ENHANCED SURFACE CHARACTERIZATION AND INSIGHT ADSORPTION STUDIES OF CR(VI) ON PYROLYZED ADSORBENTS DERIVED FROM LIGNOCELLULOSIC PRECURSOR

Dr. T.SHANMUGASUNDARI
Department of Chemistry, Excel Engineering College, TN. India.

Email: shrichem16@gmail.com

ABSTRACT

A new process for the hexavalent chromium removal by unconventional adsorbents is described. The paper has a double purpose. The first part focused how to obtain few adsorbents using a different material Sapindus emarginata. The preparation of novel adsorbents from rind and nut of Sapindus emarginata is explained. In the second part removal of hexavalent chromium by the above absorbents are studied. Chemical analysis for the adsorbents is carried out and explained. The morphology of the prepared charcoals and activated carbons of Sapindus emarginata were characterized by SEM and XRD. The influence of the following parameters such as pH, agitation time, adsorbent dosage, concentration of adsorbate is taken into account for the batch experiments. The adsorption efficiency of the chromium removal from tannery effluent also studied. The result supported that prepared adsorbent can be used efficiently for the treatment of tannery wastewater containing chromium.

Keywords: Sapindus emarginata; Activated carbon; XRD; SEM; Cr (VI) ion.

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 in the manufacture of paints, dyes, paper, Explosives and ceramics [2]. In last 2-3 decades chromium toxicity in potable water has rapidly increased [3]. Leather industry provides the necessities such as leather shoes and garments ,while using the byproducts of the meat industry. However the leather making process in turn generates byproducts and wastes. It is known that only 20% of wet salted hides are converted into commercial leather while 25% becomes chromium containing leather waste and the remainder becomes non-tanned waste and is lost in waste water as fat, soluble protein and solid suspended pollutants [4]. Chromium is considered as one of the top sixteen pollutants because of its carcinogenic characteristics for humans [5].

Chromium exists in the environment in two oxidation states that is Cr (VI) and Cr(III). In these Cr (III) is a nutrient species used for control of glucose and lipid metabolism in membranes while Cr(VI) is highly carcinogenic and mutagenic due to its high oxidative character [6].Owing to these contradicting characteristics, chromium contamination is a hot topic in modern analytical chemistry [7]. This creates a number of environmental and health problems. It increases toxicity of soil and decreases the quantity and quality of agro products. The aim of this work is to study the hexavalent chromium absorption capacity by novel adsorbents such as SERC, SENC, ACSER & ACSEN from Sapindus emarginata rind and nut. The materials are made from agricultural waste and have several beneficial properties, including low cost, easily regenerated, easily modified surfaces, and tunable porous structures[8]. The equilibrium studies are systematically carried out in a batch work covering various parameters.

MATERIALS AND METHODS

Preparation of novel absorbents

Sapindus emarginata dry fruits were collected from the local market and washed thoroughly with distilled water. Then dried in sunlight until the moisture was partially evaporated and further dried in a hot air oven at 120°c for 48 hours. From the dried material the rind and nut were separated. They are grounded into fine powder in a ball mill. One part of the rind was pyrolysed at 400°c & the nut was pyrolysed at 550°c for three hours. After burning the yield charcoal were collected. Another part of these Nut & Rind were subjected to physiochemical treatment with 50% H_3PO_4 with vigorous stirring. Charred material were kept in oven at 160 ± 5°c for 24 hours and washed with double distilled water. Then the charcoal was soaked in 5% $NaHCO_3$ solution over a night after the material was steamed for 15 minutes and dried. The dried materials were sieved to get the particle size of 10-20 µm and were used in this study. Their nomenclature is given in Table 1.

Table.1.Nomenclature

SERC	Sapindus Emarginta Rind Carbon
SENC	Sapindus Emarginta Nut Carbon
ACSER	Activated Carbon of Sapindus Emarginta Rind
ACSEN	Activated Carbon of Sapindus Emarginta Nut

Characterization of adsorbent

The characterization of SERC, SENC, ACSER & ACSEN were carried out using chemical analysis and the results are presented in **Table 2**. XRD patterns of adsorbents were recorded on Shinabzu XRD-6000 Japan. The X-ray source was copper with a voltage of 40kV and a current of 30mA. The measurement was in the scanning range of 4-90 at a scanning speed of 10°/min and is given in **Fig.1**. The surface morphology of all the four adsorbents was visualized via scanning electron microscope. The corresponding SEM 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.

Table 2. Characteristics of novel adsorbents

S.NO	Characteristics	SERC	SENC	ACSER	ACSEN
1	pH (1% solution)	8.1	7.2	5.7	5.6
2	Moisture content (%)	1.75	1.63	3.16	3.04
3	Ash content (%)	8.3	5.5	2.8	2.6
4	Conductivity (ms/cm)	0.19	0.23	0.31	0.27
5	Solubility in water (%)	0.74	0.52	0.27	0.18
6	Solubility in acid (%)	4.48	2.92	1.20	0.98

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 HCl to prevent hydrolysis of chromium ions[9].

Batch Experiments

From the stock solution 10ml was taken and 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 3.0 g of adsorbent and allowed to agitate in 300 rpm speed 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 chromium (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.

The same experimental procedure was repeated for different adsorption dosage, different agitation time, different initial concentration of Chromium and different pH. pH of the solution is adjusted by adding 0.1 N HCl (or) 0.1 N NaOH solution as required. The values of the parameters studied are given in **Table 3.**

Table 3. Experimental conditions investigated

S.NO	Parameters	Values investigated for various adsorbents
1	Adsorbent dosage (gm)	0.5 to 4.0
2	Agitation time (Min)	30 to 180
3	Initial concentration of chromium (ppm)	50 to 300
4	pH	1 to 8

Treatment of tannery waste water by novel absorbent ACSER:

Two samples were collected from ABS tannery and MM tannery in Erode. Industrial effluents were analyzed in the laboratory. The physico chemical parameters are given in **Table 4**. These two samples were treated with ACSER prepared in this work at optimized conditions of pH, agitation time & dose determined by previous experiments.

Table 4. Physico chemical characteristics of tannery effluents

Sample	pH	DO	TDS	EC	Ni	Cr	Zn
Units	-	mg/L	mg/L	μS/Cm	mg/L	mg/L	mg/L
ABST	9.1	1.3	4803	8500	0.016	3.94	3.1
MMT	6.6	1.3	6524	7100	0.015	3.59	4.3

RESULTS AND DISCUSSION

The characteristics of all the four absorbents SERC, SENC, ACSER & ACSEN are given in Table 2. The pH on SENC is neutral where as SERC has slightly alkaline pH. This may be due to its Detergent nature. The ACSER and ACSEN have low pH which may be assigned by their acid treatment. The moisture content of ACSER and ACSEN are higher than other adsorbents that may be account of the surface oxygen groups which were introduced by physio chemical treatment on them. The ash content seems to be high because the adsorbents are derived from natural products. Water and acid solubility is higher in SERC and SENC due to soluble organic compounds in their structure. Phosphoric acid activated carbon prepared from lignocellulosic materials has found to form micro porosity[10]. Raganati et al. (2021) argued that industrial efficiency depends not only on the material's adsorption capacity, but also on the utilization of the adsorbent[11]. X-ray diffraction analysis of ACSER and ACSEN 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 inorganic substances in the activated carbon [12].

Effect of agitation time

In order to estimate the adsorption capacity of adsorbent accurately, it is very much important to allow significant time required for the experimental solution to attain equilibrium. In this stage all the parameters, including temperature (30°c), absorbent dosage (3g/100 ml), pH(3),

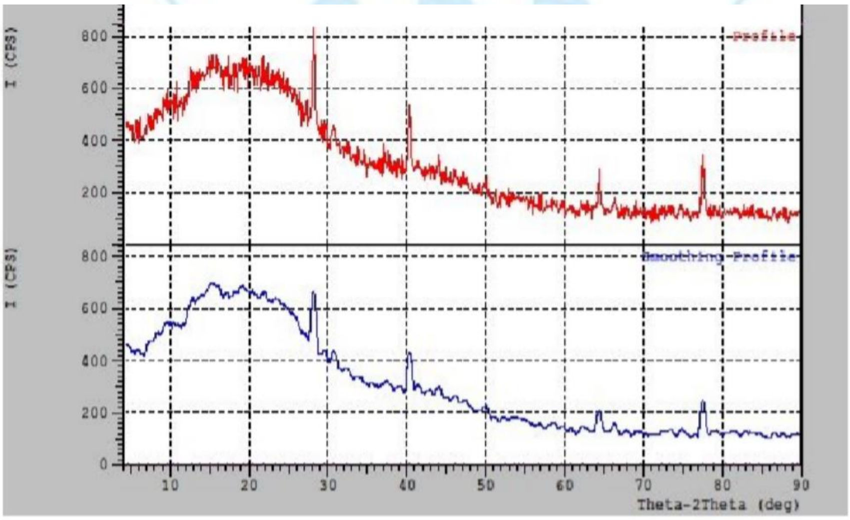

Fig 1: XRD of ACSER

Initial chromium concentrations (100 ppm) were kept constant. The effect of contact time on chromium adsorption efficiency showed in **Fig.2**. Initially the adsorption is fast. At 90 minutes SERC & at 120 minutes SENC reach the 50% of adsorption. But the activated carbons have faster rates. At 120 minutes ACSER attained

94% of adsorption. The equilibrium attained at 180 minutes.

Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface change of the adsorbent and the degree of ionization and speciation of the adsorbate[13].The results obtained are shown in Fig. 3 which shows the effect of pH on the absorption of Cr(VI) ions from the aqueous solution on to the adsorbents. SERC, SENC, ACSER &ACSEN in terms of metal ion removeal percentage. Adsorption of Cr(VI) was not significant at pH values more than 5 for SERC and SENC. It is significant upto 7 for ACSER and ACSEN shows the surface charges or positive for them.

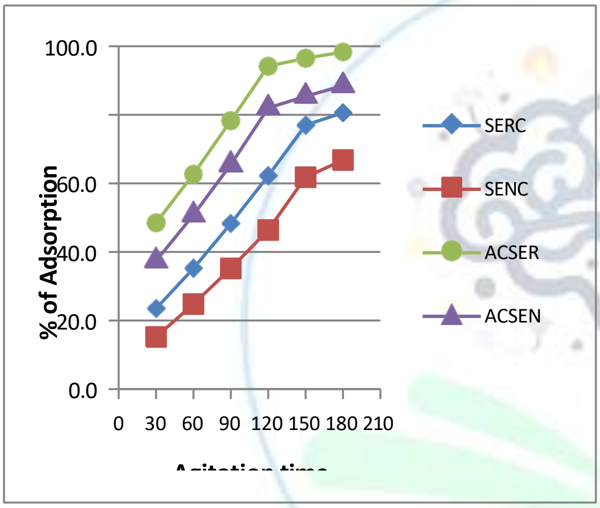

Fig: 2. Effect of agitation time

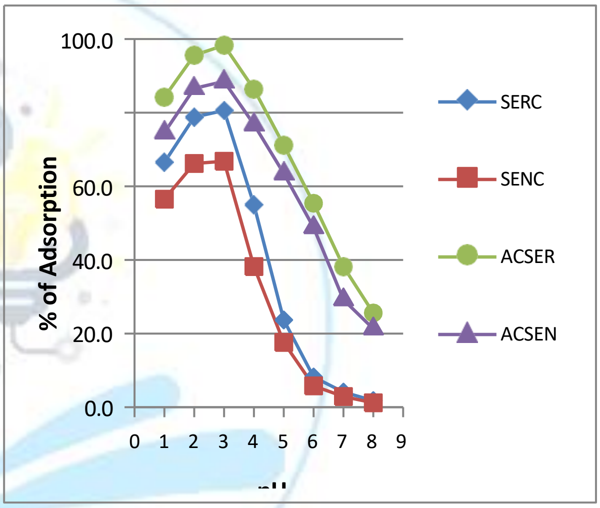

Fig: 3. Effect of pH

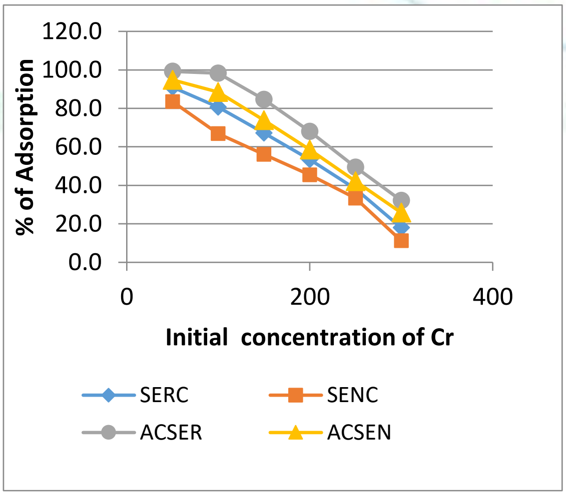

Fig: 4. Effect of initial concentration of chromium

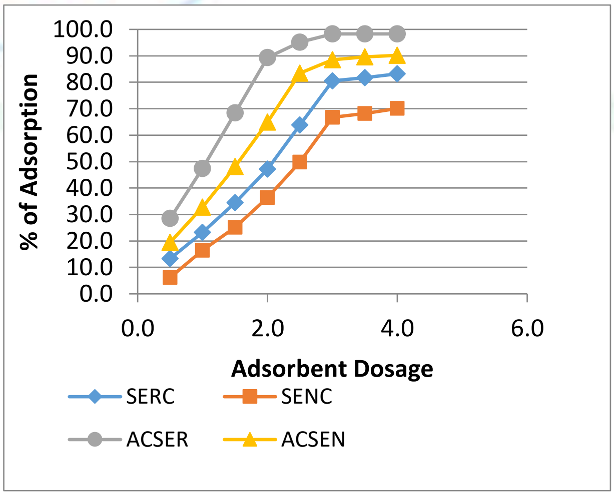

Fig: 5. Effect of carbon dose

Effect of initial concentration of chromium

Initial concentration is one of the effective factors on adsorption efficiency. **Fig. 4** shows the removal of Cr(VI) with respect to different initial concentrations. As the initial concentration of chromium increased, the percentage removal of chromium was decreased for the same agitation time of 180 minutes. The percentage removal was decreased from 99.2 to 32.1 for ACSER and it was from 83.5 to 11.2 for SENC.

Effect of carbon dose

At this stage the effect of the adsorption with various adsorbents were done under the conditions of pH 3, initial concentration 100 ppm and the time of agitation is 180 minutes. The results obtained for the effect of carbon dosage are shown in **Fig. 5**. The percentage removal of chromium gradually increases for SERC & SENC due to increase of carbon dose. But it increases rapidly for the ACSER and attain 95.2% at 2.5 g of adsorbent and it attain 90.2 % at 4.0 g of ACSEN. This clearly shows ACSER is more effective adsorbent for Cr(VI) than other three adsorbents.

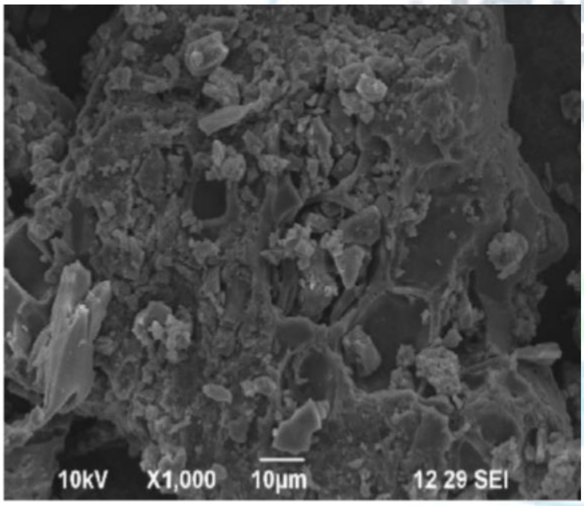

Fig: 6(a)

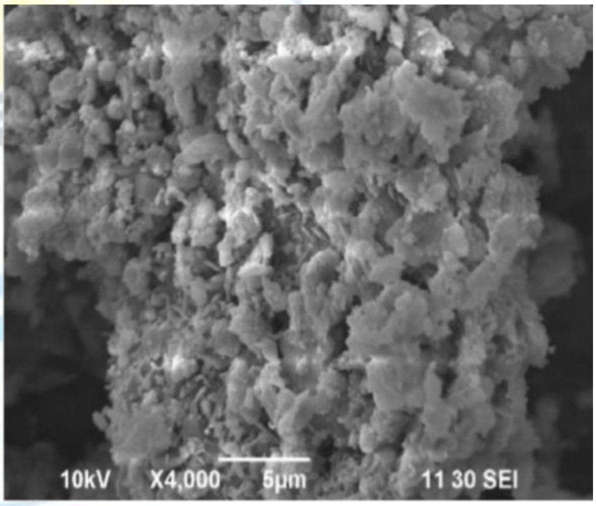

Fig: 6(b)

SEM Analysis of ACSER

Examination of SEM micrographs of the SERC, SENC, ACSER & ACSEN found to be rough areas 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 ACSER. It is observed that the morphology of unloaded ACSER in **Fig. 6(a)** is quite micro porous, heterogeneous and rough. There are voids elongated deeply inside the surface of ACSER. The phosphoric acid activation process in ACSER leads to corrode the surface of carbonaceous material and introduce micro, macro and meso pores. The loaded ACSER 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.

Treatment of tannery effluent by ACSER at optimized condition

The samples given in **Table 4** were treated by ACSER at optimized conditions pH = 3.0, dose =3g/l, agitation time = 180 minutes, determined by experiments. The removal efficiency was found 90.7% and 92.5% 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 ACSER.

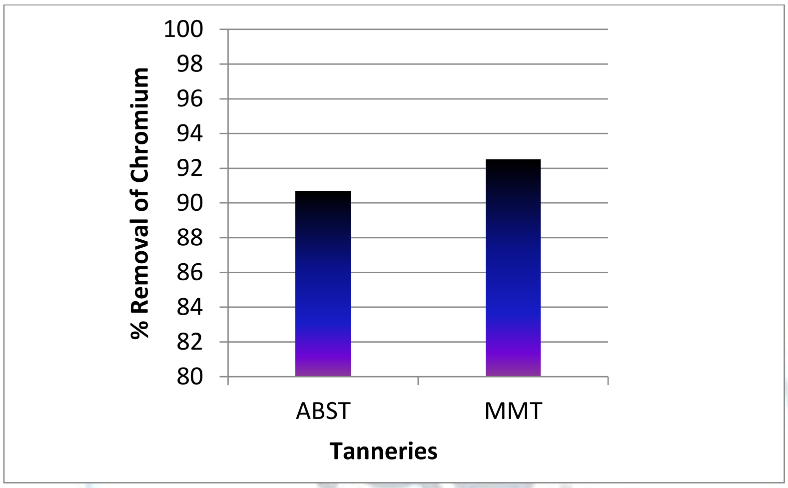

Fig: 7

CONCLUSION

Adsorbents such as SERC, SENC, ACSER and ACSEN have been prepared from Sapindus Emarginata and characterized. Effects of adsorption parameters were studied utilizing the above adsorbents. The optimum pH for the removal of Cr(VI) was found to be 3 for all the four absorbents. The uptake was maximum at adsorbent dosage of 3g/l for ACSER and 4g/l for other adsorbents. With increase in agitation time there was good effect in removal of Cr(VI) ions. Activated Carbon of Sapindus Emerginata Rind was found to be more efficient when compared with other three adsorbents and is successfully employed for the treatment of tannery effluents in optimum conditions already determined in these experiments. The results revealed the morphology of ACSER indicates that this can be applied for the treatment of effluents from tanneries and chromate mining areas. ACSER showed a good potential for Cr(VI) removal and its application is economical and ecofriendly.

REFERENCES

[1] Ramesh Chandra mishra,Santram Dwived and Sunil kumar mishra.Chromium removal by tannery effluent by phyto remediation, pollution research,2010 29(1); 69-71Andersen R A, SCi. Total Environ., **86**(1989)75-81.

[2] 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, J.of Ind.Pol.Cont 23(1),2007, pp 65-72.

[3] Shiny K.J., Remani.K.N., Jalaya.T.K., and Sasidharan,V.K., 2004. Removal of Chromium by Sasidharan, V.K.2004. Removal of chromium by two pteridophytes. J.of Environ.Sci.and Engg. Vol 463:249-251.

[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(No.1), 17-23, (1991).

[5] Torresday J.L.G, Tiemann K.J, Armendariz V.,(2000) 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),175-188.

[6] Maria C.G, Toxic and mutagenic effects of Cr(VI).A review, Polyhedran, 1996, 15(21), 3667-3981.

[7] Shajahan siraj,Monarul islam,Prakash Chandra das,Removal of chromium from tannery effluent using chitosan charcoal composite,Journal of chemical society,vol 25(1),2012,pp 53-61.

[8] Kaya GG (2023) Ultrasonication assisted urea treated biochar: an eco-friendly adsorbent for CO2 capture. ChemistrySelect 8:e202301739. https://doi.org/10.1002/slct.202301739

[9] 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),2009,pp41-48.

[10] Suganthi N.,Srinivasan K., Phosphorilated tamarind nut carbon for the removal of cadmium ions from aqueous solutions,Ind.Jrl. of Engg. And Mat.Sciences, 2010,Vol.17;382-388

[11] Raganati F, Miccio F, Ammendola P (2021) Adsorption of carbon dioxide for post-combustion capture: a review. Energy Fuels 35(16):12845–12868. https://doi.org/10.1021/acs.energyfuels.1c01618

[12] Parimalam,R.,Raj,V. and Sivakumar,P.,Adsorption isotherms,Kinetics,thermodynamics and desorption studies of reactive orange 16 on activated carbon derived from ananascomosus(l)carbo,.ARPN J.of Engg. And App.Sci.2011, 6(11):19-26.

[13] Cho.H, Oh.D, Kim. K. A study on removal characteristics of heavy metals from aqueous solutions by fly ash. J.Hazard Mater 2005 ; 127(1-3) : 187-95.

[14] 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,pp312-320 doi; 10-1016/j.jhazmat.2008.05.037.

[15] Malkoc,E,Nuhoglu y. and.Abali Y,” Cr(VI) Adsorption by waste Acorn of Quercus ithaburensis in fixed beds ; Prediction of Brakthrough Curves,”Chemical Engineering Journal, Vol-119,No.1,2006 .01.019

[16] Miretokya P, and Ciselli A.F,”Cr(VI) and Cr(III) Removal from aqueous solutions by Raw & Modified Lignocellulosic Materials : A Review,” Journal of Hazardous materials, Vol,180,2010, pp 405- 412.