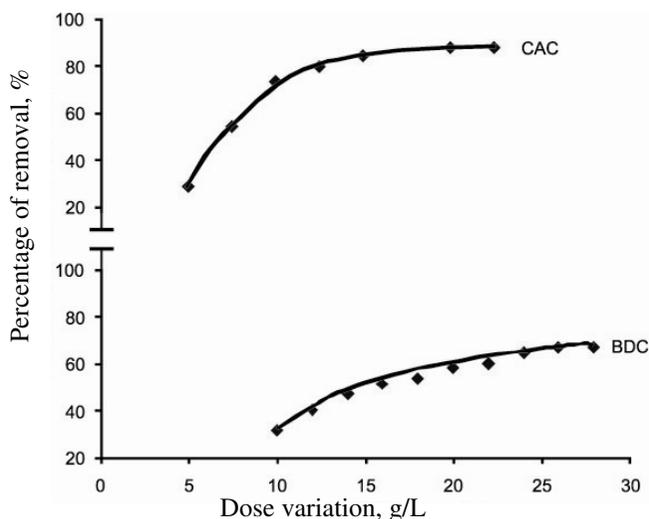


Figure 3. Effect of dose variation on the removal of lead(II) ions by BDC and CAC

This suggests that the adsorbed $Pb(II)$ ions may either block the access to the internal pores of carbons or may cause particles to aggregate and thereby minimizing the availability of active sites for adsorption.

Effect of particle size of BDC

The effect of particle size on the % removal of lead(II) ions adsorbed (range) is given in the Table 1 (Figure 4). The effect of particle size on the % removal of lead(II) ions adsorbed was studied only by varying the particle size of BDC as 45, 90, 125, 150 and 250 micron; CAC was not used, since its particle size is uniform and constant at 90 micron. The value of correlation coefficient is close to unity ($r = 0.927$). The amount of lead(II) ions adsorbed increases with the decrease in particle size of the adsorbent. This is due to the increase in the availability surface area with the decrease in particle size.

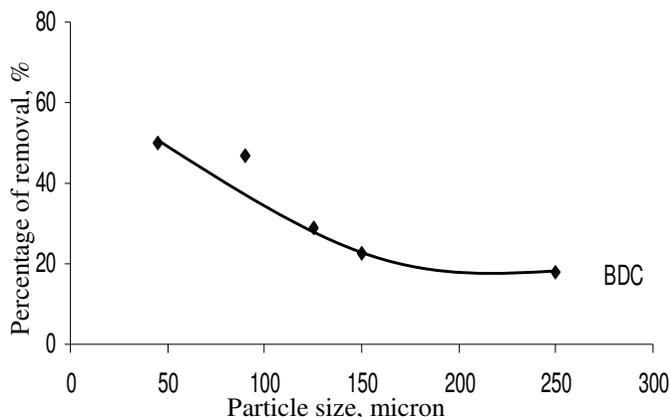


Figure 4. Effect of particle size on the removal of lead(II) ions by BDC

Effect of pH

The effect of initial pH on the extent of removal of lead(II) ions by adsorption on BDC and CAC at 30°C is given in Table 4. The adsorption of lead(II) ions on the adsorbents are found to be highly pH dependent. As pH increases, the extent of removal increases, reaches a maximum value and then decreases further increased upto optimum pH. The optimum pH for removal of Pb^{2+} ions is fixed as 7.2 for both CAC and BDC. The near neutral pH is found to be favourable. The pH value slightly decreases and change in pH ($\Delta pH = \text{initial pH} - \text{final pH}$) values after adsorption are found to decrease in the order of 0.3-0.5 units. This suggests that during the adsorption of lead species, protons are released from the surface functional groups like phenolic, carboxylic and enolic groups present on the carbons. Above pH 8.1, the Pb^{2+} ions are also precipitated as lead hydroxide.

Table 4. Effect of initial pH on the extent of removal of lead(II) ions by CAC and BDC at 30°C

Initial pH	Percentage removal	
	CAC	BDC
2.1	32.00	13.51
3.2	43.17	20.16
4.0	54.81	29.03
5.0	61.32	40.12
6.1	73.44	62.29
7.2	92.15	66.73
8.0	91.55	66.64

These adsorption data suggest that BDC could be used as an adsorbent alternative to CAC for the cost effective treatment of effluents, especially for the removal of lead (II) ions.

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