Sorption Studies of Chromium(VI) and Mercury(II) by High Temperature Activated Carbon from *Syzygium Jambolanum* Nut

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Abstract: High temperature activated *Syzygium Jambolanum* nut carbon (HSJC) has been effectively used for the removal of Cr(VI) and Hg(II) from aqueous solution by batch experiments. Effect of pH, carbon dose and equilibration time were determined. Adsorption followed Freundlich and Langmuir isotherms. Kinetic studies indicated that the removal process followed reversible first order equation. Desorption of Cr(VI) was done with 1 M NaOH and 10% H₂O₂ mixture and Hg(II) with 2% Na₂S in 1% NaOH. The performance of HSJC was compared with a commercial activated carbon (CAC).

Keywords: *Syzygium Jambolanum* nut carbon, Batch experiments, Freundlich and Langmuir Isotherms, Kinetic studies, Desorption

Introduction

Pollution caused by effluents from industries is a major environmental problem faced by many countries. Wastewater discharged from industries like electroplating, textile, leather tanning, metal finishing contains Cr(VI) while the effluent from chlor-alkali plants¹, painting, paper, pulp and pharmaceutical industries contains Hg(II). They endanger the environment, affect aquatic life and cause several health problems. Cr(VI) is carcinogenic². Hg(II) damages central nervous system and brain. It also causes chest pain, renal disturbances, impairment of pulmonary function and kidney. Hence it is imperative to treat them before discharge. Methods like precipitation technique, ion exchange method, activated sludge process, electrochemical techniques are expensive. These methods lead to incomplete removal of toxic ions and cause problems in the disposal of sludge. Clean up technology in a cost effective way is the need of the hour. Adsorption by activated carbon prepared from agricultural wastes is a novel way for the removal of toxic inorganic ions from wastewater. It is a process by which the concentration of the solute is enriched at the

surface of the adsorbent and can be desorbed by a suitable eluent. Agricultural wastes are available in plenty. Carbon prepared from agricultural wastes provides good results and involves less cost. Many agricultural wastes like coconut shell³, cotton seed⁴, *techtonea grandis* bark⁵, *pongamia* leaf powder⁶, tamarind nut⁷, bamboo dust⁸, palm pressed fibres⁹, dates nut¹⁰, turmeric wastes¹¹ *etc.* have been employed to prepare the activated carbon. *Syzygium Jambolanum* nut which has a high medicinal value is a potential agricultural waste. The study here deals with High temperature activated *Syzygium Jambolanum* nut carbon (HSJC) prepared by modified dolomite process of 20-50 ASTM particle size for the effective removal of Cr(VI) and Hg(II) from wastewater. The performance of the carbon was compared with a commercial activated carbon(CAC) of M/s LOBA chemicals of same particle size.

Experimental

The modified dolomite process¹² was used for preparation of high temperature *Syzygium Jambolanum* nut carbon. Fifty grams of *Syzygium Jambolanum* nut was placed over a bed of CaCO₃ of 1 cm thickness. The layer on top was also covered with CaCO₃ of 1 cm thickness and then subjected to pyrolysis at 600 °C for 1 h. The char was then heated and maintained at 900 °C for 30 minutes for activation by CO₂ liberated by the decomposition of CaCO₃. The activated material was repeatedly washed with water and left soaked in 10% HCl to remove the calcium oxide formed. The material was washed thoroughly with water to remove the free acid and was dried at 105±5 °C. The carbon was designated as HSJC. It was ground and sieved to get 20-50 ASTM particle size.

Evaluation of carbon characteristics

The important carbon characteristics of HSJC and CAC such as bulk density, moisture content, ash, matter soluble in water, matter soluble in acid, pH, decolourisation property, phenol number, ion exchange capacity, surface area and iron content were found out in order to determine the capacity of the carbons for the removal of contaminants by adsorption process. The results are shown in Table 1.

Table 1. Carbon characteristics.

S.No.	Control tests	HSJC	CAC
1.	Bulk density, g/cc	0.60	0.51
2.	Moisture, %	5.1	3.76
3.	Ash, %	3.81	2.69
4.	Matter soluble in water, %	1.53	1.09
5.	Matter soluble in 0.25 M HCl, %	1.66	1.10
6.	Decolourising power, mg/g	71	87
7.	Phenol number, mg	25	22
8.	Ion exchange capacity, meq./g	Nil	Nil
9.	Surface area, m ² /g [N ₂ -BET]	646	629
10.	pH	6.4	7.1
11.	Iron content, %	0.12	1.1

Batch Studies

Batch studies were done by using mechanical shaker. 100 mL of 10 mg/L Cr(VI) solutions were taken in 300 mL polythene bottles for known doses of HSJC and CAC and equilibrated for 24 h in the pH range of 1- 6. Then it was filtered and analysed for Cr(VI) by using UV- Visible spectrophotometer at 540 nm by standard methods¹³.

100 mL of 10 mg/L of Hg(II) solutions containing 10 g/L of NaCl were adjusted to different pH values in the range of 1-10 and known amounts of HSJC 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 analysed for Hg(II) content using DMA¹⁴ (Direct Mercury Analyser, Milestone Inc). In DMA, the liquid sample was initially dried and then thermally decomposed in a continuous flow of oxygen. Combustion products were carried off and further decomposed in a hot catalyst bed. Mercury vapours were trapped on a gold amalgamator and subsequently desorbed for quantisation. The Hg content was 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 methods for Cr(VI) and Hg(II) respectively.

Adsorption isotherms

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

$$\log \frac{x}{m} = \log + \frac{1}{n} \log C_e \quad (1)$$

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. Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (2)$$

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.

Freundlich and Langmuir adsorption isotherm studies were carried out with different initial concentrations and fixed doses of carbon and pH.

Adsorption kinetics

The adsorption of ions in aqueous system follows reversible first order kinetics when a single species is considered on a heterogeneous surface¹⁵. The first order rate expression¹⁶ is

$$\ln (1-U_t) = -kt \quad (3)$$

where,

$$U_t = \frac{C_{A(o)} - C_{A(t)}}{C_{A(o)} - C_{A(e)}} \quad (4)$$

$C_{A(o)}$, $C_{A(t)}$ and $C_{A(e)}$ are the concentrations in mg/L of Cr(VI) initially, at any time t and at equilibrium respectively. Kinetic studies were carried out at different time intervals whereas concentration, carbon doses and pH are fixed.

Desorption

Attempts were made to desorb the adsorbed Cr(VI) from the carbons with 1 M NaOH and 10% H_2O_2 mixture. Desorption of Hg(II) was made using 2% Na_2S in 1% NaOH^{17,18}.

Results and Discussion

From Figure 1, it could be seen that the optimum pH for Cr(VI) removal is 2. The predominant species of Cr(VI) between 2 - 4 is HCrO_4^{2-} which is adsorbed preferentially on the adsorbents. It could be inferred from Figure 2 that for 99% removal of Cr(VI) a minimum carbon dose of 0.2 g of HSJC was sufficient and for CAC 0.3 g was needed. Figure 3 indicates that an optimum time of 5 h was needed for removal of 99% of Cr(VI) and 6 h for CAC.

Figure 1. Effect of pH on removal of Cr(VI)

Figure 2. Effect of Carbon dose on removal of Cr(VI)

Figure 3. Effect of time on removal of Cr(VI).

From Figure 4, it could be inferred that HSJC 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. Figure 5 shows that the optimum carbon dose required by HSJC was 0.2 g and for CAC it was 0.3 g. Figure 6 indicates that an optimum time of 4 h was enough for Hg(II) removal and 5 h was required for CAC.

Figure 4. Effect of pH on removal of Hg(II).

Figure 5. Effect of Carbon dose on removal of Hg(II).

Figure 6. Effect of time on removal of Hg(II).

Plots of $\log x/m$ vs. $\log C_e$ are linear for HSJC and CAC for both Cr(VI) and Hg(II) (Figure 7 & 8). 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 along with the regression coefficient (R^2) values. The values of $1 < n < 10$ showed favourable adsorption of Cr(VI) and Hg(II) on both HSJC and CAC¹⁹. The regression coefficient (R^2) values were calculated and are shown in Table 2.

Figure 7. Freundlich adsorption isotherm for adsorption of Cr(VI).

Figure 8. Freundlich adsorption isotherm for adsorption of Hg(II).

Table 2. The Freundlich adsorption isotherm values.

Inorganic ion	Carbon	n	K	R^2
Cr(VI)	HSJC	3	7.59	0.9814
Cr(VI)	CAC	2.5	3.8	0.9928
Hg(II)	HSJC	1.43	3.98	0.9991
Hg(II)	CAC	1.39	2.29	0.9959

The linear plots of C_e / q_e vs. C_e showed that the adsorption obeys Langmuir model for HSJC and CAC for both Cr(VI) and Hg(II) and is shown in Figure 9 & 10. Q_0 and b were determined from Langmuir plots and are shown in Table 3 along with the regression coefficient (R^2) values. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L . $R_L = 1/(1+bC_0)$ where b is Langmuir constant and C_0 is the initial concentration of Cr(VI). R_L values between 0 and 1 indicate favourable adsorption of Cr(VI) and Hg(II) on both HSJC and CAC (Table 4). R^2 value shows that Freundlich isotherm model fits well for Cr(VI) and Hg(II) adsorption for both the carbons.

Figure 9. Langmuir adsorption isotherm for adsorption of Cr(VI).

Figure 10. Langmuir adsorption isotherm for adsorption of Hg(II).

Table 3. The Langmuir adsorption isotherm values.

Inorganic ion	Carbon	Q_0	b	R^2
Cr(VI)	HSJC	45.05	0.0588	0.9526
Cr(VI)	CAC	27.2	0.0459	0.9689
Hg(II)	HSJC	78.6	0.0364	0.9762
Hg(II)	CAC	52.9	0.0326	0.9590

Table 4. Equilibrium parameter R_L values for HSJC and CAC.

Cr(VI)		Hg(II)	
HSJC	CAC	HSJC	CAC
0.4739	0.5213	0.5790	0.6053
0.2309	0.2664	0.3144	0.3383
0.1527	0.1789	0.2157	0.2347

The straight line plot of $\ln(1 - U_t)$ vs. t indicates that the adsorption followed reversible first order kinetics for HSJC and CAC for both Cr(VI) and Hg(II) (Figure 11 & 12). The k adsorption values were calculated and are presented in Table 5.

Figure 11. Kinetic fits of Cr(VI) adsorption data **Figure 12.** Kinetic fits of Hg(II) adsorption data**Table 5.** Adsorption rate constants

Inorganic ion	Carbon	K_{ads} (h^{-1})
Cr(VI)	HSJC	0.275
Cr(VI)	CAC	0.2222
Hg(II)	HSJC	0.0999
Hg(II)	CAC	0.095

Percentage of the desorbed hexavalent chromium as chromate was found to be 81.9% for CHSJC and 80.5% for CAC. The remaining chromium which would have been reduced to Cr(III) was desorbed by adding 1 M HCl. The total chromium desorbed was found to be 91.9% for HSJC and 90.5% for CAC. Hg(II) forms a soluble complex $[\text{HgS}_2]^{2-}$ with alkaline Na_2S and the desorption was found to be 98% for HSJC and 97% for CAC.

Conclusion

The study clearly shows that the High Temperature *Syzygium Jambolanum* Nut Carbon HSJC was superior to CAC for the removal of Cr(VI) and Hg(II) from wastewater. The adsorption conforms to Freundlich and Langmuir equation based on formation of monolayer. It followed reversible first order kinetics. Hexavalent chromium could be quantitatively desorbed by treating with a mixture of 1M NaOH and 10% H_2O_2 . Mercury(II) could be quantitatively recovered by 2% Na_2S in 1% NaOH. This environment friendly adsorbent could be used as an alternative to CAC for the cost effective treatment for the removal of Cr(VI) and Hg(II) from wastewater.

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