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Removal of hexavalent chromium from aqueous system by low cost adsorbent (AAVNS)

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ABSTRACT

The presence of toxic heavy metals such as chromium (VI) contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies is one of the most important environmental problems. Adsorption is one of the effective techniques for chromium (VI) removal from wastewater. Batch adsorption experiments were carried to fix the adsorption dosage and also to find the optimum pH. The equilibrium data satisfied both Langmuir and Freundlich isotherm models. The experimental data were analysed using the pseudo –second order kinetic model. The thermodynamic study has showed that the metal adsorption phenomenon onto AAVNS was favourable, endothermic and spontaneous.

Keywords: Chromium, Acid Activated Vitex Negundo Stem (AVVNS), adsorption models, equilibrium.

INTRODUCTION

Nowadays pollution due to heavy metal contaminants from aqueous solutions is one of the most important environmental concerns due to their high toxicity and impact on human health. Cr(VI) is known to be one of the heavy metal and is widely used in many industries including electroplating, leather tanning, dye, cement and photography industries. The effluents from these industries usually contain considerable amount of chromium, which ultimately spreads into the environment through soils and water streams and finally accumulates along the food chain which causes human health hazards.

The hexavalent form of chromium has been considered more hazardous to public health due to its mutagenic and carcinogenic properties [1-2]. The recommended limit of Cr (VI) in waste water is only 0.05 mg/L. But the industrial and mining effluents contain much higher concentrations compared to the permissible limit. Therefore, the concentrations of Cr(VI) must be reduced to levels that satisfy environmental regulations for various bodies of water.

In general, chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation, etc. [3]. These methods are, however, cost intensive and are unaffordable for large scale treatment of wastewater that is rich in chromium (VI). Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular [4,5]. Other commercial adsorbents are recently reported to have been used in industries, although their versatility and adsorption capacity are generally less than those of activated carbon [6].

In the present investigation the adsorption of Chromium ion on activated carbon prepared from Acid Activated Vitex Negundo Stem. By carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared [7]. The amounts and rates of adsorption of Chromium using above activated carbon 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.

EXPERIMENTAL SECTION

Stock solution (1000 mg/L) of Cr(VI) 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. Adsorbent

The Vitex Negundo Stem collected from nearby Thiruvarur district was Carbonized with concentrated Sulphuric Acid and washed with water and activated around 400°C in a muffle furnace for 5 hrs. Then it was taken out, ground well to fine powder and stored in a Vacuum desiccators.

Batch Adsorption procedure

Batch adsorption studies were carried out in 250 mL glass-stopper Erlenmeyer flasks with 50 mL of the working Cr(VI) ion solution of different concentrations ranging from 25mg/L to 125 mg/L. A weighed amount (0.025 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 1 hours. The influence of pH (3.0–9.0), initial Cr(VI) concentration (50, 75, 100, 125 mgL^{-1}), contact time (10, 20, 30,40, 50, 60min) , adsorbent dose (0.10, 0.15, 0.20, 0.250 g/50 mL) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual Cr(VI) concentration in the solution. The amount of Cr(VI) ions adsorbed in milligram per gram was determined by using the following mass balance equation:

$q_e = (C_i-C_e)V/m$-----------------------(1)

Where Ci and Ce are Cr(VI) concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of Cr(VI) ions was calculated from the following equation:

Removal (%) = $(C_i-C_e)/C_i$ x 100-------------------(2)

Effect of contact time .

The uptake of Cr(VI) ion as a function of contact time is shown in Figure 1

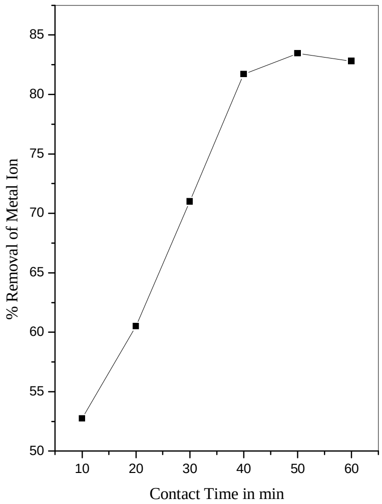

Fig:1-Effect of Contact Time on the Removal of Metal ion
[M]=50 mg/L; adsorbent dose=25mg/50ml; pH-6.5;Temp 30^0C

As illustrated in Figure 1, adsorption of Cr(VI) ion increased with rise in contact time up to 50 min. Further increase in contact time did not increase the Cr(VI) adsorption process. The equilibrium was nearly reached after 50 min for five different initial Cr(VI) ion concentrations. Hence, in the present work, 50 min was chosen as the equilibrium time. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In the later stage the sorption is likely an attachment-controlled process due to less available sorption sites. Similar findings for Cr(VI) adsorption onto other adsorbents have been reported by other investigators.[8,9]

Effect of initial Cr(VI) ion concentration

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of different initial Cr(VI) ion concentration on adsorption of Cr(VI) ion onto *AAVNS* is presented in Table 1. The percentage removal of Cr(VI) ion decreased with increasing of the initial Cr(VI) ions concentration. This can be explained by the fact that all adsorbents have a limited number of active sites and at a certain concentration the active sites become saturated. However, the adsorption capacity at equilibrium increased with increase in initial Cr(VI) ion concentration.

Table: 1. Equilibrium Parameters for the Adsorption of Chromium ion

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	1.453	1.265	1.038	1.093	47.09	47.470	47.923	47.813	95.184	94.941	85.847	87.626
50	5.283	4.841	3.217	3.009	89.43	90.307	93.564	93.980	85.433	90.307	93.564	93.980
75	11.63	10.35	10.00	9.077	126.7	129.28	129.98	131.84	84.484	86.188	86.655	87.897
100	25.76	23.26	10.00	19.62	148.4	153.46	179.98	160.75	74.231	76.732	89.991	80.375
125	41.87	37.76	21.76	30.76	166.2	174.46	206.47	188.47	66.500	69.784	82.588	75.388

It is possible that the initial concentration of the metal ions provides the necessary driving force to overcome the mass transfer resistance of Cr(VI) ion between the aqueous and the solid phase. Fig.1 plots the percentage of metal removal versus the initial metal concentration of the adsorbents. While increasing the initial metal concentration from 25.0 to 125.0 mgL^{-1}, the percentage of metal ion removal by the AAVNS from 95.18% to 66.50%, 94.94% - 69.78% and 85.84% - 82.58% respectively, the percentage removal of the metal decreased slowly in the concentration range of 25-125 mgL^{-1}, but reduced rapidly from 25 to 75 mgL^{-1} metal removal is highly concentration dependent at higher concentrations. However, with increased metal concentrations, the number of active adsorption sites is not enough to accommodate the metal ions. Therefore, the initial metal concentration was fixed at 50.0 mg L^{-1} in the following experiments.

3.3 Effect of adsorbent dose

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.

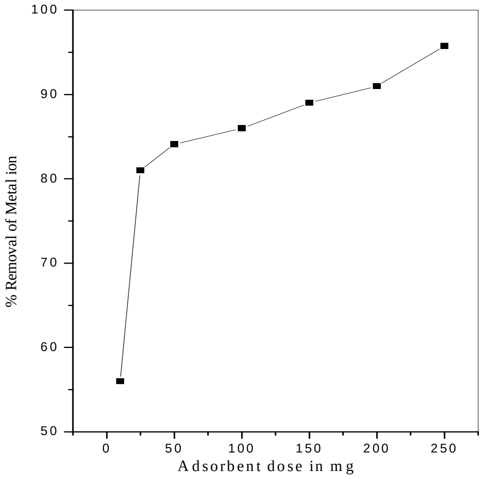

Fig.2-Effect of adsorbent dose on the removal of Metal Ion
[M]=50mg/L: Contact time=60 min: pH=6.5: Temp 30^{0}C

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

AAVNS 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.

Effect of pH

The pH of the solution is one of the most critical parameters in the adsorption process, which affects surface charge of the adsorbent material and the degree of ionization and specification of adsorbate [10]. The effect of pH on the removal efficiency of Cr(VI) ion was studied at different pH values ranging from 3.0 to 9.0, the results are given in Figure 3.

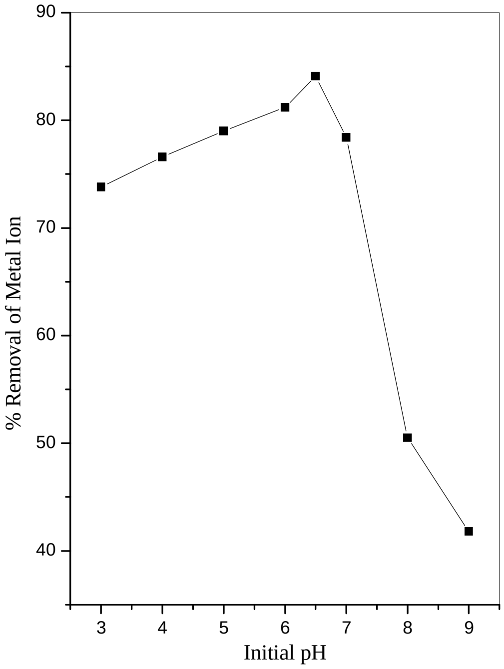

Fig.3-Effect of Initial pH on the removal of Metal Ion
[M]=50mg/L: Contact time=60 min: dose=25mg/50ml

It was observed that a sharp decrease in the Cr(VI) ion removal occurred when the pH value of the solutions changed from 3.0 to 9.0. The maximum adsorption of Cr(VI) ions are obtained at pH 6.5. So pH 6.5was selected as optimum pH for Cr(VI) ion adsorption onto AAVNS. As seen in fig 3. Cr(VI) removal by all studied adsorbents decreased significantly with increasing pH, especially between pH 3.0 to 6.5, the maximum removal percentages of Chromium onto AAVNS, were 75 to 85% respectively.

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 metal ion solutions and the contents were agitated for 50 min at 30 °C. The results had shown in the (fig.4).

it reveals that low concentration of Cl^- does not affect the percentage of adsorption of metal ion on AAVNS 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 [11]

3.6 Effect of Temperature:

It is well known that temperature plays an important role in the adsorption process. The removals of metal ions The metal 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 metal 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.

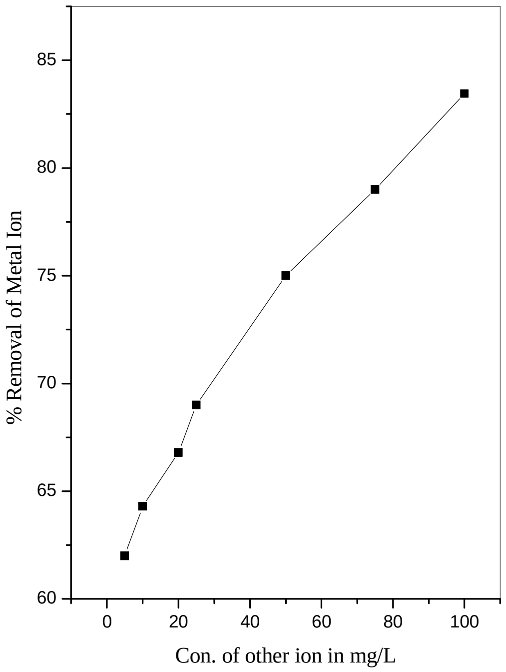

Fig.4-Effect ionic strength on the adsorption of Metal ion
[M]=50 mg/L;Contact time=60 min;Dose=25 mg/50 ml

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 AAVNS were analyzed by Langmuir and Freundlich.

3.7.2 Langmuir Isotherm

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. The Langmuir adsorption isotherm has been successfully used in many monolayer adsorption processes, the values are in table 2.

Table: 2. Langmuir and Freundlich Isotherm Parameter for the Adsorption of Chromium ion

TEMP. (C°)	LANGUMUIR PARAMETER		FRUENDLICH PARAMETER	
	Q_m	b	K_f	n
30°	183.88	0.1949	5.2056	2.6640
40°	193.91	0.2001	5.3100	2.6031
50°	249.85	0.1822	5.4542	2.0831
60°	207.88	0.2329	5.5804	2.5674

High b values indicate high adsorption affinity the monolayer saturation capacity Q_m were around. The adsorption isotherm data were analyzed by the Langmuir isotherm model in the linearised form,

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

Where q_e is the equilibrium adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium Cr (VI) concentration in solution (mg/l), q_{max} is the maximum amount of Chromium 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

$R_L=(1/(1+bCo))$ -------------------------------(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.

$R_L > 1$	Unfavourable adsorption
$0 < R_L < 1$	Favourable adsorption
$R_L = 0$	Irreversible adsorption
$R_L = 1$	Linear adsorption

The calculated R_L values are given in table 3.

Table: 3. Dimensionless Separation factor (R_L) for the Adsorption of Chromium ion

(C_i)	**TEMPERATURE °C**			
	30°C	**40°C**	**50°C**	**60°C**
25	0.1702	0.1665	0.1799	0.1465
50	0.0930	0.0900	0.0988	0.0790
75	0.0640	0.0624	0.0681	0.0541
100	0.0487	0.0475	0.0520	0.0411
125	0.0394	0.0384	0.0420	0.0332

The R_L values between 0 to 1 indicate favourable adsorption for all initial concentration (C_o) and temperatures studied.

The Freundlich isotherm model

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as[12]:

$\log q_e = 1/n \log C_e + \log K$-------------------------(5)

Where, K_F is the Freundlich constant related to sorption capacity (mg/g) (L/g)1/n and n is related to the adsorption intensity of the adsorbent. Where, K_F and 1/n can be determined from the linear plot of log q_{eq} *versus* log Ce. The evaluated constants are given in Table 2.

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 AAVNS 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 50 min. After this period the solutions then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry. The metal concentration retained in the sorbent phase (q_e, mg/g) was calculated by using Eq. (1)

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

where C_0 and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (M), V the solution volume (L) and m is the mass of AAVNS (g).

3.8 Adsorption Thermodynamics

The thermodynamic parameters for the adsorption of Cr (VI) ions by AAVNS were determined using the following equations:

$K_D = q_e/C_e$ -------------------------------------- (7)

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

$\ln K_D = (\Delta S^o/R) - (\Delta H^o/RT)$------------------------ (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 [13]. 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 4,

Table: 4. Thermodynamic Parameter for the Adsorption of Chromium ion

C_0	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	-7015	-7630.64	-8429.44	-8540.5	9.38632989	54.3721564
50	-5380.48	-5808.03	-7188.37	-7608.42	19.1399425	80.61717028
75	-4269.3	-4764.78	-5024.06	-5489.47	7.59254166	39.24356525
100	-2665.32	-3105.22	-5898.05	-3903.43	17.7326374	68.00695951
125	-1727.31	-2178.32	-4180.4 4	-3099.26	17.2451555	63.02466932

the negative values of Gibbs free energy change (ΔG^o) obtained for the adsorption of Cr (VI) ions by Acid Activated Vitex Negundo Stem Carbon at various temperatures had shown the spontaneous nature of the adsorption process. The positive values of enthalpy change (ΔH°) obtained for the adsorption of Cr (VI) ions by AAVNS 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 AAVNS Carbon at various temperatures showed the increased randomness at solid liquid inter phase during the sorption processes of Cr (VI) ions on the adsorbent AAVNS. 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 overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion [14].

The adsorption of Cr (VI) ions by AAVNS slightly increased when temperature was raised up to 60 ^{o}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 AAVNS were endothermic reactions and physical in nature which involved the strong forces of attraction between the sorbate-sorbent molecules.

3.9 Kinetic modelling 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 [15]. The pseudo-first-order rate Lagergren model is:

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

Where q (mg/g) is the amount of adsorbed heavy metals 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:

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

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:

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

where k_2,ads (g/mg min) is the rate constant of second-order adsorption. The integrated form of Eq. (12) is:

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

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

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

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

$dq_t / d_t = \alpha \exp(-\beta q_t)$ ------------------- (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 (1980) 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:

$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$--------------- (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 5.

Table: 5. The Kinetic Parameters for the Adsorption of Chromium ion

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**	51.9622	0.00293	0.996	7.91306	64.989	0.1322	0.9921	1.6524	0.9912	0.18258
	40	50.2772	0.00468	0.993	11.8314	1656.7	0.2120	0.9924	1.78181	0.9914	0.10747
	50	50.9311	0.00444	0.991	11.5391	1383.8	0.2055	0.9930	1.78183	0.9915	0.10986
	60	50.4375	0.00466	0.9960	11.8614	4751.2	0.2373	0.9915	1.80352	0.9917	0.09462
50	**30**	97.3082	0.00178	0.994	16.8508	260.38	0.0798	0.9940	1.6737	0.9918	0.15628
	40	97.1313	0.00235	0.9955	22.213	1107.8	0.0962	0.9923	1.73893	0.9919	0.12417
	50	100.160	0.00204	0.9952	20.4789	1697.7	0.0998	0.9928	1.75935	0.9921	0.11616
	60	99.3087	0.00226	0.9953	22.3059	3591.8	0.1091	0.9927	1.77693	0.9923	0.10577
75	**30**	135.809	0.00140	0.9942	25.9670	1134.4	0.0675	0.9926	1.69224	0.9925	0.12852
	40	139.108	0.00131	0.9961	25.4915	831.93	0.0631	0.9933	1.68954	0.9928	0.13526
	50	138.335	0.00150	0.9956	28.8462	2021.4	0.0707	0.9935	1.72010	0.9938	0.11896
	60	140.628	0.00144	0.9974	28.6471	1588.2	0.0674	0.9936	1.71900	0.9945	0.12338
100	**30**	160.070	0.00113	0.9941	29.0755	874.81	0.0542	0.9939	1.62190	0.9961	0.13724
	40	166.499	0.00105	0.9944	29.1198	683.98	0.0501	0.9940	1.62633	0.9967	0.14381
	50	168.186	0.00110	0.9922	31.2121	951.56	0.0517	0.9941	1.64535	0.9969	0.13679
	60	172.955	0.00104	0.9932	31.3882	1046.2	0.0506	0.9943	1.65928	0.9968	0.13485
125	**30**	175.270	0.00128	0.9973	39.392	5003.1	0.0601	0.9937	1.62049	0.9977	0.10910
	40	188.125	0.00094	0.9935	33.2868	914.40	0.0454	0.9928	1.5896	0.9975	0.13973
	50	194.228	0.0009	0.9936	33.9441	867.17	0.0435	0.9920	1.59963	0.9974	0.14172
	60	203.849	0.00083	0.9939	34.4768	922.38	0.0418	0.9919	1.62011	0.9978	0.14077

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 AAVNS adsorbent.

3.9.2 The Intra particle diffusion model

The kinetic results were analyzed by the [16] Intra particle diffusion model to elucidate the diffusion mechanism. The model is expressed as:

$q_t = K_{id} t^{1/2} + I$ -------------------------------- (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 5. The K_{id} value was higher at the higher concentrations. Intra particle 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 Intra particle diffusion was not the only rate-limiting step.

It is clear from the Table 5 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 5 that the values of the rate constant k_2 decrease with increasing initial Cr (VI) 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 AAVNS desorption experiments were carried out. The effect of strength of desorbing solution (NaOH) on the recovery of Cr(VI) is shown in Fig. 4. It is evident from the above figure that when the strength of the desorbing solution increased from 0.6 to 1.8M, Cr (VI) desorption percentage increased from 30% to 79%. Thus a significant amount of chromium is being desorbed, which shows that the AAVNS can be effectively reused after desorption.

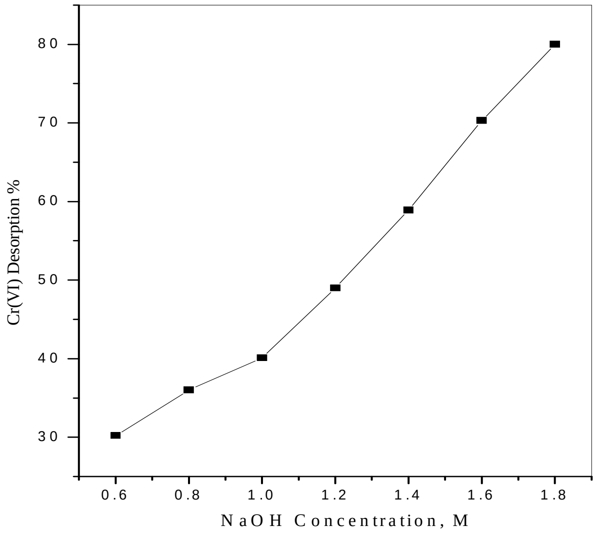

Fig.5- Effect of NaOH Concentration on Cr(VI) desorption

CONCLUSION

This AAVNS can be used as an alternative adsorbent for heavy metal ions removal in industrial wastewater due to its efficiency of Chromium ions adsorption in aqueous solution. The adsorption of Cr (VI) onto AAVNS was affected by pH, adsorbent dosage, and temperature. The Cr (VI) uptake percentage by AAVNS was found to be 95.18% when 0.025 g of adsorbent was agitated with 50mL of Cr(VI) solution of 50 mg/L for 50 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_e value with the increase of temperature implied that chemisorptions occur 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) adsorption process and the positive values of ΔH° and ΔS° showed the endothermic nature. The present findings suggest that AAVNS may be used as an inexpensive and effective adsorbent for the removal of chromium (VI) ions from aqueous solution.

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