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ADSORPTION OF CHROMIUM (VI) USING A NON-CONVENTIONAL ADSORBENT

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ABSTRACT

Activated carbon was prepared from *Passiflora foetida* plant seed by chemical activation with KOH. The prepared activated carbon was characterized and utilized for the chromium (VI) removal from the aqueous solution. The effect of pH, contact time, initial concentration of adsorbate and temperature on the adsorption of Cr (VI) was investigated. The Cr (VI) adsorption followed the pseudo second order kinetics with good correlation coefficient. The Freundlich model best described the Cr (VI) adsorption with high correlation coefficient. The thermodynamic parameters such as Free energy change (ΔG°), Enthalpy change (ΔH°) and Entropy change (ΔS°) were evaluated. The negative value of ΔG° confirmed the feasibility and spontaneity of the process. Reversibility of Cr (VI) adsorption and reuse of the adsorbent, was investigated by desorption process.

Keywords: Activated carbon, Cr (VI), Adsorption, Passiflora foetida, Kinetic models.

INTRODUCTION

Contamination of water by toxic heavy metals through wastewater discharge by industrial activity is a major environmental issue[1]. Metals and their derivatives are potential pollutants that can be particularly problematic due to their stability and mobility. Among them, Cr has become a serious health concern due to its release into the environment[2]. Chromium exists in hexavalent and trivalent forms. Hexavalent form is 500 times more toxic than trivalent one[3] and human toxicity of Cr (VI) includes skin irritation to lung cancer, as well as kidney, liver and gastric damage[4]. Considering the toxic and carcinogenic nature of Cr, the maximum levels permitted for trivalent Cr in waste water is 5 mg/L and for Hexavalent Cr is 0.05 mg/L[5,6].

Several industries like paint, steel, leather tanning, plating, fertilizer, textile, photography etc., discharge effluent containing hexavalent Cr to surface water[7]. Nearly 9,420,000 m^3 of wastewater was discharged from 2161 tanneries in India[8]. Cr removal from aqueous system can be achieved with various methods such as chemical precipitation, ion exchange, membrane processes, electro dialysis and adsorption[9]. Among all other investigated methods activated carbon adsorption is a highly promising method for the Cr (VI) removal. However, the cost of activated carbon preparation from coal and other natural sources are too expensive.

Many investigators have studied the feasibility of using inexpensive alternative materials like rice husk, saw dust, groundnut husk, coconut shell, etc. for the removal of metal ion from water and wastewater. In the present investigation the efficiency of low cost adsorbent material prepared from *Passiflora foetida* plant seed for the removal of Cr (VI) from aqueous solution was tested. The removal amount of Cr (VI) was measured in different conditions such as adsorbent dosage, initial Cr (VI) concentration, solution pH, contact time and temperature. Adsorption kinetics, equilibrium isotherm and thermodynamic parameters of the process were also investigated.

EXPERIMENTAL

Preparation of adsorbent

The *Pasiflora foetida* plant seeds are collected and dried in sun light till they lost their water content. The dried seeds were soaked in 10% KOH solution for 24 hours. At the end of 24 hours, the excess KOH solution decanted off, the material dried and carbonized in muffle furnace at 400°C for 10 minutes. The carbonized material washed several times with distilled water to remove the residual KOH. After washing, the material was dried, crushed, and ground well. Then the material was sieved to obtain average particles of 180-300µ size (ASTM Sieve). The sieved carbon was activated in a muffle furnace at 800°C for 10 minutes and then stored in an air tight container for further adsorption studies. For the convenience of discussion the adsorbent (*Pasiflora foetida* Activated Carbon) will be denoted as PAC.

Adsorption Studies

A stock solution of hexavalent Cr is freshly prepared by dissolving 2.830g of AR $K_2Cr_2O_7$ in double distilled water and diluting to one liter. This contains 1000 mg/L of Cr (VI). Experimental solutions of desired concentrations are then obtained by successive dilutions. The pH of solution was measured by using digital pH meter (Elico: Model LI-120). Cr adsorption was measured by using visible spectrophotometer (Elico Make: Model SL 207). The conductivity is measured by using Digital Conductivity Meter (Deep vision model M-180). Temperature controlled orbital shaker (Rivotek Model) is used for the equilibrium studies. The effect of pH on Cr (VI) adsorption was investigated in the initial pH range of 2-12. The initial pH of the solution was adjusted by using 0.1N HCl or 0.1N NaOH. Dried activated carbon (0.3g) was added to 100mL of solution having 40mg/L of Cr (VI) ions. After adsorption, the solutions were centrifuged and the concentrations of the solutions were determined.

For kinetic studies, 100mL of the Cr (VI) solution (initial concentrations 20, 40, 60, 80 and 100mg/L) and 0.3g activated carbon were agitated until reaching the adsorption equilibrium. After adsorption, the solutions were centrifuged and the concentrations of the solutions were determined by using a visible spectrophotometer. For isotherm studies, 0.3g of activated carbon samples were mixed with 100mL solutions of various Cr(VI) concentrations between 10mg/L and 110 mg/L in the isothermal shaker for 90 minutes at 30, 35, 40 and 45˚C constant temperatures. After adsorption, the solutions were centrifuged and the concentrations of the Cr (VI) ions remaining unadsorbed were determined as stated above. The analysis of Cr (VI) was carried out colorimetrically with the 1, 5 Diphenyl carbazide method using visible spectrophotometer[10]. The amount of adsorbed Cr (VI) was calculated from the difference in their initial and final concentrations.

RESULTS AND DISCUSSION

Adsorbent characterization

The physico-chemical characteristics of PAC are presented in Table- 1. The pH and pH_{zpc} values of PAC indicate that the adsorbent may contain acidic oxygen functional groups. Moisture content of the carbon has no effect on its adsorptive power, but it dilutes the activated carbon which necessitates the use of additional weight of carbon during the treatment process[11]. The lower bulk density value indicates the highly branched and porous carbon with more void space[11]. Acid soluble matter content was found slightly higher than the solubility in water in the activated carbon because of incorporated carbonate groups in the pores.

Higher specific gravity shows that the activated carbon was used as a good packing purpose for the removal of pollutants from wastewater. The lower ash content and volatile matter attributed to lower inorganic content and higher fixed carbon. Higher value of fixed carbon shows the activated carbon is more efficient and stable. Conductivity values mean that cations and anions in activated carbon may be responsible for the conductivity. The high surface area is considered to be the most suitable for adsorption of activated carbon in aqueous solution. Higher iodine number shows that the activated carbon has high adsorption capacity of inorganic constituents present in the aqueous solution and wastewater[11].

Effect of pH

The solution pH is one of the important parameter for the removal of heavy metals from aqueous solution because it affects the solubility of adsorbates, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction[12]. Figure- 1 shows the effect of pH on the adsorption Cr (VI) by PAC. The maximum adsorption was noticed at pH 2. This indicates that the Cr (VI) adsorption capacity of the adsorbent is dependent upon pH. Cr (VI) may exist in three different ionic forms ($HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^-) in aqueous solutions and the stability of these ions is mainly dependent on the pH of the system[13]. The Percentage of Cr (VI) removal was higher in the lower pH ranges due to high electrostatic force of attraction. As the number of H^+ ions increased with lowering the solution pH, which neutralized the negative charge on adsorbent surface and thereby increased the diffusion of chromate ions into the bulk of the adsorbent[14]. It is well known that the dominant form of Cr (VI) up to pH 4 is $HCrO_4^-$ [13]. The Cr (VI) was adsorbed the surface of activated carbon mostly in the form of $HCrO_4^-$ ions. The decrease in the removal at higher pH may be the increased number of OH^- ions in the bulk retarded the diffusion of the chromate ions. The increase in Cr (VI) adsorption at low pH, hence pH 2 was taken as the optimal values for further studies of Cr (VI) adsorption on PAC.

Table--1: Physico-chemical Characteristics of the PAC

S.No.	Parameters	Adsorbent
1	pH	9.26
2	Conductivity, μS/cm	0.4
3	Moisture, %	1.76
4	Ash Content, %	12.26
5	Bulk density (D), g/mL	0.748
6	Specific Gravity (S), g/mL	1.25
7	Porosity, %	40.2
8	Water Soluble Matter, %	0.645
9	Acid Soluble Matter, %	5.59
10	Iodine Value, mg/g	112.0
11	$pH_{(ZPC)}$	9.2
12	Surface area, m^2/g	129.0

Effect of initial metal ion concentration

The amount of Cr(VI) adsorption on PAC was studied as a function of contact time at various concentrations (20, 40, 60, 80 and 100 mg/L) of Cr(VI) at 30°C, 0.3g of adsorbent and a pH of 2.The results are shown in Figure- 2. It is evident from these Figure-, Cr (VI) adsorption is increases with contact time up to 80 minutes then saturation is almost reached. The adsorption was found to be dependent on initial concentration of Cr ion.

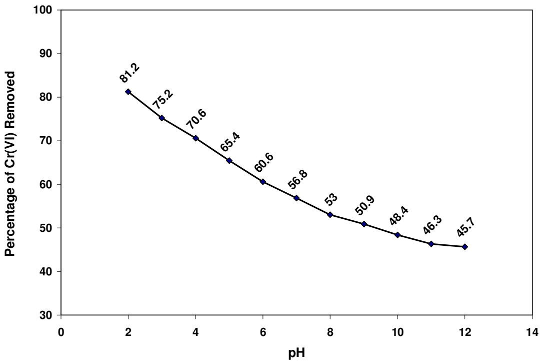

Fig.-1: Effect of pH for the adsorption of Cr(VI)

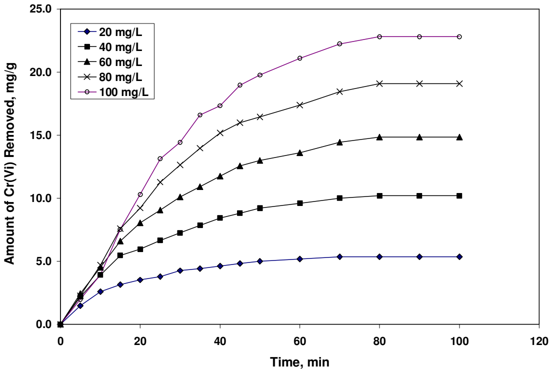

Fig.-2: Amount of Cr(VI) Adsorption – Initial Concentration variation

The amount of Cr (VI) adsorbed, q_e (mg/g), increased with increase in initial concentration. At the early stage the adsorption was rapid and then gradually decreased and became almost constant after the equilibrium point. It is because of that at lower concentration, the ratio of the initial number of Cr ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of Cr ion is dependent upon initial concentration[15,16]. Equilibrium have established at 80 minutes for all concentrations.

Effect of temperature on the adsorption of Cr (VI)

Figure-3 represents the uptake of Cr (VI) onto PAC at 30, 35, 40 and 45°C keeping the initial Cr (VI) concentration at 40 mg/L. The equilibrium sorption capacity of Cr (VI) onto PAC decreases from 10.20 to 9.22 mg/g while increasing the temperature from 30 to 45°C. The decrease in uptake with increase in temperature indicates that the sorption of Cr (VI) by PAC is an exothermic process. The decline in adsorption is due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer increases. This may have caused as a result of decrease in the mobility of the metal ions (due to decrease of kinetic energy) with the raise of temperature[17].

Kinetics of adsorption

The study of adsorption kinetics is significant as it provides valuable information about the reaction pathways and the mechanism of the reaction. The kinetics of Cr (VI) on PAC was analyzed using pseudo first order[18], pseudo second order[19], Elovich[20] and intra particle diffusion[21] models.

Pseudo first order kinetic model[18]

The pseudo first order equation, is generally expressed as:

$$\log\left(\frac{q_e}{q_e-q_t}\right)=\frac{k_1}{2.303}t \qquad (1)$$

Where q_e and q_t are the amounts of Cr (VI) adsorbed (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant of first order adsorption (min^{-1}). A plot of "log (q_e-q_t)" vs "t" at various initial Cr (VI) concentrations is shown in Figure-4. The pseudo first order constant ranged between 0.0458 to 0.0523 min^{-1} at various concentrations. The calculated q_e values obtained from pseudo first order model is in good agreement with the experimental q_e values at various concentrations. The calculated equilibrium adsorption capacity increase on increasing the initial Cr (VI) concentration.

The correlation co-efficient (r^2) at various concentrations are low for the pseudo first order kinetic model. Initial 25 minutes of the sorption data shows good correlation and after 25 minutes the data deviates from the straight line. This plot proves that initial adsorption follows first order and later on it deviates from the first order kinetics. Even though q_e(cal) and q_e(exp) values are closer, the r^2 values suggest that the adsorption data fitted poor to pseudo first order kinetics. Hence, the adsorption of Cr (VI) onto PAC is not diffusion controlled.

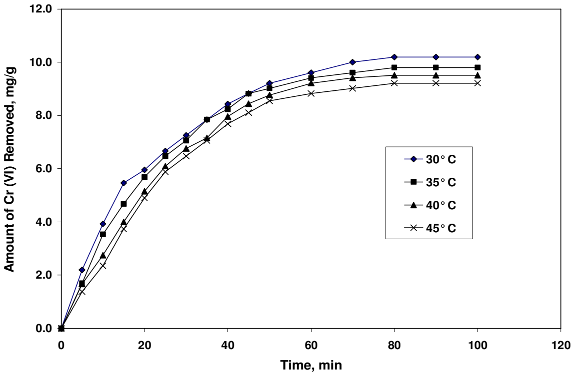

Fig.-3: Amount of Cr(VI) Adsorption – Temperature variation

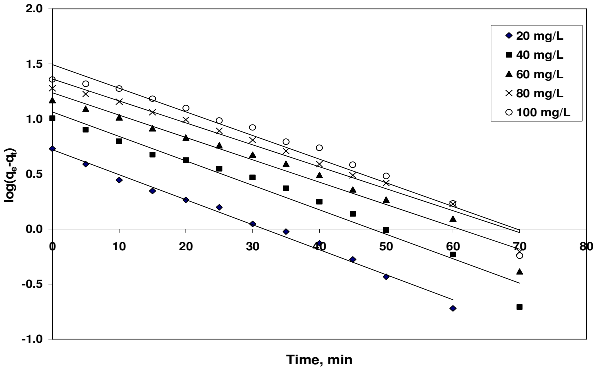

Fig.-4: Pseudo first-order plot for the Cr(VI) Adsorption

Pseudo second order kinetic model[19]

The adsorption may also be described by pseudo second order kinetic model. The liner form of the equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e} t \tag{2}$$

Where, k_2 (g/mg/min) is the second order constant for adsorption. The second order rate constants were used to calculate the initial sorption rate, h (mg/g/min) given by the following equation-

$$h = k_2 q_e^{\,2} \tag{3}$$

A plot of "t/q_t" versus "t" (Figure-5) should show a linear relationship. The values of k_2 and equilibrium adsorption capacity q_e can be calculated from the intercept and slope of the plot are given in Table- 2. The initial sorption rate (h) increases on increasing the initial concentration. The equilibrium sorption capacity (q_e) increases with concentration and sorption rate constant (k_2) decreases with increase in the initial metal ion concentration. Even though, the pseudo second order equation gives some marginal deviation in the q_e(cal) and q_e(exp), the data fits very well with good correlation co-efficient. Based on the r^2 values, we can suggest that the adsorption of Cr (VI) on to PAC follows pseudo second order kinetics. The moderate Cr (VI) uptake indicates that the rate determining step could be physisorption in nature.

Table--2: Calculated kinetic parameters for the adsorption of Cr (VI) at various initial concentrations

	Initial metal ion concentration, mg/L				
Parameters	20	40	60	80	100
$q_e$exp.(mg/g)	5.37	10.20	14.85	19.08	22.81
Pseudo first order kinetics					
k_1 (min $^{-1}$)	0.05228	0.05113	0.04675	0.04583	0.04951
$q_e$cal(mg/g)	5.26	11.61	17.31	23.09	31.18
r^2	0.9904	0.9698	0.971	0.9772	0.9601
Pseudo second order kinetics					
k_2 (g/mg/min)	0.01055	0.00356	0.00156	0.00076	0.00030
h	0.4231	0.5853	0.6481	0.6636	0.6010
$q_e$cal(mg/g)	6.33	12.82	20.41	29.50	44.44
r^2	0.9976	0.9961	0.9904	0.9507	0.7690
Elovich model					
α (mg/g/min)	0.734	0.347	0.218	0.158	0.123
β (g/mg)	2.010	6.747	15.044	25.659	39.895
r^2	0.9797	0.9874	0.9882	0.9836	0.9751
Intra particle diffusion model					
k_{id}(mg/g/min$^{1/2}$)	1.4961	0.7409	0.4471	0.3047	0.2315
r^2	0.9927	0.9873	0.9936	0.9967	0.9895

Elovich model[20]

A widely used equation to describe the kinetics of chemisorption of gas on solids was proposed by Elovich. The linear form of Elovich equation is-

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t + t_0) \tag{4}$$

Where, α and β are the parameters of the equation and $t_0 = 1/(\alpha\beta)$, α represents the rate of chemisorption at zero coverage (mg/g/min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The constants, α and β, are calculated from the plots of "q_t" vs "ln t" (Figure-6). The plot is linear with good correlation co-efficient (r^2 = 0.9691 to 0.9874). The initial adsorption rate (α) increases from 2.010 to 39.89 mg/g/min while increasing the initial concentration from 20 to 100 mg/L in conformity with the moderate initial intake observed experimentally. The other co-efficient (β) decreases with increasing the initial concentration. The constant (β) is related to extent of surface coverage. It is evident that the initial rate of adsorption increases with increase in concentration, which will decrease the availability of adsorption surface for the adsorbate.

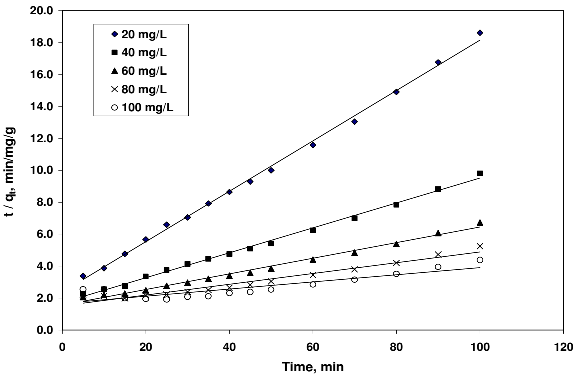

Fig.-5: Pseudo second-order plot for the Cr(VI) Adsorption

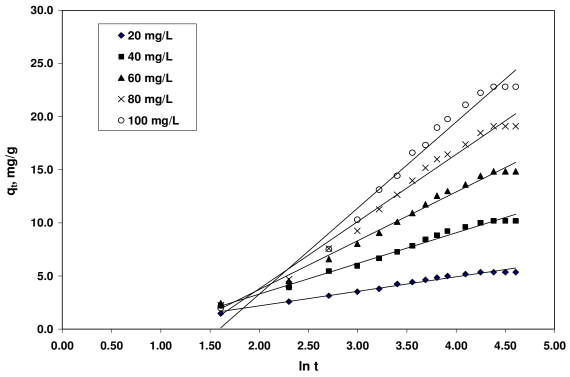

Fig.-6: Elovich plot for the adsorption of Cr(VI)

Intra-particle Diffusion Model[21]

The intra particle diffusion model is expressed as follows-

$$q_t = k_{dif} . t^{½} \quad + C \qquad (5)$$

Where, q_t is the fraction of metal ion uptake (mg/g) at time t, k_{dif} is the intra particle-diffusion rate constant (mg/g. $min^{0.5}$) and I is the intercept (mg/g). The plot of q_t versus $t^{0.5}$ (Figure-7) will give k_{dif} as slope and C as intercept. The intercept C represents the effect of boundary layer thickness. For all the concentrations employed there is a monotonous increasing trend for the sorption capacity with time. At low initial metal ion concentration, Cr is almost depleted from the aqueous solution, while for the more concentrated solutions the abstracted concentration is approximately the same ~20 mg/L. Thus, the overall sorption process is apparently not influenced by external mass transfer diffusion.

The process occurred very rapidly at low initial Cr concentrations. Increasing the initial Cr concentration, which means a strong driving force between the bulk and particle surface concentrations, a decrease in the external mass transfer coefficient is observed. These results are consistent with previous studies on vanadium sorption by chitosan. Increasing the metal concentration in the solution seems to reduce the diffusion of metal ions in the boundary layer and to enhance the diffusion in the solid. Three mechanisms appear to contribute during the process: (i) film diffusion which dominates the very beginning of the process (ii) intra-particle diffusion in the continue and (iii) a reaction which governs the largest part of the process, accompanied by an equilibrium stage when the experimental conditions slow down the transport rates.

Adsorption Isotherm

The equilibrium study on adsorption has provided sufficient information on the capacity of the adsorbent. Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. To establish the adsorption capacity of PAC various isotherm equations have been tested in the present study. Hence, four important isotherms were selected in this study, which were namely Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich (D-R) adsorption isotherm models.

Langmuir Model[22]

Langmuir Isotherm is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing finite number of identical sites. Langmuir isotherm model was chosen for estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The Langmuir isotherm can be expressed as-

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b_L} + \frac{C_e}{Q_0} \qquad (6)$$

Where, b_L is the Langmuir constant, C_e is the equilibrium metal ion concentration in solution, C_e is the initial concentration (mg/L) and Q_0 is a constant related to monolayer adsorption capacity. Straight lines were obtained by plotting C_e/q_e against C_e as shown in Figure-8. Langmuir constants, Q_0 and b were calculated from the slope and intercepts of plots of C_e/q_e against C_e, and are given in Table- 3 along with correlation coefficients (r^2).

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless equilibrium parameter, R_L, also known as the separation factor, which describes the type of isotherm:

$$R_L = 1/ (1+b_L . C_i) \qquad (7)$$

Where b_L is the Langmuir constant and C_i is the initial Cr (VI) concentration (mg/g). In all of the temperatures, the values of R_L were calculated between 0 and 1, indicating the favorable adsorption of Cr (VI) on PAC.

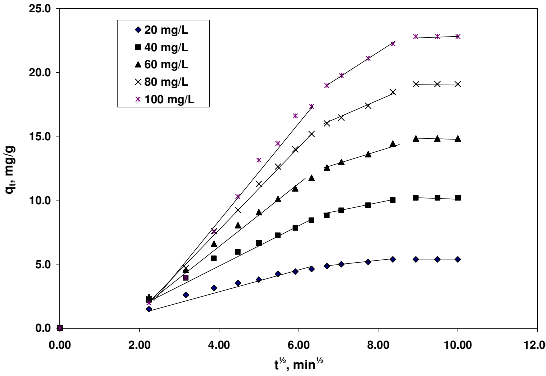

Fig.-7: Intra-particle Plot diffusion for the Adsorption of Cr(VI)

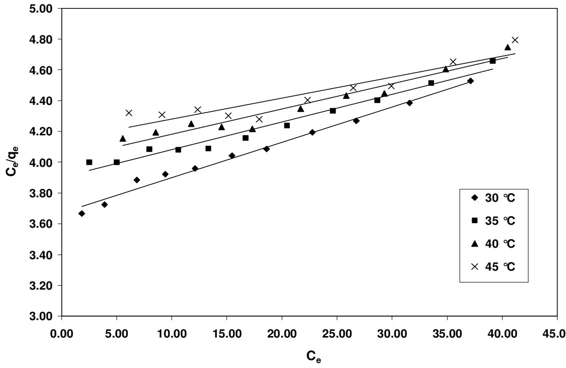

Fig.-8: Langmuir isotherm plot for the adsorption of Cr(VI)

Freundlich Model[23]

The Freundlich isotherm model is an exponential equation that applies to the adsorption on heterogeneous surfaces with interaction between adsorbed molecules and is not restricted to the formation of a monolayer. The well-known expression for the Freundlich model is given as -

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (8)$$

Where, q_e is the adsorption capacity (mg/g), C_e is the equilibrium concentration of the Cr (VI) solution (mg/L), k_f and n are Freundlich constants, which represents adsorption capacity and adsorption intensity, respectively. The Freundlich parameters k_f and n calculated by the plot of "log q_e" vs "C_e" (Figure-9) are given in Table-3.

The Freundlich constant, k_f decreases with increase in temperature. Generally a carbon that has higher q_e value at specified equilibrium concentration will be preferred for a given application. The value of n is greater than 1.0 indicating that the adsorption of Cr (VI) onto PAC is favorable[24]. Freundlich model is more appropriate to explain the nature of adsorption with a correlation co-efficient of 0.9576 to 0.9933 than Langmuir model (r^2 = 0.8506 to 0.9876).

Table--3: Results of isotherm models for the adsorption of Cr (VI) onto PAC

	Temperature °C			
Parameters	30	35	40	45
Langmuir isotherm				
Q_0 (mg/g)	43.48	55.56	60.98	73.53
b_L x10^{-3}(L/mg)	0.0063	0.0046	0.0041	0.0033
r^2	0.9876	0.9719	0.9401	0.8506
Freundlich isotherm				
n	1.37	1.22	1.07	1.00
k_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	1.92	1.32	0.86	0.67
r^2	0.9933	0.9885	0.9634	0.9576
Tempkin isotherm				
b_T (mg/g)	332.72	313.31	287.63	260.58
a_T (L/mg)	0.534	0.386	0.289	0.224
r^2	0.9496	0.9594	0.9781	0.9856
Dubinin-Raduskevich isotherm				
q_D (mg/g)	21.62	21.57	21.23	21.34
B x 10^{-6}(mol^2/J^2)	10.0	10.0	20.0	20.0
E x 10^{-3}(kJ/mol)	2.0	2.0	1.41	1.41
r^2	0.9037	0.9289	0.9135	0.924

Tempkin Isotherm[25]

Tempkin isotherm takes into account of the effect of indirect adsorbate-adsorbate interaction on adsorption and suggests that the heat of adsorption of all molecules in the adsorbent surface layer would decrease linearly with coverage. The Tempkin isotherm can be expressed in its linear form as-

$$q_e = \frac{RT}{b_T}\ln a_T + \frac{RT}{b_T}\ln C_e \qquad (9)$$

The Tempkin constants a_T and b_T are calculated from the slopes and intercepts of Figure-10 and are given in Table-3. The Tempkin sorption potential (a_T) and the Tempkin constant related to heat of adsorption (b_T) decreases up to 45°C. However, the model failed has very well for the adsorption isotherm of Cr (VI) adsorption onto PAC when compared to other isotherms with a correlation co-efficient (r^2 = 0.9496 to 0.9856).

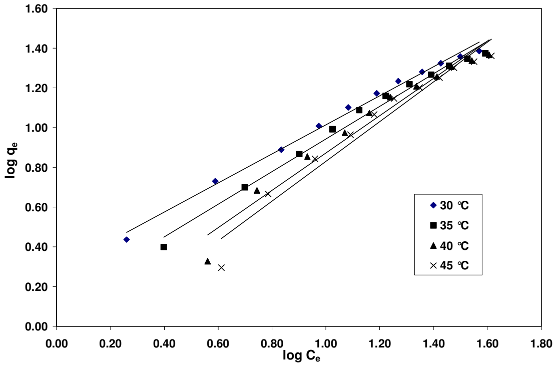

Fig.-9: Freundlich isotherm plot for the adsorption of Cr(VI)

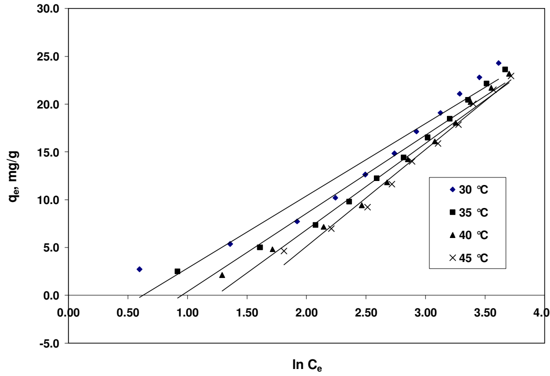

Fig.-10: Tempkin isotherm plot for the adsorption of Cr(VI)

Dubinin-Raduskevich (D-R) Isotherm[26]

The D-R model was also applied to determine the nature of the adsorption processes as either physical or chemical. The (D-R) isotherm is used to estimate the adsorption energy. This isotherm model is more general than Langmuir because it does not assume a heterogeneous surface or a constant adsorption potential. D-R model has commonly been applied in the following form-

$$\ln q_e = \ln q_D - B\varepsilon^2 \qquad (10)$$

Where B is a constant related to the mean free energy of adsorption per mole of the adsorbate ($mol^2\ kJ^{-2}$), q_D is the maximum adsorption capacity ($mg\ g^{-1}$) and ε is the polyanyi potential, which is equal to-

$$\varepsilon = RT \ln (1+1/C_e) \qquad (11)$$

The values of q_D and B were calculated from the intercept and slope of the plot "ln qe" versus ε^2. The mean free energy of adsorption E calculated from B using the following equation-

$$E = 1/ (2B)^{1/2} \qquad (12)$$

Based on this energy of activation one can predict whether an adsorption is physisorption or chemisorption. The range of mean adsorption energy at 2-20 kJ/mol could be considered physisorption in nature[27]. Figure-11 shows the D-R plot at 30, 35, 40 and 45°C and the results are given in Table-3. The D-R model constant q_D(mg/g) is found to vary too far from the experimental data. The magnitude of mean free energy E is < 8 kJ/mol, the adsorption process is physical in nature[28]. The mean free energy calculated from the constant B is found to be 10.0 to 20.0 kJ/mol. Hence, the adsorption of Cr (VI) on to PAC is physisorption in nature. However, the large deviation of q_D from the experimental data and poor correlation co-efficient obtained for D-R plot ($r^2 = 0.9037$ to 0.9289) suggests that the activation energy calculated based on D-R plot may not be the actual one. Further to confirm the nature of adsorption, it is necessary to evaluate the thermodynamic parameters.

Thermodynamics of Adsorption

Thermodynamic parameters provide in-depth information of inherent energetic changes associated with adsorption; therefore, these parameters should be accurately evaluated. Changes to ΔG^0, ΔH^0 and ΔS^0 were calculated to elucidate the process of adsorption. The Langmuir isotherm was applied to calculate the thermodynamic parameters as per the following equations.

$$\ln b_L = \frac{\Delta S^O}{R} - \frac{\Delta H^O}{R}\frac{1}{T} \qquad (13)$$

Where, b_L is a Langmuir isotherm constant, R is the gas constant (8.314×10^{-3} kJ/K/mol) and T is temperature (K). Both ΔH^0 and ΔS^0 were determined from the slope and intercept of the Van't Hoff plots of "ln (b_L)" vs "1/T"(Figure-12).The free energy of specific adsorption $\Delta G°$ (kJ/mol) is calculated from the following expression,

$$\Delta G° = \Delta H° - T\Delta S° \qquad (14)$$

The $\Delta H°$ and $\Delta S°$ values obtained from the slope and intercept of Van't Hoff plots have presented in Table-4. The values $\Delta H°$ are within the range of 1 to 40 KJ/mol indicates the physisorption. From the results we could make out that physisorption is much more favorable for the adsorption of Cr ion. The negative values of $\Delta H°$ show the exothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of Cr ion adsorption increases, this rules out the possibility of chemisorption. The low $\Delta H°$ value depicts Cr ion are physisorbed onto adsorbent PAC. The negative values of $\Delta G°$ (Table-4) shows the adsorption is highly favorable and spontaneous. The negative values of $\Delta S°$ (Table-4) shows the decreased disorder and randomness at the solid solution interface of Cr ion with PAC, while the adsorption there are some structural changes in the Cr ion and the adsorbent occur.

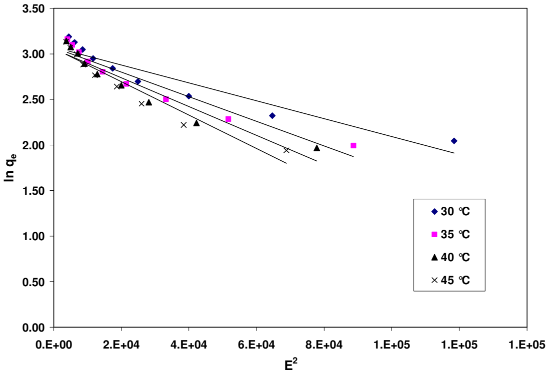

Fig.-11: D-R isotherm plot for the adsorption of Cr(VI)

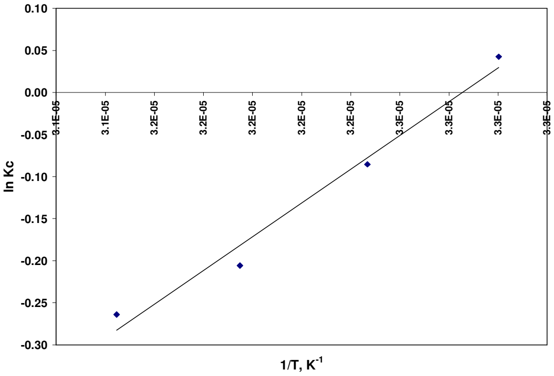

Fig.-12: Van't Hoff Plot for the adsorption of Cr(VI) onto PAC

Table--4: Results of Thermodynamic Study for the Adsorption of Cr (VI) onto PAC

Temp., °C	ΔG°, J/mol	ΔH°, KJ/mol	ΔS°, J/K/mol
30	-102.84	- 16.69	-54.84
35	-218.58		
40	-535.89		
45	-697.89		

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Cr ions. If the adsorbed Cr ions can be desorbed using neutral pH water, then the attachment of the Cr ions of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorb the Cr ion then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the Cr ions, then the Cr ions has held by the adsorbent through chemisorption. The effect of various reagents used for desorption studies (Figure-13) indicate that Sodium hydroxide is a better reagent for desorption, because we could get more than 71 % removal of adsorbed Cr ions. The reversibility of adsorbed Cr ions in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of Cr ions by mineral acids and alkaline medium indicates that the Cr ions were adsorbed onto the activated carbon through by physisorption mechanisms.

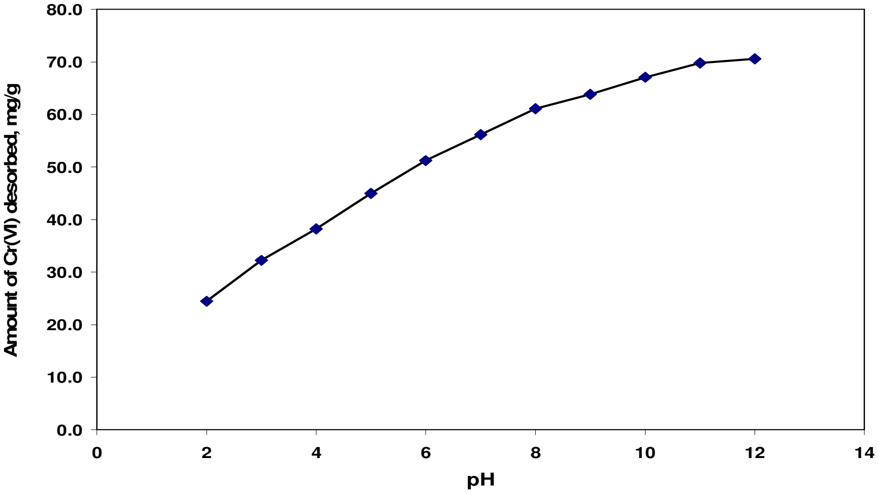

Fig.-13: Desorption of Cr (VI) – Effect of pH

CONCLUSION

Activated carbon was conveniently and economically prepared from *Passiflora foetida* plant seed by chemical activation with KOH. The characterization studies showed that the properties of PAC comparable with the commercial activated carbon. The maximum Cr (VI) adsorption was found to be at a pH of 2.0. The percentage of removal was decreased with increasing concentration. The pseudo-second order kinetic model is more appropriate than the other two, due to better prediction of the equilibrium sorption capacity. Freundlich model has better correlation coefficient than the other models in the concentration studied at all temperatures indicating the multilayer adsorption with heterogeneous surface. The negative value of ΔG° confirms the feasibility adsorbent and spontaneity of the adsorption process. The negative values of ΔH° and ΔS° shows the exothermic nature of adsorption and decreased randomness at the solid-solution interface.

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