International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.12 pp 662-673, 2015

Adsorption Studies on Chromium (VI) removal from Aqueous Solution using Activated Hibiscus sabdariffa Stem Nano Carbon

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Abstract: Batch adsorption experiments were carried to fix the adsorption dosage and also to find the optimum pH. A thermodynamic study was made on the adsorption of Cr (VI) ions in aqueous solution distinctly by the adsorbent such as activated Hibiscus sabdariffa Stem Nano Carbon. The adsorption of Chromium (VI) ions by activated Hibiscus sabdariffa StemNano Carbon increased when temperature was raised up to 60 °C. The thermodynamic study and kinetic models showed that the adsorption of Chromium (VI) ions follows pseudo second order kinetics and it was spontaneous and endothermic in nature.

Keywords: Chromium ions; Activated Hibiscus sabdariffa StemNano Carbon; adsorption models; equilibrium.

1. Introduction

With the world population set to break seven billion sometime next year, the management and use of natural resources is pushing to the forefront of world concern. With more people entering the worldwide market, an increase in products to meet their needs is inevitable. Individuals, businesses, and industries are seeing not only the long term monetary benefit of using resources wisely, but also the aesthetic and health benefits that come from environmental stewardship. This is seen from the changing of light bulbs at home to the tightening of national government and world standards for environmental quality [1].With potable water essential to life, no where else are these standards more important than the area of water quality. Not only is water essential for life, it has become the primary workhorse of industries around the world as a working fluid, transport medium, heat transfer fluid, cleaning agent, etc. Unfortunately this has often led to the degradation of water quality as harmful effluents are returned to the environment with various contaminants from these processes [1]. One of the most startling groups of water contaminants are those of chromium due to their accumulation in biological systems and their toxicity even at relatively low concentrations [2]. Sources of chromium water contamination are varied and can be seen in every step of production from mining, purification and processing, to chromium finishing and electroplating, and even end use [3]. Electroplating, the process by which chromium is deposited on a surface via an electric current, has been a major contributor to water contamination by a wide variety of chromium ions. Industry currently treats electroplating wastewater via a lime-soda precipitation technique that, although effective, essentially shifts the problem to large volumes of sludge containing chromium[4]. Not only does this method not solve the problem of chromium pollution, electroplating industries also must deal with the loss of the useable chromium which is becoming increasingly expensive due to a decrease in the quality of chromium ores [5]. What is needed is an economical method, not only for the removal of chromium from waste water, but also the recovery of thischromium.

In the present investigation the adsorption of Chromium ion on activated nano carbon prepared from *Hibiscus Sabdariffa Stem*by carbonization with con. Sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared [6]. The amounts and rates of adsorption of Chromium using above *AHSNC*from water were then measured. Three simplified kinetic models including pseudo first order, Pseudo second order equations and Elovich equations were used to describe the adsorption process.

2. Materials and methods:

All the reagents used for the current investigation were of GR grade from Scientific Equipment Company, Trichy, India. Stock solution (1000 mg/L) of Cr(VI) ions was prepared by dissolving 5.6578g of $K_2Cr_2O_7$ in double distilled water. The solution was further diluted to the required concentrations before use. Before mixing the adsorbent, the pH of each Cr (VI) solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution.

2.1 Preparation of Adsorbent:

Hibiscus Sabdariffa Stem (PulichaKeerai) was collected from local area of Thiruvarur district, Tamilnadu, India. It was dried, charred with excess quantity of concentrated Sulphuric acid keeping at 120°C for 10 hours. Then the resultant carbon was washed with excess quantity of distilled water and dried at 110°C for 1 hour and the material obtained was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to remove any residual acid. The material was thoroughly washed with hot distilled water until washings were nearly of neutral effect. To eliminate surface groups by thermal activation, the carbonized material was treated at 1100 ºC for 6 hrs in a furnace. The resulting carbons were ground in a mill, washed with pure water and finally dried at 120 ºC.

2.2 Adsorbent characterization

Adsorbent characterization was performed by means of spectroscopic and quantitative analysis. The surface area of the adsorbent was determined by Quanta chrome surface area analyzer. The pH of aqueous slurry was determined by soaking 1g of biomass in 50 mL distilled water, stirred for 24 h and filtered and the final pH was measured. The physico-chemical characteristics of the adsorbent were determined using standard procedures. The concentrations of sodium and potassium were determined by Flame Photometer (Model No. Systronics126). The equilibrium Cr(VI) concentration was determined by using 1,5-diphenylcarbazide as the complexing agent and a UV-Vis Spectrophotometer (Systronics, Vis double beam Spectrophotometer2203) at a λ_{max} of 540 nm. For stirring purpose magnetic stirrer was used. The pH of zero-point charge or pH_{ZPC} was determined based on the previous method [7].

Table: 1 physicochemical characteristics of adsorbent

Analysis	Value
pH_{slurry}	4.9237
pH_{zpc}	4.0123
Specific gravity	0.9251
Moisture content, %	0.0689
Bulk density, g cm^{-3}	0.1865
Particle density, g cm^{-3}	0.2632
Conductivity, µS/cm	36.263
Surface area, m^2/g	20.214
Na^+, mg L^{-1}	95.364
K^+, mg L^{-1}	420.24

2.3 Batch Adsorption experiments:

The Batch adsorption experiments were conducted in 250 mL Erlenmeyer flask with 50mL of standard chromium solution and were agitated in a thermo state – controlled shaker at 120 rpm. All experiment were conducted at 30-60 ºC, unless otherwise was stated.

The effect of initial pH on the adsorption of the Chromium ions onto the activated nano carbon was studied across a pH range of 2.0 – 9.0 with a fixed adsorbent concentration (25 mg/50ml of 50mgL^{-1} of chromium ion solution). The pit value of the initial chromium solution (50mgL^{-1}) was adjusted using a 0.1M HCl or NaOH solution. *AHSNC*(0.0250g) was then added to the solution and agitated for enough time to achieve equilibrium. The effect of the agitation period was also studied at a constant concentration of 50 mg L^{-1}chromium solution and a fixed adsorbent concentration of 25mg/50mL at the optimum pH. After agitation the sample solution was withdrawn at different time intervals (10-60min) and centrifuged at 3600 rpm for 10 min. Subsequently an aliquot of the supernatant was used for determination of the remaining Chromium ion concentration, and the remainder was poured back into the original solution. The determination of the effect of the initial concentration of the uptake of the chromiumion was conducted by varying the chromium concentration from 25 to 125 mg L^{-1} at a constant *AHSNC*dosage of 25 mg at optimum pH and agitation period. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms from 303 – 333K at a chromiumion concentration of 25-125mg/L.

The percentage removal of the chromium ion and the amount of chromium taken up by the adsorbent was calculated by applying following equations.

$$\%\,\mathrm{Removal} = \frac{C_i - C_t}{C_i} \times 100 \qquad (1)$$

$$Q = \frac{(C_i - C_t)}{m} V \qquad (2)$$

Where, C_i and C_t are the initial and liquid phase concentrations of Cr(VI) at time ‘t’ (mg L^{-1}) Q is the amount of chromium ion adsorbed on the adsorb of at any time (mg g^{-1}), m(g) the mass of the adsorbent sample used and V the volume of the chromium solution (L).

3. Results and Discussion:

3.1 Effect of contact time:

The Fig. 1 shows that the adsorption of Chromium ion from an aqueous solution reached equilibrium with in 40 min. The contact time significantly affected the chromiumion uptake. The adsorption of chromium by all studied adsorbents sharply increased in the first 30 min. The rapid adsorption at the initial stage was probably due to the great concentration gradient between the chromiumion in solution and the chromium in the adsorbent because there must be a number of vacant sites available in the beginning. The progressive increase in adsorption and, consequently, the attainment of equilibrium adsorption is initially due to the limited mass transfer of the chromium ions from the bulk solution to the external surface of the adsorbent, and is subsequently due to the slower internal mass transfer within the adsorbent particles[8].

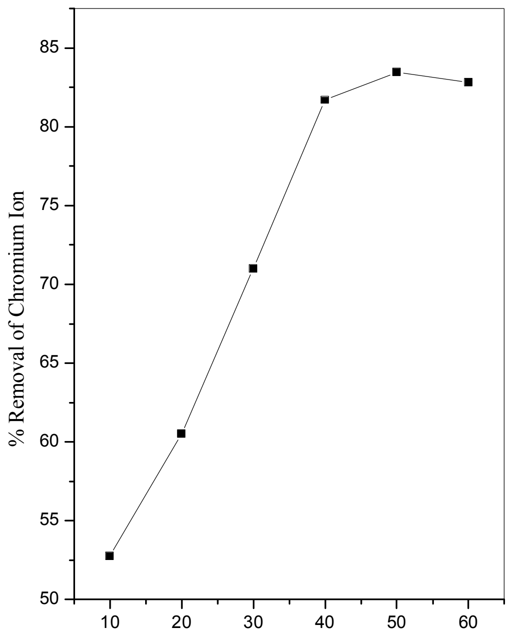

Fig:1-Effect of Contact Time on the Removal of Chromium ion
[Cr]=50 mg/L; adsorbent dose=25mg/50ml; pH-6.5;Temp 30^{0}C

3.2 Effect of initial chromiumion concentration:

Table: 2. Equilibrium Parameters for the Adsorption of Chromium ion onto *AHSNC*

M_0	Ce (Mg / L)				Qe (Mg / g)				Removed (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
25	1.3003	1.1298	0.9842	0.8939	47.399	47.740	48.031	48.2122	94.799	95.481	96.063	96.424
50	6.1555	5.4338	4.4615	3.7646	87.689	89.132	91.077	92.4708	87.689	89.133	91.077	92.471
75	13.772	12.164	10.619	9.255	122.45	125.67	128.76	131.489	81.637	83.781	85.841	87.659
100	26.791	24.752	10.619	20.483	146.41	150.49	178.76	159.033	73.209	75.248	89.381	79.517
125	41.806	39.225	22.610	34.277	166.38	171.55	204.78	181.446	66.555	68.620	81.912	72.578

The experimental results of adsorption of Chromium (VI) ions on *AHSNC* at various initial concentration (25, 50, 75, 100 and 125 mg/L) for chromium ions in terms of equilibrium data are given in table.2.The initial concentration provides an important driving force to overcome the mass transfer resistance of all of the molecules between the aqueous and solid phase, the Fig.1 plots the percentage of chromium removal versus the initial chromium concentration of the adsorbents. While increasing the initial chromiumion concentration from 25.0 to 125.0 mgL^{-1}, the percentage of chromium ion removal by the*AHSNC* decreased, the percentage removal of the chromium decreased slowly in the concentration range of 25-125 mgL^{-1}, but reduced rapidly from 25 to 75 mgL^{-1}chromium ionremovals is highly concentration dependent at higher concentrations. This can be explained by the fact that the adsorbent has a limited number of active sites that become saturated above a certain concentration. At low chromium concentrations, the ratio of surface active sites to the total chromium ions in the solution is high and hence all chromium ions may interact with the active functional groups on the surface of the carbon and be removed from the solution. However, with increased chromium concentrations, the number of active adsorption sites is not enough to accommodate the chromium ions. Therefore, the initial chromium concentration was fixed at 50.0 mg L^{-1} in the following experiments[9].

3.3 Effect of adsorbent dose

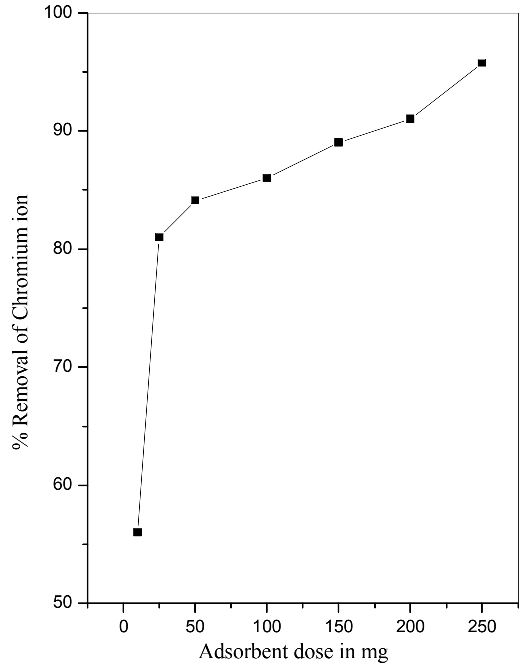

Fig.2-Effect of adsorbent dose on the removal of Chromium Ion
[Cr]=50mg/L: Contact time=60 min: pH=6.5: Temp 30^0C

In this study, Five different adsorbent dosages were selected ranging from 0.010 to 0.250 g while the Cr(VI) concentration was fixed at 50 mg/L. The results are presented in Fig. 2. It was observed that percentage of Cr(VI) ion removal increased with increase in adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent. This may be due to the decrease in total adsorption surface area available to Cr(VI) ion resulting from overlapping or aggregation of adsorption sites. Thus with increasing adsorbent mass, the amount of Cr(VI) ion adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in q_e value with increasing adsorbent mass concentration. Furthermore maximum Cr(VI) ion removal (95.18%) was recorded by 0.025 g *Hibiscus Sabdariffa Stem* Nano Carbon and further increase in adsorbent dose did not significantly change the adsorption yield. This is due to the non-availability of active sites on the adsorbent and establishment of equilibrium between the Cr(VI) ion on the adsorbent and in the solution[10]

3.4 Effect of initial solution pH:

The pH of an initial chromium solution exerts profound influence on the adsorptive uptake of adsorbate molecules, presumably due to its influence on the surface properties of the adsorbent and ionization/ dissociation of the adsorbate molecule, Therefore investigation of the effect of pH on the adsorption process is helpful to determine the optimized operational parameters for application and to reveal the adsorption mechanism[11], Adsorption of Chromium ion onto *Hibiscus Sabdariffa Stem* Nano Carbon was carried out to examine the effect of pH (in a range of 2-9) on the removal of chromium ions from aqueous solution, As seen in fig 3. Chromiumion removal by all studied adsorbents decreased significantly with increasing pH, especially between pH 2.0 and 7.0, the maximum removal percentages of Chromium onto *AHSNC*, were 80 to 89% respectively.

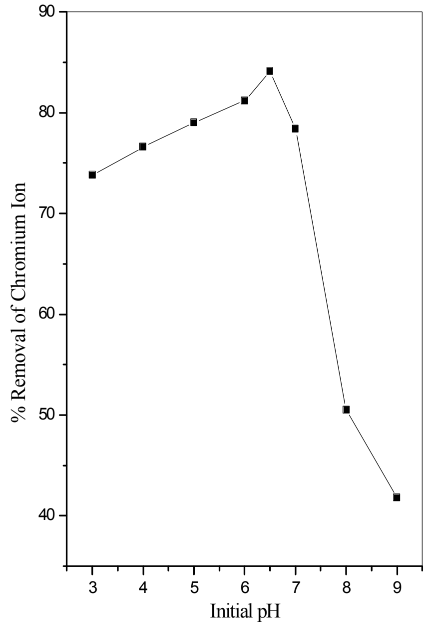

Fig.3-Effect of Initial pH on the removal of Chromium Ion
[Cr]=50mg/L: Contact time=60 min: dose=25mg/50ml

3.5 Effect of other ions:

The effect of other ions like Cl^- on the adsorption process studied at different concentrations. The ions added to 50mg/L of chromium ion solutions and the contents were agitated for 60 min at 30 °C. The results had shown in the (fig.4) reveals that low concentration of Cl^- does not affect the percentage of adsorption of chromium ion on activated *AHSNC*, because the interaction of Cl^- at available sites of adsorbent through competitive adsorption is not so effective. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions [12].

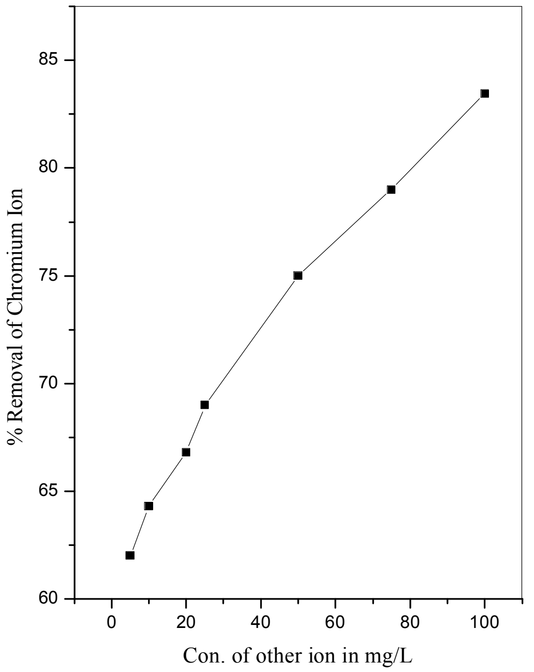

Fig.4-Effect ionic strength on the adsorption of Chromium ion
[Cr]=50 mg/L;Contact time=60 min;Dose=25 mg/50 ml

3.6 Effect of Temperature:

It is well known that temperature plays an important role in the adsorption process. The removals of chromium ions. The chromium ions removal increase rapidly from 303K to 333K, this result suggests that the experimental temperature had a greater effect on the adsorption process implying that the surface coverage increased at higher temperatures. This may be attributed to the increased penetration of chromium ions inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process. Similar result has been reported in the literature.

3.7 Adsorption Kinetic and isotherm models:

3.7.1 Adsorption Isotherms

Adsorption isotherms describe the interaction of adsorbate with adsorbents. The experimental adsorption data of Cr (VI) ions on the *Hibiscus Sabdariffa Stem*Nano Carbon were analyzed by Langmuir and Freundlich.

3.7.2 Langmuir Isotherm

Table: 3. Langmuir and Freundlich Isotherm Parameter for the Adsorption of Chromium ion onto *AHSNC*

Temp. (C°)	Langumuir Parameter		Fruendlich Parameter	
	Q_m	B	K_f	N
30°	184.88	0.1707	44.276	2.7336
40°	189.68	0.1903	47.165	2.7429
50°	253.98	0.1542	47.657	2.1049
60°	198.36	0.2492	53.668	2.7472

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules[13]. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes, the values are in table 3. The adsorption isotherm data were analyzed by the Langmuir isotherm model in the linearised form,

$$C_e/q_e = C_e/q_{max} + 1/(b\ q_{max}) \qquad (3)$$

Where,q_e is the equilibrium adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium Cr (VI) ion concentration in solution (mg/l), q_{max} is the maximum amount of Chromium ion that could be adsorbed on the adsorbent (mg/g) and b is the Langmuir adsorption equilibrium constant (L/mg). In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L by the equation

$$R_L=(1/(1+bCo)) \qquad (4)$$

Where, C_o (mg/L) is the highest initial concentration of adsorbent and b (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

$R_L > 1$ Unfavorable adsorption

$0 < R_L < 1$ Favorable adsorption

$R_L = 0$ Irreversible adsorption

$R_L = 1$ Linear adsorption

The R_L values between 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in table 4. High b values indicate high adsorption affinity the monolayer saturation capacity Q_m were around.

Table: 4. Dimensionless Separation factor (R_L) for the Adsorption of Chromium ion onto *AHSNC*

(C_i)	Temperature °C			
	30°C	**40°C**	**50°C**	**60°C**
25	0.1049	0.0951	0.1148	0.0743
50	0.0553	0.0499	0.0609	0.0386
75	0.0376	0.0338	0.0414	0.0261
100	0.0285	0.0256	0.0314	0.0197
125	0.0229	0.0206	0.0253	0.0158

3.7.3 Freundlich Isotherm

The Freundlich model can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface[14]. The experimental data were analyzed by Freundlich isotherm model in the linearised form,

$$\log q_e = 1/n \log C_e + \log K_F \qquad (5)$$

Where, K_F is the Freundlich adsorption constant and it is the maximum adsorption capacity of chromium ions (mg/g) and n is the constant illustrates the adsorption intensity (dimensionless). The values are presented in table 3 shows the favorability of the adsorption process.

3.7.4 pH optimization

The removal of Cr(VI) at different pH was studied in batch mode. A 50mL of test solution of fixed concentrations was treated with 0.025 g of *AHSNC* and agitated intermittently for 60 min. The contact time and conditions were selected on the basis of preliminary experiments, which demonstrated that equilibrium was established in 40 min. After this period the solutions then both phases were separated by filtration. The chromiumion content of the filtrate was determined by atomic spectrometry. The chromium concentration retained in the sorbent phase (q_e, mg/g) was calculated by using Eq. (1)

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (6)$$

Where, C_0 and C_e are the initial and final (equilibrium) concentrations of the chromium ion in solution (M), V the solution volume (L) and m is the mass of Activated *Hibiscus Sabdariffa Stem* Nano Carbon (g).

3.8 Adsorption Thermodynamics

The thermodynamic parameters for the adsorption of Cr (VI) ions by Activated *Hibiscus Sabdariffa Stem Nano* Carbon were determined using the following equations:

$$K_D = q_e/C_e \qquad (7)$$

$$\Delta G^o = -RT \ln K_D \qquad (8)$$

$$\ln K_D = (\Delta S^o/R) - (\Delta H^o/RT) \qquad (9)$$

where, K_D is the distribution coefficient for the adsorption in g/L, ΔG^o is the Gibbs free energy in J/mol,R is the universal gas constant in J/mol K, T is the absolute temperature in K, ΔS^o is the entropy change in J/mol K and ΔH^o is the enthalpy change in kJ/mol [15]. The values of Gibbs free energy (ΔG^o) for various temperatures were calculated from the experimental data. The values of enthalpy change (ΔH^o) and entropy change (ΔS^o) were estimated from the slope and intercept of the plot of ln K_D Vs 1/T. The estimated thermodynamic parameters were tabulated and shown in table 5, the negative values of Gibbs free energy change (ΔG^o) obtained for the adsorption of Cr (VI) ions by Activated *Hibiscus Sabdariffa Stem*Nano Carbon at various temperatures had shown the spontaneous nature of the adsorption process. The positive values of enthalpy change ($\Delta H°$) obtained for the adsorption of Cr (VI) ions by Activated *Hibiscus Sabdariffa Stem*Nano Carbon at various temperatures indicated that the adsorption reactions were endothermic. The positive values of entropy change (ΔS°) for the adsorption of Cr (VI) ions by Activated *Hibiscus Sabdariffa Stem*Nano Carbon at various temperatures showed the increased randomness at solid liquid interphase during the sorption processes of Cr (VI) ions on the adsorbent *AHSNC*. This is a direct consequence of (i) opening up of structure of adsorbent beads (ii) enhancing the mobility and extent of penetration within the adsorbent beads and (iii) overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion [16].

Table: 5. Thermodynamic Parameter for the Adsorption of Chromium ion onto *AHSNC*

C_0	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	-7312.8	-7938.5	-8579.0	-9121.4	11.0848	60.763
50	-4945.9	-5476.1	-6238.5	-6943.8	15.512	67.337
75	-3758.4	-4273.1	-4839.5	-5428.0	13.124	55.656
100	-2532.36	-2893.4	-5720.6	-3755.1	17.819	67.753
125	-1733.533	-2036.04	-4056.10	-2694.71	13.600	51.038

The adsorption of Cr (VI) ions by Activated *Hibiscus Sabdariffa Stem*Nano Carbon slightly increased when temperature was raised up to 60 °C. It might be due to the generation of new active sites on the adsorbent surface and also due to the increased rate of pore diffusion. But when the temperature was further raised, adsorption processes had slightly increased. It showed that the adsorption processes of Cr (VI) ions by Activated *Hibiscus Sabdariffa Stem*Nano Carbon were endothermic reactions and physical in nature which involved the strong forces of attraction between the sorbate-sorbent molecules.

3.9 Kinetic modeling in a batch system

In order to investigate the mechanism of adsorption kinetic models are generally used to test experimental data. Pseudo-first-order and pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations [17]. The pseudo-first-order rate Lagergren model is:

$$\frac{dq}{dt} = k_1,ads(q_e - q) \qquad (10)$$

Where, q (mg/g) is the amount of adsorbed chromium on the adsorbent at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption. The integrated form of Eq. (10) is:

$$\log(q_e - q) = \log q_e - \frac{k_1,ads}{2.303} t \qquad (11)$$

q_e the equilibrium sorption uptake, is extrapolated from the experimental data at time t = infinity. A straight line of $\log(q_e$ - q) versus t suggests the applicability of this kinetic model. q_e and k_1,ads can be determined from the intercept and slope of the plot, respectively. The pseudo-second order kinetic model is expressed as:

$$\frac{dq}{dt} = k_2,ads(q_e - q)^2 \qquad (12)$$

Where, $k_{2,ads}$ (g/mg min) is the rate constant of second-order adsorption. The integrated form of Eq. (12) is:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2,ads t \qquad (13)$$

Eq. (13) can be rearranged and linearized to obtain:

$$\frac{t}{q} = \frac{1}{k_2,ads q_e^2} + \frac{1}{q_e} t \qquad (14)$$

The plot t/ q versus t should give a straight line if second order kinetic model is applicable and q_e and $k_{2,ads}$ can be determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model the experimental estimation of q_e is not necessary.

3.9.1 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t/ d_t = \alpha \exp (-\beta q_t) \qquad (15)$$

Where, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation. Chien and Clayton [18] assumed αβt>>t and by applying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(15) becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \qquad (16)$$

If Cr (VI) ions adsorption fits with the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/β)and an intercept of (1/β)ln (αβ). The Elovich model parameters α, β, and correlation coefficient (γ) are summarized in table 6. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models. This may be due to increase the pore or active site on the *AHSNC* adsorbent.

Table: 6. The Kinetic Parameters for the Adsorption of Chromium ion onto *AHSNC*

C_0	Temp °C	Pseudo Second Order				Elovich Model			Intraparticle Diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
25	30	51.477	0.0032	0.9889	8.4749	171.335	0.1581	0.9912	0.1486	0.9886	1.7072
	40	51.569	0.0034	0.9910	8.9190	241.489	0.1656	0.9933	0.1403	0.9907	1.7243
	50	51.624	0.0036	0.9881	9.4743	348.196	0.1733	0.9904	0.1325	0.9878	1.7406
	60	51.878	0.0035	0.9892	9.4376	320.606	0.1704	0.9915	0.1344	0.9889	1.7393
50	30	95.274	0.0017	0.9883	15.2991	281.168	0.0841	0.9906	0.1517	0.9880	1.6670
	40	96.665	0.0017	0.9894	15.7686	337.004	0.0850	0.9917	0.1472	0.9891	1.6816
	50	98.315	0.0018	0.9885	17.1853	463.690	0.0868	0.9908	0.1403	0.9882	1.7042
	60	99.949	0.0018	0.9906	17.5407	446.425	0.0846	0.9929	0.1417	0.9903	1.7092
75	30	134.253	0.0011	0.9887	19.5440	263.467	0.0564	0.9910	0.1630	0.9884	1.6154
	40	136.969	0.0011	0.9880	21.2741	348.897	0.0573	0.9903	0.1556	0.9877	1.6402
	50	140.167	0.0012	0.9880	22.938	433.185	0.0574	0.9903	0.1507	0.9877	1.6615
	60	142.129	0.0010	0.9899	19.4326	586.293	0.0613	0.9922	0.1391	0.9896	1.6738
100	30	162.787	0.0008	0.9882	20.5235	175.568	0.0425	0.9905	0.1838	0.9879	1.5305
	40	166.607	0.0008	0.9893	21.7908	210.119	0.0426	0.9916	0.1778	0.9890	1.5530
	50	170.669	0.0008	0.9904	23.2943	253.726	0.0426	0.9927	0.1720	0.9901	1.5758
	60	174.318	0.0009	0.9895	26.062	350.714	0.0434	0.9918	0.1628	0.9892	1.6061
125	30	187.422	0.0006	0.9919	21.0565	132.906	0.0344	0.9942	0.2021	0.9916	1.4563
	40	192.686	0.0006	0.9920	21.9611	145.089	0.0339	0.9943	0.1991	0.9917	1.4742
	50	199.066	0.0006	0.9906	21.9964	139.079	0.0324	0.9929	0.2023	0.9903	1.4806
	60	202.357	0.0006	0.9913	24.5885	184.372	0.0332	0.9936	0.1910	0.9910	1.5137

3.9.2 The Intraparticle diffusion model

The kinetic results were analyzed by the [19] Intraparticle diffusion model to elucidate the diffusion mechanism. The model is expressed as:

$$q_t = K_{id}\, t^{1/2} + I \qquad (17)$$

Where, I is the intercept and K_{id} is the intra-particle diffusion rate constant. The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. The calculated diffusion coefficient K_{id} values are listed in Table 6. The K_{id} value was higher at the higher concentrations. Intraparticle diffusion is the sole rate-limiting step if the regression of q_t versus $t^{1/2}$ is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that Intraparticle diffusion was not the only rate-limiting step.

It is clear from the Table 6 that the pseudo- second-order kinetic model showed excellent linearity with high correlation coefficient (R^2>0.99) at all the studied concentrations in comparison to the other kinetic models. In addition the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetic model. It is also evident from Table 6 that the values of the rate constant k_2 decrease with increasing initial Cr (VI) ion concentrations. This is due to the lower competition for the surface active sites at lower concentration but at higher concentration the competition for the surface active sites will be high and consequently lower sorption rates are obtained.

3.10 Desorption studies

In order to assess the reusability of chromium-loaded Activated *Pistia Stratiotes Leave*Nano Carbon biomass desorption experiments were carried out. The effect of strength of desorbing solution (NaOH) on the recovery of Cr(VI) is shown in Fig. 5. It is evident from the above figure that when the strength of the desorbing solution increased from 0.5 to 2.0 M, Cr (VI) desorption percentage increased from 28.5% to 79%. Thus a significant amount of chromium is being desorbed, which shows that the *AHSNC* biomass can be effectively reused after desorption[20].

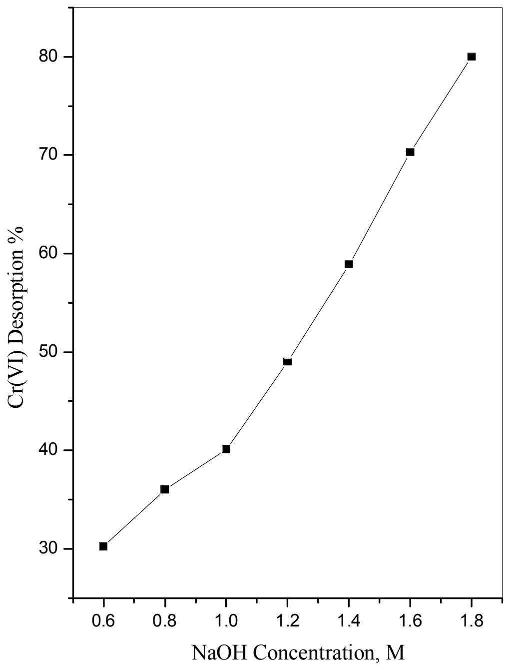

Fig.5- Effect of NaOH Concentration on Cr(VI) desorption

4. Conclusion

This study is revealed that *Hibiscus Sabdariffa Stem* Nano Carbon can be used as an alternative adsorbent for chromium ions removal in industrial wastewater due to its efficiency of Chromium ions adsorption in aqueous solution. The adsorption of Cr (VI) ion onto *AHSNC* was affected by pH, adsorbent dosage, and temperature. The Cr (VI) uptake percentage by *AHSNC* was found to be 89.804% when 0.025 g of adsorbent was agitated with 50mL of Cr(VI) ion solution of 50 mg/L for 60 min at pH. The adsorption data was fitted well by pseudo-second order kinetic indicating that chemical reaction is involved in the adsorption process. The adsorption process was found to be controlled by three steps of diffusion mechanisms. The temperature equilibrium data fitted well with Langmuir isotherm model and the monolayer adsorption capacity was found to be 207.88 mg/g at 333 K. An increase of Q_m value with the increase of temperature implied that chemisorptions occurs in the process. Thermodynamic constants were also evaluated using equilibrium constants from Langmuir isotherm. The negative values of ΔG° indicated the spontaneity of Cr(VI) ion adsorption process and the positive values of ΔH° and ΔS° showed the endothermic nature. This study illustrated that it is possible to remove Chromium ion from aqueous solution with *Hibiscus Sabdariffa Stem*Nano Carbon.

Acknowledgement

The authors sincerely thanks to the Principal, Thiru.Vika.Govt Arts College, Kidarankondan, Tamilnadu, India for the successful completion of this research work.

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