

MODELING OF ISOTHERM AND KINETICS OF EQUILIBRIUM SORPTION OF CHROMIUM HEAVY METAL FROM AQUEOUS SOLUTION ON TO ACTIVATED CARBON DERIVED FROM *CICCA ACIDA* SEEDS

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Abstract: Carbon materials are exhibited great potentials in various applications especially the removal of pollutants from aqueous solution and industrial wastewater. Therefore, the attempt has been made to study the removal of Cr(VI) ions from aqueous solution using the Nano-sorbent derived from *Cicca Acida* seeds. The sorption capacity is studied from various adsorption isotherms such as Langmuir and Freundlich models. The experimental results are correlated with FT-IR and SEM studies. The sorption capacity of Cr(VI) ions are observed much better for Nano-sorbent.

Keywords: *Cicca Acida* Seeds, Chromium, Isotherms, SEM and FTIR studies

I. INTRODUCTION

Water is one of the most abundantly available substances in nature. It is essential to all forms of life like human beings, animals and plants. It forms around 75 % of the matter of the earth's crust. It is also essential for agriculture, industries, manufacturing, transportation and countless other human activities. It is required for the satisfactory performance of various life processes as a circulatory fluid, as a carrier of nourishing food and for the removal of waste products. Water is also used as steam in many engineering operations and used as a coolant in power and chemical plants. In addition, water is widely used in other fields such as production of steel, plastics, atomic energy, textiles, chemicals, air-conditioning, drinking, bathing, sanitary, washing, irrigation and fire-fighting etc [1].

Chromium has two stable ionic forms-hexavalent and trivalent states. Cr(VI) ions is toxic but its life time in the aqueous environment is limited as it is reduced to Cr(III) by organic material. The tolerance limit of Cr(VI) ions to discharge in land surface waters has to be from 0.1- 0.05 mg/L [2]. The trivalent form is relatively innocuous, but hexavalent chromium is toxic, carcinogenic and mutagenic in nature, highly mobile in soil and aquatic system and also a strong oxidant, capable of being absorbed by the skin [3]. Chromium leads to cancer, liver damage, pulmonary congestion, oedema and causes skin irritation resulting in ulcer formation. The chromium compounds may cause epigastric pain, nausea and vomiting, severe diarrhea and hemorrhage [4]. Chromium have reported that Cr(VI) ions inhibits the respiratory activity by inactivating enzymes and may be 100 times more toxic than Cr(III) [5].

II. MATERIALS AND METHODS

2.1 PREPARATION OF *CICCA ACIDA* SEEDS NANO CARBON (CANC)

Cicca Acida Seeds Nano-sorbent (CASNS) was prepared from *Cicca Acida* tree fruits. It is commonly cultivated dry lands in most parts of India. It is one of the agricultural waste and used as fuel to a small extent. Its vegetables are mainly cultivated and consumed in developing countries. This tree stem and seeds is widely available in India. Therefore, it is low cost sorbent material, used for the removal of Cr(VI) ions from aqueous solution and also wastewater treatment.

2.2 EXPERIMENTAL METHODS

The adsorption experiments were carried out by batch equilibrium method. 100 mg of adsorbent mixed with 100 mL of the adsorbate solution of desired concentration taken in an iodine flask and the mixture was agitated with different time intervals by

using water-bath shaker with temperature controller at a constant speed of 180 rpm was used for adsorption studies. The solutions were centrifuged at regular time intervals and the residual concentration of Cr(VI) ions present in the filtrate at each stage were determined using UV-Visible Spectrophotometer (Systronics169, India). All experiments were carried out twice. The amount of metal ions adsorption was calculated based on the difference of Cr(VI) ions concentration in aqueous solution before and after adsorption [2]. The experimental variables were considered as follows,

Adsorption capacity is calculated using the following formula,

$$\text{Adsorption capacity } (q_e) = \frac{(C_0 - C_e)}{W} V$$

$$\% \text{ of Removal} = \frac{(C_0 - C_e)}{C_0} 100$$

where, C_0 = Initial concentration of metal ions (mg/L)

C_e = Final concentration of metal ions (mg/L)

V = Volume of the metal ions solution (mL)

W = Weight of the sorbent (g).

III. RESULTS AND DISCUSSION

3.1. Effect of Sorbent Dosage, pH and Agitation Time

These experiments are done by using 25 mg to 150 mg of sorbent, 100 mL of 25 mg/L of Cr(VI) solution and agitation of various time intervals. The results indicate that the optimum dose is fixed as 100 mg due to the quantity of Cr(VI) uptake more [6], the optimum pH is fixed as 2 due to maximum removal of Cr(VI) and the optimum agitation time is fixed as 40 minutes after this time removal of Cr(VI) was constant [7].

3.2. Effect of Initial Concentration and Temperature

The results of initial concentration and temperature with respect of percentage of Cr(VI) removal are shown below in **Table 3.1**. It revealed that, the amount of Cr(VI) adsorbed (q_e) increases with the percentage removal slightly decreases while the increase in initial concentration of Cr(VI) from 5 to 25 mg/L. This indicated that there exists a reduction in immediate solute adsorption owing to the lack of available active sites on the sorbent surface, compared with the relatively large number of active sites required for the high initial concentration of Cr(VI).

Table 3.1 Equilibrium parameters for the removal of Cr(VI) by CASNS

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 CASNS		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
5	0.6006	0.3636	0.0877	4.3994	4.6364	4.9123	87.99	92.73	98.25
10	1.5325	1.2078	0.8961	8.4675	8.7922	9.1039	84.68	87.92	91.04
15	2.9383	2.5487	2.0682	12.0617	12.4513	12.9318	80.41	83.01	86.21
20	4.5877	4.0292	3.3831	15.4123	15.9708	16.6169	77.06	79.85	83.08
25	6.7110	6.2175	5.4513	18.2890	18.7825	19.5487	73.16	75.13	78.19

The percentage removal was dependent on initial concentration of Cr(VI) solution. It increases with increase in temperature. This may be due to the increase in temperature; the rate of sorption increased if the adsorption process is endothermic in nature. The increasing in sorption with temperature may be due to the relative decrease in the escaping tendency of Cr(VI) ions from the solid phase to the bulk phase[8].

3.3. Adsorption Isotherms

Langmuir and Freundlich isotherm models at three different temperatures are shown in the **figure 3.1, 3.2** and **table 3.2**. In Langmuir isotherm, the values of monolayer adsorption capacity (Q_0) decreases with increase of temperature, suggesting that adsorption are favored by lower temperature. The energy of adsorption (b_L) values suggests the affinities of binding sites with the metal ions are favourable.

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 favoured at high temperature. The intensity of adsorption (n) values are greater than unity signifies that the forces between the Cr(VI) ions and sorbent surface are attractive which leads to the favourable adsorption and adsorption process is physical in nature. The goodness of fit of the experimental data is measured by the determination of correlation coefficients. Therefore, the Freundlich model showed better fit followed by Langmuir model and also it indicates that the metal adsorption by the sorbent was governed by physical adsorption [9].

Table 3.2 Results of isotherm models for the adsorption of Cr(VI) on CASNS

Temp. (°C)	Langmuir Isotherm			Freundlich Isotherm		
	Correlation coefficient	Constants		Correlation coefficient	Constants	
	r^2	Q_0 (mg/g)	b_L (L/mg)	r^2	k_f	N
30	0.996	26.737	0.304	0.997	6.218	1.692
40	0.991	23.923	0.517	0.999	7.809	2.011
50	0.977	21.786	1.077	0.991	10.539	2.985

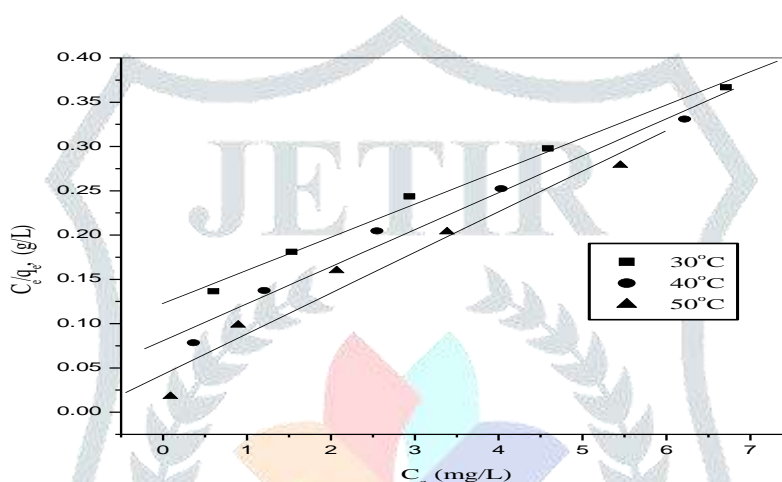


Figure 3.1 Langmuir isotherm for the adsorption of Cr(VI) on CASNS

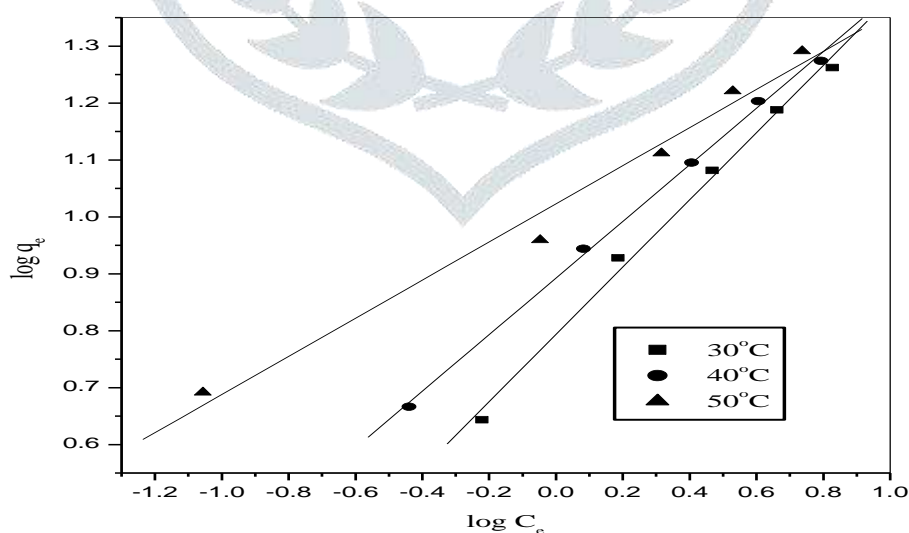


Figure 3.2 Freundlich isotherm for the adsorption of Cr(VI) on CASNS

3.4 Fourier Transform Infrared Spectroscopic (FTIR) Studies

The FTIR spectra of CASNS are taken before and after adsorption of Cr(VI) ions and shown in **figures 3.3 and 3.4**. The FTIR spectrum of CASNS before adsorption spectrum at 3840 - 3750 cm^{-1} indicated the presence of -OH group of nano - sorbent. The aromatic -CH stretching observed at 2923 cm^{-1} . A peak at 2758 - 2677 cm^{-1} indicated the presence of -CH stretching group of aldehydes. The presence of alkynes group at 2359 cm^{-1} and strong acyclic stretching group at 1708 cm^{-1} . The region from 1607 - 1403 cm^{-1} indicated the -C=C stretching groups. The peaks from 683 - 415 cm^{-1} indicated -C-X stretching of halogen groups. After the adsorption of Cr(VI) on CASNS, there is 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 CASNS[10].

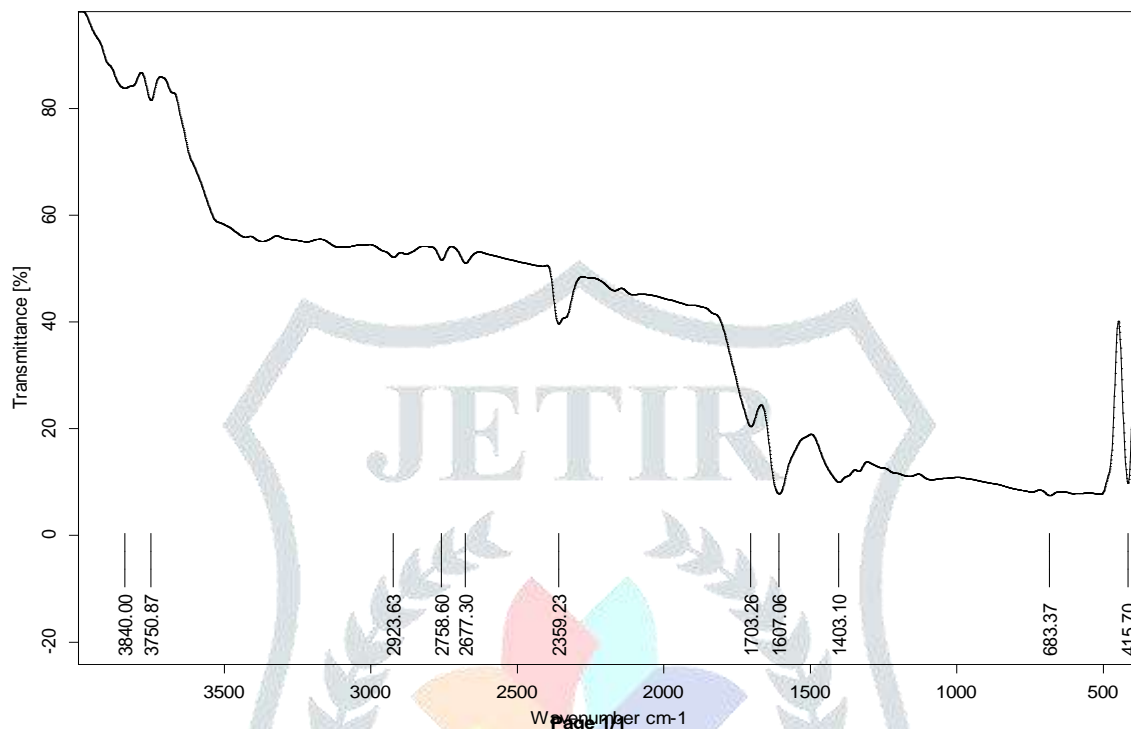
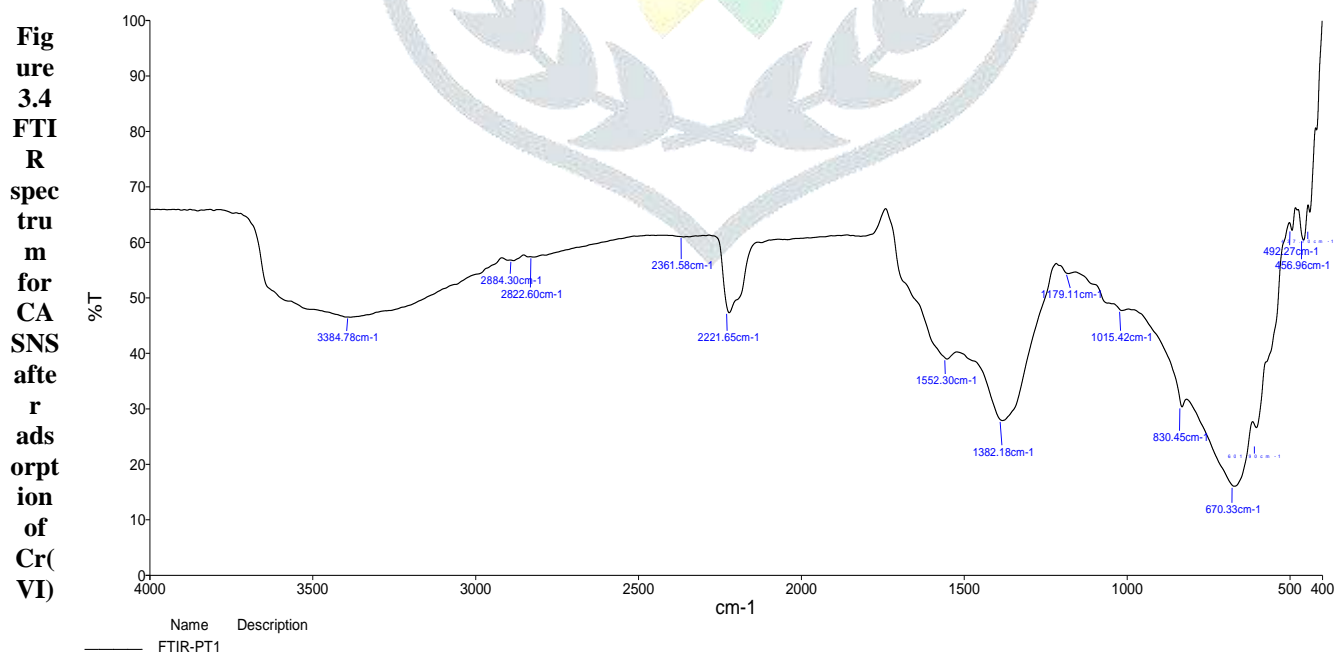


Figure 3.3 FTIR spectrum for CASNS before adsorption of Cr(VI)



3.5.

Scanning Electron Microscope (SEM) Studies

The SEM photographs of CASNS before and after adsorption are shown in the **figures 3.5 and 3.6**. It is clearly stated that the presence of porous structure of the nano - sorbent before adsorption. They have holes and cave type openings on the surface of the nano - sorbent which could definitely increase the surface area available for adsorption. After adsorption of Cr(VI), SEM

photographs are clearly seen that the surface of nano-sorbent were the caves, pores and surfaces of sorbents covered by Cr(VI) ions. It is evident that the adsorbent structure is changed upon the adsorption of Cr(VI) ions.

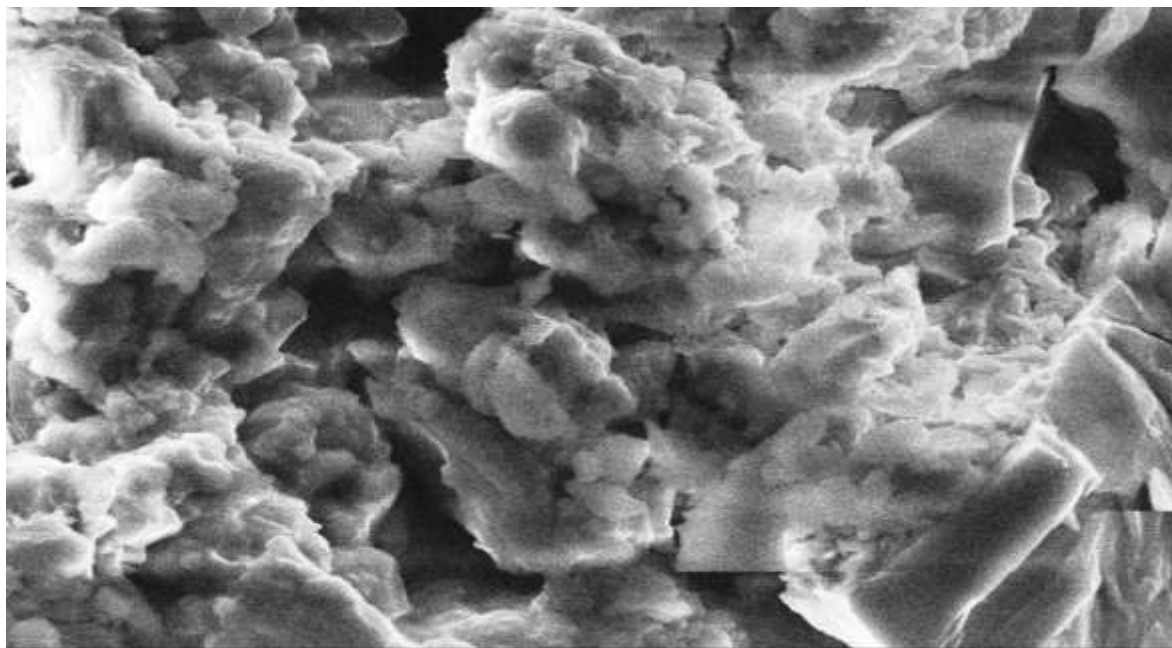


Figure 3.5 SEM photograph before adsorption of Cr(VI) on CASNS

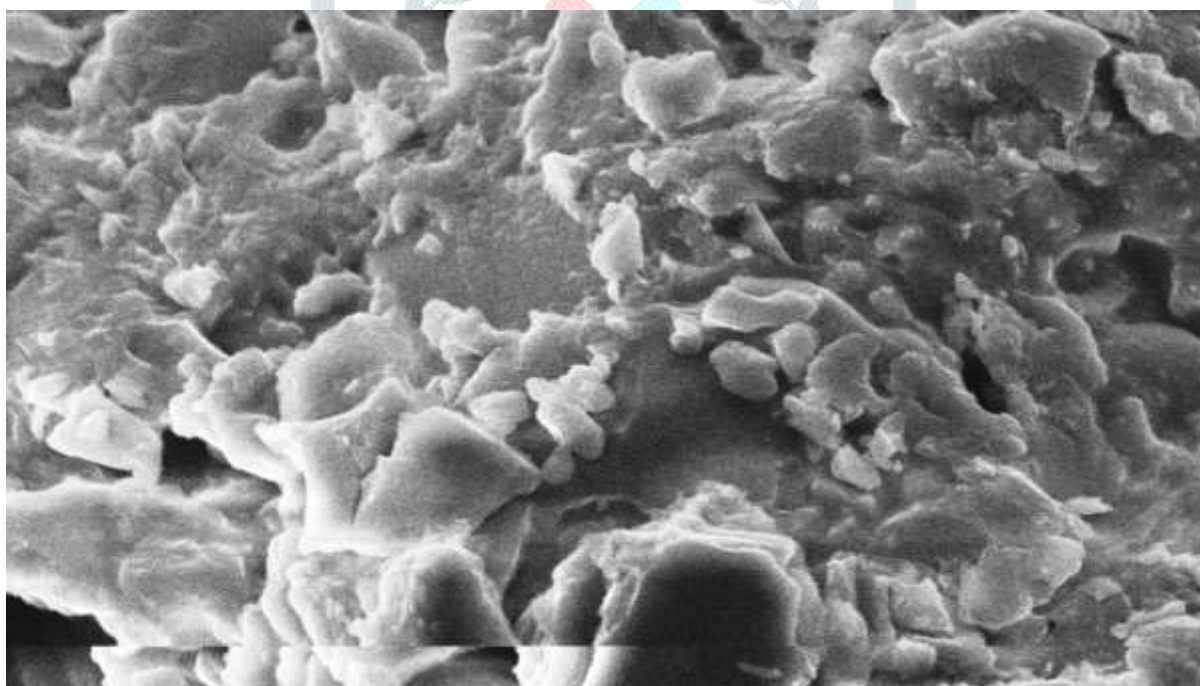


Figure 3.6 SEM photograph after adsorption of Cr(VI) on CASNS

IV.CONCLUSION

Cicca Acida Seeds Nano-sorbent (CASNS) is easily available, environmental friendly and low cost material, could be used as a potential sorbent for the removal of Cr(VI) from aqueous solution. The Freundlich adsorption isotherm model describes the adsorption behaviour with good correlation coefficient followed by the Langmuir model. The optimum pH of the solution is 2, the optimum contact time is 40 minutes and adsorbent dosage is 100 mg used for the removal of Cr(VI). The sorption of Cr(VI) is characterised with FTIR and SEM studies. The percentage of removal of Cr(VI) increased with increase the temperature from 30 to 50°C.

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