A Novel Approach for Hexavalent Chromium Removal from Tannery Effluents by Nanosize Activated Carbon Derived Utilizing Sapindus Emarginata Rind

T.Shanmugasundari*[1], S.Chitra[2]

[*1]*Department of Chemistry, K.S.R.College of Engineering, Tiruchengode, India*

[2] *Department of Chemistry, A.R.Engineering college, Villupuram, India*

Abstract

A process for the hexavalent chromium removal by a novel nano adsorbent is discussed in this work. This paper has a double purpose. The first part described how to obtain a nanosize adsorbent using a different material Sapindus emarginata rind. Here the preparation of novel activated carbon from the rind by pyrolysis method is explained. Chemical analysis for the nano adsorbent is carried out and analyzed. The morphology of the prepared nano activated carbon is characterized by SEM, TEM and XRD. In the second part removal of hexavalent chromium by the above nano absorbent is studied. The influence of the following parameters such as pH, agitation time and adsorbent dosage is taken into account for the batch experiments. The adsorption efficiency of the chromium removal from tannery effluent also studied. The result showed that prepared nano adsorbent can be used efficiently for the treatment of tannery wastewater containing chromium.

Keywords: *Nano material; Sapindus emarginata; Ortho Phosphoric acid; XRD; TEM; SEM.*

I. INTRODUCTION

A tremendous increase in human population and the rapid growth of industries in India have created more problems of waste disposal and fresh water contamination mainly in last few decades[1]. Among several heavy metals chromium compounds are used extensively in industrial process such as leather tanning, textile dyeing, electro plating, and manufacture of paints, dyes, paper, explosives and ceramics[2]. Leather industry provides the necessities such as leather shoes and garments; however the leather making process in turn generates byproducts and wastes[3]. Chromium is considered as one of the top sixteen pollutants because of its carcinogenic characteristics for humans[4]. This creates a number of environmental and health problems. It increases toxicity of soil and decreases the quantity and quality of agro products. To avoid these severe problems, the industrial effluents have to be treated and disposed off before released into the environment. Among various water treatment techniques described, adsorption is generally preferred for the removal of Chromium due to its high efficiency[5]. Nano structured material based technologies are promising in removing toxic chemicals because they have large specific surface areas which are useful for impurity removal[6]. The aim of this research work is to study the Cr(VI) adsorption capacity by nano adsorbent prepared from Sapindus emarginata rind. The studies are systematically carried out in a batch work covering various parameters.

II. MATERIALS AND METHODS

A. Preparation of Nano Activated Carbon

Sapindus emarginata dry fruits were collected from the local market and washed thoroughly with distilled water.They were dried in sunlight until the moisture was partially evaporated and further dried in a hot air oven at 120°c for 72 hours.From the dried material the rinds were separated.They were grounded into fine powder in a ball mill. After this the material was screened to obtain particle sizes ranging from 50 to 200µm.The rind powder was treated by 50% H_3PO_4 with vigorous stirring. The phosphoric acid impregnated material was kept in oven at 430 ± 5°c for 16 hours and washed with distilled water. Then the charcoal was soaked in 5% $NaHCO_3$ solution over a night and washed with double distilled water then followed by absolute ethanol. The dried Phosphoric acid Activated Carbon of Sapidus Emarginata Rind (PACSER) was collected in airtight bottles and used in this study.

B. Characterization of Adsorbent

The characterization of PACSER is carried out using chemical analysis and the results are presented in

Table1.X-ray Diffraction (XRD) pattern of PACSER was recorded on Shinabzu XRD-6000 Japan. The X-ray source was copper with a voltage of 40kV and a current of 30mA.The surface morphology of PACSER was visualized through Scanning Electron Microscopy (SEM) and the micrographs being obtained using a JSM-6090 JEOL JAPAN. The SEM of metal loaded and unloaded samples were taken at an accelerated voltage of 10 kV. Transmission Electron Microscopy (TEM) studies were carried out on the adsorbent PACSER using a model JEOL-2010 microscope with an accelerating voltage of 100kV.

C. Preparation of Stock Solution

1000ppm of stock solution of $K_2Cr_2O_7$ was prepared by dissolving 2.82g of $K_2Cr_2O_7$ in double distilled water. The above stock solution contains few drops of concentrated Hydrochloric acid to prevent hydrolysis of chromium ions [7].

D. Batch Experiments

From the stock solution 10ml was make up to 100ml in a standard measuring flask. This test sample is examined in spectrophotometer for initial %Transmittance. Then the solution was treated with 0.6 g of PACSER and allowed to agitate in a rotary shaker for about 180 minutes at pH 3. After this, the sample was allowed to settle and then filtered through whatmann filter paper. The filtrate of the sample was examined in spectrophotometer to measure final %Transmittance. The percentage removal of chromiu (VI) was calculated as

$$\% \text{ Removal} = [(C_o - C_t) / C_o \mathbf{X} 100]$$

Where C_o = Initial concentration of chromium

C_t = Chromium concentration after adsorption by adsorbent.

Table 1. Characteristics of PACSER

Characteristics	***Values***
pH (1% solution)	5.7
Moisture content (%)	3.16
Ash content (%)	2.8
Conductivity (ms/cm)	0.31
Solubility in water (%)	0.27
Solubility in acid (%)	1.20
Particle Size (nm)	18 to 65

Table 2. Experimental Conditions Investigated

S.NO.	***Parameters***	***Range of Values Investigated***
1	Adsorbent dosage (gm)	0.1 to 0.8
2	Agitation time (Min)	30 to 180
3	pH	1 to 8

The same experimental procedure was repeated for different agitation time, different pH, and different dosage of PACSER. The range of the parameters studied is given in Table 2.

E. Treatment of Tannery Waste Water by Novel Absorbent PACSER:

Two samples were collected from ABS tannery and MM tannery in Erode. Industrial effluents were analyzed in the laboratory. The Heavy metal analysis is given in Table 3. These two samples were treated with nano material PACSER prepared in this work at optimized conditions of pH, agitation time & dose determined by previous experiments.

III. RESULTS AND DISCUSSION

A. Characterization of adsorbent

The characteristics of Nano activated carbon PACSER is given in Table 1. PACSER has low pH that may be assigned due to its acid treatment. The higher moisture content of nano adsorbent may be on account of the surface oxygen groups which were introduced by chemical treatment on it. The ash content seems to be high because the adsorbent is derived from natural product. Particle size analysis represent the range of PACSER is 18nm to 65nm. X-ray diffraction analysis of PACSER in Fig.1 show broad peaks at 2θ values in the range of 15-40. This indicates the amorphous form of carbons. There is no major peak obtained. This may be due to lack of the Inorganic substances in the activated carbon [8]. TEM analysis of PACSER clearly confirms its nano level structure. This is shown in Fig.2 which represents its agglomerated form.

Table 3. Heavy Metal Analysis of Tannery Effluents

Sample	***Pb***	***Ni***	***Cr***	***Zn***
Units	mg/L	mg/L	mg/L	mg/L
ABST	0.18	0.014	3.94	4.2
MMT	0.15	0.017	3.59	3.9

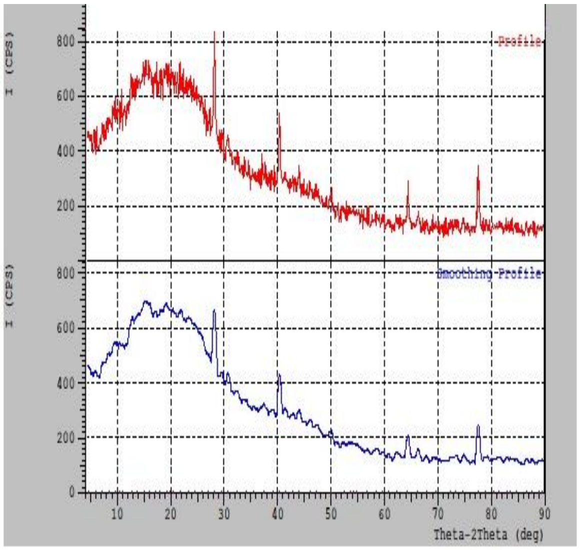


Fig. 1. XRD of PACSER

B. Batch Experiments

1) Effect of Agitation Time

In this stage all other parameters, including absorbent dosage (0.6g/L),pH 3.0 were kept constant. The effect of contact time on chromium adsorption efficiency by the nano activated carbon is shown in Fig.3. Initially the adsorption of PACSER is fast. At 120 minutes PACSER attained 94% of adsorption. After this there is no appreciable change in the percentage of adsorption.

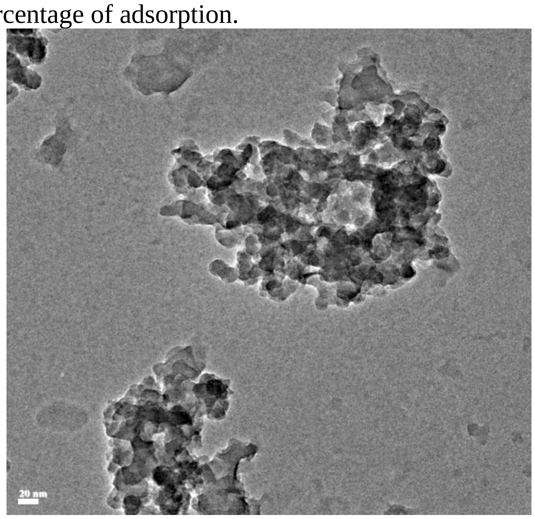
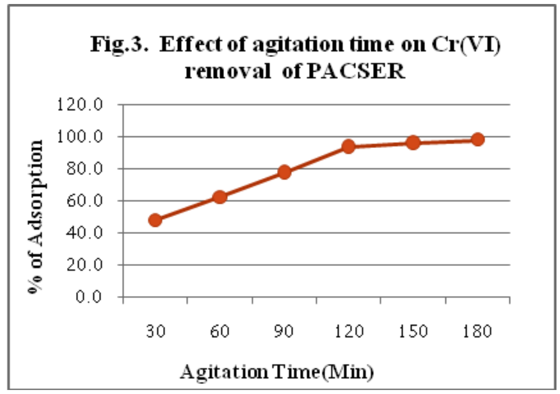


Fig. 2. TEM of PACSER

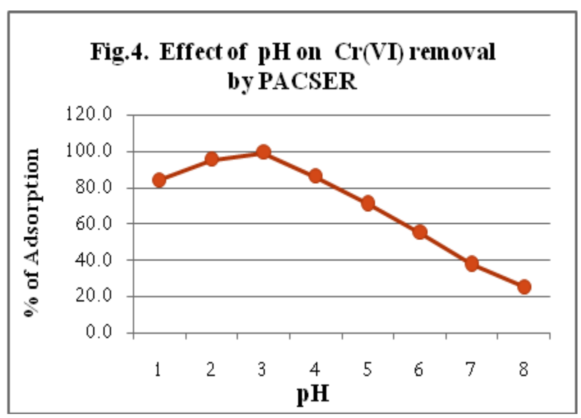


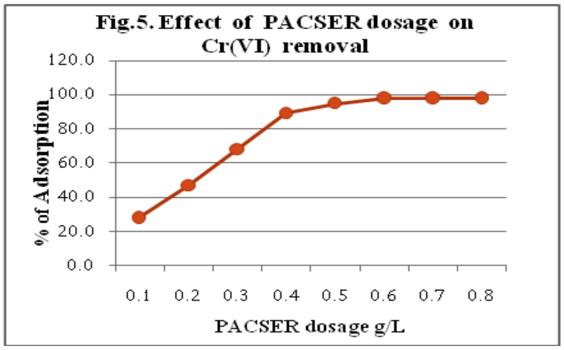
2) Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals. The results obtained are shown in Fig.4 which shows the effect of pH on the absorption of Cr(VI) ions from the aqueous solution on to the novel adsorbent PACSER in terms of metal ion removal percentage. It is clear that the Cr(VI) ions were effectively adsorbed in the pH range of 2 to 3. In general adsorption of anion is favoured at very low pH. In this pH, chromium ions exist in the form of $HCrO_4^-$, As the pH increases equilibrium shifted from $HCrO_4^-$, to CrO_4^{2-} and $Cr_2O_7^{2-}$ [9]. The maximum adsorption of 99.3% occurs at 3.0 pH. When move from pH of 3 to higher values there is a drastic decrease of adsorption.

3) Effect of Carbon Dose

At this stage the effect of the PACSER was done under the conditions of pH 3.0 and the time of agitation is 180 minutes. The results obtained for the effect of nano carbon dosage are shown in Fig.5. The percentage removal of chromium increases rapidly for PACSER and attain 98.3% at 0.6g. This is possible due to the nanosize of the adsorbent. This clearly shows PACSER is more effective adsorbent for Cr(VI) .





C. *SEM Analysis of PACSER*

Examination of SEM micrographs of the PACSER found to be rough area on the surface of the carbon and the micro pores were identifiable. Fig.6(a) and 6(b) represent the SEM photographs of Cr(VI) ion unloaded and loaded PACSER.It is observed that the morphology of unloaded PACSER in Fig.6(a) is quite corroded, having voids and heterogeneous. Micro porosity is formed when phosphoric acid activated carbon prepared from lignocellulosic materials [10]. The loaded PACSER in Fig.6(b) seems to be having less porosity and less roughness. This indicates the surface turns smooth after the adherence of Cr(VI) ions.

D. *Treatment of Tannery Effluent by PACSER at Optimized Condition*

The samples given in Table.3 were treated by PACSER at optimized conditions of pH 3.0, dose 0.6g/L, agitation time 180 minutes, determined by experiments. The removal efficiency was found 93.4% and 96.8% for effluents of ABST & MMT respectively. This representation is given in **Fig.7**. The efficiency of adsorption here is seems to be less than that of standard chromium solution (98.3%). This may be due to the presence of other metals in tannery effluents which competed with Chromium to adsorb on PACSER.

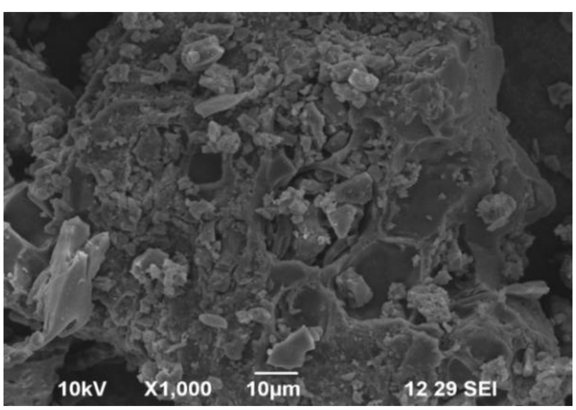


Fig: 6(a). Morphology of unloaded PACSER

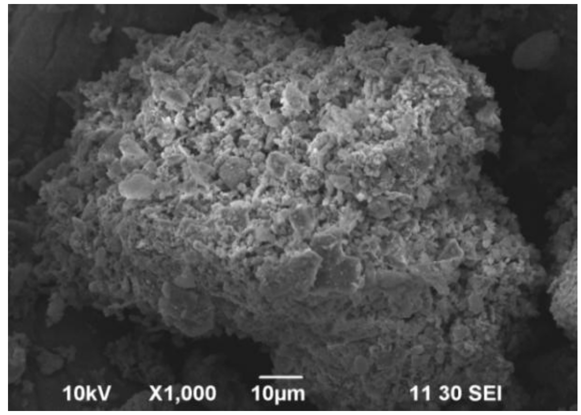
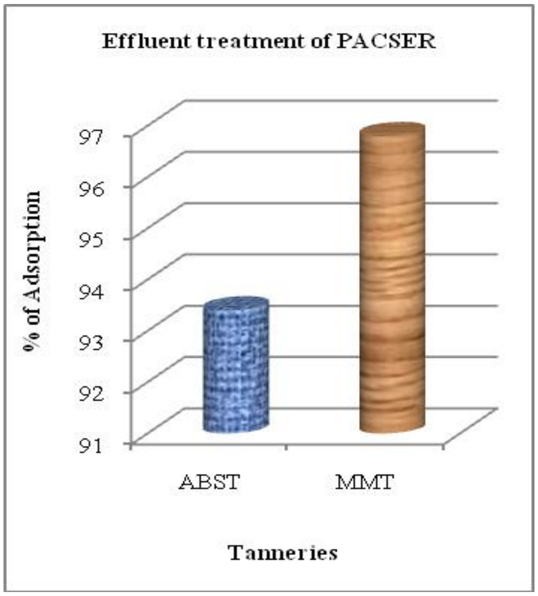


Fig: 6(b). Morphology of Cr(VI) loaded PACSER

IV. CONCLUSION

Nanosize activated carbon PACSER has been prepared from Sapindus Emarginata rind and characterized. Effects of adsorption parameters were studied utilizing the PACSER. The optimum pH for the removal of Cr(VI) was found to be 3.0 for the nano absorbent. The uptake was maximum at adsorbent dosage of 0.6g/l for PACSER and with increase in agitation time there was good effect in removal of Cr(VI) ions. Nano activated Carbon of Sapindus Emerginata Rind was found to be more efficient and is successfully employed for the treatment of tannery effluents in optimum conditions determined in these experiments. The results revealed the morphology of PACSER indicates that this can be applied for the treatment of effluents from tanneries and chromate mining areas. PACSER showed a good potential for Cr(VI) removal and its application is economical.



ACKNOWLEDGEMENT

The authors would like to acknowledge the department of biotechnology, Karunya University, Coimbatore for providing XRD & SEM facilities and CARISM Laboratory, Sasthra University, Thanjavur for providing Particle size analyzing & TEM facilities.

[1] REFERENCES

[2] Ramesh Chandra mishra, Santram Dwived and Sunil kumar mishra.Chromium removal by tannery effluent by phyto remediation, pollution research, 29(1); pp 69-71,(2010).

[3] Shanmugavalli.R, Madhavakrishnan.S, Kathirvelu.K, Rasappan.K,MohanRaj.R and Pattabhi.S, Adsorption studies on removal of chromium(VI) from aqueous solution using using silk cotton hull carbon, Journal of Industrial .Pollution Control, 23(1); pp 65-72,(2007).

[4] Alexander K.T.W, Corning D.R , Cory N.J, Dorohue V.J, Sykes R.L, Environmental and safety issues, clean technology and environmental auditing, J.soc, Leather Technol.Chem. vol.76(1); pp17-23, (1991).

[5] Torresday J.L.G, Tiemann K.J, Armendariz V,characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural by products of Avena monida (oat) biomass., J.Harzard Mater, 80(1-3); pp175-188.(2000).

[6] Nederlof,M.M.,Van Riemsdijk ,W.H. and Koopal, L.K.. Determination of adsorption affinity distributions - A General frame work for methods related to local isotherm approximations. J.Colloid Interface Sci.135; pp410-26.(1990).

[7] Cao,A.M, Monnel,J.D., Matranga,C., Wu,J.M., Coa,L.L & Cao,D. Nano size copper oxide in removal of Arsenic(III) from wastewater, J Phys Chem C,111; pp12624-28. (2007).

[8] Sara khatoon,Jameel anwar,Mukhtar-ul-Hassan,Hafza bushra Fatima,Dania Ahmad, Removal of chromium(VI) by using Eucalyptus bark,Journal of Scientific rearch,34(1); pp41-48,(2009).

[9] Parimalam,R.,Raj,V .and Sivakumar, P.,Adsorption isotherms, Kinetics, thermodynamics and desorption studies of reactive orange16 on activated carbon derived from ananascomosus (l)carbo,. RPN J.of Engg. And App.Sci., 6(11); pp19-26. (2011).

[10] Bansal M, Garg.U, Singh.D & Garg V.K, “removal of Cr(VI) from aqueous solution using pre-consumer processing agricultural waste, a case study of rice husk,” journal of hazardous materials, Vol.162, No.1, 2009; pp 312-320 .(2008).

[11] Suganthi N.,Srinivasan K., Phosphorilated tamarind nut carbon for the removal of cadmium ions from aqueous solutions, Int. Jrl. of Engg. And Mat.Sciences, vol.17; pp382-388,(2010,).