

Mercury(II) Removal by Bicarbonate Modified Tamarindnut Carbon

A. RAMADEVI and K. SRINIVASAN*

Department of Chemistry, College of Engineering, Salem-636 011, India

E-mail: srins52@sancharnet.in

The carbon obtained by treatment of tamarindnut with concentrated sulphuric acid under a weight ratio of 1 : 1 followed by soaking in 10% sodium bicarbonate solution exhibited a significant removal of Hg(II) from aqueous solutions over the pH range of 3–10 and commercially activated carbon in the pH range of 2–3 in batch studies. Based upon the findings, column studies were mainly conducted under optimum conditions to evaluate the removal of Hg(II) for large scale applications. For bicarbonate modified tamarindnut carbon an optimum flow rate of 13 mL/min with optimum bed height of 10.3 cm in 2.5 cm diameter column with optimum weight of 15 g of carbon was maintained. In the case of commercially activated carbon, 15 g of carbon with optimum flow rate of 5 mL/min was maintained with the optimum bed height of 5.8 cm. The breakthrough capacities of bicarbonate modified tamarindnut carbon and commercially activated carbon under optimum conditions were found to be 1440 and 52 mg respectively per 15 g of carbon. Common anions and cations affected the removal of Hg(II) on both the carbons. Breakthrough capacities were found out in the presence of wastewater containing Hg(II) and the potential of bicarbonate modified tamarindnut carbon was found to be 10 times superior to commercially activated carbon in the removal of Hg(II).

Key Words: Bicarbonate treated Tamarindnut carbon, Commercially activated carbon, Mercury(II) removal.

INTRODUCTION

The application of activated carbon for the removal of Hg(II) from water and wastewater is of recent interest only¹. Activated carbon adsorption generally increases with decrease in pH condition^{2–4}. Both powdered and granular commercially available activated carbons have been applied for the removal of mercury(II) and the results show that with the increase in dose of carbon, residual concentration of metal ions generally decreases in the treated water⁵. The treatment of activated carbon is gaining interest because of the advantage offered by this method in terms of ease and general reliability over conventional methods involving ion exchange or precipitation. Considering the importance of activated carbon from the economic point of view, cheaper varieties of carbon developed

from rice husk⁶, coconut shell⁷, peanut hull⁸ by treatment with sulphuric acid were tried for the removal of cadmium, lead and mercury. This paper describes the investigation carried out with respect to the removal of Hg(II) from aqueous solutions by bicarbonate modified tamarindnut carbon (BTNC) by column studies.

EXPERIMENTAL

The commercially available activated carbon was procured from the market directly (SD Fine Chemicals). Tamarindnut procured from the market was broken into small pieces. It was treated with concentrated sulphuric acid in the weight ratio of 1 : 1 and then kept in an air oven at 140–160°C for 24 h as per the procedure described elsewhere⁶. The carbonized material was washed with water to remove excess acid and dried at 110°C. The sulphuric acid treated tamarindnut carbon was then soaked in 10% sodium bicarbonate solution for 24 h and after perfect washing, it was dried once again at 110°C. The carbon characteristics of the bicarbonate modified tamarindnut carbon (BTNC) and commercially activated carbon (CAC) were determined by ISI procedure (Table-1).

TABLE-1
CHARACTERISTICS OF BICARBONATE MODIFIED TAMARIND NUT CARBON (BTNC) AND COMMERCIAL ACTIVATED CARBON (CAC)

S. No.	Control tests	BTNC	CAC
1.	Bulk density (g mL ⁻¹)	0.7191	0.5617
2.	Moisture (%)	4.66	0.2692
3.	Ash (%)	15.20	6.100
4.	Solubility in water (%)	7.698	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	56.3
9.	Ion exchange capacity (m equiv g ⁻¹)	0.668	Nil
10.	Surface area (m ² g ⁻¹)	77.0	421
11.	Iron %	6.1	3.23
12.	Porosity %	20.1	2.40

Stock solutions of 1000 mg/L of Hg(II) were prepared in distilled water by weighing AR mercuric chloride 1.345 g/L. Appropriate volumes of stock solution were suitably diluted with distilled water to obtain a concentration of 200 mg/L which were used in column studies.

Column studies

The investigation of column studies was done with sufficient weight of BTNC packed in a cylindrical tube of 2.5 cm diameter fitted with a teflon stopper valve to control the flow of Hg(II) solution 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 13 mL/min with the optimum bed height of 10.3 cm was employed to assess the potential of BTNC carbon.

Similarly, another column of same diameter containing commercially available activated carbon (CAC) was packed under an optimum bed height of 5.8 cm and a flow rate of 5 mL/min was maintained.

The initial concentrations of Hg(II) employed were prepared in distilled water of 200 and 20 mg/L for BTNC and CAC, respectively. Since initial studies with CAC in respect of Hg(II) removal were found to be less when compared with BTNC, a lower concentration of 20 mg/L of Hg(II) was employed in column studies. Percolation of Hg(II) solution was stopped as soon as Hg(II) concentration in the effluent exceeded the permissible limit⁹ of 0.01 mg/L (break point). 200 mL of lot volumes were collected in both cases and analyzed for Hg(II) content by following Rhodamine 6G spectrophotometric procedure¹⁰.

Regeneration and recycling of BTNC carbon was done by treating with dilute solution of 0.1 N hydrochloric acid followed by soaking in 10% solution of sodium bicarbonate. The CAC was regenerated with 0.1 N hydrochloric acid and thoroughly washed and reloaded in the column after drying.

Breakthrough studies pertaining to Hg(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 conditions for both the carbons.

RESULTS AND DISCUSSION

Examination of carbon characteristics show that the BTNC has higher bulk density and ion exchange capacity. The moisture content of BTNC suggests that the acid treatment has made the carbon more 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.

Effects of pH

Fig. 1 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 calculations¹¹ that in the presence of chloride, the predominant species of Hg(II) at pH > 4.0 is $\text{Hg}(\text{OH})^+$, HgO and at pH < 4.0 it is HgCl_2 . The formation of HgCl_2 has been found to decrease the Hg(II) sorption on to a commercial FS-400 GAC¹². 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. This is in agreement with the studies made by various authors on the effects of pH on mercury sorption by activated carbon FS-300¹³, FS-400¹² and peanut hull carbon⁸.

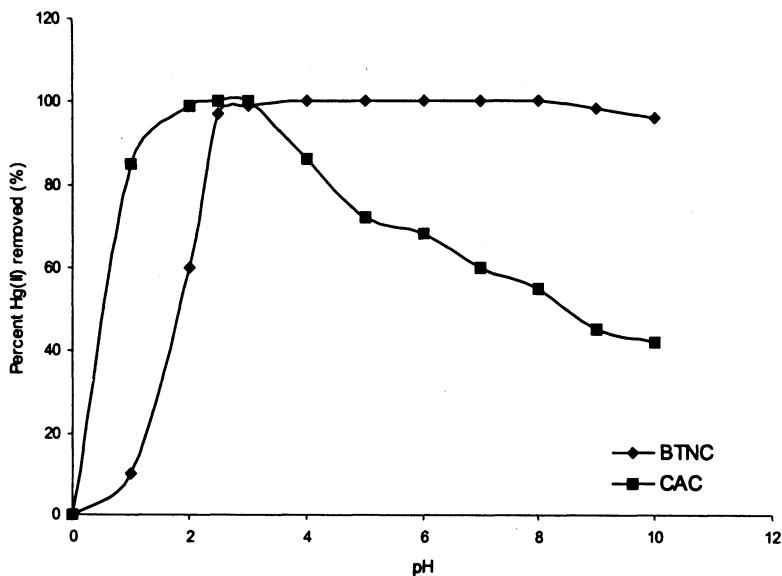


Fig. 1. Effect of pH on the removal of Hg(II) by BTNC and CAC (Carbon dosage = 100 mg/100 mL; equilibration time = 3 h; Hg(II) concentration 10 mg/L for BTNC and carbon dosage = 100 mg/100 mL; equilibration time = 4 h; Hg(II) concentration = 10 mg/L for CAC).

In the case of BTNC, the following mechanism is suggested. Based upon the work of Frumkin¹⁴, the surface oxide groups available on the surface of a carbon can undergo hydrolytic reactions with the result that proton exchangeable sites such as $C_xOH_2^{2+}$, C_xOH^+ may be formed. Since the BTNC was prepared upon treatment with sulphuric acid in hot condition followed by sodium bicarbonate soaking, groups such as C_xONa^+ , $C_xONa_2^+$, 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:

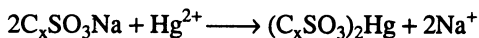
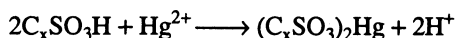
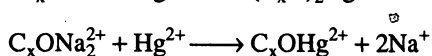
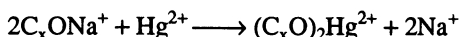
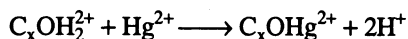
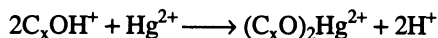


Table-2 indicates the breakthrough capacities of carbons under optimum flow rate and bed height conditions of BTNC and CAC from which one could conclude that BTNC shows a higher removal capacity when compared with CAC.

TABLE-2
BREAKTHROUGH CAPACITIES OF CARBONS

Optimum flow rate (BTNC) = 13 mL/min; Optimum flow rate (CAC) = 5 mL/min
Optimum weight of carbon = 15 gm

Condition	Breakthrough capacity in mg	
	BTNC	CAC
Room temperature	1440	51.737

Table-3 indicates the effect of common anions and cations that may be present in water on the removal of Hg(II) by BTNC and CAC. Decreases in the capacities were noted in both BTNC and CAC. Bicarbonate and especially calcium and magnesium ions affect the breakthrough capacities to a larger extent. The decrease in the removal of Hg(II) may probably be due to formation of unionizable chloro complexes of mercury and calcium; magnesium ions present in the tap water may also compete with mercury for ion exchange sites during the sorption process.

TABLE-3
EFFECT OF COMMON ANIONS AND CATIONS ON THE REMOVAL OF Hg(II)
UNDER OPTIMUM FLOW RATE AND BED HEIGHT CONDITIONS

Carbon	HCO ₃ ⁻ ions	Cl ⁻ ions	SO ₄ ²⁻ ions	Ca ²⁺ ions	Mg ²⁺ ions
	1000 mg/L	1000 mg/L	1000mg/L	1000 mg/L	1000 mg/L
BTNC	40	240	80	40	40
CAC	3.328	18.834	7.688	3.284	3.486

BTNC showed constant breakthrough capacity values in distilled water under different regeneration cycles indicating that carbon is effective in the removal of Hg(II) over the number of cycles and it was not undergoing any significant degradation in particle size because of its hardness. However, CAC capacity was very much affected by the different cycles and also showed nil value at the end of the IV cycle (Table-4).

TABLE-4
REGENERATION CYCLES

Cycle	BTNC	CAC
I	1479.99	51.730
II	1520.00	43.197
III	1480.00	13.910
IV	1440.00	3.487
V	1440.00	—

Table-5 indicates the experiments with synthetic wastewater similar to that of Chlor-Alkali plant and its characteristics were as shown. BTNC shows the capacity value as 10.576 mg/15 g whereas CAC showed nil capacity value even upon 10 times dilution with wastewater. Hence, it may be concluded that BTNC

could be employed for the removal of Hg(II). However, cost of BTNC will have to be assessed before utilizing the same.

TABLE-5
MERCURY(II) WASTEWATER CHARACTERISTICS

Parameters	Amount in mg/L	
	BTNC	CAC
Hg(II)	120.00	12.00
Chlorides	1140.00	114.00
Sodium	753.40	75.34
Calcium	150.00	15.00
Magnesium	120.00	12.00

ACKNOWLEDGEMENTS

The authors are thankful to V. Palanisamy, Principal, College of Engineering, Salem for granting permission to carry out this research work and providing laboratory facilities. Thanks are also due to C. Jayabharathi, Project Associate, CIRT in the documentation work.

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