RESEARCH ARTICLE

BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING HUSK OF *ANACARDIUM OCCIDENTALE L.*

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Manuscript Info	*Abstract*
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Chromium (Cr) (VI) is an acutely toxic and carcinogenic metal ion. It is mobile in environment and is widely used in electroplating, stainless steel production, leather tanning, paint and textile manufacturing. Due to its known harmful effects, a focus on methods to remove this harmful metal ion is very important. In our study, we examined the potential ability of pre-treated testa (husk) of *Anacardiumoccidentale* (Cashew) in removal of Cr (VI) from aqueous solutions when usedas an adsorbent. We looked at effects of temperature, pH, initial concentration of adsorbate, and adsorbent dosage on effective removal of Cr (VI). Data obtained was analyzed using Freundlich and Langmuir adsorption isotherms at different temperatures and related parameters for each adsorption isotherm were determined. The Langmuir adsorption potential was found to be 56.9 mg/g and the Freundlich constants K_f and n were 1.002 [mg/g (1/mg) ^{n}] and 3.4. The study also included results on the kinetic dimensions of adsorption of the Cr (VI) on derived adsorbent. Fourier transform infrared spectroscopy (FTIR) studies confirmed that carboxyl and hydroxyl groups were the main groups involved in the metal uptake.
Abbreviations:-Cr- Chromium; FTIR – Fourier transform infrared spectroscopy; ppm – parts per million.

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Introduction:-

Many researchers looked at methods for metal removal from waste water because of ecological effects of toxic metals (Volesky B, 1990; Kratochvil D and Volesky B, 1998). Water pollution due to ejection of toxic heavy metals containing effluents from industries such as textile, paint, leather tanning remain as a major environmental concern worldwide.

Chromium, in its hexavalent form, has been reported to be hazardous with group "A" carcinogenic property. It has been shown to play a role in modification of DNA transcription process resulting in chromosomic aberrations. Subsequently, chronic exposure to hexavalent chromium can inflict many health problems, including allergic contact dermatitis and other immunomodulatory diseases (International Agency for Research on Cancer (IARC), 1982). Effluents from above mentioned industries contain concentrations upto 100ppm of Cr (VI) indicating the significant need for methods for its efficient removal.

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A number of physiochemical techniques are available for chromium removal such as chemical precipitation, ion exchange, electrochemical precipitation, ultrafiltration, solvent extraction, reverse osmosis, etc (Aksu Z et al., 1996; Juang RS and Shiau RC, 2000). All these techniques are economically expensive and have major disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal.

In such circumstances, an efficient and environment friendly adsorption technique is of utmost importancewith its easy operation, low cost, versatility, and ability to allow kinetics and equilibrium measurements without any highly sophisticated instruments (Volesky B and Holan ZR, 1995). Such heavy metal removal using biological materials is called biosorption. Consequently, various potential adsorbents have been researched for their ability to remove specific heavy metals from wastewater (Selvaraj K et al., 1997; Orhan Y and Büyükgüngor H, 1993; Hamadi NK, 2001;Selvaraj K et al., 2003). Much work has been carried out using seaweeds, molds, yeast, bacteria, shells, agricultural waste products like peat, coffee, coconut husk, crushed coconut shell, waste tea, defatted rice bran, rich hulls, soybean hulls, cotton seed hulls, etc (Dakiky M et al., 2002; Marshall WE and Champagne ET, 1995; Ahalya N et al., 2005; Ahalya N et al., 2010; Srinivasan K et al., 1988). These adsorbents having distinct advantage over activated carbon because of their low and easy availability. Based on our literaturereview,the adsorptive properties of testa (husk) of *AnacardiumoccidentaleL.*, which is easily available, has not been looked at so far.

Testa (husk) of *AnacardiumoccidentaleL.* is an agricultural waste byproduct that is available in plenty in certain areas of India and can be potentially used for the removal of chromium (VI) ions from aqueous solution. The objective of our study was to test the feasibility of using testa (husk) of *AnacardiumoccidentaleL.* as a biosorbent and examine the effects of temperature, pH, initial concentration of adsorbate, and adsorbent dosage on effective removal of Cr (VI).

Materials and Methods:-
Preparation of biosorbent:-
Husk from *AnacardiumoccidentaleL.*(cashew) was procured from a cashew processing unit. Brownish color husk with high moisture content was washed thoroughly with tap water to remove large adhered particles and then rinsed with double distilled water. Subsequently, husk was boiled to remove color and impurities and dried at $80^{\circ}C$ for 5 hours. The dried material was then ground in a well cleaned porcelain mortar. Finally, it was sieved to get a fine powder (0.15mm) and stored in desiccators for subsequent use.

Reagents and equipments:-
A 1000 ppm stock solution of Cr (VI) is prepared by dissolving 2.8287 of analytical grade (99.9%) potassium dichromate ($K_2Cr_2O_7$) in ultra-pure double distilled water. The complexing reagent, 0.5% diphenyl carbazide, was prepared in acetone and stored in a brown bottle for use during the study. Concentration of diphenyl carbazide complex with chromium solutions were monitored on UV-Vis Spectrophotometer with 10 mm matched quartz cuvettes, Model Lambda 25 (M/s Perkin Elmer Ltd, USA) over a wavelength of 540 nm. The pH was adjusted using Systronics calibrated pH meter. Remi Manufacturers mechanical shaker was used for adsorption and kinetic studies.

Experiments:-
Adsorption studies:-
The preliminary part investigations were carried out in batches using 100 ml borosil conical flasks at different conditions of pH, concentration, time, amount of adsorbent, temperature, etc., to check the effects on adsorption process. After multiple meticulous trials, concentration ranges of 40-200 ppm and adsorbent amount of 1.5 g/L were chosen. The effect of adsorbent amount was studied using varied amounts in the range of 0.5-4 g/L with initial concentration of Cr (VI) of 100ppm. The mixture was sporadically shaken and then kept for certain period for saturation. Subsequently supernatant liquid was filtered through Whatmann Filter Paper No.42 and the amount of metal ion adsorbed was determined spectrophotometrically at 540 nm. All experiments were performed in triplicates.

Kinetic studies:-
Kinetic studies were carried out to measure the rates of reaction under various experimental conditions. These objective of these studies was to determine influence of concentration and temperature on rates of reaction and also to determine time requirement for the attainment of equilibrium during the adsorption process. For different initial concentrations of chromium solution ranging 40-100 mg/L with definite pH, known amount of adsorbent was taken

at different temperature with periodic shaking. The solutions were then filtered at different time intervals using Whatmann Filter Paper No.42 and evaluated spectrophotometrically for the amount of toxic metal.

Characterization of adsorbent:-
FTIR analyses were performed on KBr discs with 1% finely ground sample. They were analysed in a Perkin Elmer, Model Spectrum BXI FTIR spectrophotometer. Spectral data were processed using Spectrum 6.2 version software. The infrared spectra were recorded in the range of wave number 650-4000 cm^{-1} at a resolution of 4 cm^{-1}. The cashew husk with and without adsorbed metal, were analyzed. The surface structure and metal adsorption on biosorbent was examined using Scanning Electron Microscope (SEM) combined with Energy Dispersive X-ray spectroscopy. The samples were covered with a thin layer of gold and electron acceleration voltage of 20 KV was applied. The percentage of elements was evaluated using Energy Dispersive X-ray spectroscopic study which revealed the percentage of chromium in the biomass after biosorption.

Results and Discussion:-
Sorption equilibria studies:-
In order to evaluate the chromium (VI) adsorption capacity, studies were performed with a constant adsorbent dose (1 g/L) with different initial adsorbate concentration (40-200 mg/L) solutions and applicability of the data to the Langmuir adsorption isotherm was tested. Tests were run for sufficient time to get equilibrium at an initial pH 2. These results were adjusted to the Langmuir model that can be expressed as equation (1) shown below: (Kadirvelu K and Namasivayam C, 2000).

$$(1) \qquad q_e = \frac{b\,q_{max}\,C_e}{1 + b\,C_e}$$

In the above equation,q_e is the metal uptake at equilibrium (mg/g of biomass),q_{max} is the maximum Langmuir uptake (mg/g),C_e is the final metal concentration at equilibrium (mg/L), and$b$ is the Langmuir affinity constant (L/mg of the metal). The Langmuir affinity constant correlates to the affinity between the biomass and a certain metal, with higher value indicating greater affinity. These sorption parameters can be calculated from the isotherm using a linear representation of the Langmuir model(C_e/q_e vs C_e) as shown in equation (2) below:

$$(2) \qquad \frac{C_e}{q_e} = \frac{C_2}{q_{max}} + \frac{1}{b\,q_{max}}$$

The Langmuir isotherm is based on the following assumptions (Langmuir I, 1918).
a) Metal ions are chemically adsorbed at a fixed number of well-defined sites.
b) Each site can hold only one ion.
c) All sites are energetically equivalent and there is no interaction between the ions.

The linear plot of C_e/q_e vs C_e showed that the adsorption followed the Langmuir adsorption model (Figure 1). The correlation coefficient was 0.99. q_{max} and b were calculated from the slope and intercept of the plot and were 76.9 mg/g and 0.209 L/mg respectively.
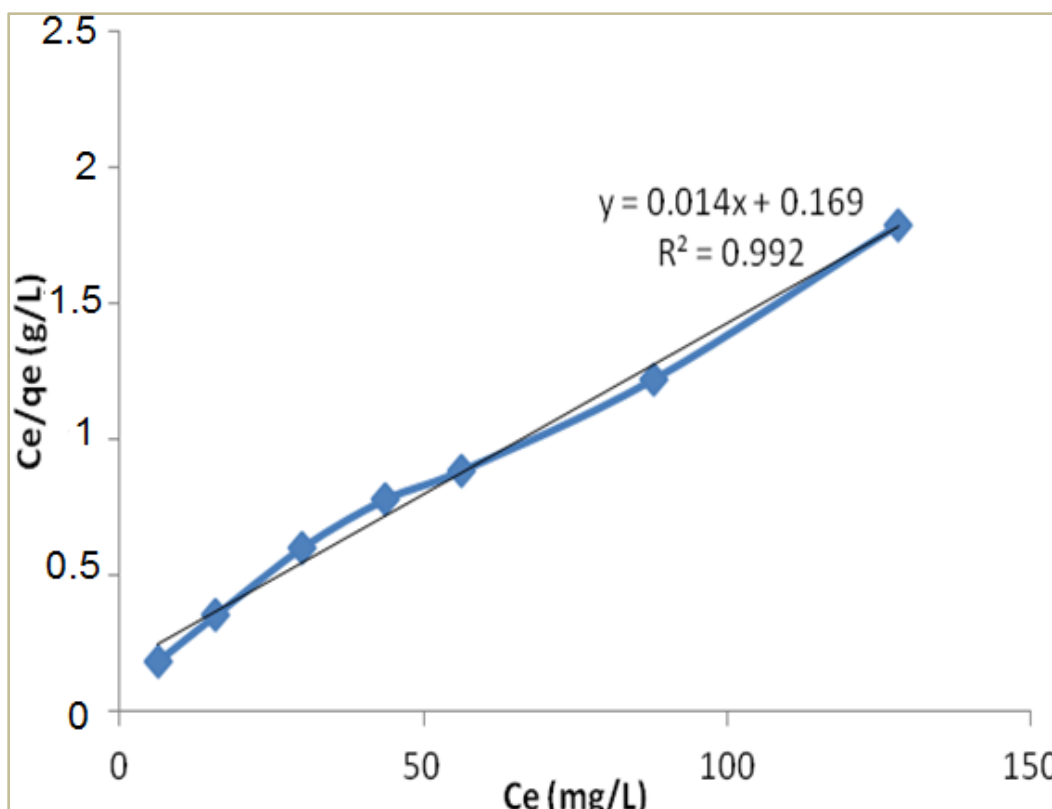
Fig.1:-Langmuir plot for Cr(VI) adsorption. Agitation time: 80 min, initial pH: 2.0, initial adsorbate concentration: 40-200 mg/L, adsorbent dosage: 1 g/L, temperature: 30°C.

Separation factor - R$_L$:-

The necessary characteristics of the Langmuir isotherms wasexpressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which was defined as shown in equation (3) below where C_o is initial concentration in mg/L and b is Langmuir constant:

(3) $$R_L = \frac{1}{1+bC_o}$$

According to McKay G et al. (1982), R_L values between 0 and 1 indicate favorable adsorption (Table 1).The R_L values obtained in our study were less than 1 for Cr (VI) adsorption indicating favorable adsorption (Table 2).

Table 1:-Relation between separation factor (R_L) and type of isotherm.

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L < 1$	Favorable

Table 2:-Initial adsorbate concentration (C_o) and resulting values of separation factor (R_L)

| C_o	R_L
40	0.116
60	0.095
80	0.073
100	0.059
120	0.049
160	0.037
200	0.030

Freundlich adsorption was also applied in our study of adsorption of Chromium (VI) on to biosorbent. The Freundlich isotherm is represented by the equation (4) shown below (Freundlich H, 1906):

(4) $q = K_f C_{eq}^{1/n}$

In the above equation, C_{eq} is the equilibrium concentration (mg/L), q is the amount adsorbed (mg/g), K_f is the Freundlich constant, and n is the heterogeneity factor representing the deviation from linearity of adsorption, also known as Freundlich coefficient. The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and was represented as equation (5) below:

(5) $\ln q = \ln K_f + \dfrac{1}{n}\ln C_{eq}$

K_f and n were calculated from the slope of the Freundlich plots (Figure 2). A n value between 1 and 10 represent beneficial adsorption and in our study, the value of n was significant at 3.4.
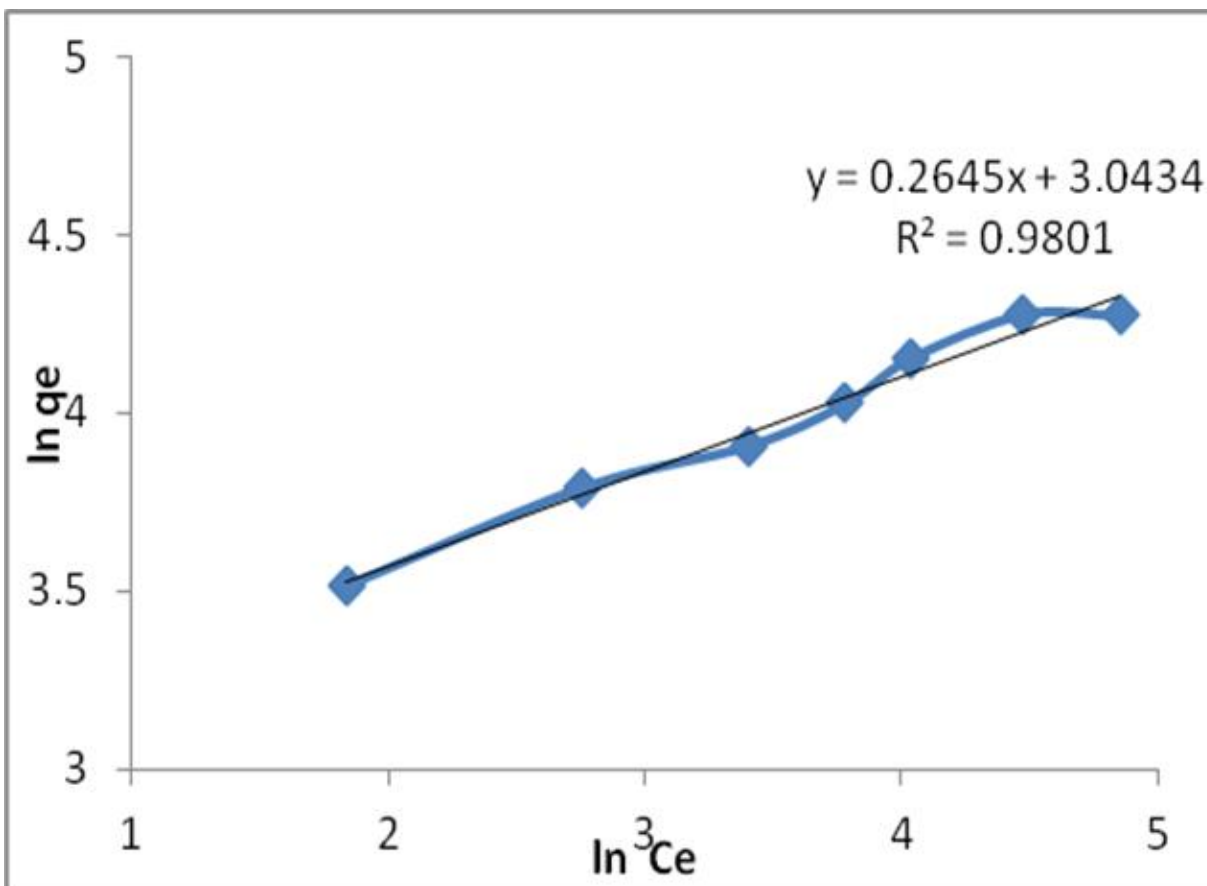

Fig. 2:-Freundlich plot for Cr (VI) adsorption. Agitation time: 80 min, initial pH: 2.0, initial adsorbate concentration: 40-200 mg/L, adsorbent dosage: 1 g/L, temperature: 30°C.

Effect of pH on adsorption:-

To optimize the pH for maximum Cr (VI) removal which is an important factor, batch experiments were performed with 50 ml of different concentration (mg/L) of metal ion solution by varying the pH between 2-6 and results were analysed. The metal chromium is known to exhibit pH dependent equilibria in aqueous solutions. As the pH shifts, the equilibrium also shifts. In the pH range of 2-6, $HCrO_4^{-}$ and $Cr_2O_7^{2-}$ ions are in equilibrium. But in the case of lower pH (pH< 2.0) values, $Cr_3O_{10}^{-}$ and $Cr_4O_{13}^{2-}$ species are produced.

The optimum initial pH for biosorption of hexavalent chromium using our biosorbent was 2.0 in our study. The experimental results showed that the percentage adsorption increased as the pH was lowered and reached 99% and 97% respectively for 20 and 40 mg/L Cr (VI) concentrations (Figure 3). The decrease in percentage removal of chromium ion at higher pH is likely due to negative charges on surface of adsorbent repelling the ions.
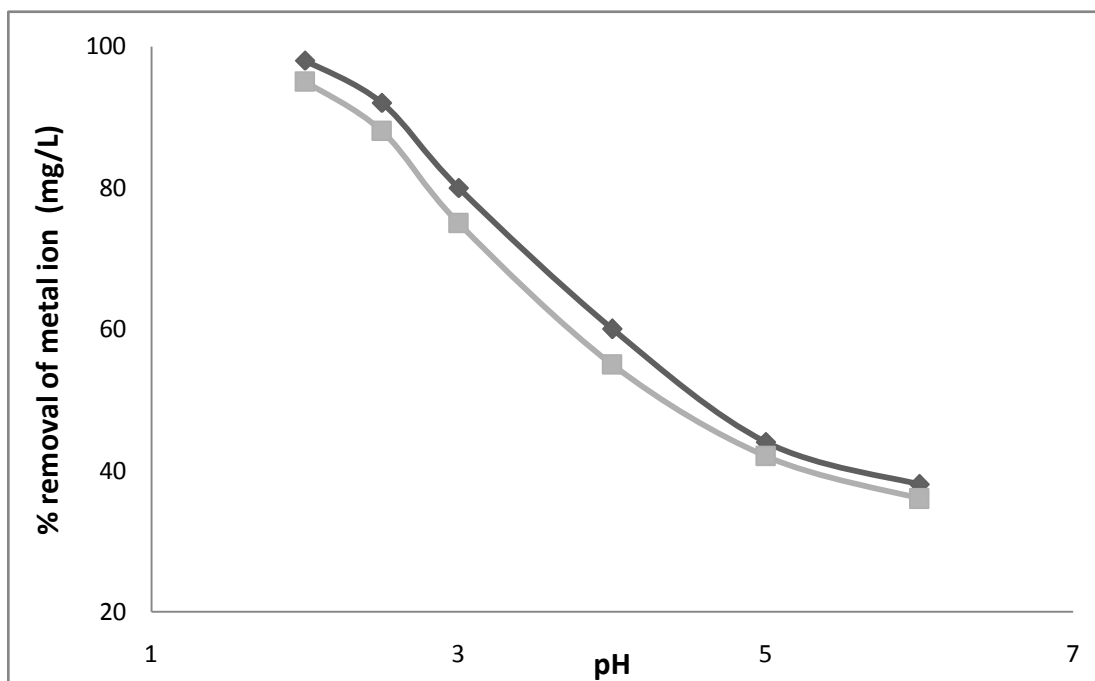
Fig. 3:-Effect of pH on Cr(VI) adsorption at different initial Cr(VI) concentrations. Initial concentration: 20 mg/L (black line), 40 mg/L (gray line).

Recently, information is available that Cr (VI) can be reduced to Cr (III) by contact with biomass due to high reduction potential values. This has been supported by X-ray photoelectron spectroscopy analysis (Park D et al., 2004). At the time of Cr (VI) reduction some of the organic carbons of the biomass are converted to inorganic carbon (HCO_3^- and CO_2). Thus in our study, with decreasing pH, the protons were consumed during adsorption and more polymerized chromium oxide species were noted.

Effect of agitation time and initial Cr (VI) concentration on Cr (VI) adsorption:-
In our study, there were two stages of adsorption process noted. First stage was rapid where about 75% biosorption was completed within first 15-20 min and the second stage represented a slow progressive biosorption. The first stage was likely rapid due to accumulation of metals on the large available surface area of biosorbent. With the progressive decrease in available sites on biosorbent, adsorption process was slower during the second stage. Moreover, the initial deposited metal ions are known to penetrate the interior of the biosorbent through intra-particle diffusion which contributes to the slower process as well (Sangi MR et al., 2008).

We observed that the biosorption process attained equilibrium in 1 hour. The effect of agitation time for various initial concentrations was studied at pH 2. The percentage removal of Cr (VI) improved with an increase in agitation time and the equilibrium attained varied for different Cr (VI) concentrations. The time required to attain equilibrium for 40 mg/L Cr(VI) initial concentration was 60 minutes and for 100 mg/L Cr(VI) initial concentration was 80 minutes. The maximum percentage adsorption was 99% and 75% respectively (Figure 4).
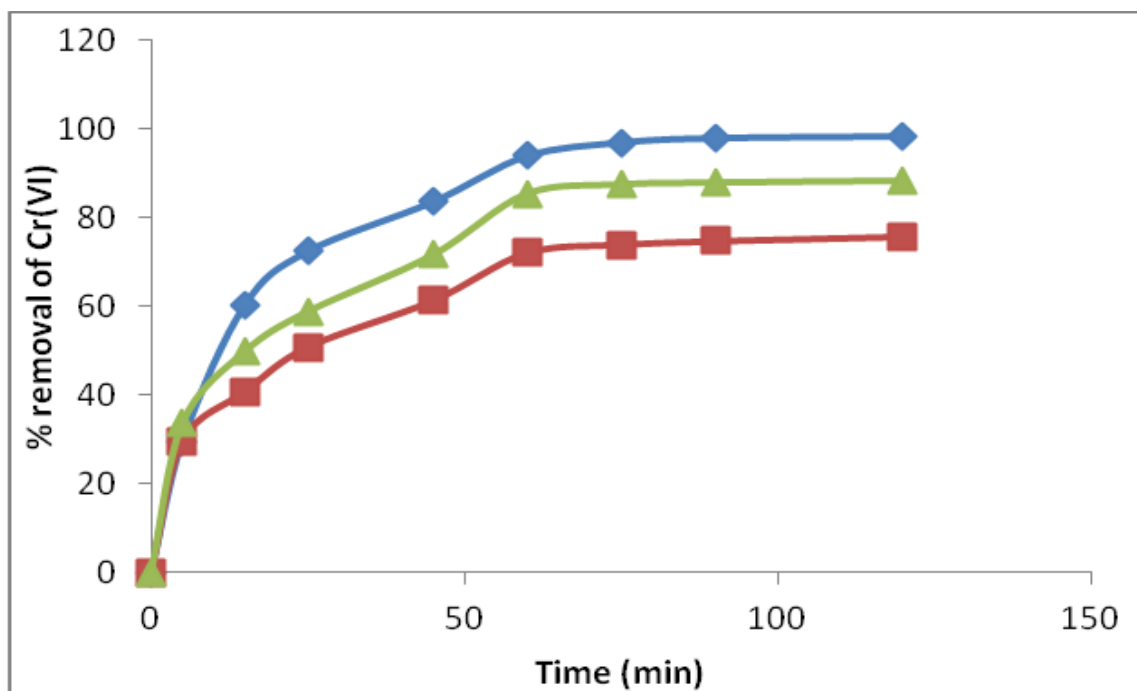
Fig. 4:-Effect of agitation time and initial Cr (VI) concentration. pH 2, initial concentrations: 40 mg/L (◊), 80 mg/L (Δ), and 100mg/L (□).

Effect of adsorbent dose on adsorption:-
The percentage absorption of chromium (VI) was studied in relation to increasing adsorbent dose from 0.5 to 5 g added to 50 ml aqueous solution with absorbate concentration of 100 mg/L. We noted increased percentage removal from 65% to 99% as the dosage increased from 1 to 5 g but the adsorption capacity decreased (Figure 5).

The increase in percentage removal with increase in adsorbent dosage is due to increased availability of number of adsorption sites. However, the decrease in adsorption capacity can be explained by the fact that more sites remain unsaturated with increase in adsorbent dosage (Sharma DC and Forster CF,1993).
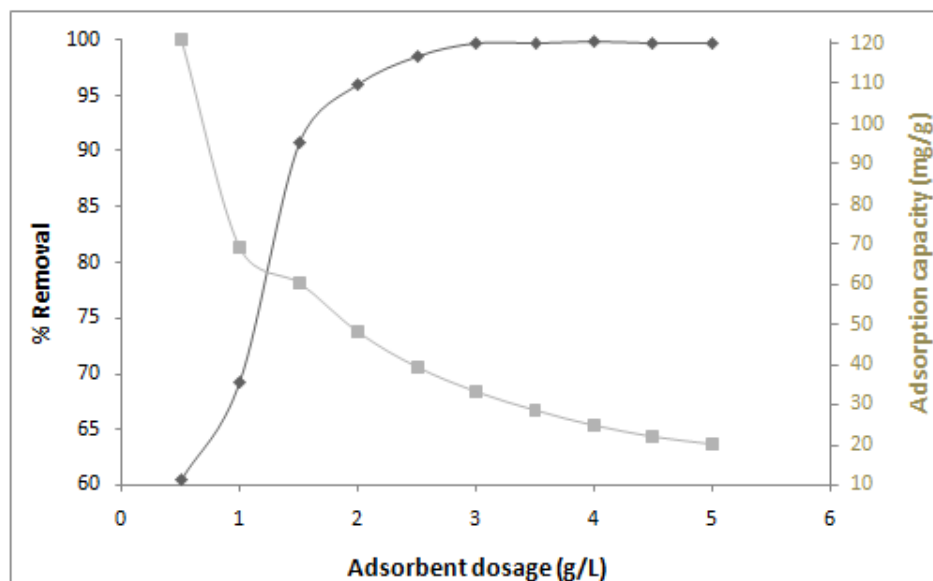
Fig. 5:-Effect of adsorbent dose on Cr(VI) adsorption. Time: 60 min, temperature: 30°C.

FTIR spectral analysis:-
For further analysis, unreacted, chromium treated husk pellets were prepared and scanned using FTIR and percentage transmission for various wave numbers were studied. We identified absorption bands using obtained spectra and assigned them to corresponding functional groups (Figure 6).
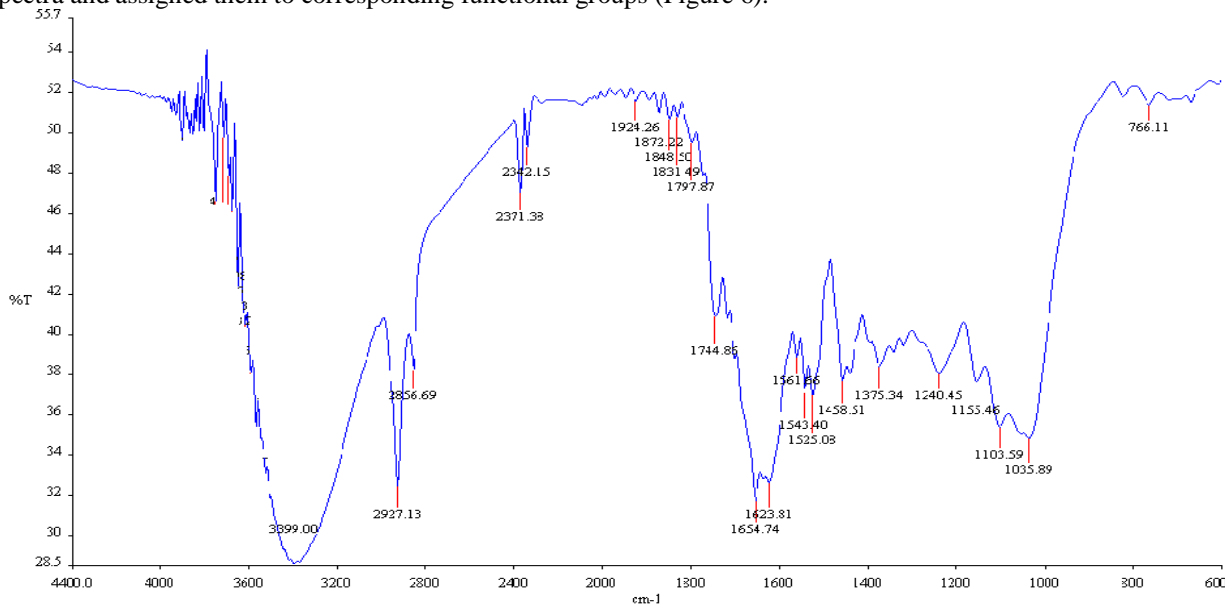
Fig. 6. Fourier transform infrared spectroscopy(FTIR) spectral analysis

Wave numbers of 3000 and 3750 cm^{-1} indicated presence of OH groups on the bisorbent surface. The trough that was observed at 2926 cm^{-1} and 893 cm^{-1} indicated presence of C-H groups. The 1649 cm^{-1} band was a result of CO stretching mode conjugated to a NH deformation mode and was indicative of amide band. The trough at 1154 cm^{-1} was due to CO or CN groups. Out data reflected the presence of several functional groups for binding Cr (VI) ions on biosorbent surface.

Conclusion:-
Results from our study strongly support the ability of cashew husk as an excellent alternative for removal Cr (VI) from solutions. The FTIR bands related to –OH and –COOH groups indicate that linocellulosic moieties of biosorbent that hold these groups play an important role in biosorption. Hydrogen of these groups is competent of ion exchange with metal ions.

We found maximum adsorption of Cr (VI) was at pH of 2. The percentage removal increased with increase in adsorbent dosage and the equilibrium experiments showed that equilibrium was attained within 70 minutes. Langmuir isotherm showed Cr (VI) on cashew husk with maximum capacity of 56.9 mg/g. Our study, through multiple analyses, showed that cashew husk can serve as an effective biosorbent for Cr (VI).

Cashew husk contains less amount of nitrogen (protein) and is advantageous over protein rich algal and other biomass projected metal biosorbents because proteinaceous materials are more likely to putrefy. Cashew husk, which is available in large quantities at various places in India, can be processed easily and in a very inexpensive manner to get sufficient adsorbent readily. Cashew husk as a biosorbent can be used in large scale industries to remove chromium ions from effluents and can be an effective alternative compared to other costly biosorbents and process.

Conflict of Interest:- The author has no conflicts of interest to disclose.

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