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Batch Adsorption Studies for Removal of Hg(II) from Wastewater using *Syzigium jambolanum* Nut Carbon

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Activated carbon prepared from *Syzigium jambolanum* nut was found to be useful for the removal of mercury(II) as $[HgCl_4]^{2-}$ from wastewater. Quantitative removal of 99 % takes place when batch studies were done at an optimal carbon dose of 0.1 g, pH of 5 and equilibration time of 3 h. The adsorption follows Freundlich and Langmuir adsorption isotherms and obeys first order rate equation. The efficiency of *Syzigium jambolanum* carbon was compared with a commercial activated carbon.

Key Words: *Syzigium jambolanum* nut carbon, Adsorption, Isotherm, Kinetics, Commercial activated carbon.

INTRODUCTION

Mercury is widely used in chlor-alkali plants[1], painting, pharmaceutical, pulp and paper industries. The health problems[2] of mercury and its compounds include damage of central nervous system, impairment of pulmonary function and kidney, chest pain, renal disturbances and damage to brain. So it becomes imperative to remove it before the discharge of effluents.

Though several techniques like coagulation, lime softening, ion exchange, reverse osmosis, chemical precipitation and use of biological materials[3] are used for removal of mercury, adsorption using low cost activated carbons from agricultural wastes like coconut shell[4], coconut oil cake residue[5] have been employed.

In chlor-alkali plant effluents, mercury mostly exists in the form of $[HgCl_4]^{2-}$. The present work deals with the chemically activated high temperature *Syzigium jambolanum* nut carbon (CHSJC) of 20-50 (mesh) ASTM particle size which effectively removes Hg(II) as $[HgCl_4]^{2-}$ without promoting reduction to elemental state. The performance of the carbon was compared with a commercial activated carbon (CAC) of Loba chemicals of same particle size for removal of Hg(II) from wastewaters.

EXPERIMENTAL

Preparation of *Syzigium jambolanum* nut carbon (CHSJC): 100 g of *Syzigium jambolanum* nut was treated with 100 mL of con. H_2SO_4 for carbonization purpose in the presence of oxidizing chemicals like $(NH_4)_2S_2O_8$ or H_2O_2[6]. The material was left in an air oven maintained at 140-160 ºC 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 ºC. The dried material was subjected to thermal activation in CO_2 atmosphere by sandwitching the material between powdered $CaCO_3$ beds in a closed container at 800-850 ºC for 0.5 h. 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 ºC. The carbon was referred to as CHSJC.

Evaluation of carbon characteristics: The important carbon characteristics of *Syzigium jambolanum* nut carbon (CHSJC) and commercial activated carbon (CAC) such as bulk density, moisture content, ash, matter soluble in water, matter soluble in acid, pH, decolourization property, phenol number, ion exchange capacity, surface area and iron content were carried out and the results are shown in Table-1.

TABLE-1
CARBON CHARACTERISTICS

Control tests	CHSJC	CAC
Bulk density (g/cc)	0.63	0.51
Moisture (%)	4.90	3.76
Ash (%)	3.28	2.69
Matter soluble in water (%)	1.42	1.09
Matter soluble in 0.25 M HCl (%)	1.54	1.10
Decolourizing power (mg/g)	81	87
Phenol number (mg)	28	22
Ion exchange capacity (meq/g)	Nil	Nil
Surface area (m^2/g)[N_2-BET]	660	629
pH	6.3	7.1
Iron content (%)	0.12	1.1

Batch studies: 100 mL of 10 mg/L of Hg(II) solutions containing 10 g/L of NaCl were adjusted to different pH values and known amounts of CHSJC and CAC under study were added to these solutions taken in 300 mL polythene bottles. The solutions were equilibrated for 24 h in a mechanical shaker. The solutions were filtered and analyzed for Hg(II) content using DMA[7] (Direct Mercury Analyzer, Milestone Inc).

In direct mercury analyzer, 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 quantisation. The Hg content is determined using atomic absorption spectrophotometry at 254 nm.

Other parameters such as effect of carbon dose at optimum pH and effect of equilibration time under optimum pH and carbon dosage were also established by the above method. Adsorption isotherm studies were carried out with different initial concentrations of Hg(II) and fixed doses of carbon. Kinetic studies were carried out at different time intervals and fixed Hg(II) concentration, carbon doses and pH.

RESULTS AND DISCUSSION

As the carbons prepared in the presence of $(NH_4)_2S_2O_8$ or H_2O_2 behaved similarly, it was decided to carry out all the investigations with the carbon prepared in the presence of $(NH_4)_2S_2O_8$.

Effect of pH: Fig. 1 represents the effect of pH on the removal of Hg(II) as $[HgCl_4]^{2-}$ with the carbon doses of 0.5 g for both the carbons. It was found that both CHSJC and CAC were effective for the quantitative removal of Hg(II) over the pH range 2-10. So for further studies the optimum pH was fixed as 5.

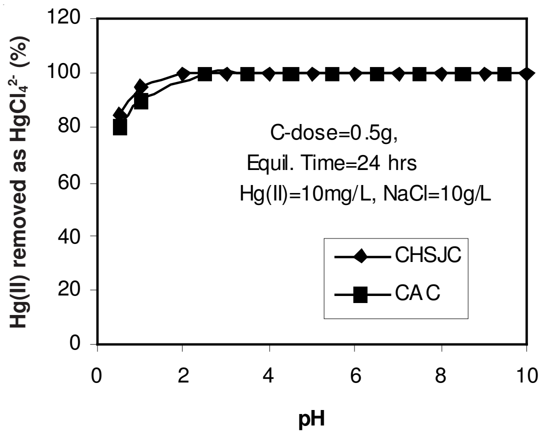

Fig. 1. Effect of pH on removal of Hg(II)

Effect of carbon dose: Fig. 2 represents the effect of carbon dose on the removal of Hg(II) as $[HgCl_4]_{2-}$ at pH of 5 and equilibration time of 24 h by CHSJC and CAC. For 99 % removal of Hg(II) a minimum dose of 0.1 g of CHSJC and 0.3 g of CAC were required. Therefore the optimum carbon dose required by CHSJC was found to be thrice as effective as CAC.

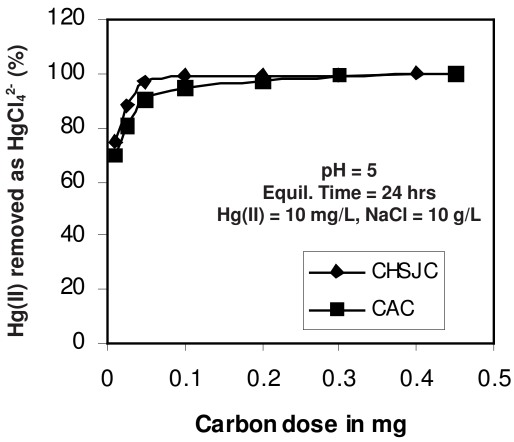

Fig. 2. Effect of carbon dose on removal of Hg(II)

Effect of equilibration time: Fig. 3 represents the effect of equilibration time on removal of Hg(II) as $[HgCl_4]^{2-}$ by 0.1 g CHSJC and 0.3 g CAC at an optimum pH of 5. For CHSJC, an optimum time of 3 h was enough for 99 % Hg(II) removal and 5 h was needed for CAC. It was evident that optimum time required by CHSJC was 1.67 times less than that of CAC.

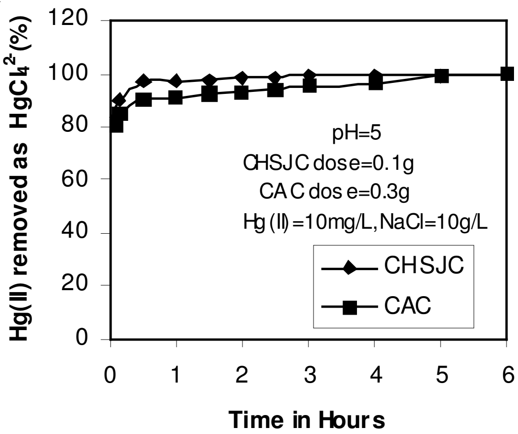

Fig. 3. Effect of equilibration time on removal of Hg(II)

Desorption studies: Attempts were then made to desorb the Hg(II) using Na_2S in alkaline medium[8,9]. The use of 100 mL of 2 % Na_2S in 1 % NaOH was found to be sufficient to desorb Hg(II) completely from the carbons.

Adsorption isotherms: Freundlich and Langmuir adsorption isotherm equation are the most widely used to characterize the adsorption data for adsorption in any aqueous solution. Freundlich Isotherm is represented by the equation.

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e$$

k and 1/n are the adsorption capacity and intensity of adsorption x is the amount of solute adsorbed, m is the weight of the adsorbent and C_e is equilibrium concentration in mg/L.

Plots of log x/m *versus* log C_e are linear for both CHSJC and CAC (Fig. 4). The straight line nature of the plots indicates that the process followed were of Freundlich adsorption type. The k and n values for both the carbons were calculated from the intercepts and slopes, respectively and are shown in Table-2. The values of $1 < n < 10$ showed favourable adsorption of Hg(II) on both CHSJC and CAC[10].

Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$$

where C_e is equilibrium concentration in mg/L, q_e is the amount adsorbed at equilibrium (mg/g), Q_o and b are the Langmuir constants related to adsorption capacity and energy of adsorption.

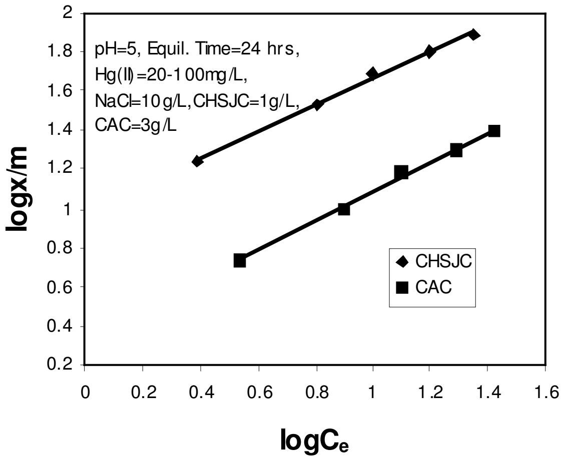

Fig. 4. Freundlich plots for adsorption of Hg(II)

TABLE-2
K AND N VALUES OF FREUNDLICH ADSORPTION ISOTHERM

Carbon	N	k
Syzigium jambolanum nut carbon	1.4815	9.5500
Commercial activated carbon	1.3929	2.2909

The linear plots of C_e/q_e *versus* C_e showed that the adsorption obeys Langmuir model for both CHSJC and CAC and is shown in Fig. 5. Q_o and b were determined from Langmuir plots and are shown in Table-3. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L. $R_L = 1/L + bC_0$ where b is Langmuir constant and C_0 is the initial concentration of Hg(II). R_L values between 0 and 1 indicate favourable adsorption of Hg(II) on both CHSJC and CAC (Table-4).

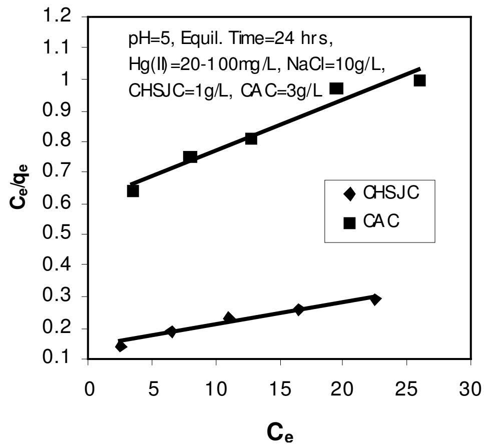

Fig. 5. Langmuir plots for the adsorption of Hg(II)

TABLE-3
Q_o AND b VALUE OF LANGMUIR ADSORPTION ISOTHERM

Carbon	Q_o	b
CHSJC	125.0	0.0640
CAC	52.9	0.0326

TABLE-4
EQUILIBRIUM PARAMETER R_L VALUES FOR CHSJC AND CAC

CHSJC	CAC
0.4386	0.6053
0.2809	0.4340
0.2066	0.3383

Adsorption kinetics: The kinetics of Hg(II) adsorption of both CHSJC and CAC followed the first order rate expression[11].

$$Ln(1 - U_t) = -kt$$

where $U_t = \frac{C_{A(o)} - C_{A(t)}}{C_{A(o)} - C_{A(e)}}$

$C_{A(o)}$, $C_{A(t)}$ and $C_{A(e)}$ are the concentrations in mg/L of Hg(II) initially, at any time t and at equilibrium, respectively. k is the adsorption rate constant. The straight line plot of Ln(1- U_t) *versus* t indicates that the adsorption followed first order kinetics for both CHSJC and CAC (Fig. 6). The k adsorption values were calculated and are presented in Table-5.

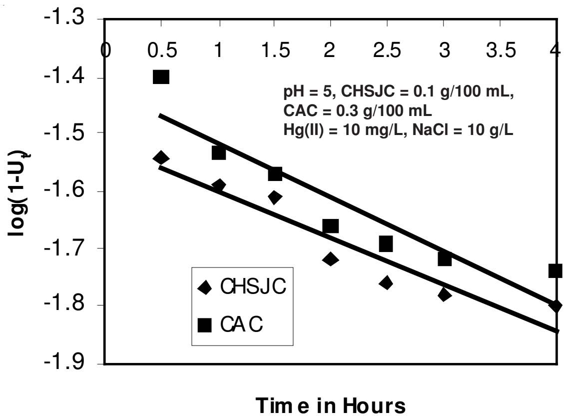

Fig. 6. Kinetic fits of Hg(II) adsorption data

Conclusion

The foregoing study clearly shows that activated high temperature *Syzigium jambolanum* nut carbon is an effective adsorbent for the removal of Hg(II) present as $[HgCl_4]^{2-}$ from aqueous solution. Its adsorption capacity is much higher than commercial activated carbon. It conforms to Freundlich and Langmuir equation based on formation of monolayer. The adsorption followed first order reversible kinetics. The CHSJC could be used for commercial purposes for economic treatment of wastewater containing Hg(II).

TABLE-5
ADSORPTION RATE CONSTANTS

Carbon	k_{ads} (h^{-1})
CHSJC	0.11
CAC	0.095

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