

## SEM and FT-IR Studies on Nature of Adsorption of Mercury(II) and Chromium(VI) from Wastewater using Chemically Activated *Syzygium jambolanum* Nut Carbon

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The chemically activated carbon prepared from *Syzygium jambolanum* nut [CHSJC], an agricultural waste, after activation with ammonium persulphate, an oxidizing chemical in the presence of sulphuric acid followed by thermal activation by modified dolomite process was successfully used to remove mercury(II) and chromium(VI) from wastewater in batch studies by adsorption process. Surface morphology of the carbon was analyzed by scanning electron microscope (SEM) before and after the adsorption of Hg(II) and Cr(VI) and the results revealed the presence of micropores which are responsible for adsorption. Fourier transform infrared (FT-IR) spectroscopic studies of the carbon showed that physisorption took place on the surface of the carbon and the functional groups responsible for adsorption. SEM and FT-IR analysis of high temperature activated *Syzygium jambolanum* nut carbon [HSJC] and a commercial activated carbon (CAC) before and after the adsorption of Hg(II) and Cr(VI) were also carried out for comparison purposes.

**Key Words:** *Syzygium jambolanum* nut, Chemical activation,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , Adsorption, Scanning electron microscope, Micropores, Fourier transform infrared spectra.

### INTRODUCTION

Water is one of the most vital natural resources for all forms of life on earth. The purity of water plays an important role in determining the health of the people. At present, various ill effects of health caused by the use of polluted water looms large on the horizons of developing countries. The major source of water pollution is the effluent from industries which contains heavy metal ions like Hg(II) and Cr(VI) which are discharged even at trace levels into the natural water bodies. Water pollution makes water unsuitable for the desired use.

Mercury(II), a highly toxic metal ion, causes pollution of water due to the discharge of effluents from chlor-alkali plants<sup>1</sup>, pharmaceutical, pulp, paint, plastic industries<sup>2</sup> and also by agricultural sources such as fertilizers and fungicidal spray<sup>3</sup>. Compounds of mercury find widespread use as a catalyst in the production of polyvinyl acetate and polyvinyl chloride<sup>4</sup>. The permissible limit of Hg(II) in potable

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water is 0.002 mg/L as per USEPA (United States Environment Protection Agency) standard<sup>5</sup> and 0.001 mg/L as per Indian standard<sup>6</sup>.

A variety of approaches have been described for the treatment of mercury and chromium containing wastewater which include ion exchange<sup>7</sup>, reverse osmosis<sup>8</sup> and precipitation<sup>9</sup> electrochemical reduction<sup>10</sup>, electrocoagulation<sup>11</sup>, *etc.* These processes have considerable disadvantages including incomplete removal, generation of toxic sludge or other waste products that require disposal, need of expensive equipment, monitoring system and energy requirements. In addition, the recovery of these species is limited.

Alternate method using adsorbents have been studied extensively during the last three decades. It is a process by which the concentration of solute is enriched at the surface or interface between two phases. It provides reliable results without much cost and working efforts. In addition, it is capable of producing effluent free of suspended solids. Activated carbons prepared from a variety of agricultural wastes such as coconut shell<sup>12</sup>, peanut hull<sup>13</sup>, walnut shell<sup>14</sup>, hazelnut shell<sup>15</sup>, almond shell<sup>16</sup>, date palm seed<sup>17</sup>, *etc.* have been employed for the removal of toxic inorganics and organics from water and wastewater.

*Syzygium jambolanum* nut is one of the potential agricultural wastes. *Syzygium jambolanum* tree is an evergreen tropical tree. A tropical tree also grows easily in sub-tropical climates and grows largely all over India. It is commonly called java plum, jambul, jamun, jaman, black plum, Indian blackberry, jambol, jambolan, *etc.* It grows to 50 to 100 feet tall with oblong opposite leaves. Jamun has fragrant white flowers and purplish-black oval edible berries. The berry has a single nut which is used for the treatment of diabetic and blood pressure. Even though, it is used for medicinal purposes, a large amount of nuts remains a waste. As the production rate of the nut is high, this has prompted the studies on the use of *Syzygium jambolanum* nut for the removal of toxic inorganic ions from wastewater.

The present work deals with the chemically activated high temperature *Syzygium jambolanum* nut carbon (CHSJC) of 20-50 mesh ASTM particle size which effectively removes Hg(II) as  $[\text{HgCl}_4]^{2-}$  and Cr(VI) as dichromate ions. Surface morphology of the carbon particles were carried out by using scanning electron microscope (SEM) to analyze the pores on the surface of the carbon particles where the adsorption takes place and Fourier transform infrared (FT-IR) spectroscopic studies were done to find the type of adsorption *i.e.* whether physical or chemical adsorption had taken place and the groups responsible for adsorption. High temperature *Syzygium jambolanum* nut carbon (HSJC) and commercial activated carbon (CAC) of M/s LOBA Chemicals of same particle sizes were taken for comparison purposes.

## EXPERIMENTAL

**Preparation of CHSJC and HSJC:** *Syzygium jambolanum* nut was treated with conc.  $\text{H}_2\text{SO}_4$  (1:1.5 weight ratio) for carbonization purpose in the presence of oxidizing chemical  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0.1 part). 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<sub>3</sub> solution to remove the free acid and finally left immersed in 2 % NaHCO<sub>3</sub> 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<sub>2</sub> atmosphere by sandwiching the material between powdered CaCO<sub>3</sub> beds in a closed container at 800-850 °C for 0.5 h (modified dolomite process<sup>18</sup>). The material was washed thoroughly with water and then soaked in 10 % HCl to remove CaO as well as unspent CaCO<sub>3</sub>. After separating the material, it was washed with distilled water, dried at 105 ± 5 °C. The carbon was referred to as CHSJC.

HSJC was prepared by the modified dolomite process by keeping the *Syzygium jambolanum* nuts between CaCO<sub>3</sub> beds at 600 °C for 1 h for pyrolysis and maintained at 900 °C for 0.5 h for activation by CO<sub>2</sub> liberated by the decomposition of CaCO<sub>3</sub>. Commercial activated carbon (CAC) of M/s LOBA chemicals was used for comparison purposes. All the carbons were ground and sieved to separate 20-50 mesh ASTM particles.

**Batch studies:** Batch studies were performed by using mechanical shaker to find out the optimum pH, minimum carbon dose and equilibration time for maximum removal of Hg(II). Mercury(II) content was analyzed using DMA<sup>19</sup> (Direct Mercury Analyzer, Milestone Inc.) and Cr(VI) was analyzed by UV-visible spectrophotometer [PGI 1901] at 540 nm by standard methods<sup>20</sup>.

For batch studies, 100 mL of 10 mg/L of Hg(II) solutions containing 10 g/L of NaCl were adjusted to pH of 2.0 to 10.0 and 0.5 g each of CHSJC, 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 analyzed for Hg(II). 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. The equilibration time needed for maximum removal of mercury(II) was 3 h for CHSJC, 4 h and 5 h for HSJC and CAC, respectively.

Similarly 100 mL of 10 mg/L chromium(VI) solutions were taken in 300 mL polythene bottles and adjusted to pH of 1.0 to 6.0 with 0.5 g each of CHSJC, HSJC and CAC and equilibrated for 24 h. For maximum Cr(VI) removal as HCrO<sub>4</sub><sup>-</sup> species, the optimum pH was fixed at 2.0 at which dichromate [HCrO<sub>4</sub><sup>-</sup>] ions were predominant. The minimum carbon dosage was 0.1 g, 0.2 g and 0.3 g for CHSJC, HSJC and CAC, respectively for the quantitative removal of Cr(VI). The equilibration time needed for maximum removal was 4 h for CHSJC, 5 h and 6 h for HSJC and CAC, respectively<sup>21</sup>.

The carbon particles after filtration were collected separately after Hg(II) and Cr(VI) removal and dried for SEM and FT-IR analysis. In addition, all the three carbons before batch studies were also taken for analysis.

The SEM and FT-IR analysis of the carbon samples were carried out before and after adsorption of mercury(II) and chromium(VI).

## RESULTS AND DISCUSSION

**Scanning electron microscope studies:** SEM study is used to study the morphology and surface characteristics of adsorbent material<sup>22</sup>. The pores present in activated carbon can be divided into three basic classes<sup>23</sup> viz., (1) macropores (2) transitional pores and (3) micropores. Pores of effective radius greater than 500-1000 Å are classified as macropores. In activated carbon, the effective radius of macropores, frequently lies in the range of 5000-20000 Å having surface area ranging between 0.5 and 2.0 m<sup>2</sup>/g. The effective radius of transitional pores usually falls within 40-200 Å and their surface area lies between 20-70 m<sup>2</sup>/g. Micropores, which have radius less than 20 Å usually amounts to at least 95 % of total surface area. Micropores are of greatest significance for adsorption due to their large surface area<sup>24</sup>.

SEM picture of CHSJC before adsorption is shown in Fig. 1. The picture shows isolated pores of varying dimensions from micro to transitional pores. The SEM picture of HSJC before adsorption is shown in Fig. 2 shows irregular pores of large dimensions. Layers of carbon that are interconnected are clearly seen. The pores extend from one layer to the other layer. The SEM picture of CAC before adsorption is shown in Fig. 3. The pores appear to have a fewer dimensions than CHSJC and HSJC. Presence of inorganic irregular deposits is also seen on the commercial carbon.

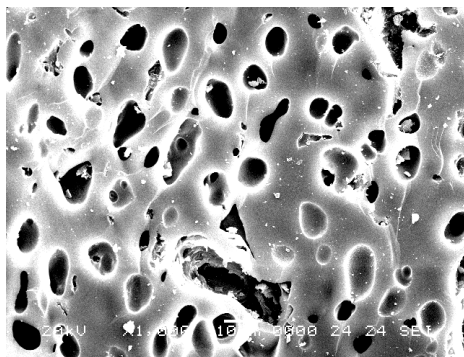


Fig. 1. Chemically activated high temperature *Syzygium jambolanum* nut carbon (CHSJC)

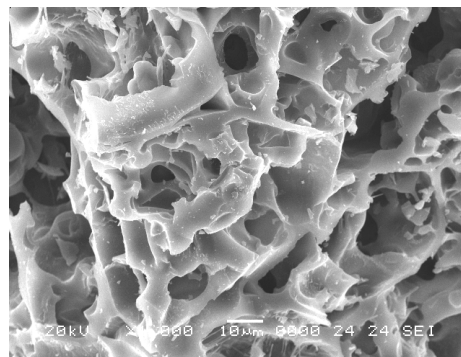


Fig. 2. High temperature *Syzygium jambolanum* nut carbon (HSJC)

The SEM picture of CHSJC after adsorption of Hg(II) is shown in Fig. 4. The surface morphology is changed completely after adsorption of Hg(II). The SEM picture of HSJC after adsorption of Hg(II) is shown in Fig. 5 in which the surface morphology appears smooth. The pore size also appears reduced. The SEM picture of CAC after adsorption of Hg(II) is shown in Fig. 6. It displays nearly similar characteristics as that of the parent carbon. Hence after adsorption studies, the surface morphology changes in the case of CHSJC and HSJC. But in case of CAC, no change is observed.

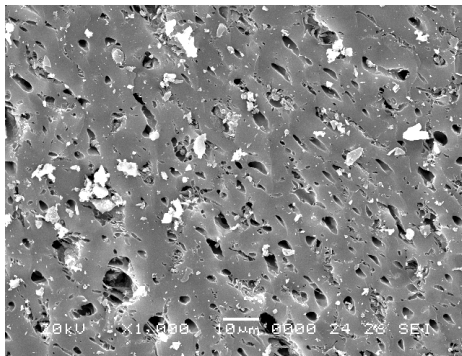


Fig. 3. Commercial activated carbon (CAC)

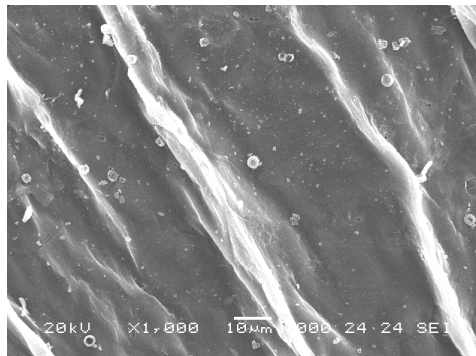
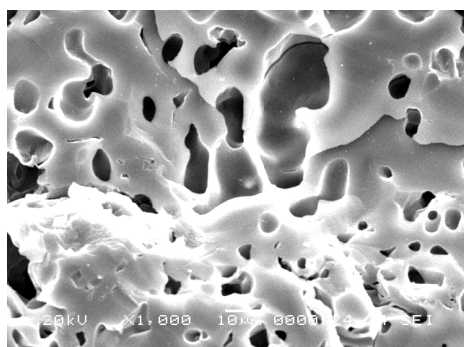
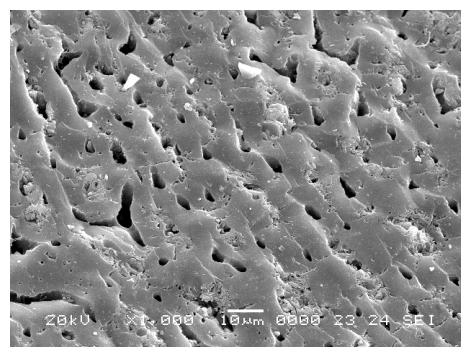
Fig. 4. Chemically activated high temperature *Syzygium jambolanum* nut carbon (CHSJC) after adsorption of mercury(II)Fig. 5. High temperature *S. jambolanum* nut carbon (HSJC) after adsorption of mercury(II)

Fig. 6. Commercial activated carbon after adsorption of mercury(II)

The SEM picture of CHSJC after adsorption of Cr(VI) is shown in Fig. 7. Although the carbon appears porous, the porosity appears to be larger after adsorption. The presence of inorganic deposits in most of the pores is also evident from the figure. But in the parent carbon, the deposits are very low. The SEM picture of HSJC after adsorption of Cr(VI) is shown in Fig. 8. Here also, the presence of inorganic deposits inside the pores is clearly evident. The SEM picture of CAC after adsorption of Cr(VI) is shown in Fig. 9. Here, the surface appears smooth when compared to parent carbon. Pile up layers of carbon is seen. Inorganic deposit scattered over the terrace of carbon is also seen.

Inorganic deposits appear more on CHSJC than HSJC and CAC. It is also in line with the investigation that CHSJC is superior to HSJC and CAC.

**Fourier transform infrared (FT-IR) spectroscopic studies:** FT-IR studies are used to identify the groups responsible for adsorption and also the nature of adsorption. The adsorptive properties of activated carbon are determined not only

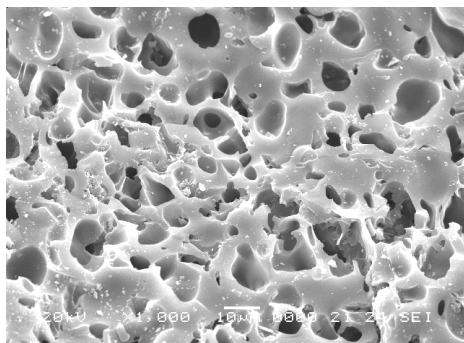


Fig. 7. Chemically activated high temperature *Syzygium jambolanum* nut carbon (CHSJC) after adsorption of chromium(VI)

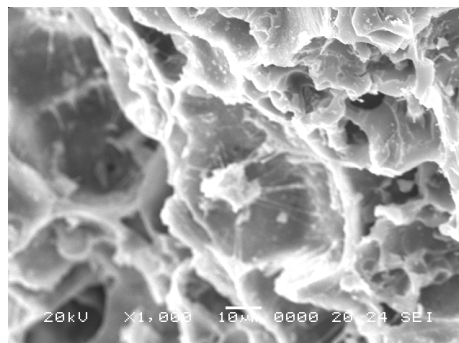


Fig. 8. High temperature *Syzygium jambolanum* nut carbon (HSJC) after adsorption of chromium(VI)

by its porous structure but also by its chemical composition. Activated carbon contains chemically bonded elements such as oxygen and hydrogen. These elements are derived from the starting material and they remain as a result of imperfect carbonization or they can become chemically bonded to surface during activation.

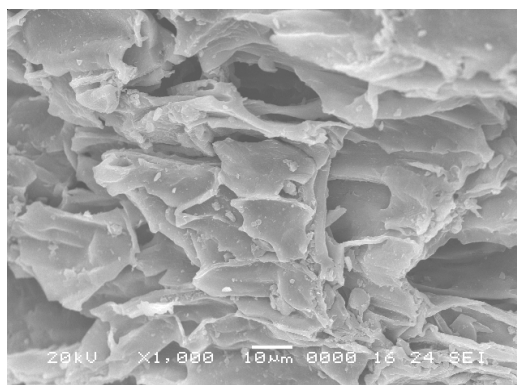


Fig. 9. Commercial Activated Carbon (CAC) after adsorption of chromium(VI)

In FT-IR spectrum of CHSJC, the broad and intense peak at  $3432\text{ cm}^{-1}$  is due to O-H stretching vibration of carbon. It is confirmed by its C-O stretching vibration occurring at  $1109\text{ cm}^{-1}$ . The peaks at  $2922\text{ cm}^{-1}$  and about  $2820\text{ cm}^{-1}$  are due to asymmetric and symmetric stretching vibrations of  $-\text{CH}_2-$  groupings. The corresponding bending vibrations occur at  $1382$  and  $1450\text{ cm}^{-1}$ . Trace amount of adsorbed water is partly evident by its  $\text{OH}_2$  bending vibration occurring at about  $1630\text{ cm}^{-1}$ . The intense peak in the higher energy region also includes O-H stretch of water. Hence the IR spectrum reveals presence of residual O-H and  $-\text{CH}_2-$  groupings on the carbon.

The FT-IR spectrum of HSJC display nearly similar characteristics as that of CHSJC. Hence, chemical treatment and subsequent temperature treatment produce carbon with characteristics same as that of temperature treated carbon. The FT-IR spectrum of CAC reveals similar characteristics as that of CHSJC.

Though the three spectra of CHSJC, HSJC and CAC show similar characteristics for all the carbons, there is slight difference with respect to the intensity of the O-H stretching vibration occurring in the higher energy region. CHSJC shows more intensity than the commercial activated carbon which in turn shows more intensity than HSJC. As this peak is due to mainly O-H stretching vibration, it could be depicted that CHSJC could have higher adsorption properties than the other two carbons. The O-H groups can have covalent interaction with metal ions or hydrogen bonding interaction with any anionic species during adsorption.

FT-IR spectrum of CHSJC after adsorption of mercury(II) shows similar characteristics as shown in FT-IR spectrum of CHSJC before adsorption. Hence the free O-H groups of carbon might not exert covalent interactions with the metal ion. In addition, the O-H groups do not exhibit even hydrogen bonding interaction with  $\text{HgCl}_4^{2-}$ . This observation suggests that these O-H groups might not be present inside the pores where the adsorption is expected to occur. But the O-H groups might be close to each other as there is peak broadening.

The FT-IR spectrum of HSJC after adsorption of  $\text{HgCl}_4^{2-}$  shows nearly same characteristics as presented in FT-IR spectrum of HSJC before adsorption. Hence, the similar to CHSJC, after adsorption of Hg(II), it is suggested to carry O-H groups not inside the micropores where the adsorption actually occurs. The FT-IR spectrum of CAC after adsorption of Hg(II), also displays similar characteristics as shown in FT-IR spectrum of CAC before adsorption. Hence, the adsorption of Hg(II) on the surface of carbon does not lead to any change in the vibration of O-H groupings. Therefore, adsorption of  $\text{HgCl}_4^{2-}$  on CHSJC, HSJC and CAC is exclusively controlled by vander Walls forces. In other words, there might be exclusive physical adsorption.

The FT-IR spectra of CHSJC, HSJC and CAC after Cr(VI) adsorption carry similar features. Hence, after adsorption of Cr(VI), there is no change in the vibrations of O-H groupings. So, here also there must be physical adsorption of Cr(VI) in the pores of the carbons.

Therefore, from the IR spectral analysis, it can be said that there is exclusive physio-sorption of Hg(II) and Cr(VI) in the pores of the carbons.

## Conclusion

Based on the experimental analysis of carbon prepared from *Syzygium jambolanum* nut before and after adsorption of Hg(II) and Cr(VI) with SEM studies, it was found out that micropores were responsible for adsorption. More inorganic deposits present in the pores of CHSJC than HSJC and CAC showed that CHSJC was superior to HSJC and CAC for the removal of mercury(II) and chromium(VI)

from wastewater which was also in line with the results from batch studies. From FT-IR spectral analysis, it could be concluded that there was exclusive physio-sorption of Hg(II) and Cr(VI) on CHSJC, HSJC and CAC.

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