Agricultural solid waste for the removal of inorganics: Adsorption of mercury(II) from aqueous solution by Tamarind nut carbon

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The adsorption of Hg(II) on modified tamarind nut carbon (Bicarbonate treated tamarindnut carbon – BTNC) was investigated to assess the possible use of this adsorbent for the processing of mercury removal from 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.

Keywords: Tamarind nut carbon, mercury(II) adsorption, Langmuir and Freundlich isotherm, first order kinetics

IPC Code: B01D17/00; C02F101/20

Mercury is viewed as the most toxic inorganic pollutant available in natural waters due to the discharges from chloralkali, paper and pulp, oil refining and battery manufacturing industries. It has been noted that the tolerance level of Hg(II) for discharge into inland surface waters is 2 μg /L and for drinking water 2 μg/L[1]. Mercury is capable of affecting central nervous system, chromosomes, pulmonary function and kidney damage[2,3]. The biochemical kinetics of mercury methylation in water under naturally occurring condition of pH and temperature has confirmed that inorganic mercury could be easily converted into the more toxic organic mercury by certain micro organisms[4]. Polystyrene divinyl benzene containing benzimidazolyazo groups as an ion exchange resin has been used to remove mercury from environmental, medicinal and geological samples[5]. Granulated slag of a steel plant is used to remove mercury in elemental form and as mercuric sulphide[6]. Activated carbon derived from peanut hull was also examined for the removal of Hg(II) and found out that the capacity of peanut hull carbon was superior to the commercial activated carbon[7]. Removal of trace level mercury from surface water using different sorbents in column was also carried out[8]. In the present investigation, it has been shown that out of various non conventional

adsorbents, modified tamarind nut carbon has adsorption capacity for Hg(II) removal from aqueous solutions. This work reports the results of batch and kinetic studies on the removal of Hg(II) from aqueous solution by adsorption technique, using bicarbonate treated tamarind nut carbon (BTNC) as adsorbent. The effect of various parameters like equilibration time, pH, amount of adsorbent etc., has been studied. Reversible first order rate equation has also been applied to the present study to understand the mechanism.

Experimental Procedure
Preparation of BTNC

Tamarind nut procured from the market was washed with distilled water, dried at 110ºC, cut into small pieces and sieved to 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±5ºC for 24 h. The carbonized material was washed with distilled water to remove the free acid and dried at 105±5ºC. Then it was repeatedly soaked in 1% sodium bicarbonate until effervescence ceased and further soaked in the same solution for two days to remove any residual acid. The material was then washed with distilled water, dried at 105±5ºC and again sieved to 20-50 ASTM size (BTNC). Preliminary studies were carried out with raw tamarind nut, sulphuric acid treated tamarind nut carbon and BTNC for the Hg(II)

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removal. Based upon their efficiency, BTNC was chosen for further studies. The characteristics of carbon were found out using BTNC. Subsequent experiments were carried out with the BTNC. The CAC (SD fine chemicals) was procured from the market and sieved to 20–50 ASTM mesh size and its characteristics were found out. The characteristics of BTNC and CAC are summarized in Table 1.

Batch experiments

A stock solution of Hg(II) was prepared by dissolving 0.3385 g of HgCl$_2$ in 100 mL distilled water containing 0.1 mL concentrated hydrochloric acid and diluting to 250 mL. This solution was diluted as required to obtain standard solutions containing 10–20 mg/L of Hg(II). One hundred mL of Hg(II) solution of a desired concentration adjusted to a desired pH were taken in polythene bottles of 300 mL capacity. Known amounts of BTNC or CAC were added and pH was adjusted using dilute hydrochloric acid (0.01, 0.1 or 1.0M) or dilute sodium hydroxide (0.01, 0.1 or 1.0M) solutions. All the chemicals used were of Analar grade and were obtained from Ranbaxy, BDH, and Merk. The solutions were agitated for a predetermined period at 30 ±1°C in a horizontal shaker, the carbons were separated by filtration and the filtrate was analyzed by spectrophotometric procedure for Hg(II) content[9]. Adsorption isotherm studies were carried out with different initial concentrations of Hg(II) while maintaining the carbon dosage at constant level. For pH effects, 10 mg /L of Hg(II) and a BTNC or a CAC dose of 100 mg/100 mL were used. In order to correct for any adsorption of Hg(II) onto the containers, control experiments were carried out without adsorbent. It was found that there was no adsorption by the container walls. In addition, all mixing vessels were kept sealed throughout the duration of each isotherm test to minimize mercury loss to the atmosphere.

Results and Discussion

Examination of carbon characteristics (Table 1) shows that BTNC has higher bulk density and ion exchange capacity. The moisture content of BTNC suggests that the acid treatment has made the carbon porous. Even though BTNC shows lower surface area when compared with CAC, it has shown considerable ion exchange capacity through which the Hg(II) removal may be taking place.

Table 1—Characteristics of bicarbonate treated tamarind nut carbon (BTNC) and commercial activated carbon (CAC)

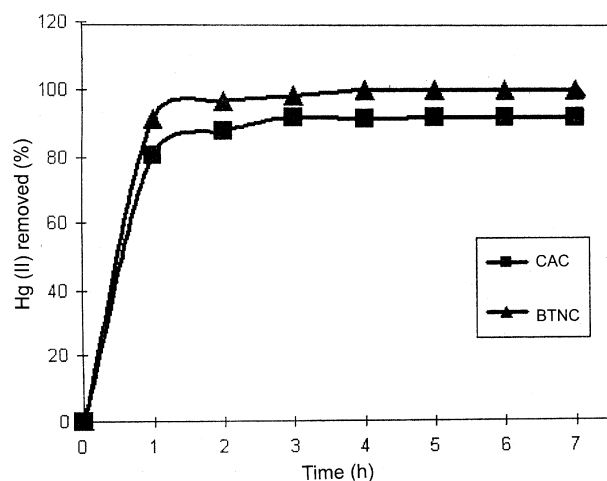| Sl. No	Control test	BTNC	CAC
1	Bulk density (g mL^{-1})	0.72	0.56
2	Moisture (%)	4.66	0.27
3	Ash (%)	15.20	6.10
4	Solubility in water (%)	7.69	3.66
5	Solubility in 0.25 M HCl (%)	34.49	5.70
6	pH	6.96	9.84
7	Decolorizing power (mg g^{-1})	7.20	2.25
8	Phenol number	73.00	56.00
9	Ion exchange capacity (m equiv g^{-1})	0.67	Nil
10	Surface area (m^{2}g^{-1})	77	421
11	Iron (%)	6.10	3.23
12	Porosity (%)	20.10	2.40

Fig. 1—Effect of contact time for the removal of Hg(II) by BTNC and CAC (pH=5.0).

Effect of agitation time

Figure 1 shows the effect of agitation time on the removal of Hg(II) by BTNC and CAC. The removal increases with time and attains equilibrium in 3 h for BTNC and 4 h for CAC for an initial Hg(II) concentration of 10 mg /L for a carbon dosage of 100mg/ 100 mL (100 % removal of Hg(II) in case of BTNC and 92% removal in case of CAC).

Effect of carbon dose

Figure 2 shows the removal of Hg(II) as a function of carbon dosage by both BTNC and CAC. It is evident that for the quantitative removal of 10 mg/L of Hg(II) in 100 mL, minimum carbon dosage of 80 mg is required in case of BTNC and 150 mg for CAC. The data clearly show that the BTNC is nearly two
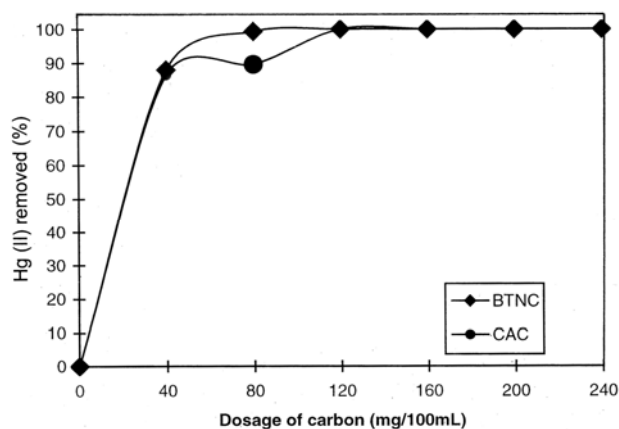
Fig. 2—Effect of carbon dosage on the removal of Hg(II) by BTNC and CAC (pH=5.0, Equilibration time =3h. Concentration of Hg(II), 10 mg/L for BTNC, and Equilibration time=4 h. Concentration of Hg(II), 10 mg /L for CAC).

times more effective than CAC. This may be due to the moderate ion exchange capacity of BTNC compared to CAC.

Effect of pH

Figure 3 presents the effects of initial pH on the removal of Hg(II) by BTNC and CAC. It is clear that BTNC is effective for the quantitative removal of Hg(II) over the pH range of 4.0-10.0. However, CAC is effective within a narrow range of pH 2.0 to 3.0. It can be shown by the stability constant calculations that in the presence of chloride, the predominant species at pH >4.0 is Hg (OH) $^+$, HgO and at pH <4.0 is $HgCl_2$[10]. The formation of $HgCl_2$ has been found to decrease the Hg(II) sorption onto a commercial FS–400 GAC[11]. Accordingly, the Hg(II) adsorption decreased when the pH was less than 1.0 with hydrochloric acid for BTNC and less than 2.0 for CAC. In the case of CAC, an increase in pH above 4 shows a decreasing trend in the adsorption probably because of the formation of insoluble hydroxyl complexes of mercury[17] such as $HgOH^+$, Hg_2OH^{+3}, $Hg_2(OH)_2^{+2}$. This is in agreement with the studies made by various authors on the effect of pH on mercury sorption by activated carbon FS- 300[12], and FS – 400[11] and peanut hull carbon[7].

In the case of BTNC the following mechanism is suggested. Based upon the work of Frumkin[13] the surface oxide groups available on the surface of a carbon can undergo hydrolytic reactions with the result proton exchangeable sites such as $C_xOH_2^{2+}$, C_xOH^+ may be formed. Since BTNC was prepared
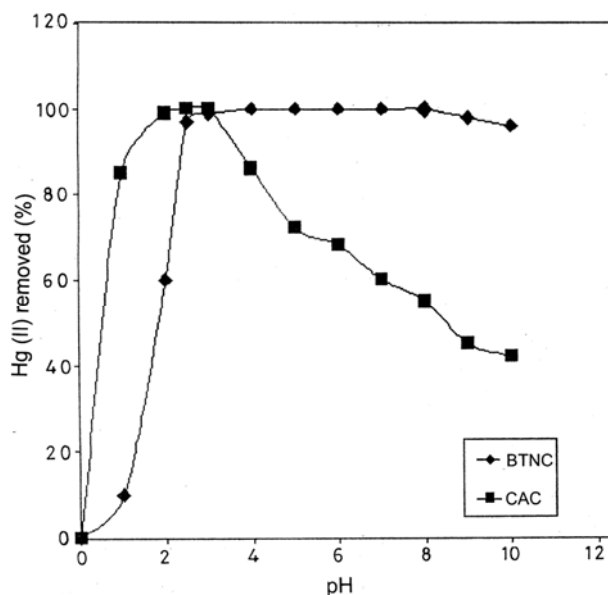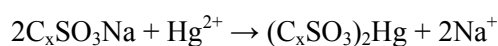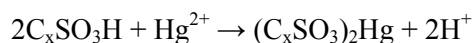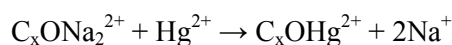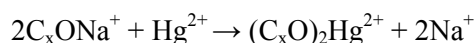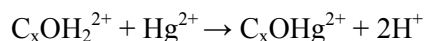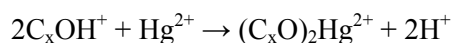

Fig. 3—Effect of pH on the removal of Hg(II) by BTNC and CAC (Carbon dosage =100 mg /100 mL, Equilibration time=3 h. Hg(II) concentration, 10 mg/L for BTNC and Carbon dosage =100 mg / 100 mL, Equilibration time=4 h. Hg(II) concentration, 10 mg /L for CAC).

upon treatment with sulphuric acid followed by sodium bicarbonate soaking, groups such as C_xONa^+, $C_xONa_2^{2+}$, C_xSO_3H and C_xSO_3Na may be present. Hence, it is expected that Na^+ in the group got exchanged with Hg(II) and soluble complexes of Hg(II) as follows.

$$2C_xOH^+ + Hg^{2+} \rightarrow (C_xO)_2Hg^{2+} + 2H^+$$

$$C_xOH_2^{2+} + Hg^{2+} \rightarrow C_xOHg^{2+} + 2H^+$$

$$2C_xONa^+ + Hg^{2+} \rightarrow (C_xO)_2Hg^{2+} + 2Na^+$$

$$C_xONa_2^{2+} + Hg^{2+} \rightarrow C_xOHg^{2+} + 2Na^+$$

$$2C_xSO_3H + Hg^{2+} \rightarrow (C_xSO_3)_2Hg + 2H^+$$

$$2C_xSO_3Na + Hg^{2+} \rightarrow (C_xSO_3)_2Hg + 2Na^+$$

Adsorption isotherms

The Langmuir equation was applied for adsorption equilibrium for both BTNC and CAC.

$$C_e/q_e = 1/Q_ob + C_e/Q_o$$

where C_e is the equilibrium concentration mg/L, qe is the amount adsorbed at equilibrium (mg/g) and Q_o and *b* are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plots of C_e/q_e versus C_e show that the adsorption

obeys the Langmuir model for both BTNC and CAC and it is shown in Fig. 4. Q_o and b were determined from the Langmuir plots and found to be 60.24 mg/g and 2.075 mg/L respectively for BTNC and 62.5 mg/g and 0.8 mg/L respectively for CAC. The ratio of Q_o values of BTNC and CAC works out to be 0.96. 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 $R_L = 1/(1+bC_o)$, where b is Langmuir constant and C_o be the initial concentration of Hg(II)[14]. R_L values indicate favourable adsorption of Hg(II) on both BTNC and CAC at the concentration studied at room temperature 30±1°C.

The Freundlich isotherm is represented by the equation[14].

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 BTNC or CAC(mg/g). Plots of log (x/m) versus log C_e are linear for both BTNC and CAC. Figure 5 shows the Freundlich adsorption isotherms for BTNC and CAC, in tap water and distilled water. The straight line nature of the plots indicates that the processes followed were of Fruedlich adsorption type. The K and n values for both the carbons were calculated from the intercepts and slopes, respectively and were shown in Table 2. The values of 1<n<10 show favourable adsorption of Hg(II) on both BTNC and CAC[13].

Adsorption kinetics

The kinetics of mercury adsorption on both BTNC and CAC follows the first-order rate expression[15].

$Ln(1-U$t$) = - k$t

Where Ut = $(C_0-C_t) / (C_0-C_e)$

C_0, C_t and C_e are the concentrations in mg/L of mercury initially at any time t and at equilibrium, respectively. The straight line plot of $Ln(1-U$t$)$ versus t indicates that the adsorption process follows first order kinetics(Figs 6 & 7). The straight line portions of the curves were used for calculating the slope values which give the overall rate constant K of the process. The forward (k_1) and backward (k_2) rate constants are calculated using the following equation.
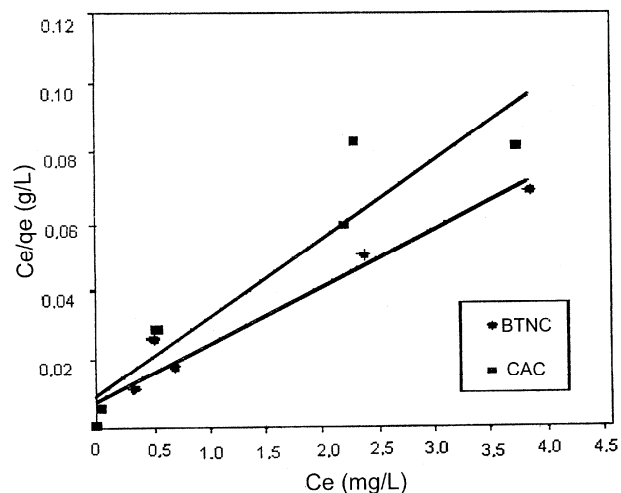
$K = k_1 + k_2$

$k_2 = (k_1/K_c)$

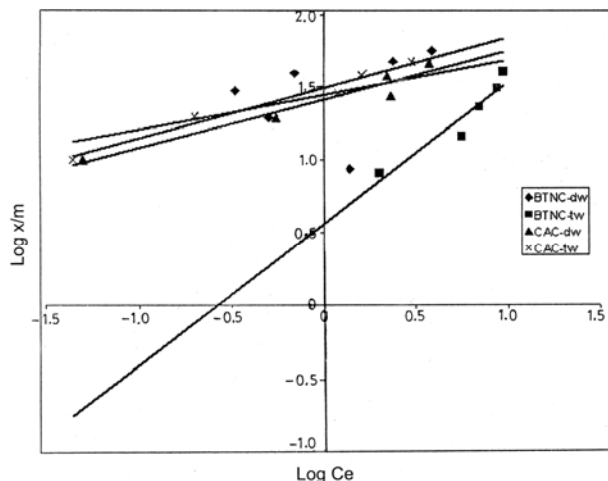Fig. 4—Langmuir adsorption isotherm for mercury with BTNC and CAC systems.

Fig. 5—Freundlich adsorption isotherm for mercury in distilled (dw) and tap water (tw) for BTNC and CAC systems.

Table 2—K and n values of Fruendlich adsorption isotherm

Carbon	Distilled water		Tap water	
	K	n	K	n
BTNC	38.02	3.89	3.98	1.10
CAC	25.12	2.50	3.16	2.50

$K = k_1 (1+1/K_c)$

$K_c = k_1/k_2$

where K_c is the equilibrium constant. The kinetic data are furnished in Table 3. It is evident that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is
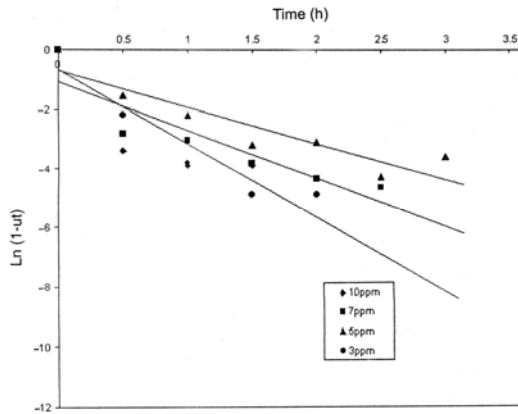
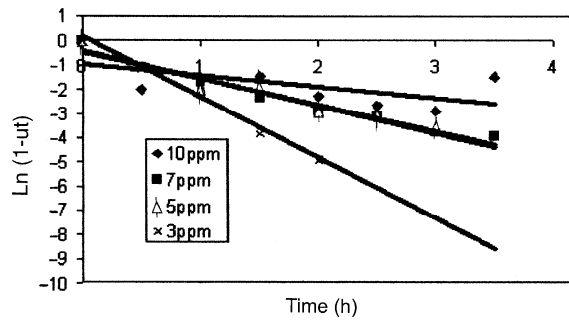Fig. 6—Kinetic fits for the adsorption of Hg(II) in case of BTNC system.

Fig. 7 —Kinetic fits for the adsorption of Hg(II) in case of CAC system.

clearly dominant for BTNC and CAC. The ΔG values were also calculated for BTNC and CAC using the equilibrium constant values of the adsorption process (k_1/k_2) for each concentration of the metal ions. It was found that for BTNC and CAC the average values of ΔG were worked out to be -2950 and -2829 calories respectively. The values indicated clearly that the adsorption on BTNC was found to be more spontaneous when compared with CAC.

In order to assess the nature of the diffusion process responsible for the adsorption of mercury on BTNC and CAC, attempts were made to calculate the pore and firm diffusion coefficients for various concentrations of Hg(II) using the following equation[16].

$$D_p = 0.03 \times r_o^2 / t_{1/2}$$

where D_p is the pore diffusion coefficient expressed in $cm^2 \ s^{-1}$, r is the radius of the sorbent expressed in cm, and $t_{1/2}$ is the half life period in sec.

$$D_f = 0.23 \times r_0 \delta \times C^*/C \ t_{1/2}$$

where D_f is the film diffusion coefficient expressed in $cm^2 \ s^{-1}$, δ is the film thickness expressed in cm, and C^*/C is equilibrium loading of the sorbent. According to Michelsen et al.[15] for the adsorption of heavy

Table 3—Rate constants for the removal of mercury by BTNC at a pH of 5.0 and CAC at a pH of 2.5

Name of carbon	Concentration of Hg(II) mg L^{-1}	K Overall rate constant (h^{-1})	k_1 Forward rate constant (h^{-1})	k_2 Backward rate constant (h^{-1})
	10	0.9230	0.9202	0.0028
	7	1.0714	1.0520	0.0194
BTNC				
	5	1.2000	1.1813	0.0187
	3	2.9230	2.9018	0.0212
	10	0.8667	0.8558	0.0109
	7	0.9000	0.8763	0.0237
CAC				
	5	1.0000	0.9956	0.0044
	3	2.7142	2.6940	0.0202

Table 4—Diffusion coeffficients for the removal of mercury by BTNC and CAC

Conc. of Hg(II) in mg/L	Diffusion coefficient of BTNC in cm^{2}s^{-1}		Diffusion coefficient of CAC in cm^{2}s^{-1}	
	Pore diffusion	Film diffusion	Pore diffusion	Film diffusion
10	7.0679×10^{-9}	1.8788×10^{-9}	5.5660×10^{-9}	1.4600×10^{-9}
7	1.5615×10^{-9}	4.0900×10^{-9}	1.8930×10^{-9}	4.9100×10^{-10}
5	2.3845×10^{-9}	6.2619×10^{-9}	5.1400×10^{-9}	1.3660×10^{-9}
3	2.4960×10^{-8}	6.6082×10^{-9}	1.3547×10^{-9}	3.5860×10^{-9}

metals on carbon surface, for film diffusion to be the rate determining process, the values of film diffusion coefficient (D_f) should be between 10^{-6} and 10^{-8} cm^2 s^{-1}. If pore diffusion Dp were to be rate determining process, its value should be in the range of 10^{-11} to 10^{-13} cm^2 s^{-1}. It is evident the removal of mercury (II) follows film diffusion process, since the coefficient values are close to the range of 10^{-6} to 10^{-8} cm^2 s^{-1}, and the values are shown in Table 4.

Conclusion

Activated carbon prepared from the tamarind nut waste generated in the agricultural sector is capable of removing Hg(II) effectively from aqueous solution. The bicarbonate treated tamarind nut and commercial activated carbon, conforms to a Freundlich and Langmuir equation based on the formation of monolayer. The adsorption capacity of BTNC is found to be more and quantitative than commercial activated carbon based upon its wider pH range for adsorption of mercury (II) and also on the carbon dosage. It is also available as a cheap alternative agricultural waste material which can be processed in the place of commercial activated carbon. The adsorption of Hg(II) on both the carbons follows first order reversible kinetics with film diffusion being the essential rate controlling step. The kinetic data would be useful for the fabrication and designing of wastewater treatment plants. It is concluded that in addition to above advantages the activated carbon prepared from tamarind nut carbon could also be considered for commercial applications based on its high mechanical strength and bulk density.

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