

UTILIZATION OF AGRICULTURAL WASTE ECONOMICALLY AS AN ADSORBENT FOR REMOVAL OF CHROMIUM POLLUTANT FROM AQUEOUS SOLUTION AND INDUSTRIAL WASTEWATER

P. Thamilarasu*¹, M. Mohan¹, V. Dharmalingam¹, R. Sharmila²
and K. Karunakaran³

¹Department of Chemistry, Paavai Engineering College, Namakkal, India.

²Department of Chemistry, Vivekanandha College of Engineering, Namakkal, India.

³Department of Chemistry, Sona College of Technology, Salem, India.

*E-mail: thamilarasu2011@gmail.com

ABSTRACT

This paper presents the feasibility of the removal of hexavalent chromium ions from aqueous solution and industrial wastewater by using activated carbon prepared from *Cajanus Cajan(L) Milsp.* It was carbonized and activated by treating it with concentrated sulfuric acid followed by heating for 5 h at 500°C. Batch adsorption experiments were carried out as a function of pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature. The experimental data fitted well to the Freundlich isotherm. Thermodynamic parameters such as ΔH° , ΔS° , and ΔG° were calculated, which indicated that the adsorption was spontaneous and endothermic in nature. The adsorbents used in this study were characterized by FT-IR and SEM before and after the adsorption of metal ions. The results indicate that *Cajanus Cajan(L) Milsp* seed shell can be employed as a low cost alternative and commercial adsorbents in the removal of chromium(VI) from aqueous solution and wastewater.

Keywords: Agricultural waste, Adsorption, Kinetics, Chromium and *Cajanus Cajan(L) Milsp.*

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INTRODUCTION

Rapid increase in population and industrial growth are responsible for the inclusion of heavy metals in the environment. These heavy metals and their compounds are potential pollutants that could be particularly problematic due to their stability, mobility and toxicity. The pollution due to heavy metals has received wide spread attention in recent years¹, due to the toxicological problems in the ecosystem, agriculture and human health, which has led to the development of alternative technologies for the effective removal of these pollutants from aquatic ecosystems. Low cost and waste biomaterials used as adsorbents of dissolved metal ions have been shown to provide cost effective solutions to this global problem². In this work, it has been shown that an adsorbent (CCC: *Cajanus Cajan(L) Milsp* seed shell activated carbon) can be used in an effective, economically and eco-friendly way for the removal of Cr(VI) ions from wastewaters.

Chromium is a highly toxic pollutant generated from various industries such as leather, electroplating, dye, paint and paper. Chromium exists in the aquatic environment mainly in two states; trivalent chromium and hexavalent chromium. Hexavalent chromium is primarily present in the form of chromate and dichromate ions³. The USEPA has set the maximum contaminant level (MCL) for chromium in drinking water at 0.1 mg L⁻¹. These standards are based on the total concentration of the trivalent and hexavalent forms of the dissolved chromium. Chromium has the potential to cause the following health effects from long-term exposures at levels above the MCL; damage to liver, kidney, circulatory and nerve tissues and dermatitis. Furthermore, chromium has serious effects on the health of human⁴. Some of the conventional methods that are used to remove the dissolved heavy metal ions are: chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment and evaporative

recovery. However, these highly technological processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipments and monitoring systems, high reagent or energy requirements or generation of toxic sludge and or other waste products that require addressing of disposal problems⁵.

Adsorption on activated carbon has been found to be an effective process for Cr(VI) removal, although this method is too expensive. Large quantities of natural materials are available and certain waste products from industrial or agricultural operations may have the potential to be used as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Most of the low cost sorbents have the limitation of low sorption capacity and thereby for the same degree of treatment they possess disposal problems. Therefore, there is a need to explore low cost biosorbents having high contaminant sorption capacity⁶. Consequently, numerous low cost alternatives have been studied including beech sawdust⁷, eucalyptus bark⁸, walnut sawdust⁹, seaweeds¹⁰, coir pitch¹¹, peanut husks carbon¹², Zeolite tuff¹³, activated carbon fabric cloth¹⁴, bagasse fly ash¹⁵, activated slag¹⁶ etc. In spite of all these, new economical, easily available and highly effective adsorbents are still needed. Generally, biosorption processes can reduce the capital costs by 20%, operational costs by 36% and the total treatment costs by 28%, compared with other conventional methods¹⁷.

A detailed literature survey shows that *Cajanus cajan* (L) Millsp has not been tried for use as adsorbent for the removal of chromium ions. It is an important pulse crop in India known as Pigeonpea or Arhar or Tur. It is mainly cultivated and consumed in developing nations. This crop is widely grown in India making it the largest producer and consumer in the world. It accounted for about 20 percent of the total pulse production of the country during the year 2000–2001. It can be used as a low-cost material adsorbent for the removal of Cr(VI) in wastewater. The objectives of the present study is to remove the Cr(VI) from aqueous solution by batch mode studies.

EXPERIMENTAL

Preparation of adsorbent

Activated carbons were prepared from *Cajanus cajan* (L) Millsp seed shell (CCC). The raw material was procured from local vendors. The material was washed in hot distilled water to remove earthy matter, cut into small pieces and dried. It was prepared from the above material, impregnated with concentrated sulfuric acid. For impregnation, a 1:1 of acid volume to weight ratio was employed. After that, the charred material was washed several times in water and distilled water until the pH of the washings becomes neutral. The material was then dried and carbonized at 500°C in a muffle furnace. Finally, the activated material was ground and sieved using 180–300 µm standard sieves. The same adsorbent was modified by the treatment of polymerization of pyrrole and to obtain the another adsorbent. Commercially available analytical grade other reagents (Merck, SRL, India and SD-fine, India) were used for this study.

Batch mode studies

50 mL of a known concentration of Cr(VI) solution was taken in a 100 mL screw-cap conical flask with 50 mg of adsorbent. The mixture was agitated at 120 rpm in a thermostatic shaker water bath at 30°C for a 60 min of contact time and the solution was centrifuged. The remaining concentration of Cr(VI) was measured using a UV-Visible spectrophotometer (Systronics 169) with 1,5-diphenyl carbazide in acid medium. The amount of Cr(VI) adsorbed in mg/g at time (t) was computed by the following equation¹⁸.

$$q_t = (C_0 - C_t) \frac{V}{M} \quad (1)$$

Where, C_0 = Initial concentration of Cr(VI), C_t = Concentration at a given time t ,
 V = volume of the Cr(VI) solution in L and M = weight of activated carbon in g.

The percentage of removal Cr(VI) ions in solution was calculated using the following equation,

$$R(\%) = \frac{C_0 - C_i}{C_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Adsorbent Characterization

All the parameters were analyzed using standard testing methods¹⁸. Activated carbons are widely used as adsorbent due to their high adsorption capacity, high surface area, micro porous structure and high degree of surface adsorption. The chemical nature and pore structure usually determine the sorption activity. Some important physico-chemical characteristics of CCC and Ppy/CCC are given in Table-1. The lower ash content values are attributed to lower inorganic content and higher fixed carbon. The high surface area is considered to be most suitable for adsorption of adsorbates in the aqueous solution. The lower bulk density value indicates the highly branched and porous carbon with more void space. Acid soluble matter content was found higher in the carbon because of the incorporated carbonate groups in the pores. Sodium and potassium content may be due to the presence of mineral sodium and potassium in the CCC seed shell¹⁹.

Table-1: Characteristics of the CCC

S.No.	Parameter	CCC	Ppy/CCC
1	pH	7.48	8.06
2	pH _{zpc}	5.24	5.78
3	Moisture content (%)	2.80	2.60
4	Bulk density (g/mL)	0.48	0.36
5	Solubility in water (%)	0.81	0.69
6	Solubility in 0.25 M HCl (%)	4.91	2.86
7	Porosity (%)	59.10	71.43
8	Specific gravity	1.07	1.26
9	Volatile matter (%)	8.15	5.26
10	Ash content (%)	3.86	3.65
11	Fixed carbon (%)	85.19	88.49
12	Sodium (mg/L)	67.00	62.00
13	Potassium (mg/L)	3.30	3.10
14	Phenol adsorption capacity (%)	36.20	39.34
15	Conductivity (mS/cm)	1.85	1.89
16	Surface area (m ² /g)	532	560
17	Iodine number (m ² /g)	453	440

Effect of adsorbent dosage, pH and agitation time

These experiments are done by using from 50mg to 300mg of adsorbents, 50ml of 10ppm of Cr(VI) solution and agitation of various time intervals. The results indicate that the optimum dose is fixed as 50mg due the quantity of Cr(VI) uptake was more, the optimum pH is fixed as 2 due to maximum removal of Cr(VI)²⁰. All the experiments were conducted at optimum conduct time of 60 min²¹.

Effect of Initial concentration and Temperature

In the present investigation, 50 mg of adsorbents (CCC) were treated with 50 mL of Cr(VI) solutions of different concentration. Sorption experiments were carried out at the most suitable pH value of 2 for each sorbent. As seen from Table-2, at 30°C, as the initial Cr(VI) ion concentration was increased from 2 to 10 mg/L, Cr(VI) the adsorption removal decreased from 79.4 to 77.5% and the uptake capacity of CCC increased from 1.6 to 7.9 mg/g. The increase in the uptake capacity of CCC with the increase in Cr(VI) ions concentration is due to the higher availability of Cr(VI) ions in the solution for the adsorption. Moreover, higher initial Cr(VI) concentration increased the driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collisions between Cr(VI) ions and the adsorbent. This also results in higher metal uptake²². The rise in adsorption capacity with temperature is because of the rise in kinetic energy of the sorbent particles. Thus the collision frequency between adsorbent and adsorbate increases, resulting in the enhanced sorption onto the surface of the adsorbent. Secondly, at higher temperatures due to the rupture of bonds of the functional groups on adsorbent surface, there may be an increase in the number of active sorption sites, leading to enhanced sorption with rise in temperature.

Table-2:Equilibrium parameters for the removal of Cr(VI) by CCC

Initial conc. of Cr(VI) (C_0), mg/L	Equilibrium conc. of Cr(VI) (C_e), mg/L			Quantity of Cr(VI) adsorbed at equilibrium (q_e), mg/g			Cr(VI) removal (%) by CCC		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
2	0.405	0.367	0.335	1.595	1.634	1.665	79.74	81.68	83.27
4	0.825	0.744	0.673	3.175	3.256	3.327	79.38	81.40	83.17
6	1.291	1.185	1.083	4.709	4.815	4.918	78.49	80.25	81.96
8	1.799	1.633	1.467	6.201	6.367	6.533	77.52	79.59	81.66
10	2.250	2.042	1.844	7.750	7.958	8.156	77.50	79.58	81.56

Adsorption Isotherms

The adsorption equilibrium data presented in Table-2 are described by the Langmuir, Freundlich and Tempkin isotherm models at three different temperatures are shown in figure-1. In Langmuir isotherm, the values of monolayer adsorption capacity (Q_0) increases with temperature, suggesting that adsorption are favored by higher temperature. This may be attributed to the fact that Cr(VI) ions diffuse into adsorbate particles at a faster rate with rise of adsorption system temperature. The energy of adsorption (b_L) values suggests the affinities of binding sites with the metal ions are favourable. R_L values shown the range between 0 to 1 for the adsorption of Cr(VI) at different concentrations which indicated the favorable adsorption of Cr(VI) by CCC. These results indicated the efficiency of the adsorbents are good under investigation.

In Freundlich isotherm, the values of adsorption capacity (k_f) increases with increase in temperature of the solution from 30 to 50°C. It is shown that the adsorption is favored at high temperature. Further the value of intensity of adsorption (n) was greater than unity signifies that the forces between the Cr(VI) and adsorbents surface are attractive which leads to the favourable adsorption and adsorption process is physical in nature. The equilibrium binding constant values and heat of adsorption values are shown to the minimum binding energy and minimum heat of adsorption during the adsorption of Cr(VI) on CCC²³. The goodness of fit of the experimental data is measured by the determination of correlation coefficients. The correlation coefficients (r^2) of Langmuir, Freundlich and Tempkin isotherm models and their constants are presented in Table 3. Comparing these three adsorption isotherm models, the linear form of Freundlich isotherm has high correlation coefficient values at all temperatures. Therefore, the Freundlich model showed

better fit followed by Langmuir model followed by Tempkin model and also it indicates that the metal adsorption by the adsorbents was governed by physical adsorption.

Table-3: Results of isotherm models for the adsorption of Cr(VI) on CCC

Temp.(°C)	Langmuir Isotherm			Freundlich Isotherm			Tempkin Isotherm		
	Correlation coefficient	Constants		Correlation coefficient	Constants		Correlation coefficient	Constants	
	r^2	Q_0 (mg/g)	b_L (L/mg)	r^2	k_f	n	r^2	b_T (kJ mol ⁻¹)	a_T (L/mg)
30	0.973	45.46	0.089	0.999	3.694	1.097	0.958	0.578	3.075
40	0.962	45.87	0.101	0.999	4.137	1.094	0.969	0.619	3.389
50	0.945	52.36	0.098	0.996	4.630	1.086	0.971	0.705	4.089

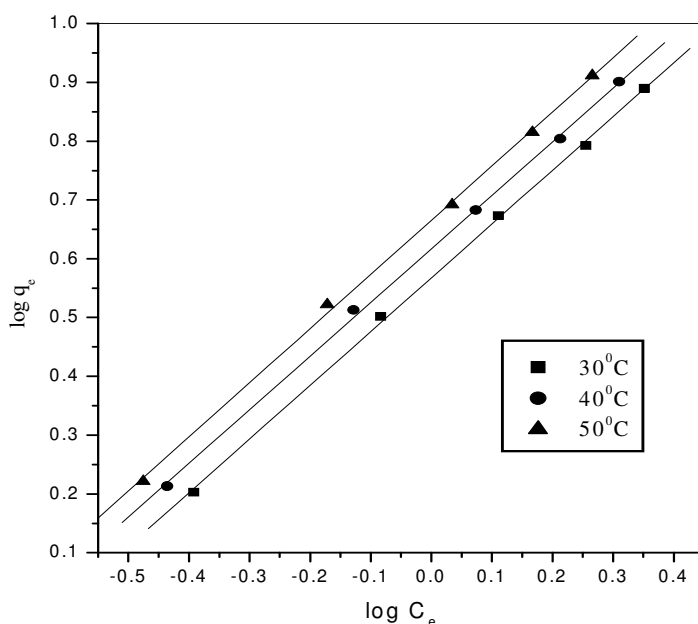


Fig.-1: Freundlich isotherm for the adsorption of Cr(VI) on CCC

Thermodynamic Parameters

The standard free energy change, enthalpy and entropy changes along with equilibrium constants are calculated and given in Table 4. From the results, the endothermic nature of adsorption is indicated by an increase in equilibrium constant (K_0) with rise in temperature. The results indicated that the standard free energy values increase with increasing initial Cr(VI) concentration. The standard free energy values are negative and range from -4.3 to -3.1 kJ mol⁻¹, which mean that the adsorption process is spontaneous in nature. The amount adsorbed at equilibrium must increase with increasing temperature, because standard free energy decreases with increasing temperature of the solution.

In the present study the enthalpy change observed in the range from 9 to 11 kJ mol⁻¹ for CCC. These values indicated that there might be physical interaction between the adsorbent and the adsorbate. Positive values of standard enthalpy suggested that the adsorption process is endothermic, so an increase of temperature encourages Cr(VI) adsorption. The standard entropy values for the adsorption process are positive which was the range from 41 to 45 J K⁻¹ mol⁻¹ for CCC. This observation suggests a high degree of disorderness at the solid-solution interface during the adsorption of the Cr(VI) on active carbons.

Further the positive values of entropy reflect the affinity of the adsorbent material for adsorption of Cr(VI) and also suggest some structural changes in the adsorbate and adsorbent²³.

Table-4: Thermodynamic parameters for the adsorption of Cr(VI) on CCC

C_o , mg/L	K_o			ΔG° (kJ mol ⁻¹)			ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)
	30°C	40°C	50°C	30°C	40°C	50°C		
2	3.935	4.457	4.976	-3.451	-3.889	-4.309	9.752	43.605
4	3.848	4.377	4.940	-3.395	-3.842	-4.290	10.376	45.402
6	3.649	4.064	4.543	-3.261	-3.649	-4.064	9.104	40.813
8	3.448	3.900	4.453	-3.118	-3.541	-4.011	10.634	45.369
10	3.444	3.897	4.422	-3.115	-3.540	-3.992	10.384	44.560

Kinetics of Adsorption Studies

A good agreement of adsorption capacities between the calculated and experimental results were found in pseudo-second order model while comparing to pseudo-first order kinetic model and the values shown in Table 5 and also figure 2. The experimental data obtained for the adsorption of Cr(VI) with high correlation co-efficient ($r^2 = 0.999$) and very less percentage relative deviation in pseudo-second order model. From the above results, the pseudo-second order model was the best fit for the adsorption of Cr(VI) than the pseudo-first order model. Many studies reported that the first order equation of Lagergren does not fit well to the adsorption process. The first order kinetic model has been used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the pseudo-second order kinetic model assumes that the rate-limiting step may be physical adsorption. In many cases, the second order equation correlates well to the adsorption studies²⁴.

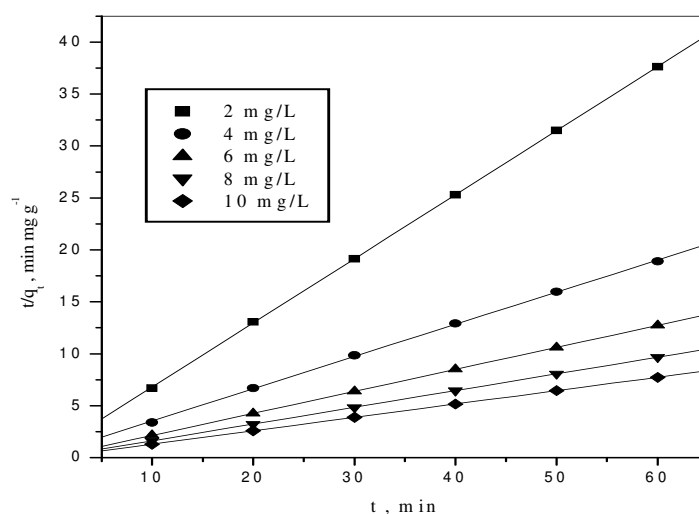


Fig.-2: Pseudo-second order kinetic model for the adsorption of Cr(VI) on CCC

Fourier Transform Infrared Spectroscopic Studies

The CCC spectrums are shown in figure 3a and 3b at 3914-3383 cm⁻¹ indicated the presence of -OH groups of activated carbons. The aromatic -CH stretching observed at wave number from 3100-3000 cm⁻¹. A peak at 2857-2686 cm⁻¹ indicated the presence of -CH and -CO stretching group of aldehydes. The region from 1624-1585 cm⁻¹ indicated the N-H bending of primary amines and -C-C stretching of aromatic groups.

The region from 1370-1350 cm^{-1} indicated $-\text{CH}$ stretching of alkanes group. The regions from 1250-1020 cm^{-1} and 910-665 cm^{-1} indicated the presence of $-\text{CN}$ stretching and $-\text{NH}$ stretching of aliphatic amines. The region from 850-550 cm^{-1} indicated the presence of $-\text{C}-\text{Cl}$ stretching of alkyl halides. After the adsorption of Cr(VI) on activated carbons, there was a small shift in wave number and some of the wave number regions were not observed. This observation indicated the participation of adsorption of Cr(VI) on CCC, and Ppy/CCC activated carbons. The identification of functional groups present in the adsorbents was found with results of Viboon Sricharoenchaikul et al (2008) studies²⁵.

Table-5: Pseudo-first and second order constants for the adsorption of Cr(VI) on CCC

C_o (mg/L)	$q_e(\text{exp})$ (mg/g)	pseudo-first order kinetic model				pseudo-second order kinetic model			
		$q_e(\text{cal})$ (mg/g)	k_1 (min^{-1})	r^2	P	$q_e(\text{exp})$ (mg/g)	k_2 (g mg^{-1} min^{-1})	r^2	P
10	1.595	0.228	0.069	0.998	85.73	1.621	0.608	0.999	1.62
20	3.175	0.371	0.039	0.978	88.31	3.225	0.221	0.998	1.57
30	4.709	0.394	0.144	0.936	91.64	4.721	1.500	0.999	0.26
40	6.201	0.159	0.074	0.970	97.43	6.219	1.002	0.999	0.28
50	7.750	0.214	0.081	0.982	97.25	7.770	0.846	0.999	0.26

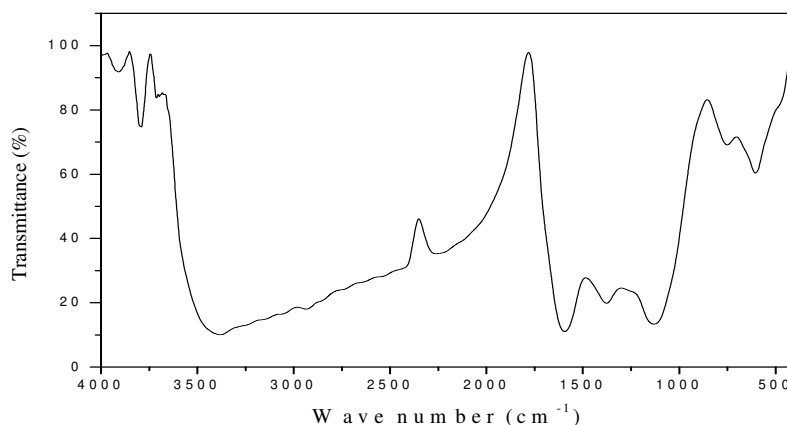


Fig.-3a: FTIR spectrum for CCC before adsorption of Cr(VI)

Scanning Electron Microscope Studies

The SEM photographs of CCC and Ppy/CCC before and after adsorption are studied and shown in the Figures-4a and 4b. It is clearly stated that the presence of porous structure of the active carbon before adsorption. They have holes and cave type openings on the surface of the active carbon which could definitely increased the surface area available for adsorption. After adsorption of Cr(VI), SEM photographs are clearly seen that the surface of active carbons are the caves, pores and surfaces of adsorbents was covered by adsorbate. It is evident that the adsorbent structure is changed upon the adsorption of Cr(VI) ions.

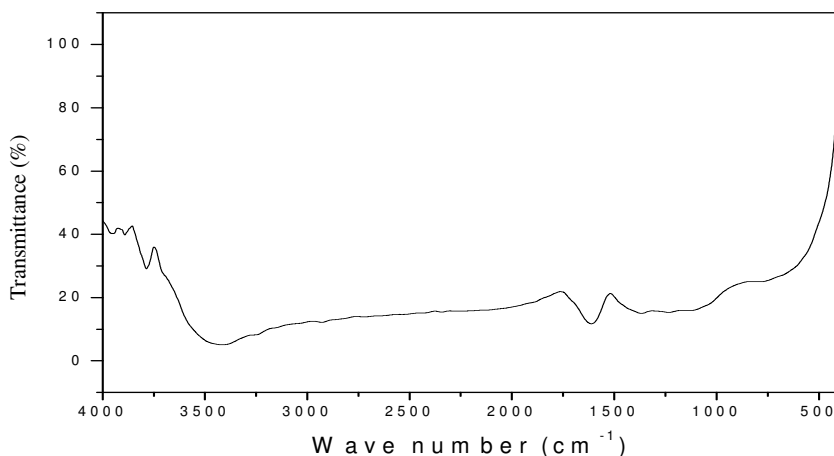


Fig.-3b: FTIR spectrum for CCC after adsorption of Cr(VI)

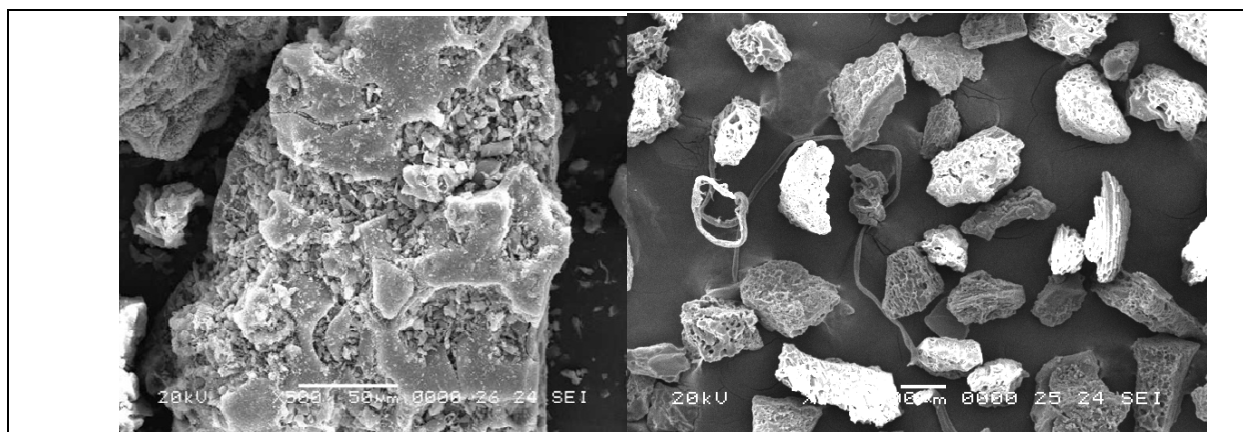


Fig.-4a: SEM photograph before adsorption Fig.-4b: SEM photograph after adsorption

Industrial Waste Water Treatment

The electroplating wastewater was acidic, highly concentrated with iron, nickel, chromium, sulphate, chloride and total solids. The wastewater containing large amount of chromium was diluted to the analyzing range of the aqueous solution. To study the effect of adsorbent dosage on Cr(VI) removal, 10 mg/L of solution was prepared by diluting the electroplating wastewater. The effect of adsorbent dosage of Cr(VI) removal from the waste water with pH 2 and the contact time for 60 min. For the Cr(VI) aqueous solution, the amount of adsorbent required was 300 mg/50 mL for 90 % removal of 10 mg/L of Cr(VI). It was found that percentage of Cr(VI) removal from electroplating wastewater increases with increase in adsorbent dosage and reached 90 % with an adsorbent dosage of 700 mg/50 mL for CCC and 650 mg/50 mL for py/CCC. It is higher than that of the removal of Cr(VI) from aqueous solution. This may be due to the presence of other competitive ions present in the electroplating wastewater.

Cost Analysis

The preparation of 1 kg of CCC, it requires 3 kg of precursor. The amount of H₂SO₄ required to the process 3 kg of precursor is one litre. The rate of commercial H₂SO₄ is Rs. 185/L. Therefore, the expense for the preparation of 1 kg of adsorbent is Rs. 185. The rate of commercial charcoal is Rs. 250/kg. For treating 100 M³ of industrial wastewater, the 50kg optimum dose of CCC is Rs. 9,250 in Indian rupees and 50kg commercial charcoal is Rs. 12,500 in Indian rupees.

CONCLUSION

Cajanus Cajan(L) Milsp seed shell activated carbon(CCC) that was prepared from an abundant, environmentally friendly and economically cheap agricultural waste, could be used as a potential adsorbent for the removal of Cr(VI) from aqueous solution containing heavy metals and industrial wastewater. The Freundlich adsorption isotherm model describes the adsorption behavior with good correlation coefficient. The adsorption of Cr(VI) depended on the pH of the solution. Based on the results, the optimum contact time is 60 min and adsorbent dosage is 50 mg. The metal ion adsorption obeyed the pseudo-second order kinetic model. The removal of Cr(VI) simultaneously increased with increase in the temperature from 30°C to 50°C.

REFERENCES

1. N. Bishnoi, M. Bajaj, N. Sharma and A. Gupta, *Bioresour. Technol.*, **91**, 305(2004).
2. D. Park, S.Y. Yun and J.M.Park, *Chemosphere*, **60**, 1356(2005).
3. L. Khezami and R. Capart, *J. Hazard. Mater.*, **123**, 223(2005).
4. USEPA, National Primary Drinking Water Regulations, Ground Water and Drinking water, Consumer factsheeton: Chromium. (1995).
5. Z. Aksu, F. Gonen, and Z. Demircan, *Process Biochem.*, **38**, 175(2002).
6. G.S Agarwal, H.K. Bhuptawat, and S. Chaudhari, *Bioresour. Technol.*, **97**,949 (2006)
7. F.N. Acar, and E. Malkoc,, *Bioresour.Technol.*, **94**, 13(2004).
8. V.Sarin, and K.K. Pant, *Bioresour. Technol.*, **97**, 15(2002)
9. B. Yasemin, T. Zeki, *Fresen. Environ.Bull.*, **12**, 376(2003).
10. K. Vijayaraghavan, J. Jegan, K. Palanivelu and M. Velan, *Separ. Purif. Technol.*, **44**,53 (2005).
11. K. Kadirvelu, K. Thamaraiselvi and C. Namasivayam, *Separ. Purif. Technol.*,**24**, 497 (2001).
12. S. Ricordel, S. Taha, I. Cisse, I. and G. Dorange, *Separ. Purif.Technol.*, **24**, 389(2001).
13. A. Al-Haj, and R. El-Bishtawi, *J. Chem. Tech. Biotechnol.*, **69**, 27(1999).
14. D. Mohan, K.P Singh ,and V.K. Singh, *Ind. Eng. Chem. Res. (ACS)*, **44**,1027(2005).
15. V.K. Gupta, K.T. Park, S. Sharma and D. Mohan, *Environmentalist*, **19**, 129(1999).
16. S.K. Srivastava, V.K. Gupta and D. Mohan, *J. Environ. Eng. (ACSE)*, **123**, 461(1997).
17. M. X. Loukidou, A.I. Zouboulis, T.D. Karapantsios and K.A. Matis, *Colloid Surfaces A*, **242**, 93(2004).
18. F.W. Gilcreas, M.J. Tarars and R.S. Ingols, Standard methods for the examination of water and wastewater 12th edition, American Public Health Association(APHA) Inc, New York, 213–220, (1965).
19. S. Karthikeyan, P. Sivakumar and P.N. Palanisamy, *E-J. of Chemistry*, **5**,409 (2008).
20. D. Mohan, K.P. Singh and V.K.Singh, *J. Hazard. Mater.*, **135**, 280(2006).
21. L.D. Benefield, J.F. Judkins and B.L. Weand, Process chemistry for water and wastewater Treatment, EnglewoodCiffs, NJ, 433–435, (1982).
22. N. Tewari, P. Vasudevan and B.K. Guha, *Biochem. Eng. J.*, **23**, 185(2005).
23. Y. C Sharma, V. Srivastava, C. H. Weng, and S. N. Upadhyay, *Can. J. Chem. Eng.*, **87**, 921(2009).
24. Y. Sag, and Y. Aktay, *Biochem. Eng. J.*, **12**, 143(2002).
25. Viboon Sricharoenchaikul, Chiravoot Pechyen, Duangdao Aht-ong and D. Atong, *J. Am. Chem. Soc.*, **22(1)**,31(2008).

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