Sorption kinetics and equilibrium studies on the removal of toxic Cr(VI) ions employing modified Indian almond nut shells

N.Muthulakshmi Andal*[1]& G.Gohulavani[2&3]
1.Assistant Professor, Dept. of Chemistry, PSGR Krishnammal College for Women, Coimbatore, Tamilnadu, India
2. Research Scholar, Dept. of Chemistry, PSGR Krishnammal College for Women, Coimbatore, Tamilnadu, India
3. Assistant Professor,Dept. of Chemistry, Hindusthan Institute of Technology, Coimbatore, Tamilnadu, India
* andaldr@gmail.com

Abstract
Exploring the use of novel agricultural based adsorbents in controlling Cr(VI) pollution in waste water is one of the main areas of research on pollution control due to its high toxicity, posing threat to the human and environment. Adsorption has attracted attention as a cost-effective tool for the removal of such heavy metal ions. This paper presents the experimental results carried out for the sorption of Cr(VI) ions from aqueous solutions employing modified *Terminalia catappa* nut shell (TTCNS). The characterization of TTCNS is investigated using BET, BJH, FTIR, SEM and EDAX analysis. The effect of variable parameters viz., particle size, contact time, initial concentration, sorbent dose and pH were studied. The system has been optimized to achieve suitable parameters for maximum removal of Cr(VI) which are: 0.18mm particle size and 200 mg adsorbent dose of selected sorbent material,11 mg/L initial concentration of adsorbate species, 30 minutes contact time and pH 2 for the solution medium. Adsorption equilibrium and kinetics were verified by Langmuir, Freundlich isotherms and Lagergren first order, Pseudo second order models. The applicability of the methodology developed is also tested with real effluent sample collected from chrome plating industry.

Keywords: adsorption, isotherm, kinetics, equilibrium, nut shells

1. Introduction

Chromium is one of the heavy metals of concern due to its toxic and non-biodegradable nature. Industrial activities such as mining, electroplating, tanning, metallurgical operations and manufacturing have led to the release of this pollutant into the environment. It exists in two stable forms as Cr(III) and Cr(VI), the trivalent ion is known to be an essential trace element in plants and animal metabolism, the hexavalent chromium is carcinogenic and mutagenic. This is due to its easy penetration into biological membranes resulting in health hazards such as skin disorders,respiratory tract problems,lung carcinoma, acute tubular necrosis of kidney and even death in extreme cases(R.Mehra 2003). As per USEPA, the permissible potable limit of Cr(VI) in drinking water is 0.1ppm and irrigation water is 100 ppm (US Department of Health and Human Services, 1991). It is therefore imperative to determine this metal ion concentration in water bodies.

Environmental concerns have motivated many physico-chemical techniques for heavy metal removal from aqueous solutions like reduction, co-precipitation, ion-exchange, reverse osmosis, dialysis and resin chelation(J.N.Egila et al., 2011). These techniques however, posses their own disadvantageslike incomplete metal removal, high reagent cost and energy requirements. Therefore, the need for cost effective alternative technologies is essential for this task. Adsorption using natural adsorbents, an innovative and economical method, has evolved the frontline of defense especially for metals that could not be effectively removed by other techniques.

Several natural sorbents from agricultural, aquatic and forest wastes have been utilized as such and in modified forms by various researchers in the sequestration of chromium ion from aqueous solutions and industrial effluents. Husk of Toor dal (*Cajanuscajan*) was investigated for the removal of Cr(VI) and Fe(III) ions from aqueous solution by N.Ahalya et al(2007).F.N.Acar and E.Malkoc(2004) employed beech saw dust *Fagusorientalis L*, to elaborately examine the removal of Cr(VI).Uptake of Cr(VI) and Ni(II) from aqueous solutions had been investigated by O.O.Kehinde et al.,(2009),usinglow cost agricultural by-products like coconut husk and teak tree bark. Recently low cost adsorbents are activated/modified by various methods for metal removal. Zinc chloride activated *Terminaliaarjuna* nuts(KaustubhaMohantyet al.,2005) and phosphoric acid activated tamarind hulls(A.Verma et al.,2006) have been utilized to trap Cr(VI). Dried biomass of *Oscillatorialaete-virens* was found to posses the potential to remove heavy metals like Cr(VI) and Ni(II) from polluted water (Suman Das, 2012).

The objective of the present study is to investigate the feasibility of employing modified *Terminalia catappa* nut shells for the adsorption of Cr(VI) from aqueous solutions. Until this present work, little or no information is available on the suitability of using this selected agricultural waste in the removal of toxic Cr(VI) and seldom work has been reported in literature so far.

2. MATERIALS

2.1 Sorbent and Sorbate

The tropical Almond *Terminalia catappa* (Indian almond) belongs to the family Combrataceae. It is a large spreading tree distributed throughout the tropics and coastal environment (Species profiles, 2006). The fruit is a sessile, laterally compressed, ovoid to ovate and smooth skinned drupe. The oil containing seeds are encased in a tough fibrous husk with a fleshy pericarp. Thiscorky fibrous endocarp (nut) of the fruit was collected from various localities in Coimbatore, Tamilnadu, India. The nut shells were thoroughly washed with double distilled water,dried in air, then powdered and sieved to various sizes viz., 0.18mm, 0.24mm, 0.30mm, 0.42mm and 0.71mm. The powdered sieved adsorbent was first treated by boiling in 0.1 N HCl for three hours. After decanting the solution, the residue was boiled again with 0.1 N NaOH for three hours. The treated sorbent of varying sieve sizes were washed well several times with double distilled water. Later, they were soaked in water for sufficient time interval,to ensure swelling, as it would make more sorption sites available and finally, the sorbent materials were dried in sunlight. The chemically treated *Terminalia catappa* nut shell powder was used for further experiments and henceforth shall be denoted as TTCNSin the forthcoming discussions.

HCl, NaOH and $K_2Cr_2O_7$of AR gradewere purchased from RanbaxyChemicals.A stockCr(VI) solution of 1000 mg/L was prepared by dissolving 2.828 g of $K_2Cr_2O_7$in 1000 ml of double distilled water for the adsorption experiments.

2.2 Characterization of Sorbent

Table-1 depicts the various physicochemical parameters of TTCNS. Surface area, micropore area, micropore volume and average pore diameter were determinedby *Micrometrics Surface Analyzer*, (facilitated with Belsorp adsorption/desorption software; using nitrogen adsorption at 77 K).The FTIR spectrum of the native and Cr(VI) loaded adsorbent were recorded with a *Thermo Nicolet Infrared Spectrophotometer*. The surface morphology of the treated adsorbent,both loaded and unloaded was examined using the *Scanning Electron MicroscopeJEOL JFM- 6390* (Japan). After drying, the samples were covered with a thin layer of platinum (10 nm) using a sputter coater (SCD 0050 –Baltec, Liechenstein) and observed using the microscope (20 kV) under thevacuum of 1.33 x 10^{-6} m Bar.

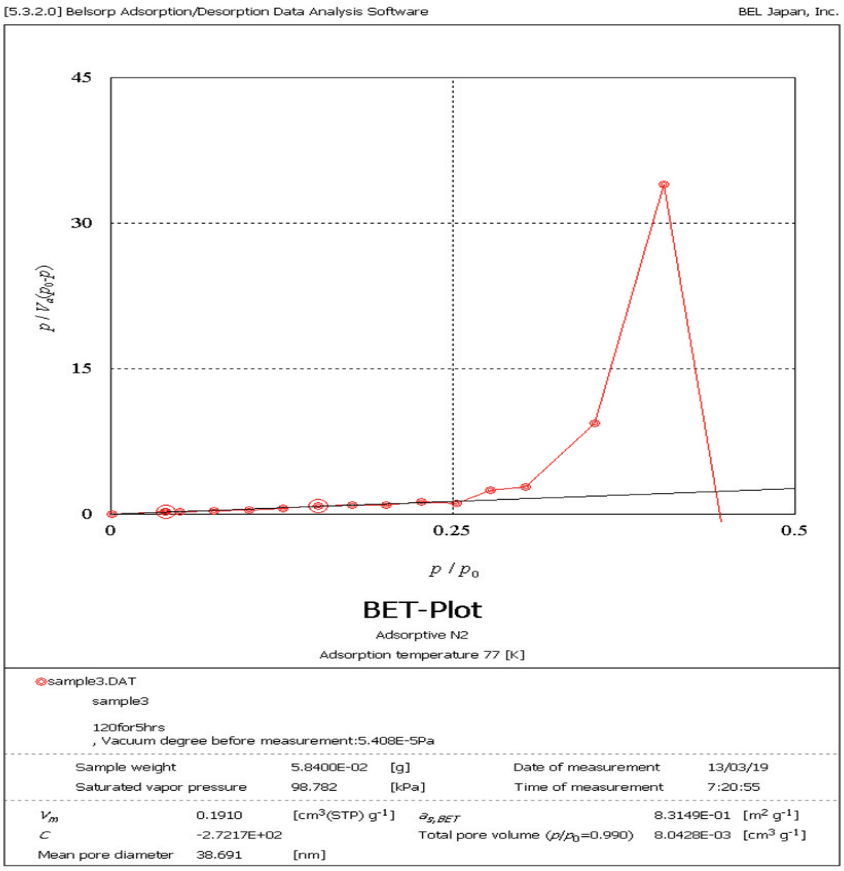
Table 1 Physiochemical Characteristics ofTTCNS

Parameters	**Values**
Surface area (m^2/g)	83.14
Mean Pore diameter (nm)	38.69
Porosity%	94.95
Specific gravity	4.45
Bulk Density	0.25
Ash Content %	9.09
Ion exchange capacity(meq/g)	0.40
pHzpc	6.20
Moisture %	8.51
Pore volume cm^3/g	6.80

3. Methods

3.1. BET surface analysis

BET and BJH methods are used for the evaluation of the particle and mesopore size distribution. Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC manual., 1982)i.e [micropores diameter(d<20A°),mesopores (20A°< d< 500A°) and macropores (d > 500A°].The adsorbents for liquid phase adsorbates should have predominantly mesopores in their structure, due to the larger sizes of liquid molecules(V.C.Srivastava et al., 2006). Surface characteristic values depicted in table 1, proves that, TTCNS lie in the mesopore category and has wide pore size distribution (Fig.1) providing wide distribution of surface area.



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sample3.DAT
     sample3

     120for5hrs
     , Vacuum degree before measurement:5.408E-5Pa

    Sample weight              5.8400E-02   [g]          Date of measurement        13/03/19
    Saturated vapor pressure   98.782       [kPa]        Time of measurement        7:20:55

  Vm                   0.1910        [cm3(STP) g-1]   as,BET                             8.3149E-01  [m2 g-1]
  C                    -2.7217E+02                    Total pore volume (p/p0=0.990)     8.0428E-03  [cm3 g-1]
  Mean pore diameter   38.691        [nm]
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Figure 1:BET plot for TTCNS

3.2Equilibration Experiments

Batch equilibration studies were carried out at 25±1^0 C. At varying initial concentrations, TTCNS dosage varying in the range of 0.18mm-0.71mm particle sizes, 50-250 mg dosages were added to samples separately and the iodine flasks were agitated in an orbital mechanical shaker at predetermined time intervals. pH of the solutions were adjusted to different values accordingly using 0.1 M HCl and 0.1 M NaOH. The contents of the flasks were then filtered and the residual metal ion concentrations were determined using *Shimadzu (AA 6200) Atomic Absorption Spectrophotometer*.The solution volume V ml was kept constant (50ml). The metal ion sorption percentage at any instant of time was determined by using the following equation (1)

$$\%\ \text{adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

where C_o and C_e are the initial and final concentrations of Cr(VI) respectively.

3.3 Specifications of Isothermal and Kinetic Studies

The equilibrium study on adsorption has provided sufficient information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values that express the surface properties and affinity of the sorbent (Ahmed and Mustafa, 2008). It can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. Theadsorption isotherm models were applied to the experimental data obtained from parameter study conducted for various initial concentrations of the Cr(VI) ion. The linear equation (2) was used to plot the Langmuir model

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \qquad (2)$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in solution (mg/L), q_m is the maximum monolayer adsorption capacity of the sorbent (mg/g) and b is the Langmuir sorption constant (L/mg) related to the free energy of sorption. The Langmuir constants q_m and b can be determined from the linear plot of C_e/q_e versus C_e, which has a slope of $1/q_m$ and intercept of $1/bq_m$.

Freundlich isotherm was plotted by applying its standard straight-line equation (3)

$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

where, K_F and 1/n are the Freundlich's constants related to the adsorption capacity (mg/g) and adsorption intensity of the adsorbent respectively, which vary with the heterogeneity of the adsorbent.

The adsorption kinetics were investigated with an aim of obtaining a deep insight into how the amount of adsorbed metal changes with time and the process time required to achieve equilibrium between the aqueous and the solid phase. In order to clarify the adsorption kinetics of Cr(VI) onto TTCNS, two kinetic models viz., Lagergren's Pseudo-first –order and Pseudo-second-order models were applied to the experimental data

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (4)$$

where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t, respectively and k_1 is the rate constant for pseudo-first-order adsorption (min^{-1}).

The linear form of the Pseudo-second-order rate equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

where, k_2 is the rate constant for pseudo-second-order adsorption (g/mg min). The slopes and intercepts of plots of t/q_t versus t were used to calculate q_e and k_2.

3.4. FT-IR Characterization

Examination of the spectra of TTCNS after Cr(VI) adsorption (figure 2b) show a shift in absorption of the–OH stretching frequency from 3386.48$\text{cm}^{-1}$to 3369.33cm^{-1} corresponding to unloaded spectra(figure 2a). This can be interpreted as that O-H stretching is associated with metal adsorption. The –CH stretching at around 2923.09 cm^{-1} is also slightly shifted in the Cr(VI) loaded spectra. The peak at 1423.37 cm^{-1} characteristic of–COO stretching is also found to shift to around 1425.10 cm^{-1} in the corresponding metal loaded spectra, which is indicative of theparticipation of these groups in metal binding.

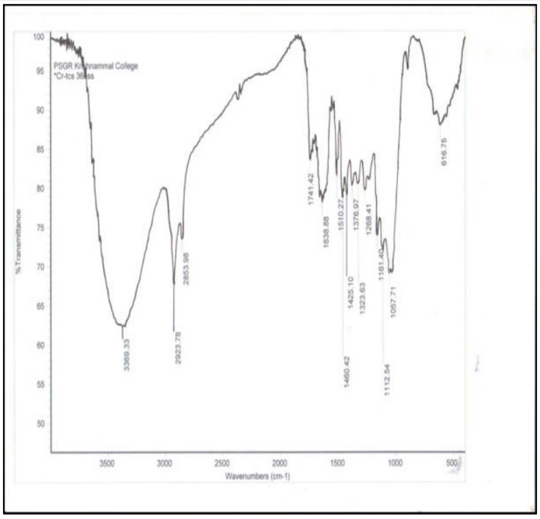

Figure 2a: FT-IR of unloaded TTCNS

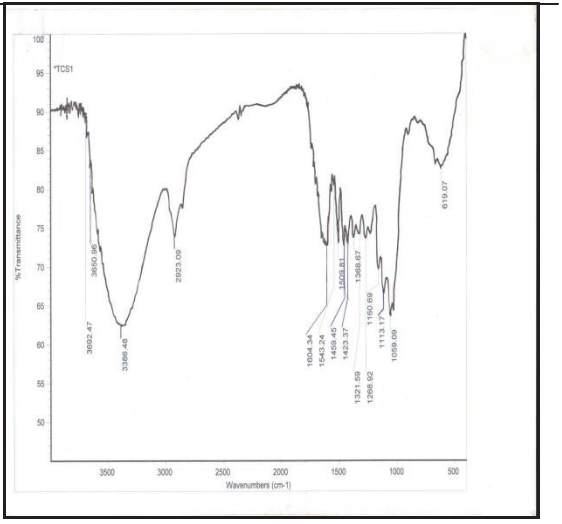

Figure 2b: FTIR of Cr(VI) loaded TTCNS

3.5 SEM and EDAX Analysis

It can be observed from the SEM figures (3a&3b) that the TTCNS is found to posses'surface rugosity in such a way to adhere the solute species onto the surface of the adsorbent. Therefore,the adsorptive characteristics of TTCNS is expected to be effective on Cr(VI) adsorption. EDAX (figure 4b) shows the presence of new peakrepresenting chromium so that it substantiatesthat the adsorption had occurred.

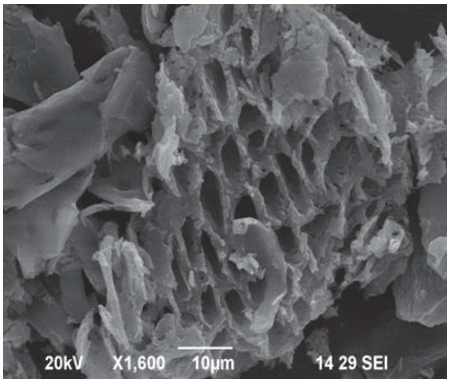

Figure 3a: SEM of unloaded TTCNS

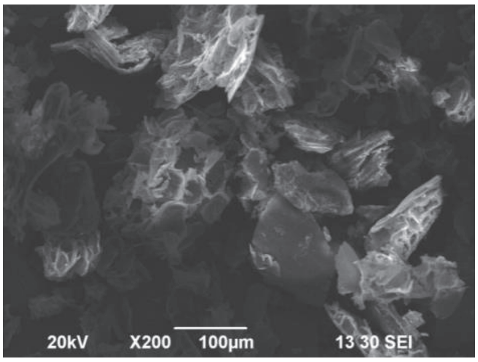

Figure 3b: SEM of loaded TTCNS

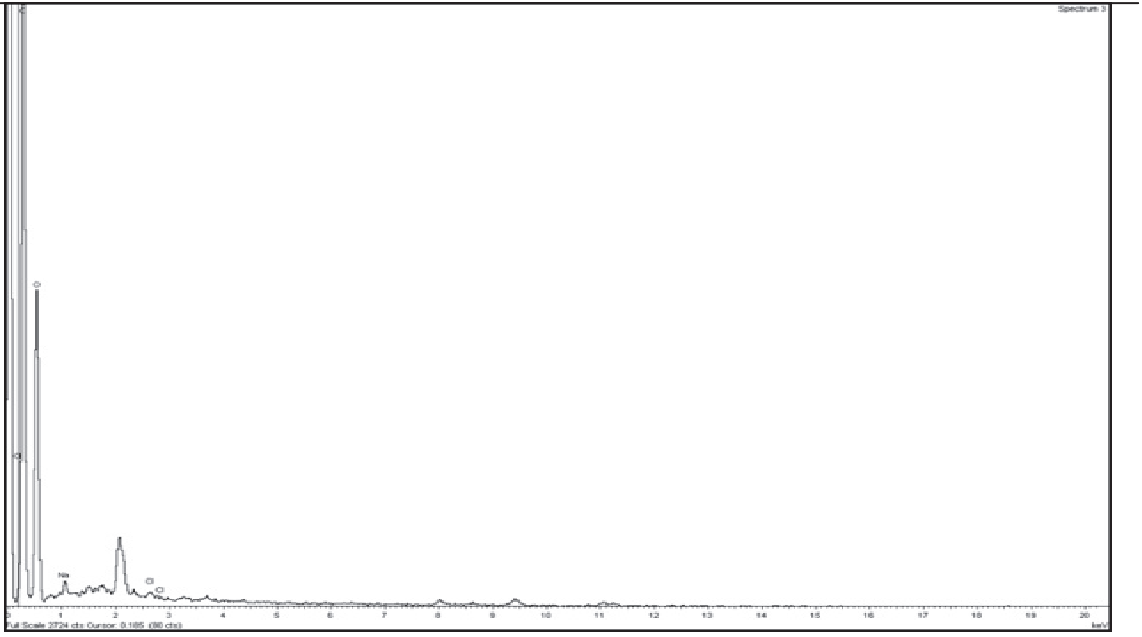

Figure 4a: EDAX spectrum of unloaded TTCNS

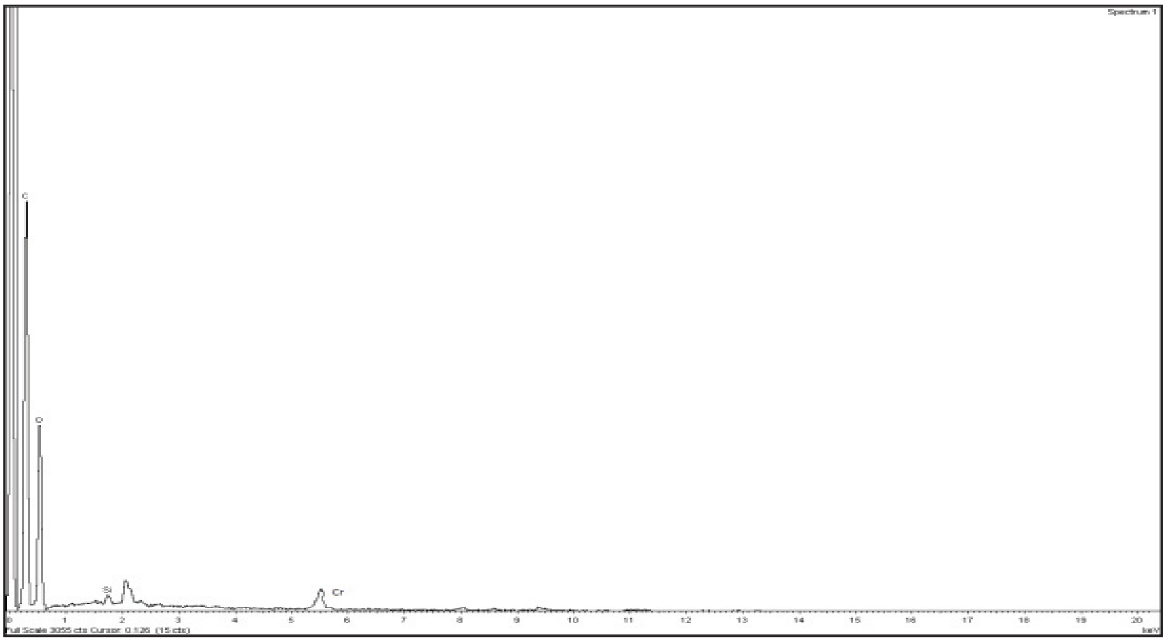

Figure 4b: EDAX spectrum of loaded TTCNS

4. Results and Discussion

4.1 Effect of Particle Size

Five different particle sizes of the sorbent, ranging from 0.18 mm to 0.71mm were utilized to investigate the influence of the adsorbent particle size for the metal removal. It is observed from the smooth and continuous curves (figure 5) that 0.18mm sizes of TTCNS had registered enhanced sorption capacity, showing a maximum uptake of 26.8 mg/g to be the optimum particle size.The relatively higher adsorption with smaller adsorbent particle size may be attributed to the fact that smaller particles yield large surface areas and indicate that chromium ion adsorption occurs through a surface mechanism(IAGC, 2010). So, the studies pertaining to other parameters were carried out employing 0.18mm TTCNS.

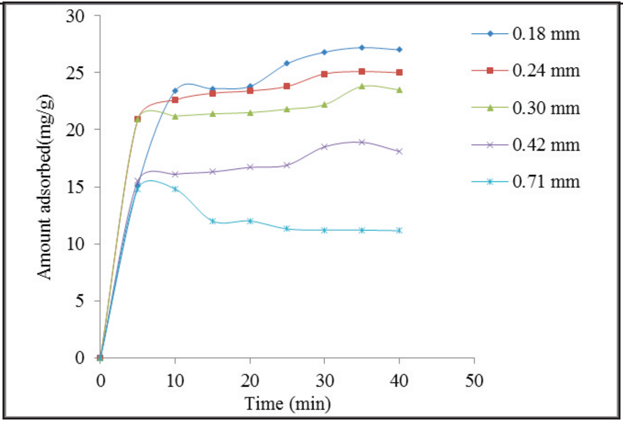

Figure 5: Effect of particle Size (TTCNS)

4.2 Effect of Contact Time and Initial Concentration

The agitation period for the adsorption of Cr(VI) by the sorbentwas investigated to identify the rate of metal removal. The amount adsorbed per gram of the adsorbent for Cr(VI) at different initial concentrations ranging from 3 to11 ppm are listed in table 2. At 30 minutes, higher amounts of Cr(VI) was adsorbed onto TTCNS and the values were 11.85, 22.8, 23.8, 27.2 and 37.4 mg/g for initial concentrations of 3,5,7,9 and 11 ppm respectively(Fig.6).The amount of Cr(VI) getting adsorbed increased with contact time but at a particular point of time, the system attained equilibrium (i.e) the % removal of chromium was observed upto 30 minutes of agitation time later no further increase was registered(Carlos Green- Ruiz,2006). In this view point, optimum initial concentration of 11 ppm of Cr(VI) and an optimum contact time of 30 minutes has been fixed for the forthcoming experiments.

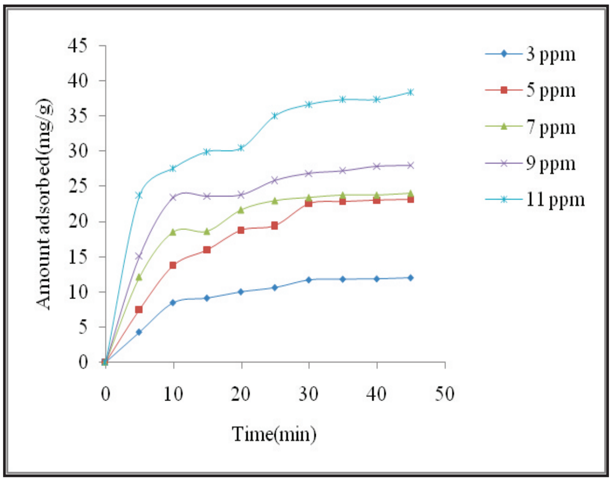

Figure 6: Effect of contact time and initial concentration [Cr(VI)onto TTCNS]

4.3 Effect of Dosage

The variation in doses (50-250mg; 50mg interval) was experimentally verified. The decrease in the amount adsorbed beyond 200 mg was observed to decrease from 54.4 to 52.3 mg/g, as evident from the steep rise in the curve upto 200mg and later a decline for 250 mg (fig.7). This may be basically due to electrostatic interactions between the adsorbent particles and interference between the binding sites(Hameed and Khaiary,2008).

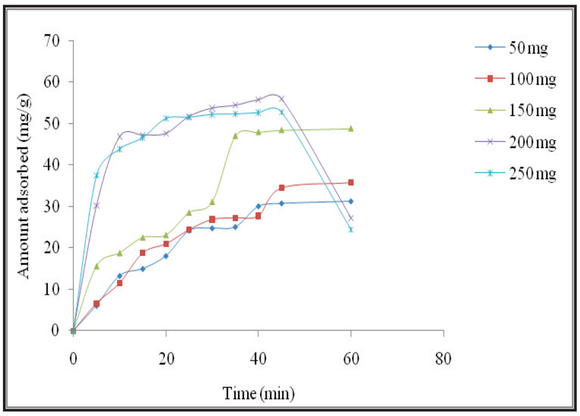

Figure 7: Effect of Dosage(TTCNS)

4.4 Effect of pH

Cr(VI) removal by TTCNS was investigated as a function of solution pH over the range 1-8, for two different initial concentrations, as depicted in figure 8. Maximum uptake was observed at pH 1.78. At increasing pH environments, a sharp decline in uptake was observed, which is in good agreement with previous reports (Emine Malkoc,2007 &HuiGao, 2008). The speciation studies of Cr(VI) in aqueous solution shows that H_2CrO_4 predominates at pH less than 1.0, $HCrO^{4-}$ for pH between 1.0 and 6.0 and CrO_4^{2-} at pH above 6.2 (Lyn Patrick,2006).

Adsorption of Cr(VI) at pH 1.78 onto TTCNS is due to the electrostatic attraction between the positively charged surface of the adsorbent with $HCrO^{4-}$ ions. But, in highly acidic medium (pH=1.0), H_2CrO_4 (neutral form) is the predominant species of Cr(VI). Hence, percentage removal decreased due to the involvement of less number of $HCrO^{4-}$ anions to the positive surface. At higher pH value, the reduction in adsorption may be due to the dual competition of both OH^- and CrO_4^{2-} ions to get adsorbed on the surface of the adsorbent among which OH^- predominates (Manjeet Bansal et al., 2006)

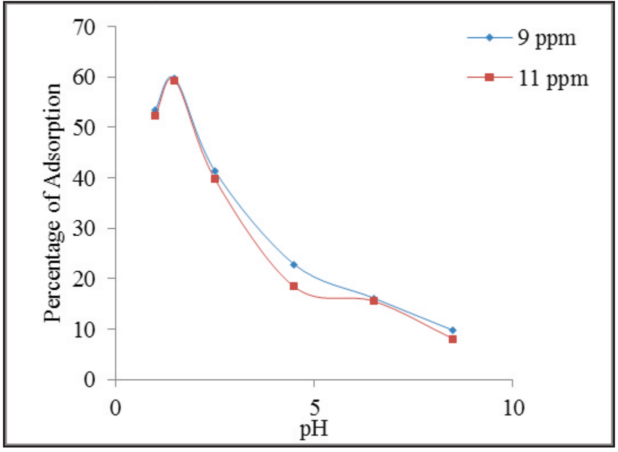

Figure 8: Effect of pH[Cr(VI)onto TTCNS]

4.5 Langmuir adsorption isotherm

The Langmuir constant q_m which is a measure of the monolayer adsorption capacity of TTCNS,Langmuir constant b, (free energy of sorption) and the correlation coefficient R^2 for Cr(VI) ion with the adsorbent,presented in table 3, indicates a good agreement between the experimental values and the isothermal parameters. This also confirms the monolayer adsorption of the Cr(VI) by adsorbent surface. The R_L (table 2) values calculated with initial concentration range 3-11 mg/L were between (0<RL<1) which is consistent with the requirement for a favourable adsorption process.

Table 2 Equilibrium parameter (R_L)

Conc. of metal ion (mg/L)	(R_L) Cr(VI)-TTCNS
3	0.47
5	0.34
7	0.27
9	0.23
11	0.19

4.6 Freundlich isotherm model

The plot of log q_e versus log $C_e$for the adsorption of Cr(VI) onto TTCNS (fig.9) was employed to generate the intercept value of K_F and the slope of 1/n, which illustrates that adsorption of Cr(VI) onto TTCNS obeyed Freundlich isotherm very well. K_F derived from the equation (3) is an indicator of adsorption capacity of a given adsorbent. The results obtained indicate that TTCNS have higher capacity to adsorb Cr(VI).The value of 'n' greater than 1(Table 3) implies favourable nature of adsorption.

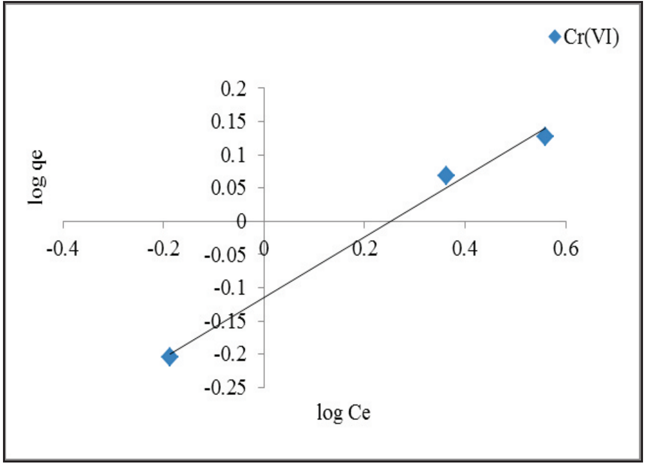

Figure 9: Freundlich isotherm plot

Table 3 Linear regression data ofAdsorption isotherms for Cr(VI) sorption

Langmuir model			Freundlich model		
q_{max}	b	R^2	K	1/n	R^2
18.6	0.38	0.9997	14.26	1.005	0.9356

(Initial metal ion concentration:3-11 ppm, pH:1.78, Temp:303K)

From the values of correlation regression co-efficients obtained from these models, it was suggested that the data fitted well to the Langmuir isotherm model, indicating both monolayer adsorption and heterogeneous surface conditions (Vinodhini and Das,2010). Based on the q_{max} values, it is noteworthy that TTCNS has appreciable potential for the removal of Cr(VI) from aqueous solutions.

4.7 Lagergren First order kinetic model

The pseudo-first-order rate expression of equation (4) was used to test the experimental data for Cr(VI) onto TTCNS. The values of k_1, pseudo-first-order rate constant and q_e calculated obtained by the plot of log (q_e-q_t) versus t (Fig.10) are presented in table 4,

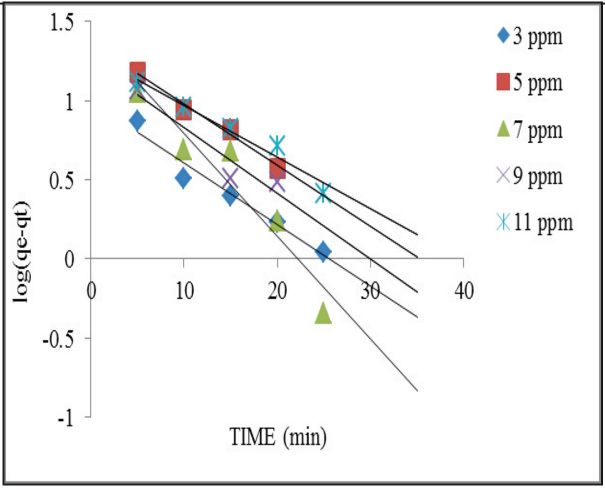

Figure 10: Pseudo-first order Kinetic model

4.8 Pseudo second order Kinetic model

The values of pseudo-second-order rate constants obtained by the plot of t/q_t versus t (Fig.11). The R^2 values observed for pseudo-second-order model were greater than the other employed systems. The decrease in K_2 and increase in q_e values with an increase in metal concentration was observed. The increase in q_e with concentration may be due to the more efficient utilization of the sorptive capacities of the adsorbent due to greater driving force (Amudha et al.,2009). As the increase in the metal concentration reduced the diffusion of metal ions at the boundary layers, K_2 decreased with concentration (Anirudhan,2008)

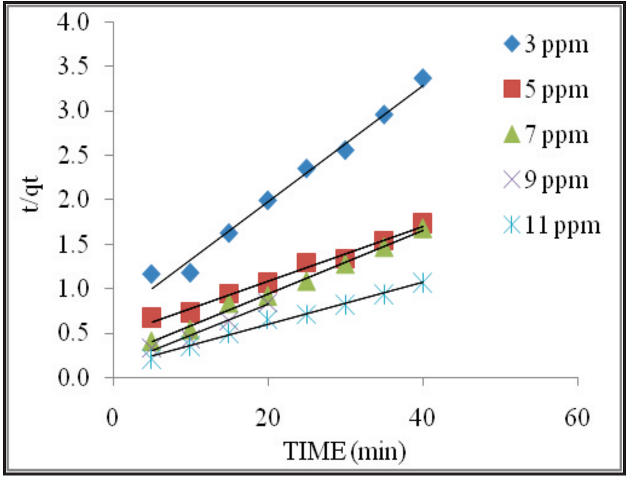

Figure 11: Pseudo-second order Kinetic model

Table 4 First-order and second-order kinetic constants for adsorption of Cr(VI)ion

First Pseudo-order			Second Pseudo order		
q_e	K_1X10^{-3}	R^2	q_e	$K_2X\ 10^{-3}$	R^2
19.70	7.53	0.9947	42.37	6.3	0.9922

(Initial metal ion concentration:3-11 ppm, pH:1.78, Temp:303K)

The kinetic data showed good compliance with first-order model rather than the second-order indicating a surface-complexation mechanism.

4.9 Effect of TTCNS on Industrial Effluent containing chromium

The industrial effluent sample collected from Chromium plating industry was diluted thrice and a volume of 50 ml was employed for the batch study. The efficiency of the selected adsorbent materials on industrial effluent was analyzed for the optimised particle size of 0.18mm at a contact time of 30 minutes by batch study. Batch adsorption studies were carried out with different adsorbent dosages (50-500 mg; 50 mg interval). The effluent pH was adjusted to nearly 2.0 for Cr(VI),as low pH conditions favoured Cr(VI) removal. A dosage of 450 mg of TTCNS was sufficient for approximately 50% removal of Cr(VI) as depicted in Fig.12

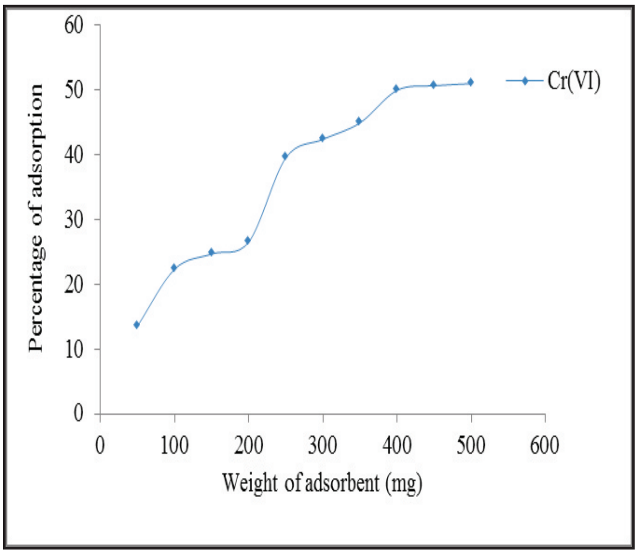

Figure 12. Effect of TTCNS on industrial effluent containing chromium

Conclusion

This study identified Indian almond (*Terminalia catappa)* nut shell as a suitable biosorbent forCr(VI) removal employing batch equilibration method. The adsorption process was found to be pH dependent and optimized as 1.78 for Cr(VI)-TTCNS system.The probable mechanism of adsorption was surface complexation, as observed from Langmuir isothermal data and Lagergren first order kinetic model. Present research also confirmed the potentiality of Indian almond nut shell for the removal of toxic chromium from electroplating industry effluent.

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