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Column Studies on Adsorption of Hg(II) on Chemically Activated High Temperature *Syzygium jambolanum* Nut Carbon

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ABSTRACT

The present work focuses on the remediation of toxic Hg(II) from wastewater using ecofriendly as well as cost effective adsorbents. Syzygium jambolanum nut is locally abundant. Besides medicinal uses, it is expected to be a potential adsorbent for cleanup technology. Chemically activated Syzygium jambolanum nut carbon (CHSJC) has been developed using $(NH_4)_2S_2O_8$*. A series of column adsorption experiments have been carried out to evaluate the effect of flow rate, bed height and the presence of salts for the removal of Hg(II) as* $[HgCl_4]^{2-}$ *uptake by (CHSJC). The breakthrough capacity has found to be 5.33 mg/g. The adsorbed* $[HgCl_4]^{2-}$ *could be quantitatively recovered as Hg(II) by employing alkaline* Na_2S*. The capacity remained unaffected even after 5 cycles of operation and the treated water was found to be free from Hg(II). The efficiency of CHSJC was compared with high temperature Syzygium jambolanum nut carbon (HSJC) and commercial activated carbon (CAC).*

Keywords: *Syzygium jambolanum* nut; Chemical activation; Column studies; Regeneration, Recycling

INTRODUCTION

Mercury(II), a highly toxic metal ion threatens the aquatic environment due to effluents discharged from chlor-alkali plants [1], pharmaceutical, pulp, paint, plastic industries and also by agricultural sources such as fertilizers and fungicidal spray [2]. As a cumulative toxin, discharging of mercury and its compounds into the water bodies at any level has the potential to adversely affect the water ecosystem. Mercury(II) released in water becomes methylated where it accumulates in the fish and ultimately enters the human through the food chain which further frighten the community. Hg(II) causes permanent neurologic, kidney and pulmonary impairment [3], chest pain, renal disturbances, and damage to brain.

Clean up technologies which can treat large volumes of water contaminated with Hg(II), in a cost-effective way is highly imperative. Several techniques such as ion exchange [4], reverse osmosis [5], ultrafiltration [6] etc. have been used for the removal of toxic ions from wastewater. Alternate but cheap treatment techniques has focused attention on the use of biowastes which are available in plenty and expected for the removal of heavy metal ions. Activated carbons prepared from biowastes are cost effective and provides reliable results for removing heavy metal ions from wastewater by sorption technique. Many biowastes such as coconut shell [7], sugarcane fiber [8], grape stalks and yohimbe bark [9], walnut hull [10], Thespesia Populnea bark [11], maple leaves [12], African palm fruit [13], apple peels [14], cashew nutshell [15], pyras pashia leaves [16] etc. have been employed for the removal of various heavy metal ions. *Syzygium jambolanum* nut a biowaste is a potential material to prepare sorbent. *Syzygium jambolanum* tree is an evergreen tropical tree. Although a tropical tree, it also grows easily in sub-tropical climates and it grows largely all over India.

The present work deals with the chemically activated high temperature *Syzygium jambolanum* nut carbon (CHSJC) of 20-50 ASTM particle size which effectively removes Hg(II) as $[HgCl_4]^{2-}$, the form of mercury in chlor-alkali plant effluents without promoting reduction to elemental state. The performance of the CHSJC was compared with high temperature *Syzygium jambolanum* nut carbon (HSJC) and also a Commercial Activated Carbon (CAC) of LOBA Chemicals of same particle size for removal of Hg(II) from wastewater for this study.

MATERIALS AND METHODS

One hundred gram of *Syzygium jambolanum* nut was treated with 100 mL of con. H_2SO_4 for carbonization as well as activation purposes in the presence of oxidising chemicals like $(NH_4)_2S_2O_8$. The material was left in an air oven maintained at 140-160°C for 24 h. The material was repeatedly washed with distilled water followed by 2% $NaHCO_3$ solution to remove the free acid and finally left immersed in 2% $NaHCO_3$ solution overnight. After separating the material, it was washed with distilled water, dried at 105 ± 5°C. The dried material was subjected to thermal activation in CO_2 atmosphere by sandwiching the material between powdered $CaCO_3$ beds in a closed container at 800-850°C for 30 minutes. The material was washed with water and then soaked in 10% HCl to remove CaO and undecomposed $CaCO_3$. After separating the material, it was washed with distilled water, dried at 105 ± 5°C. The carbon was referred to as CHSJC [17].

HSJC was prepared by keeping the *Syzygium jambolanum* nut at 600°C for direct carbonisation followed by thermal activation in CO_2 atmosphere in the temperature range of 800-850°C for 30 min [18]. A commercial activated carbon (CAC) of LOBA chemicals was used for comparison purposes. All the carbons were ground and sieved to separate 20-50 mesh ASTM size particles.

In column studies, Hg(II) is analysed using DMA-80 (Direct Mercury Analyser, Milestone Inc). In DMA-80, the liquid sample is initially dried and then thermally decomposed in a continuous flow of oxygen. Combustion products are carried off and further decomposed in a hot catalyst bed. Mercury vapours are trapped on a gold amalgamator and subsequently desorbed for quantitation. The Hg content is determined using Atomic Absorption Spectrophotometry at 254 nm.

Experimental procedure

Studies were carried out systematically by batch and column experiments. The influence of parameters such as effect of pH, carbon dose and equilibration time were established by batch studies. For removal of Hg(II) content, the optimum pH was fixed at 5.0 for all the three carbons. The minimum carbon dosage for 99% removal was 0.1 g, 0.2 g and 0.3 g for CHSJC, HSJC and CAC respectively. Whereas the equilibration time needed for maximum removal of Hg(II) was 3 hours for CHSJC, 4 hours for HSJC and 5 hours for CAC [17].

Column studies were carried out using 15 g each of CHSJC and HSJC and 20 g of CAC packed in a 2.5 cm diameter glass column to evaluate the effect of bed height and flow rate. The carbon under study was made into slurry with distilled water and transferred slowly to the glass column packed at the bottom with glass wool. The bed was washed several times with water.

Mercury(II) solution was stored in polythene containers of 5 L capacity. Polythene tubes were connected to the bottles with a tap at the bottom. The other end of the tubing was connected to a socket containing a flow regulating valve. The outlet of the valve was fixed to the top of the glass column which was kept at a lower level. The columns were provided with pinch cocks at the bottom to control the flow rates. For the column experiments a pressure head of 10-15 cm (4”-6”) was maintained over the carbon beds. The inflow and outflow rates were maintained constant.

To establish the optimum flow rate for maximum uptake of Hg(II), column experiments were carried out using 10 mg/L of Hg(II) solution containing 10 g/L of NaCl adjusted to a pH of 5.0 in the varying flow rates of 10-20 mL/min to percolate through the carbon under study. Under the experimental conditions, Hg(II) forms an anionic complex $[HgCl_4]^{2-}$ with NaCl and inhibited the reduction of Hg(II) to Hg^0 by the elemental carbon. Each lot of 200 mL was separately collected and analysed for Hg(II) content using Direct Mercury Analyser (DMA). Percolation of Hg(II) solution was stopped as soon as the concentration of Hg(II) exceeded the permissible limit (0.002 mg/L) in the eluent.

To find the influence of bed height on the removal of Hg(II), column experiments were conducted for bed heights in the range of 4-16 cm. Hg(II) content was analysed as before. The influence of presence of bicarbonate and sulphate on the uptake of Hg(II) as $[HgCl_4]^{2-}$ was evaluated by adding their sodium salt in the concentration range of 100-1000 mg/L after adjusting the pH to 5.0 Each lot of 200 mL was collected and analysed as before.

RESULTS AND DISCUSSION

Systematic studies with 10 mg/L of Hg(II) containing 10 g/L of NaCl at pH 5.0 showed that rate of flow has considerable influence on Hg(II) removal and is maximum when maintained between 10-16 mL/min for all carbons. So, a flow rate of 14 mL/min was fixed for further studies. The amount of Hg(II) removed varied with bed height. In the case of CHSJC and HSJC, a minimum bed height of 8.0 cm provided by packing the 2.5 cm diameter column with 15 g of carbons should be maintained for the capacity per unit weight of carbon to remain constant. In the case of CAC, the minimum bed height should be 10.5 cm which was provided by 20 g of the carbon. At optimum bed height and flow rate, the uptake of Hg(II) by CHSJC, HSJC and CAC were found to be 80 mg/15 g, 60 mg/15 g and 40 mg/20 g respectively. This corresponds to the removal of 5.33 mg/g, 4 mg/g and 2 mg/g by CHSJC, HSJC and CAC respectively. The presence of anions like bicarbonate and sulphate did not have any significant change on the uptake of Hg(II) in the column studies.

Regeneration studies

Attempts were made to recover Hg(II) quantitatively from the exhausted carbon beds when the concentration of Hg(II) in 200 mL lot collected exceeded 0.002 mg when adsorption was done using 15 g of CHSJC/HSJC and 20 g of CAC at a bed height of 8 cm for CHSJC/HSJC and 10.5 cm for CAC and flow rate of 14 mL/min. Hg(II) was desorbed using 2% Na2S in 1% NaOH. Hg(II) forms soluble $[HgS_2]^{2-}$ with Na_2S in alkaline medium. For CHSJC the recovery was 99%, for HSJC 98.3% and for CAC 97%.

Recycling of carbon beds

The regenerated carbons were put to repeated use after washing the column with 1M HCl followed by distilled water till the pH of the wash water was 7.0. There is no change in the capacity even after 5 cycles of adsorption and desorption. The particle size degradation was found to be only around 1 % with all the carbons which is negligible. The summary of the results obtained are presented in Table 1.

Table 1. Removal and Recovery of Hg(II) by Column mode.

Description	CHSJC	HSJC	CAC
Hg(II) removal (mg)	80	60	40
Hg(II) recovery (mg)	79.2	59	38.8
Hg(II) recovery (%)	99	98.3	97

Hg(II)=10 mg/L; pH=5; NaCl=10 g/L; Flow rate=4 mL/min

Bed Height CHSJC and HSJC=8 cm, Bed Height CAC=10.5 cm

Application

In chlor-alkali plants, mercury is used as a moving cathode in the cell. Chlor-alkali plant wastewater contains Hg(II) content in the range 5-10 mg/L and chlorides in the range 10-50 g/L. Synthetic chlor-alkali plant wastewater containing 10 mg/L of Hg(II) with 50 g/L of NaCl was tested with the different carbons for their suitability. The synthetic solution was percolated through a column containing 15 g of CHSJC/HSJC and 20 g of CAC which provides a height of 8 cm and 10.5 cm and flow rate of 14 mL/min as described in column studies. The adsorbed Hg(II) was completely recovered as soluble $[HgS_2]^{2-}$ complex using 2% Na_2S in 1% NaOH. The regenerated carbon after washing as above was put to repeated use. The capacity remains unaffected even after 5 cycles of adsorption and desorption operation. The results are presented in Table 2.

Table 2. Application of activated carbon for the treatment of synthetic chlor-alkali plant wastewater.

Carbon	Hg(II) removal and recovery	Cycle No					Average value (mg)	Particle size degradation after 5 cycles (%)
		I	II	III	IV	V		
CHSJC 15g	Hg(II) removed	80	80	80	79.999	79.999	79.9996	1.16
	Hg(II) recovered	79.2	79	79	79.19	79.15	79.108	
HSJC 15g	Hg(II) removed	60	60	59.999	60	60	59.9998	1.34
	Hg(II) recovered	59	58.7	59	58.5	59	58.84	
CAC 20g	Hg(II) removed	40	40	40	40	39.999	39.996	1.38
	Hg(II) recovered	38.9	38.8	38.8	38.7	38.7	38.78	

Hg(II)=10 mg/L; pH=5.0; NaCl=50g/L; Flow rate=14mL/min

CONCLUSION

Column adsorption studies on Hg(II) removal showed that sorption capacity depends on flow rate, bed height. At optimum bed height of 8.0 cm and flow rate of 14 mL/min, the uptake of Hg(II) by CHSJC was 5.33 mg/g. The adsorbed $[HgCl_4]^{2-}$ could be quantitatively recovered as Hg(II) by using alkaline Na_2S. The capacity of regenerated carbon remained unaffected even after 5 cycles of operation and the treated water was found to be free from Hg(II). So chemically activated *Syzygium jambolanum* nut can be used as an efficient adsorbent for environmental remediation of industrial wastewater containing Hg(II).

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