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Research Article

INFLUENCE OF ACID AND BASE SURFACE MODIFICATION ON Cr (VI) IONS ADSORPTION ONTO ACTIVATED CARBONS PREPARED FROM BARK OF *THESPESIA POPULNEA*-ISOTHERM AND THERMODYNAMICS STUDY

H. Sivasankari[1], K. Ramesh*[1], A. Rajappa[2]
[1]Department of chemistry, Poompuhar College (Affiliated to Bharathidasan University), Melaiyur, Nagapattinam, India
[2]Department of chemistry, Sri Manakula Vinayagar Engineering College, Madagadipet, Puducherry, India
*Corresponding author: rameshchem82@gmail.com

ABSTRACT

Thespesia populnea barks were utilized to prepare activated carbon by using orthogonal array experimental design method with the parameters such as microwave radiation power, radiation time and concentration of H_3PO_4. Optimized conditions were found to be; radiation power 850W, radiation time 15 min, 50% of H_3PO_4 and impregnation time 24 hours. Carbon prepared was designated as TPBC (*Thespesia populnea* Bark Carbon). Ten g TPBC was impregnated with 20% concentrations of hydrochloric acid and sodium hydroxide solution separately and heated in a microwave oven (radiation power 850W, radiation time 10 min) to improve the structural characteristics of the adsorbents for enhanced Cr(VI) ions removal. These two carbons were designated as A20TPBC (20% HCl acid surface modified *Thespesia populnea* Bark Carbon) and B20TPBC (20% NaOH base surface modified *Thespesia Populnea* Bark Carbon). Influence of the parameters such as initial metal ion concentration and temperature on adsorption was studied. Equilibrium data were fitted with Langmuir, Freundlich, Tempkin and D-R isotherms. The order of best describing isotherms was given based on R^2 value. Various thermodynamic parameters such as $\Delta H°$, $\Delta S°$, and $\Delta G°$ have been evaluated using Vant Hoff plots. Analysis of these values inferred that this adsorption was endothermic, spontaneous and proceeded with increased randomness.

Keywords: *Thespesia populnea,* Thermodynamic parameters, Activated carbon, Orthogonal array.

1. INTRODUCTION

Use of water has been increasing since last few decades. Water availability is falling to crisis levels in more than 80 countries, 40% of the world's population are already facing water shortages by the year 2020 [1]. However, some observers have estimated that by 2025 more than half of the world population will be facing water-based vulnerability. Water pollution may generally be defined as the degradation of the quality of water by the introduction of chemical, physical or biological parameters into the water [2]. Heavy metals are non-biodegradable and the concentration of such metal ions and salts get accentuated through bioaccumulation through food chain in living tissues leading to serious metabolic changes. These metal form complexes with organisms in the environment thereby increasing their mobility in the biota and manifest toxic effects [3]. Chromium is one of the most common ubiquitous and abundant pollutant in the aquatic environment [4], does not found naturally in the pure metallic form. Chromium is a redox active soil contaminant, but it has dramatic alterations in toxicity and mobility with changes in its oxidation states [5].

In this present study, Microwave assisted phosphoric acid activated carbon (TPBC) was prepared from *Thespesia populnea* bark [6]. They are merely a waste material. Microwave energy has been widely used in recent researches and industrial processes. Compared with other heating techniques, microwave heating has the additional advantages [7]; higher heating rates, interior heating, greater control of the heating process, selective heating, no direct contact between the heated materials and heating source and reduced equipment size and waste. Hence microwave radiation is used to prepare activated carbon from the plant material instead of conventional heating methods [8].

2. EXPERIMENTAL AND RESULTS

2.1. Preparation of Adsorbents

The small pieces of dried barks were powdered in a pulveriser. Twenty five g of the powdered barks was mixed with 100 mL of phosphoric acid solution of desired concentration (25, 50 and 75 %). To ensure the access of the H_3PO_4 to the *Thespesia Populnea* Bark, the slurry was kept at room temperature for 24 hours. The slurry was then placed to microwave heating (450, 600 and 850 watts and 10, 12 and 15 minutes) for simultaneous carbonization and activation. Carbonized samples were washed with cold distilled water followed with 0.5 M HCl, hot distilled water and cold distilled water until the pH of the washings reached to 7. The carbon was filtered and dried at 425 K. Adsorption of *Thespesia populnea* Bark carbon with H_3PO_4 generates more interspaces between carbon layers to more surface area and micro porosity. The increase in porosity with H_3PO_4 activation suggests that the porosity created by this reactant is due to spaces left by H_3PO_4 after the corresponding washing. H_3PO_4 activation causes electrolytic action termed as swelling in the molecular structure of cellulose, which leads to the breaking of lateral bonds in the cellulose molecules resulting in increased inter and intra voids. Totally 27 numbers of activated carbons were prepared by varying preparation parameters. The carbon showing maximum percentage removal was chosen for further adsorption study and designated as TPBC (*Thespesia Populnea* Bark carbon). Ten g of the prepared carbons were mixed with 20% solutions of HCl and NaOH and placed in a microwave oven for 10 minutes. Then the carbons were again washed with hot distilled water and cold distilled water and designated as A20TPBC and B20TPBC (HCl 20 % *Thespesia Populnea* Bark carbon and NaOH 20% *Thespesia Populnea* Bark carbon).

2.2. Preparation of stock Solution

AR grade Potassium dichromate was used as such. The Cr(VI) ions stock solution was prepared in double distilled water to a concentration of 1000mg/L. The experimental solutions were prepared by proper dilution.

2.3. Adsorption experiments

The effect of parameters such as adsorbent dose, initial concentration of Cr(VI) ions and contact time was studied by batch mode technique because of its simplicity. Pre-determined dose of the adsorbent and pre-determined concentration of the 50mL adsorbate solution was taken in 250 mL iodine flask with pH of the solution brought to 2 by adding concentrated HCl. Then the content of the flask was agitated using rotary shaker with 200 rpm for pre-determined duration. Then 1 ml of aliquot was taken from sample and diluted to 25 ml by double distilled water, adsorbents were then separated by centrifugation and concentration of the solution was determined by diphenyl carbazide method [9]. The percentage removal of the Cr(VI) ions from the solution was calculated by the mass balance relationship [10]. To study the effect of pH were brought to 2 to 10 by adding 5 N HCl and 5 N NaOH.

2.4. UV-Vis Spectrometric Analysis of Samples:

A 0.25% (W/V) solution of diphenyl carbazide was prepared in 50% (V/V) acetone. One mL of the sample solution was pipetted out into 25 mL standard flasks. To the mixture, 1 mL of 6 N H_2SO_4 was added followed by 1 mL of prepared diphenyl carbazide and the total volume was made up to 25 mL using double distilled water. Concentration of Cr(VI) ions was estimated by the intensity of the pink colour developed due to complex formation using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 540 nm (λ=540 nm).

2.5. Effect of adsorbent dosage

The adsorption of Cr (VI) ions onto TPBC, A20TPBC and B20TPBC were studied by varying the dose of the adsorbent from 10 mg/50 mL to 50 mg/50 mL by taking 10 mg/L to25 mg/L of the Cr(VI) ions, respectively. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose in all the cases which were shown in fig. 1. This is due to the increased carbon surface area and the availability of more adsorption sites. Based on these results, the remaining parts of the experiments were carried out with the adsorbent dose of 20 mg/50 mL of adsorbate solution for Cr(VI) ions solution was used for the adsorption onto TPBC, A20TPBC and B20TPBC.

2.6. Effect of contact time

The effect of contact time on the percentage removal of Cr (VI) ion from aqueous solution was studied by taking 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L solutions as initial concentrations for TPBC, A20TPBC and B20TPBC.

2.7. Effect of pH

Fig. 3 shows the effect of initial pH of the solution on the removal of Cr(VI) ions. The adsorption capacities of Cr(VI) ions onto TPBC, A20TPBC and B20TPBC increased significantly with a decrease of pH value and the maximum removal was attained at pH 2.0. The reason for the high percentage of removal of Cr(VI) ions at lower pH range was explained as below. The Cr(VI) ions exists in different forms such as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^-ions in aqueous solution and the stability of these forms is dependent on pH of the system. The active form of Cr(VI) ion adsorbed is $HCrO_4^-$ ions [11, 12]. This form is stable at only lower pH range which leads to high removal of chromium. The concentration of this form decreases with the increase of pH.

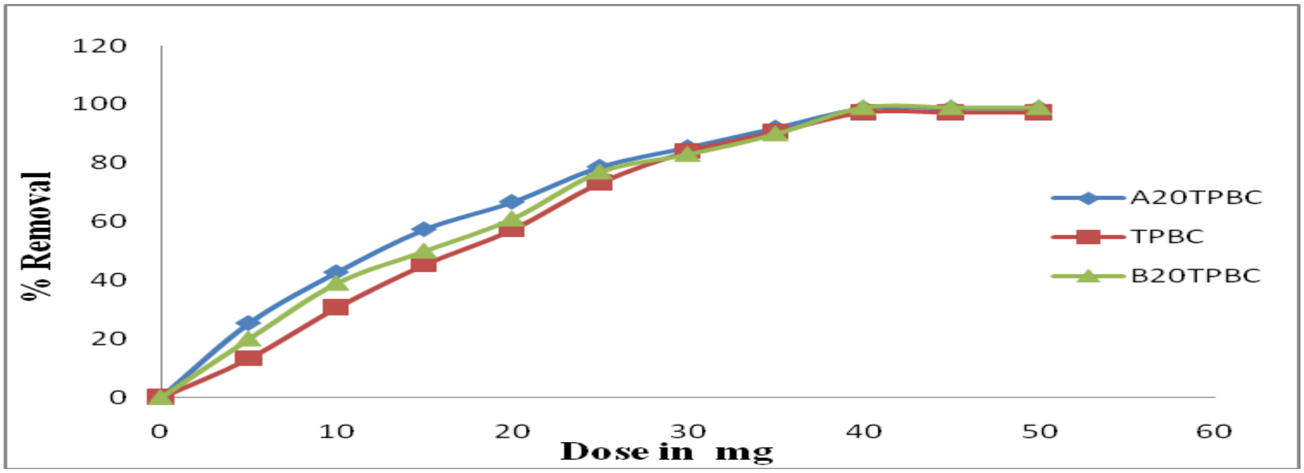


Fig. 1: Effect of Dose for Cr (VI) onto TPBC, A20TPBC & B20TPBC

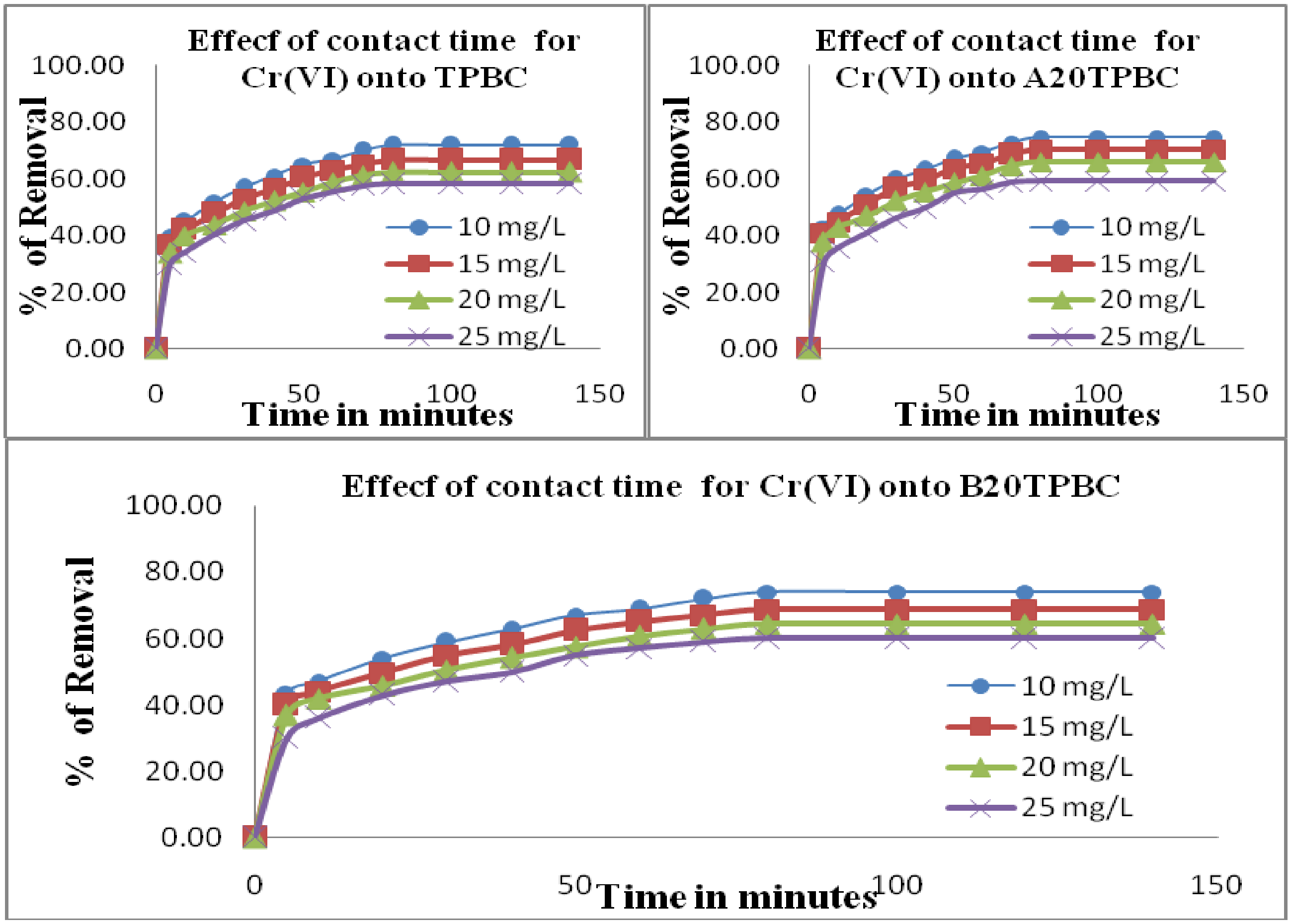


Fig. 2: Effect of Contact time for Cr (VI) ions onto TPBC, A20TPBC & B20TPBC

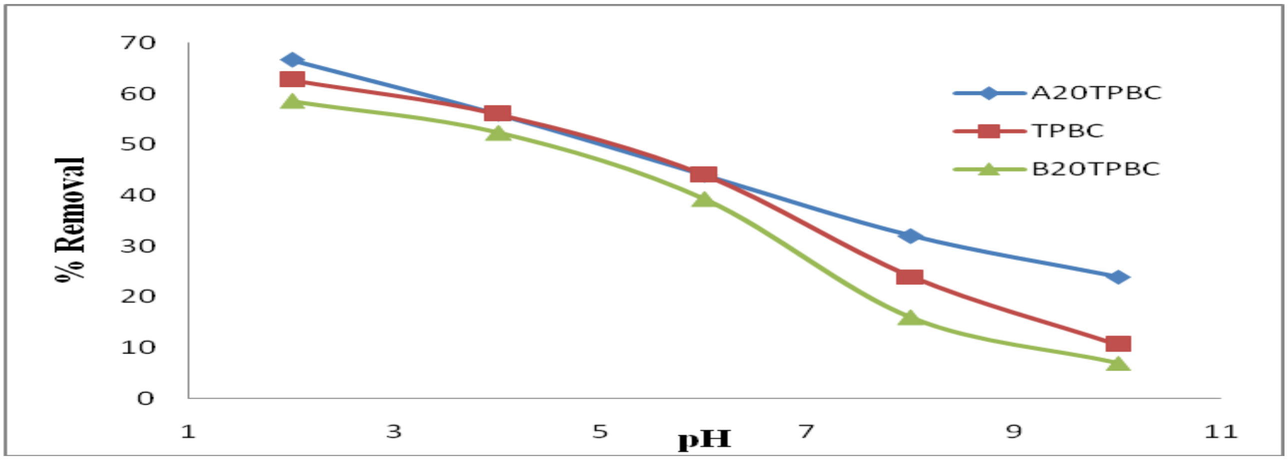


Fig. 3: Effect of pH for Cr (VI) onto TPBC, A20TPBC & B20TPBC

2.8. Isotherm studies

2.8.1. Langmuir isotherm

Langmuir is based on the following assumptions such as,

- Adsorption limited to monolayer coverage
- All surface sites being alike one site accommodates one species of the adsorbates and the ability of a molecule to be adsorbed on a given site independent of its neighbouring sites occupancy.

Linear formof Langmuir equation is written as [13]

$$C_e/Q_e = 1/Q_m b + C_e/Q_m$$

Where Q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), Q_m is the maximum monolayer adsorption capacity (mg/g) and bis the adsorption energy. The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation,

$$R_L = 1 / (1 + bC_0)$$

Where C_0 is the initial concentration of the adsorbate solution. The separation factor R_L indicates the shape of the isotherm and the nature of the adsorption process as given below:

R_L value	Nature of the process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The mono layer adsorption capacity $Q_m$values (mg/g) for adsorption of Cr (VI) ion onto TPBC, A20TPBC and B20TPBC system, the values ranged from 21.310 to 22.959, 20.822 to 23.408 and 21.739 to 23.697, respectively. A20TPBC seems to have a higher adsorption capacity than other two carbons with respect to adsorption of Cr (VI) ion for all the studied temperatures. The adsorption capacity increased with the increase of temperature. The values of Langmuir constant 'b', the adsorption energy ranges from 0.155 to 0.329 for all the three systems. These values indicate that the apparent energy of sorption is less and rules out the possibility of strong interaction between the solute and adsorption site. The dimensionless separation factor R_L values calculated for various initial concentrations at different temperatures are lie between 0 and 1 which indicates the favourable adsorption of Cr (VI) onto TPBC, A20TPBC and B20TPBC. These R_L values are presented in table 1.

2.8.2. Freundlich Isotherm

Freundlich Isotherm is the most popular model for a single solute system based on the distribution of solute between the solid phase and aqueous phase at equilibrium. The Freundlich model describes the adsorption within a restricted range only. It is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents.

Linear form of Freundlich Isotherm equation is written as [14]

$$\log q_e = \log K_f + 1/n \log C_e$$

Where q_e is the amount of adsorbate adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of adsorbate in solution (mg/L) and K_f and n are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

Freundlich constant K_f (mg/g) for adsorption of Cr (VI) ion onto TPBC, A20TPBC and B20TPBC systems, the values ranged from 4.18 to 5.20, 4.79 to 6.00 and 4.50

to 5.62 respectively. The adsorption intensity constant ‘n’ values are ranged from 1.86 to 2.25 for all the studied systems, *i.e.*, between 1 and 10, which indicates the favourable physical adsorption. ‘n’ value increases with an increase of temperature for all the studied systems. In general Freundlich constant values infer a better performance for all the studied systems.

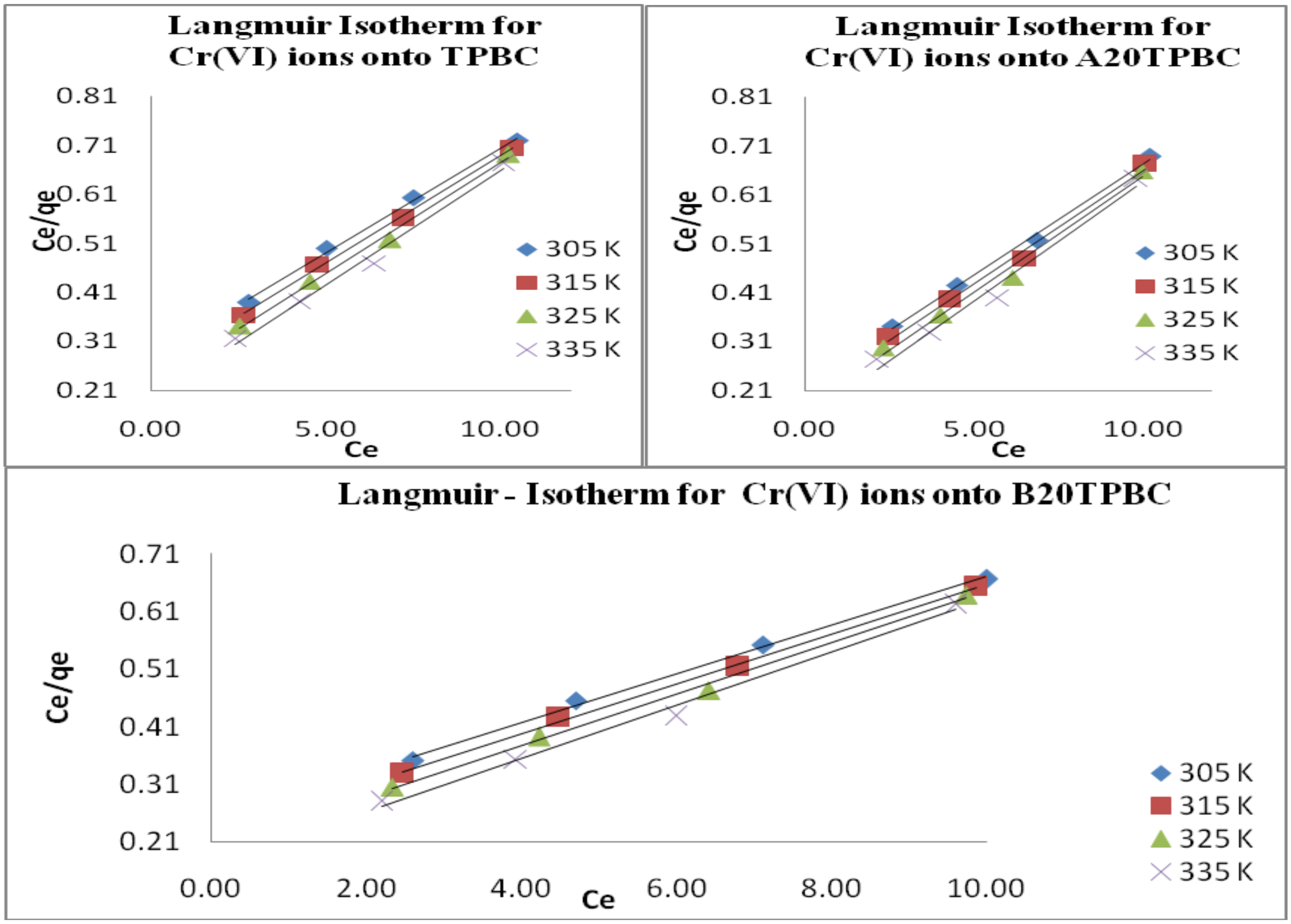


Fig. 4: Langmuir Isotherm plots for Cr (VI) ions onto TPBC, A20TPBC & B20TPBC

Table 1: Langmuir isotherm results for the adsorption of Cr (VI) ions Onto TPBC, A20TPBC and B20TPBC

Adsorbent	Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
				10mg/L	15mg/L	20mg/L	25 mg/L	
TPBC	305	21.310	0.155	0.392	0.300	0.244	0.142	0.9972
	315	22.179	0.176	0.363	0.275	0.222	0.186	0.9987
	325	22.673	0.202	0.331	0.248	0.198	0.165	0.9962
	335	22.959	0.241	0.293	0.217	0.172	0.142	0.9904
A20TPBC	305	20.822	0.202	0.331	0.248	0.198	0.108	0.9967
	315	21.445	0.232	0.301	0.223	0.177	0.147	0.9927
	325	21.953	0.271	0.269	0.197	0.156	0.128	0.9873
	335	23.408	0.329	0.233	0.169	0.132	0.108	0.9817
B20TPBC	305	21.739	0.170	0.371	0.282	0.228	0.130	0.9971
	315	22.470	0.193	0.341	0.257	0.206	0.172	0.9986
	325	23.095	0.223	0.309	0.230	0.183	0.152	0.9965
	335	23.697	0.268	0.272	0.199	0.157	0.130	0.9916

[pH=2; Dose = 20 mg/50 mL]

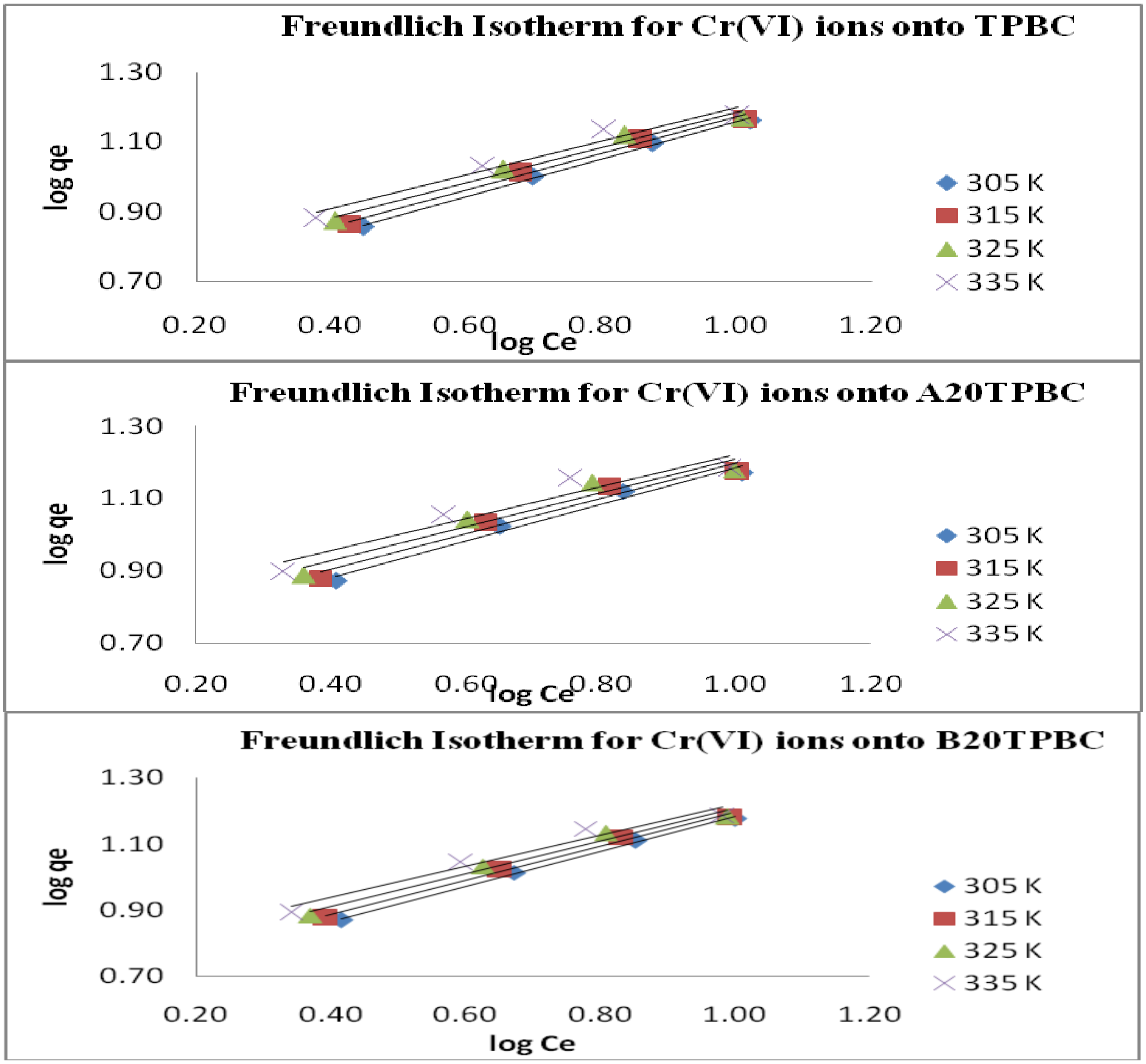


Fig. 5: Freundlich Isotherm plots for Cr (VI) ions onto TPBC, A20TPBC & B20TPBC

Table 2: Freundlich isotherm results for the adsorption of Cr (VI) ion onto TPBC, A20TPBC and B20TPBC

Adsorbent	Temperature (K)	n	k_f(mg/g)	R^2
TPBC	305	1.86	4.18	0.9982
	315	1.92	4.46	0.9930
	325	1.98	4.79	0.9815
	335	2.07	5.20	0.9608
A20TPBC	305	1.98	4.79	0.9792
	315	2.05	5.12	0.9660
	325	2.13	5.51	0.9446
	335	2.25	6.00	0.9127
B20TPBC	305	1.89	4.50	0.9981
	315	1.95	4.81	0.9927
	325	2.02	5.16	0.9811
	335	2.11	5.62	0.9605

[Cr (VI) ion, pH = 2; Dose = 20 mg/ 50 mL]

2.8.3. *Tempkin isotherm*

The Tempkin isotherm assumes that the heat of sorption in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. Further the fall in the heat of adsorption is not logarithmic as stated in Freundlich expression.

The linear form of Tempkin equation is, [15]

$$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e$$

Where, b_T is the Tempkin constant related to the heat of sorption (J/mg) and a_T the equilibrium binding constant corresponding to the maximum binding energy (L/g) The Tempkin constants a_T and b_T were calculated from the slopes and intercepts of q_e versus ln C_e Equilibrium binding constant 'a_T' values (L/g) for adsorption of Cr(VI) ions onto three carbons. Systems are ranged from 1.267 to 1.839 for TPBC, 1.574 to 2.485 for A20TPBC and 1.385 to 2.060 for B20TPBC. The Tempkin constant related to heat of sorption, b_T values are ranged from 4.48 J/mg to 5.56 J/mg for the four studied temperatures viz. 305, 315, 325 and 335 K for Cr(VI) ions onto TPBC, A20TPBC and B20TPBC.

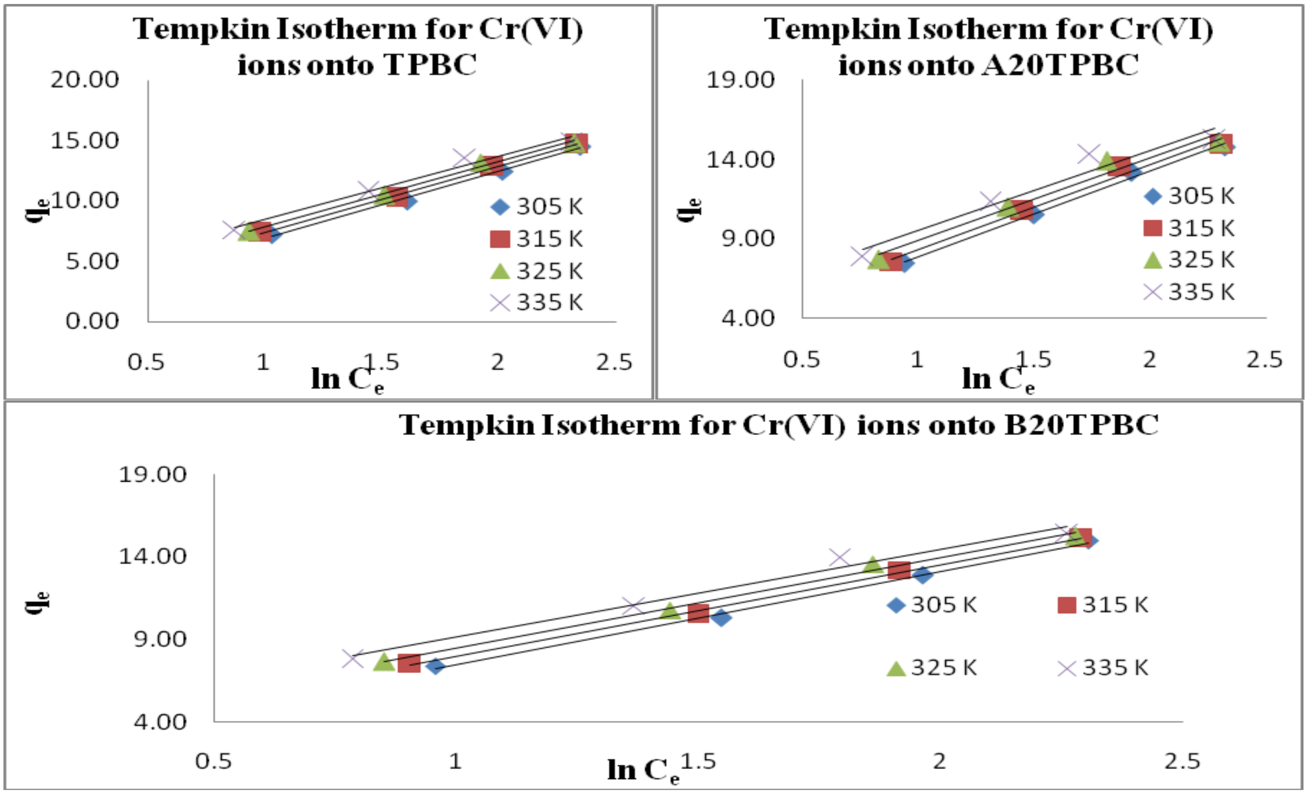


Fig. 6: Tempkin Isotherm plots for Cr (VI) ions TPBC, A20TPBC & B20TPBC

Table 3: Tempkin isotherm results for the adsorption of Cr (VI) ions onto TPBC, A20TPBC and B20TPBC

Adsorbent	Temperature (K)	a_T	b_T	R^2
TPBC	305	1.267	4.56	0.9961
	315	1.405	4.77	0.9978
	325	1.578	5.01	0.9939
	335	1.839	5.29	0.9805
A20TPBC	305	1.574	4.68	0.9948
	315	1.782	4.93	0.9859
	325	2.055	5.21	0.9691
	335	2.485	5.56	0.9408
B20TPBC	305	1.385	4.48	0.9961
	315	1.545	4.71	0.9976
	325	1.749	4.95	0.9937
	335	2.060	5.24	0.9804

[Cr (VI) ions, pH = 2; Dose = 20 mg/ 50 mL]

2.8.4. Dubinin – Radushkevich isotherm

The Linear form of Dubinin-Radushkevich isotherm is [16]

$$\ln q_e = \ln q_D - B\varepsilon^2$$

Where, q_D is the theoretical saturation capacity (mg/g) B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) and ε is polanyi potential which is related to the equilibrium as given below

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

The constants q_D and B were calculated from the slope and intercept of straight line obtained from the plot of ln q_e versus ε^2. The mean free energy of adsorption E calculated from B using the following equation.

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

E is a parameter used in predicting the type of adsorption. An E value less than 8kJ/mol is an indication of physisorption. The results obtained from Dubinin- Radushkevich (D - R) model for the removal of Cr (VI) ion onto TPBC, A20TPBC and B20T PBC were represented in table 4. Concerned isotherm plots were shown in fig. 7.

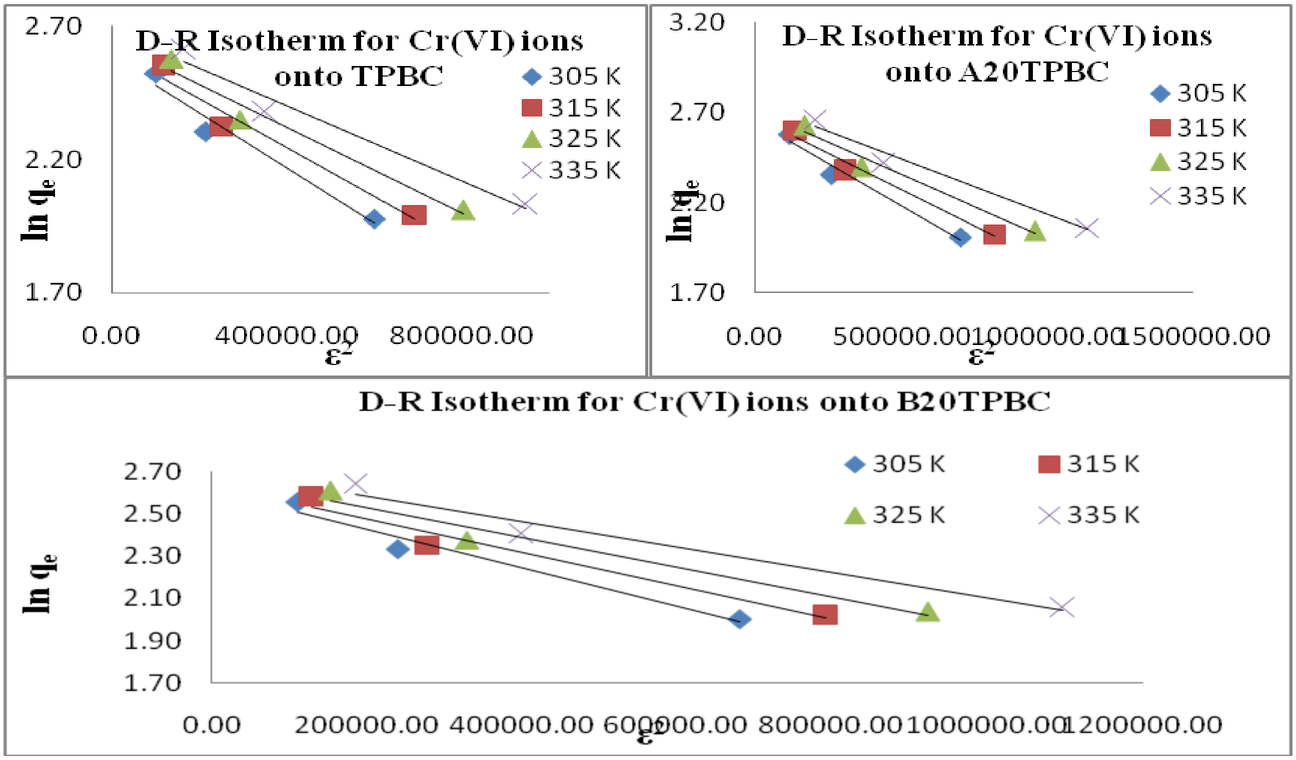


Fig. 7: D-R Isotherm plots for Cr (VI) ions onto TPBC, A20TPBC & B20TPBC

Table 4: D-R isotherm results for the adsorption of Cr (VI) ions onto TPBC, A20TPBC and B20TPBC

Adsorbent	Temperature (K)	Q_D	E kJ	R^2
TPBC	305	166.38	0.622.	0.9638
	315	176.93	0.618	0.9629
	325	195.58	0.613	0.9643
	335	208.54	0.610	0.9674
A20TPBC	305	194.40	0.614	0.9726
	315	206.26	0.611	0.9721
	325	222.18	0.607	0.9737
	335	242.94	0.603	0.9770
B20TPBC	305	177.46	0.618	0.9626
	315	188.23	0.615	0.9618
	325	202.44	0.612	0.9631
	335	220.80	0.607	0.9664

[Cr (VI) ion, pH = 2; Dose = 20 mg/50 mL]

The mono layer adsorption capacity $q_D$values (mg/g) for adsorption of Cr(VI) ions onto TPBC, A20TPBC and B20TPBC system are ranged from 166.38 to 208.54for TPBC, 194.40 to 242.94 for A20TPB Cand 177.46 to 220.80for B20TPBC.A20TPBC seems to have a higher saturation adsorption capacity than other two carbons with respect to adsorption of Cr(VI) ions for all the studied temperatures.

Further it is noticed that adsorption capacity increased with an increase in temperature. Values of the mean free energy of adsorption were ranged 0.622 kJ/molto 0.610kJ/molfor TPBC, 0.614 kJ/molto 0.603kJ/molfor A20TPBCand 0.618 kJ/molto 0.607kJ/molfor B20TPBC. The magnitude of E is below 8kJ/mol in all the studied systems infers the physisorption interaction, whereas the value of $8<E<16$ is an indicator of the chemical adsorption.

2.9. Thermodynamic study

To evaluate the feasibility of the adsorption process, thermodynamic parameters such as change in free energy ΔG° (kJ/mol), enthalpy ΔH°(kJ/mol) and entropy ΔS° (J/K/mol) can be determined using the following equations [17].

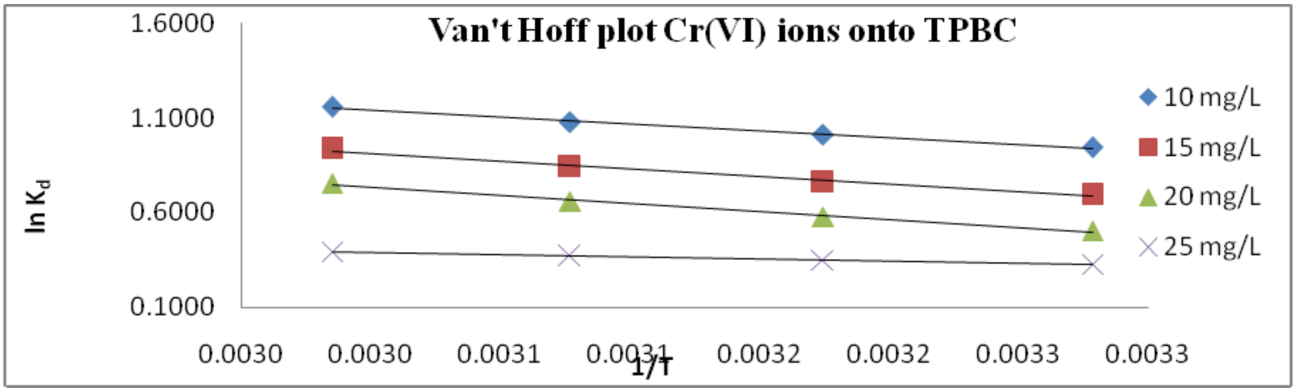
$$k_d = C_{solid} / C_{liquid}$$

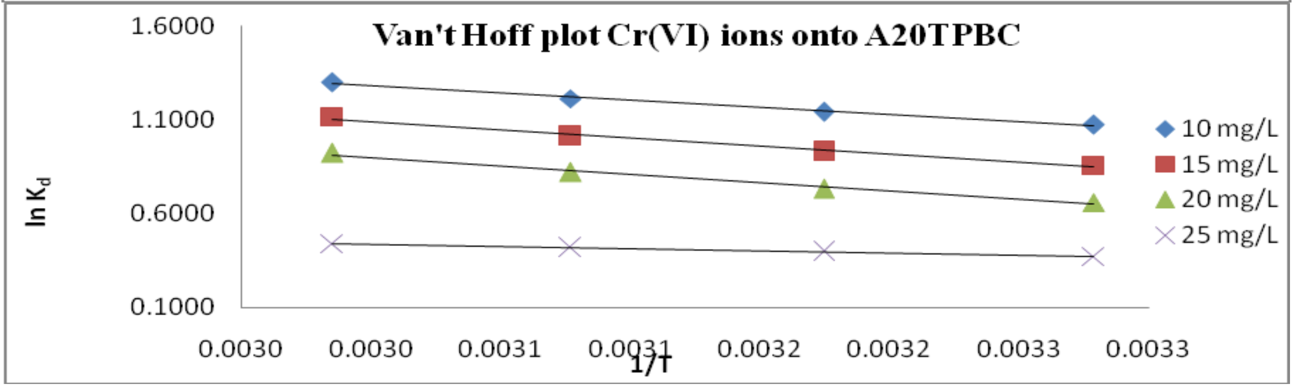
$$\Delta G^\circ = -RT\ln k_d$$

$$\log k_d = \Delta S^\circ / (2.303RT) - \Delta H^\circ / (2.303R)T$$

Where k_d is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), $C_{liquid}$is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The Vant Hoff plots are drawn between $\ln k_d$ versus 1/T. ΔH° and ΔS° values were evaluated from the slope and intercept of the plot respectively.The positive value of ΔH° indicates endothermicity and negative value indicates the exothermicity of the adsorption process. Positive value of ΔS° indicates that the adsorption accompanies increased randomness while the negative value infers that the adsorption accompanies reduction in the randomness. Spontaneity of the adsorption can be understood from the sign of ΔG° value. Negative sign indicates the spontaneous process while the positive sign indicates the non-spontaneity of the process.

The negative values of ΔG° (table 5) show that the adsorption is highly favourable and spontaneous for all the studied systems.The ΔH° values were within the range of 1 to 93 kJ/mol which indicates the favorability of physisorption. The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. This fact supports the physical adsorption and rules out the possibility of chemisorptions. The positive values of ΔS° show the increased disorder and randomness at the solid solution interface.





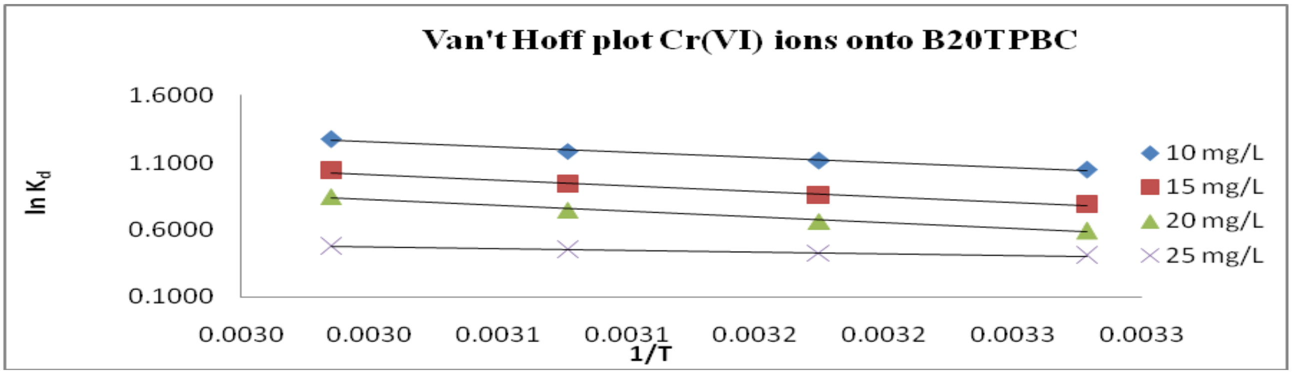


Fig. 8: Van't Hoff plotsfor Cr (VI) ions onto TPBC, A20TPBC & B20TPBC

Table 5: Thermodynamics results for the adsorption of Cr (VI) ions onto TPBC, A20TPBC and B20TPBC

Adsorbent	Temperature (K)	ΔG	ΔH	ΔS	R^2
TPBC	305	-1.56	7.03	27.19	0.9903
	315	-1.76	6.79	27.99	0.9875
	325	-1.99	6.00	27.51	0.9940
	335	-2.26	1.90	08.96	0.9959
A20TPBC	305	-1.87	7.42	29.74	0.9935
	315	-2.09	7.31	30.99	0.9867
	325	-2.33	6.43	29.96	0.9896
	335	-2.63	1.92	09.40	0.9958
B20TPBC	305	-3.07	7.24	28.59	0.9945
	315	-2.41	7.06	29.63	0.9883
	325	-1.90	6.34	29.43	0.9909
	335	-1.17	1.93	9.70	0.9960

[Cr (VI) ions, pH = 2; Dose = 20 mg/ 50 mL]

3. CONCLUSION

Microwave assisted phosphoric acid activated carbon prepared from *Thespesia Populnea barks* found to have good capacity of adsorption. Experimental data indicated that A20TPBC was effective in removing Cr(VI) ions from aqueous solution. Equilibrium adsorption was achieved in about 80 minutes for the dosage of 20 mg/50 mL of solution at room temperature of 305 K for the initial concentration of Cr(VI) ions solutions ranging from 10 to 25 mg/L. Langmuir and Tempkin isotherm represents the equilibrium adsorption data well when compared to other isotherms studied. The separation factor RL values indicated that the adsorption was favourable. Thermodynamic study revealed that the adsorption system was spontaneous, endothermic with increased randomness.

Conflict of interest

None declared

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