



STUDIES ON THE ADSORPTION OF Cr (VI) FROM AQUEOUS SOLUTION BY LOW COST ACTIVATED CARBON

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ABSTRACT

The efficiency of activated carbon prepared from *Azadirachta indica* stem carbon (AZSC) for the adsorption of Cr(VI) from aqueous solution using batch mode experiment has been studied as a function of agitation time, adsorbent dosage, initial dye concentration, temperature and pH of adsorbate solution. The ideal conditions for the adsorption have been shown up and tests were led to discover the Langmuir constants, Freundlich constants, Lagergren, Bhattacharya-Venkobachar and kinetic parameters. The percentage removal of Cr(VI) increases with the increase of the dose of the adsorbent and decreases with the increase of the concentration of adsorbate solutions. Similarly, the minimum time required to achieve maximum adsorption also increases with the increase of the dose of the adsorbent. Studies pertaining to FT-IR, SEM, effect of temperature and desorption studies revealed the existence of physisorption.

Keywords: Activated carbon (AZSC), reactive red 2, Adsorption isotherm, Equilibrium, Kinetic parameters.

1. INTRODUCTION

Chromium, a commonly toxic and carcinogenic heavy metal, is widely found in industrial wastewaters [1-3]. Therefore, the elimination of this element from the wastewater to prevent its entry into the aquatic environment, which is the objective of this study, is of prime importance. Chromium can be found in trivalent (Cr(III)) and hexavalent (Cr(VI)) forms in natural waters. The trivalent species are one of the trace elements for living organisms whereas the hexavalent species are hazardous to humans and other living organisms even at very low concentrations due to toxicity, mutagenicity and carcinogenicity. Some of the adverse effects of exposures to the Cr(VI) include injury to the central nervous system, the kidneys damage, anemia, lung cancer and gastrointestinal cancer. Annually a large volume of wastewater containing Cr(VI) is discharged to the environment from several industries such as steel, textile, electrical plating and chromium plating industries.

In order to achieve the satisfactory water quality in relation to these determined limits, removal of Cr(VI) from discharges of industries is necessary. In this regard, various approaches such as chemical precipitation [4], ion exchange [5], membrane filtration [6] and

adsorption were examined for Cr(VI) removal from industrial effluents. Among these methods, the adsorption is known as an efficient method due to ease of use, low-cost, high efficiency and eco-friendly [7].

In the present investigation, the investigator has chosen the activated carbon prepared from *Azadirachta indica* stem carbon (AZSC), as the adsorbent and carried out batch mode experiments to study the effect of contact time on the removal of Cr(VI) with the variation of the dose of the adsorbent, Variation of the initial concentration of the solution, variation of pH, variation of size of the adsorbent and variation of temperature. Various models such as Lagergren [8], Bhattacharya-Venkobachar [9], Langmuir [10] and Freundlich [11] were tested and the results were interpreted.

2. MATERIAL AND METHODS

2.1. Experimental techniques

Preparation of activated carbon from the plant *Azadirachta indica* comprises of the following stages like procurement of raw material for carbonization, impingement with doping agents like H₂SO₄, ZnCl₂ or H₃PO₄, carbonization and activation. For the selection of an appropriate raw material for preparation of porous carbon, several factors are taken into consideration.

Industrially, inexpensive material with high carbon and low inorganic (*i.e.* low ash) content is preferred as raw material for the production of activated carbon. The plant *Azadirachta indica* procured locally, cut into small pieces after the removal of their bark and dried.

Pyrolysis is the process in which AZSC heated, decomposed and eventually converted into desired product in absence of air in the fixed bed reactor. During carbonization, most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting materials. Thus carbonization involves thermal decomposition of carbonaceous material, eliminating non-carbon species producing a fixed carbon mass and rudimentary pore structure [12].

Activation is carried to enlarge the diameters of the pores which are created during the carbonization process and to create some new porosity thus resulting in the formation of pore structure with very large surface area.

Chemical activation was carried out with AZSC as the starting material. Initially, wood was impregnated with a concentrated solution of activating agents. It resulted in degradation of cellulosic material. Chemical-impregnated materials were then pyrolysed between 400 and 600°C in the absence of air. Product was cooled and washed to remove activating agents, which was recycled. On calcinations, impregnated and chemically dehydrated raw material resulted in charring and aromatization, and creation of porous structure. The activation agents used were sulphuric acid and calcium chloride [13]. All the activating agents were dehydrating agents which influenced the pyrolytic decomposition, inhibited tar formation and decreased the formation of acetic acid, methanol etc., and enhanced the yield of carbon.

A pseudo-activated carbon has been prepared by reacting AZSC with concentrated sulphuric acid or phosphoric acid and heated to 120-130°C. The activated AZSC obtained from different process were ground using a mortar and pestle sieved into several size fraction using American Standard Testing Mesh. The sieved particles were then dried in a hot air oven over night at 110°C. These particles after removing from the oven were cooled in desiccators. Then they were stored in air-tight containers for further characterization.

The activated AZSC samples were examined using Perkin-Elmer FT-IR spectrophotometer. The surface morphologies of activated AZSC were observed with Scanning Electron Microscope at CECRI, Karaikudi.

3. RESULTS AND DISCUSSION

The prepared AZSC are of particle size 75-125 μ , bulk density 0.3576g/cc, moisture content 1.85%, loss on ignition 85%, acid insoluble matter 2.78%, water soluble matter 0.62%, pH 6.4, pH_{zpc} 6.45 and surface area 346.8m²/g.

Similarly the FT-IR spectra of raw activated carbon AZSC shown in fig. 1(a). The band at 3412.7 cm⁻¹ is due to stretching of O-H group. The band at 2361.4 cm⁻¹ shows the presence of C=C stretching. The N-H bending vibrations occur in the region of 1590.9 cm⁻¹ and C-O-C stretching vibrations occur in the region of 1156.3 cm⁻¹.

The adsorption of metal Cr (VI) ion on AZSC is shown in fig. 1(b). Slight reduction of stretching vibration absorption band could be seen, which indicates the adsorption of metal ion on the adsorbent by physical forces.

3.1. SEM Images

The SEM images of raw activated carbons of AZSC and the same after Cr(VI) adsorption are shown in fig. 2 (a) and (b), respectively. The bright spots show the presence of tiny holes on the crystalline structure of raw activated carbons. After treatment with Cr(VI), the bright spots have become dark which reveal that the adsorption of metal on the surface of the carbon by means of physisorption [14-16]. SEM images of AZSC shows that the adsorbent has a rough surface with almost non-compact structure. It is obvious that the sorbent has considerable number of pore spaces, where appropriate conditions exist for Cr(VI) ions to be trapped and adsorbed into the pores. The SEM images also illustrate that the Cr(VI) ion can be homogeneously adsorbed on the surface of adsorbent. The surfaces of AZSC were found to be not so random but rough in such a way to adhere the solute species on to the surface of the adsorbent which is revealed from the SEM images. Hence, the adsorptive characteristics of AZSC are expected to be highly effective.

3.2. Effect of dosage of AZSC

The table-1 presents the results of the effect of dose of the adsorbent, namely, 2.0, 4.0, 6.0, 8.0 and 10.0 g/L respectively on the adsorption potential of Cr(VI) and minimum time required for the maximum Cr (VI) removal. Fig.3(a) represents the plot of Cr(VI) adsorbed in percentage for various doses of the adsorbent. This showed that as the dose of the adsorbent increases, adsorption of Cr(VI) also increases.

This may be due to the increased carbon surface area and availability of more adsorption sites [17-19].

3.3. Effect of contact time

During the process of adsorption, the rate of removal of Cr(VI) increases with increasing time, up to a certain period, and thereafter, the rate of removal of the solute becomes constant. At one stage, it may even become insignificant. It is understood from the table-1 that the residual concentration of Cr(VI) drops steeply in the first 150 min and then only marginal increase in adsorption rate of Cr(VI) ions was observed [20, 21]. The initial step drop of the residual concentration of

Cr(VI) is due to the rapid removal of Cr(VI) ions which occurs as a result of the presence of large number of active adsorption sites available on the surface of the adsorbent, when compared to the number of adsorbate species in the solution. Hence for the present study, 180 min is fixed to be the equilibration time, which means that, 180 min appear to be sufficient for maximum adsorption of Cr(VI) by the chosen adsorbent under the given set of experimental conditions. The maximum amount of Cr(VI) adsorbed corresponding to the equilibration time is found to be 84.9% for a weight of 2 g/L of the adsorbent shown in fig. 3(b).

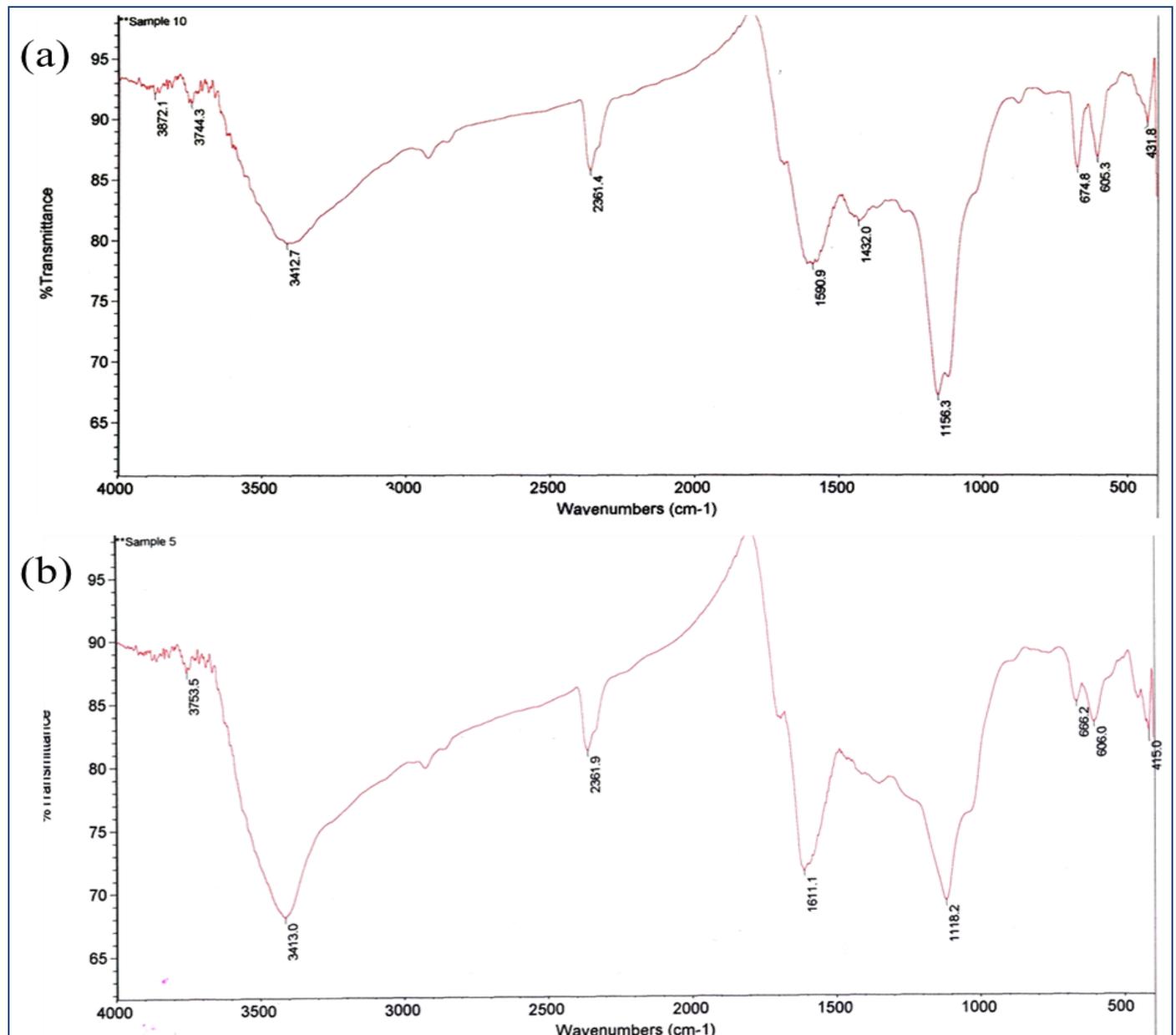


Fig. 1: FT-IR spectrum of (a) raw AZSC and (b) AZSC after Cr (VI) adsorption

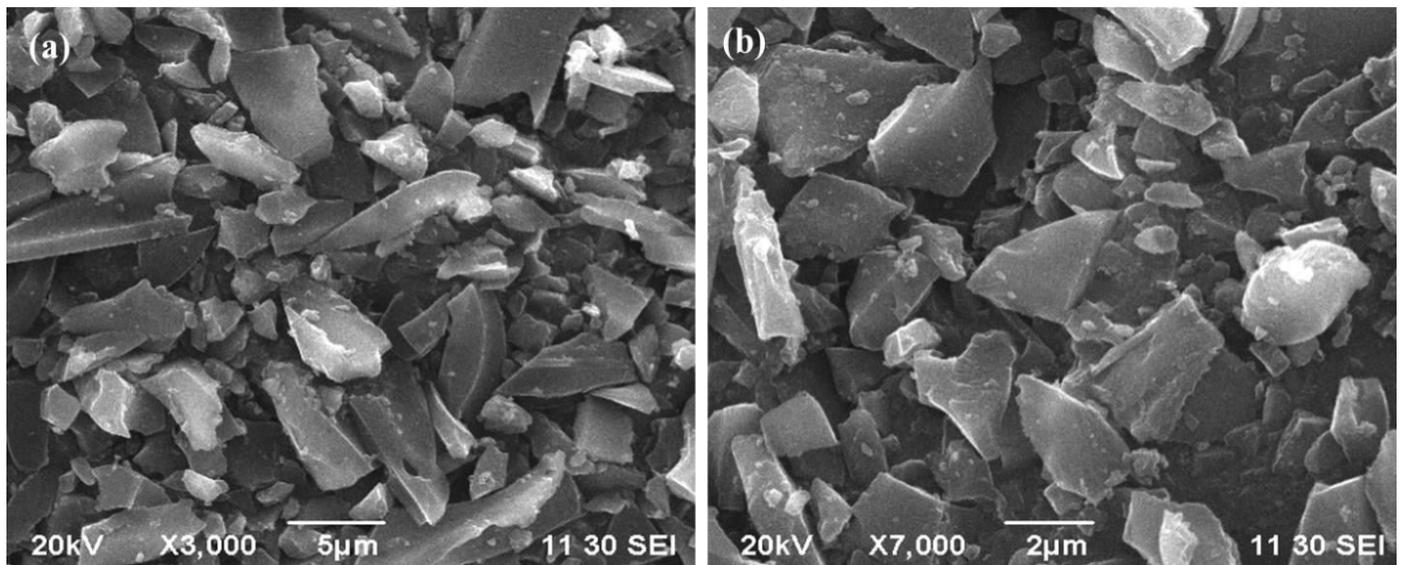


Fig. 2: SEM image of (a) raw AZSC and (b) AZSC after Cr (VI) adsorption

Table 1: Effect of adsorbent dose, contact time and metal ion concentration on the removal of Cr(VI)

S. No	Effect of adsorbent		Effect of contact time		Effect of concentration	
	Dose of the adsorbent m, g/ L	Maximum adsorption, %	Contact time, min	[Cr(VI)] _{adsorbed} at equilibrium, %	Metal ion Concentration of Cr(VI), mg/L	[Cr(VI)] _{adsorbed} at equilibrium, %
1	2.0	84.9	30	61.2	50	84.9
2	4.0	86.7	60	62.8	100	44.8
3	6.0	91	90	70.6	150	32.8
4	8.0	92.4	120	79.7	200	26.7
5	10.0	98.3	150	82.4	250	22.7
6			180	84.9	300	19.8
7			210	85.1	400	15.7
8					500	13.08

3.4. Effect of initial metal ion concentration

A series of experiments were conducted at different concentrations namely, 50, 100, 150, 200, 250, 300, 400 and 500 mg/L, keeping all other experimental conditions constant, with a view to obtaining information about the influence of concentration on both the maximum removal of Cr(VI) and the minimum time for maximum removal.

The values in table-1 indicate that the percentage removal of Cr(VI) ions decreases with the increasing concentration of the solution. It is also interesting to know that the amount of Cr(VI) adsorbed at equilibrium time is 84.9%, when the concentration of the solution is 50 mg/L, and the corresponding Cr(VI) removal at equilibrium time for 500 mg/L is 13.08 %. This showed that as the concentration of the solution increases the percentage of adsorption of Cr(VI)

decreases [10, 22]. Fig.3(c) represents the plot of Cr(VI) adsorbed in percentage against the various concentrations of adsorbate solutions. The curve in this figure is a single, smooth, and continuous, suggesting the probability of the formation of monolayer coverage of Cr(VI) on to the outer surface of the adsorbent.

3.5. Effect of pH

Experiments were conducted using Cr(VI) ion concentration around 50 mg/L and the weight of the adsorbent around 2.0 g/L at different pH values viz., 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0. The percentage removal of Cr(VI) and the corresponding pH shown in table-2 and fig. 4(a). It is found that the adsorption of Cr(VI) is maximum [23-26] at the pH range of 1.5 to 2. Accordingly, the present study has been carried out at pH 1.5.

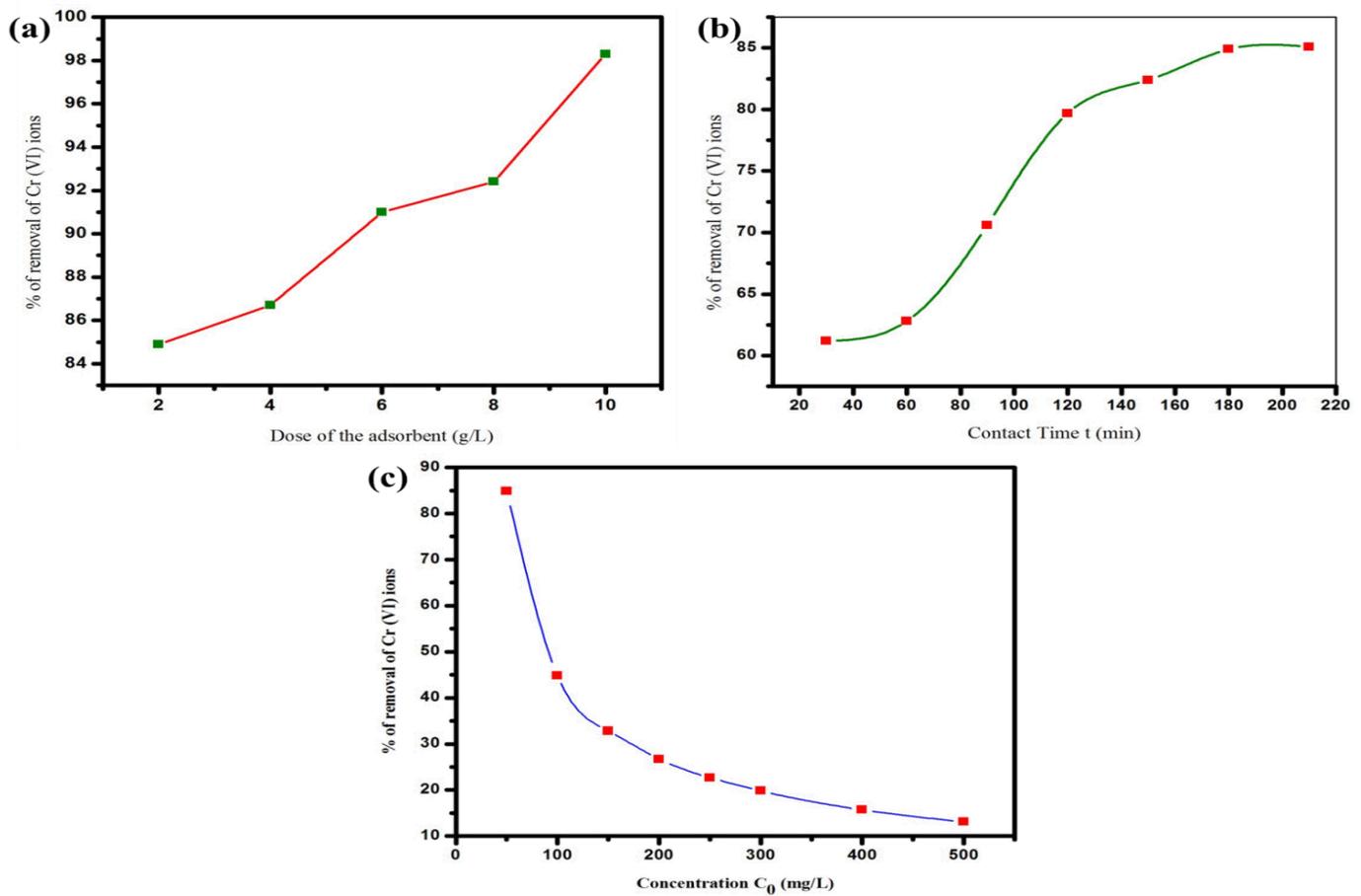


Fig. 3: Effect of (a) Adsorbent dose, (b) Contact time and (c) Concentration of metal ions on the removal of Cr(VI)

3.6. Effect of Temperature

A series of isotherms were determined at four different temperatures, viz., 35, 40, 45 and 50°C in a thermostatic shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of $\pm 0.5^\circ\text{C}$. The percentage removal of Cr(VI) at different temperatures is shown in fig. 4(b) and the respective data are shown in table 2. The result indicates that as the temperature of the solution increases, percentage adsorption of Cr(VI) also increases. It is clear that the adsorption is maximum at higher temperature and found to be an endothermic process [27-31].

3.7. Effect of Size of the Adsorbent

The experimental results of adsorption of Cr(VI) ion on to the activated carbon with various sizes (75-125, 125-200, 200-250, 250-300 μ) of the adsorbent are shown in table 2 and the corresponding values for the effect of size of the adsorbent on removal of Cr (VI) are plotted in fig.4 (c). It was found that the adsorption is much

favorable with the 75-125 μ size of the adsorbent revealing that smaller the size, larger is the surface area [11, 32].

3.8. Adsorption Kinetics

The experimental data obtained for the adsorption of Cr(VI) on to the surface of AZSC under the given set of conditions were analyzed in the light of Lagergren equation, with the view to evaluating the mechanistic parameters associated with the process of adsorption. $\log_{10}(q_e - q) = -k_{\text{Lagergren}} t / 2.303 + \log_{10} q_e$ where, q_e , q , $k_{\text{Lagergren}}$ and t are the amount of metal ions adsorbed at equilibrium, amount of metal ions adsorbed per unit weight of the adsorbent at time t , Lagergren rate constant and time respectively. The Lagergren equation [8] suggests linearity for the plot of $\log_{10}(q_e - q)$ against time, t . The fig. 5 and table 3 represents the relation between $\log_{10}(q_e - q)$ and t under a given set of experimental conditions at temperature 35°C (C_e , q_e for 2.0, 4.0, 6.0, 8.0, 10.0 g/L are 6.9, 5.7, 4.5, 3.8, 0.85mg/L and 21.6, 11.1, 7.6, 5.8, 4.9mg/g

respectively). From the slope of each line, the rate constants were determined.

The values of $k_{Lager} \times 10^4, s^{-1}$ obtained for different doses of the adsorbents are presented in Table 5. The results thus obtained were further confirmed by Bhattacharya-Venkobachar equation [9].

$\log_{10} [1-U_t] = -k_{Bhatt} t / 2.303$ where $U_t = [(C_0 - C_t) / (C_0 - C_e)]$, k_{Bhatt} , C_0 , C_t and C_e are Bhattacharya-Venkobachar rate constant, concentration of metal ion initially, concentration of metal ion at time, t and concentration of metal ion at equilibrium respectively

The fig.6 and table 4 represent the relation between $\log_{10} [1-U_t]$ and t under a given set of experimental conditions at temperature $35^\circ C$ (C_e for 2.0, 4.0, 6.0,

8.0, 10.0 g/L are 6.9, 5.7, 4.5, 3.8, 0.85 mg/L respectively). From the slope of each line, the rate constants were determined. The values of $k_{Bhatt} \times 10^4, s^{-1}$ obtained by using different doses of the adsorbent at pH 1.5, are presented in the table 5. It is found that the k_{Bhatt} values are also similar to those of k_{Lager} . These values reveal the decreasing trend with the increase of the dose of the adsorbent from 2 to 4 g/L and increases as well as remain almost same for 6 to 10 g/L [30]. Furthermore, the applicability of the both Lagergren and Bhattacharya-Venkobachar equations confirm the formation of a monomolecular layer of Cr(VI) ions on to the surface of the adsorbent, as well as the first order kinetic nature of the process.

Table 2: Effect of pH, Temperature and size on the removal of Cr(VI)

S. No	Effect of pH		Effect of Temperature		Effect of size	
	pH	[Cr(VI)] _{adsorbed} at equilibrium, %	Temperature, °C	[Cr(VI)] _{adsorbed} at equilibrium, %	Size of the adsorbent μ	[Cr(VI)] _{adsorbed} at equilibrium, %
1	0.5	76.4	35	84.9	75-125	84.9
2	1	58.3	40	91.6	125-200	82.08
3	1.5	85.3	45	95.6	200-250	79.59
4	2	84.6	50	98.4	250-300	73.88
5	3	71.2				
6	4	53.4				

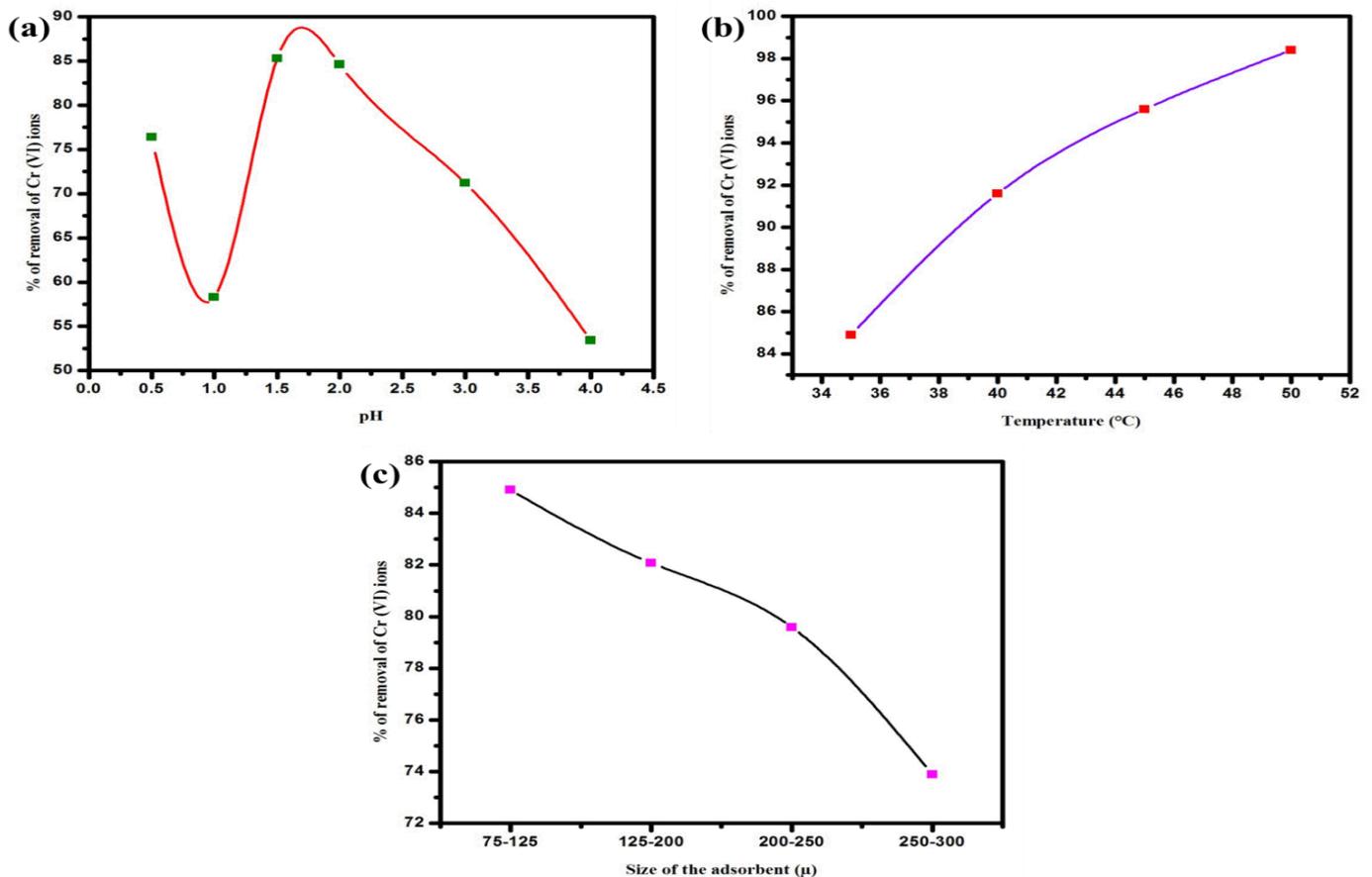


Fig. 4: Effect of (a) pH, (b) Temperature and (c) Size of the adsorbent on the removal of Cr(VI)

Table 3: Effect of contact time on Cr(VI) removal-adsorbent dose variation

S. No.	Contact time t, min	$2+\log_{10}(q_e-q)$				
		Adsorbent Dose (g/L)				
		2.0	4.0	6.0	8.0	10.0
1	30	2.79	2.52	2.32	2.14	2.13
2	60	2.76	2.45	2.23	1.91	1.95
3	90	2.59	2.36	2.01	1.50	1.45
4	120	2.20	2.11	1.177	1.14	
5	150	1.97	1.72	1.0		
6	180	1.47	1.38			
7	210	1.39				
8	240	0.69				

Table 4: Effect of contact time on Cr(VI) removal - adsorbent dose variation

S. No.	Contact time t, min	$2+\log(1-U_t)$				
		Adsorbent Dose (g/L)				
		2.0	4.0	6.0	8.0	10.0
1	30	1.46	1.47	1.44	1.37	1.44
2	60	1.43	1.39	1.35	1.15	1.26
3	90	1.25	1.31	1.13	0.74	0.76
4	120	0.87	1.05	0.29	0.38	
5	150	0.64	0.67	-0.005		
6	180	0.14	0.33			
7	210	0.07				
8	240	-0.63				

Table 5: Effect of the dose of the adsorbent on k_{Lager} and k_{Bhatt}

S. No.	Dose of the adsorbent m, g/ L	$k_{Lager} \times 10^4, s^{-1}$	$k_{Bhatt} \times 10^4, s^{-1}$
1	2.0	3.87	3.37
2	4.0	2.59	2.95
3	6.0	4.72	4.68
4	8.0	4.37	4.37
5	10.0	4.41	4.41

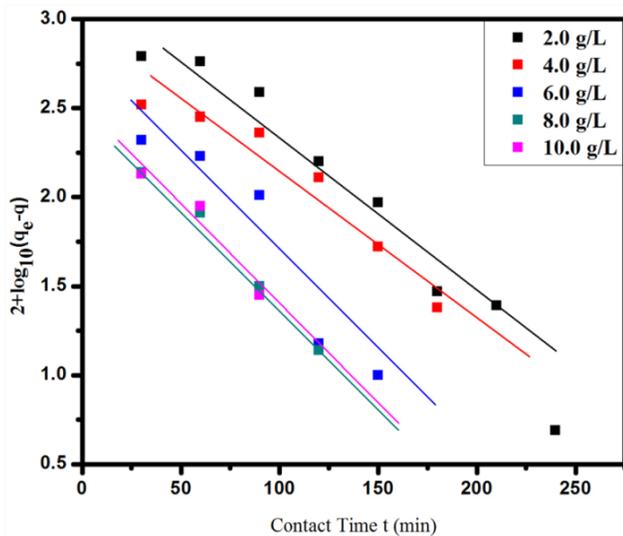


Fig. 5: Lagergren plot-dose variation

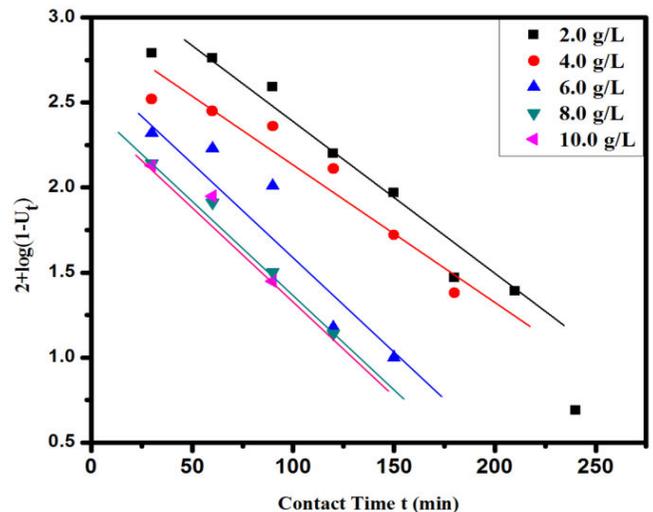


Fig. 6: Bhattacharya-Venkobachar plot-dose variation

3.9. Adsorption Isotherm

The Langmuir isotherm is represented by $C_e / q_e = 1 / Q_m b + C_e / Q_m$ Where C_e , q_e , Q_m , and b were the equilibrium concentration, amount adsorbed at equilibrium, Langmuir constants related to adsorption efficiency and energy of adsorption respectively. The data for Langmuir and Freundlich isotherms at different temperatures viz., 35, 40, 45 and 50°C are presented in tables 6-9. The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms shown in fig. 7. Values of Q_m and b were determined from slope and intercepts of the plots and are presented in table 11. From the results, it is clear that the value of adsorption efficiency Q_m and adsorption energy b of the carbon increases on increasing the temperature. Further, it confirms the endothermic nature of the processes involved in the system.

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter R_L . $R_L = 1 / (1 + b C_0)$ Where b was the Langmuir constant and C_0 is the initial concentration of the Cr (VI) ions. To confirm the favorability of the adsorption process, the separation factor (R_L) has been calculated and presented in table 11. The values were found to be between 0 and 1 and confirmed that the adsorption process is favorable [16, 25, 32].

The Freundlich isotherm was represented by $\log q_e = \log K_F + 1/n \log C_e$ Where q_e , C_e , K_F and n were the amount of Cr (VI) ions adsorbed, equilibrium concentration of metal ion in solution and Freundlich constants respectively. From fig. 8, the linear plot of $\log q_e$ versus $\log C_e$ shows that the adsorption of Cr(VI) ion follows the Freundlich isotherm. Values of K_F and n were calculated and presented in the table-10. However, the values of n is greater than one indicating the adsorption is much more favorable [25, 26, 32].

The rate constant for intra-particle diffusion [15, 16, 25, 33] is obtained by using the equation, $q = K_p t^{1/2} + C$ Where, K_p (mg/g/min) is the intra-particle diffusion rate constant. The data for intra particle diffusion plot for different doses are presented in table 12. The respective plots are represented in Fig. 9. The Weber-Morris plot of q versus $t_{1/2}$ gives a straight line and the K_p values obtained from the slope of the linear portions of the curves for the different doses of the adsorbent viz., 2.0, 4.0, 6.0, 8.0 and 10.0 g/L at 35°C were 0.6061, 0.3755, 0.2355, 0.1355, 0.1392 mg/g/min. It is understood from table 13 that the K_p values decrease with increase in the dose of the adsorbent, which reveals that the rate of adsorption is governed by the diffusion of adsorbed Cr(VI) ion within the pores of the adsorbent.

Table 6: Data for Langmuir and Freundlich plots (at 35°C)

S.No.	Cr(VI) _{ini} , C ₀ , mg/L	x, mg/L	C _e , mg/L	log C _e	(x/m), q _e , mg/g	log q _e	C _e /q _e
1	50	42.5	7.5	0.8750	21.25	1.3273	0.35294
2	100	44.8	55.2	1.7419	22.4	1.3502	2.46428
3	150	49.2	100.8	2.0034	24.6	1.3909	4.0975
4	200	53.4	146.6	2.1661	26.7	1.4265	5.4906
5	250	56.8	193.2	2.2860	28.4	1.4533	6.8028
6	300	59.4	240.6	2.3812	29.7	1.4727	8.1010
7	400	62.8	337.2	2.5278	31.4	1.4969	10.7388
8	500	65.4	434.6	2.6380	32.7	1.5145	13.2905

Table 7: Data for Langmuir and Freundlich plots (at 40°C)

S.No.	Cr(VI) _{ini} , C ₀ , mg/L	x, mg /L	C _e , mg/L	log C _e	(x/m), q _e , mg/g	log q _e	C _e /q _e
1	50	45.8	4.2	0.6232	22.9	1.3598	0.1834
2	100	52.8	47.2	1.6739	26.4	1.42160	1.7878
3	150	59.5	90.5	1.9566	29.75	1.4734	3.0420
4	200	65.8	134.2	2.1277	32.9	1.5171	4.0790
5	250	71.6	178.4	2.25139	35.8	1.5538	4.9832
6	300	77.8	222.2	2.3467	38.9	1.5899	5.7120
7	400	83.5	316.5	2.5003	41.75	1.6206	7.5808
8	500	90.2	409.8	2.6125	45.1	1.6541	9.0864

Table 8: Data for Langmuir and Freundlich plots (at 45°C)

S.No.	Cr(VI) _{ini.} , C ₀ , mg/L	x, mg/L	C _e , mg/L	log C _e	(x/m), q _e , mg/g	log q _e	C _e /q _e
1	50	47.8	2.2	0.3424	23.9	1.3783	0.09205
2	100	57.2	42.8	1.6314	28.6	1.4563	1.4965
3	150	66.8	83.2	1.9201	33.4	1.5237	2.4910
4	200	75.4	124.6	2.0955	37.7	1.5763	3.3050
5	250	81.2	168.8	2.2273	40.6	1.6085	4.1576
6	300	91.8	208.2	2.3184	45.9	1.6618	4.5359
7	400	97.2	302.8	2.4811	48.6	1.6866	6.2304
8	500	105.2	394.8	2.5963	52.6	1.7209	7.5057

Table 9: Data for Langmuir and Freundlich plots (at 50°C)

S. No.	Cr(VI) _{ini.} , C ₀ , mg/L	x, mg /L	C _e , mg /L	log C _e	(x/m), q _e , mg/g	log q _e	C _e /q _e
1	50	49.2	0.8	-0.0969	24.6	1.3909	0.03252
2	100	62.4	37.6	1.57518	31.2	1.4941	1.20512
3	150	74.8	75.2	1.8762	37.4	1.5728	2.01069
4	200	85.4	114.6	2.0591	42.7	1.6304	2.6838
5	250	94.2	155.8	2.1925	47.1	1.67302	3.3078
6	300	105.2	194.8	2.2895	52.6	1.7209	3.7034
7	400	116.2	283.8	2.4530	58.1	1.7641	4.8846
8	500	125.5	374.5	2.5734	62.6	1.7965	5.9824

Table 10: Langmuir and Freundlich isotherm constants for adsorption of Cr(VI) on AZSC

S.No	Temp. °C	Correlation Coefficient (R ²)	Q _m (mg/g)	b (L/mg)	K _F (mg/g)	n (L/mg)	Correlation Coefficient (R ²)
1	35	0.9928	33.898	0.0357	0.1800	8.9600	0.8537
2	40	0.9810	47.169	0.0254	0.2034	6.7476	0.8684
3	45	0.9781	55.248	0.0249	0.2467	6.5746	0.8562
4	50	0.9713	66.225	0.0233	0.2209	3.5560	0.9949

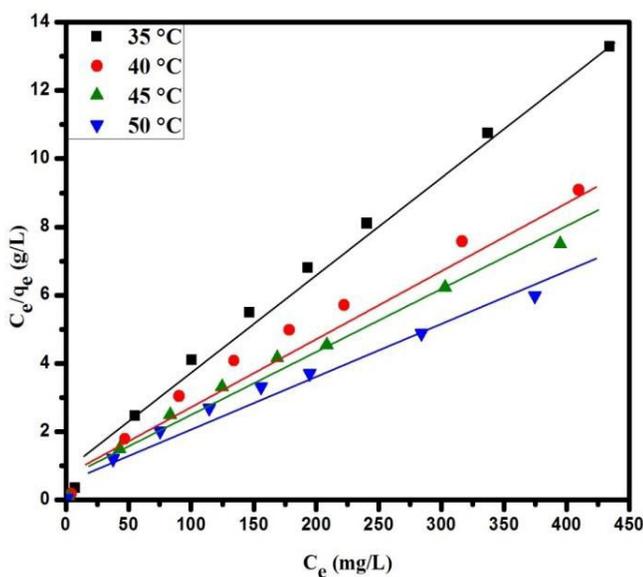


Fig. 7: The data for Langmuir isotherm

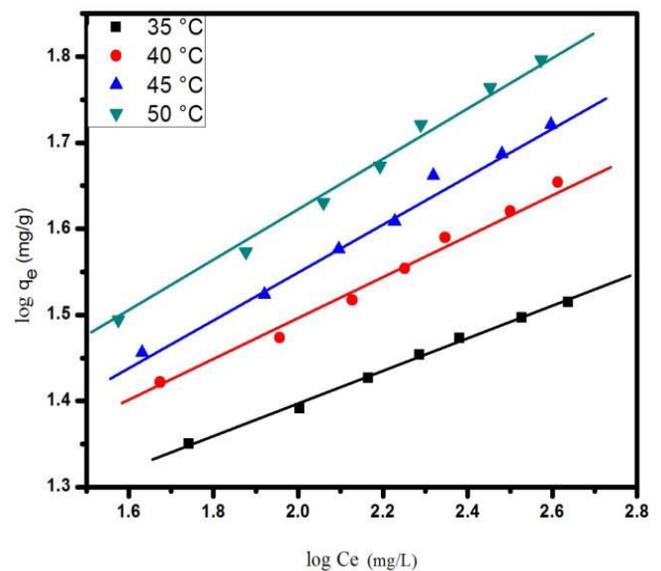


Fig. 8: The data for Freundlich isotherm

Table 11: Values of R_L for Cr(VI) adsorption on AZSC

S. No	[Cr(VI)] _{ini.} , C ₀ (mg/L)	Temp. °C			
		35°C	40°C	45°C	50°C
1	50	0.3590	0.4405	0.4454	0.4618
2	100	0.2188	0.2824	0.2865	0.3003
3	150	0.1573	0.2079	0.2111	0.2224
4	200	0.1228	0.1644	0.1672	0.1766
5	250	0.1007	0.1360	0.1384	0.1465
6	300	0.0853	0.1160	0.1180	0.1251
7	400	0.0654	0.0896	0.0912	0.0968
8	500	0.0530	0.0729	0.0743	0.0790

Table 12: Data for the Weber and Morris plot-variation of the dose of the adsorbent

S. No.	Contact time t, min	t ^{1/2}	(x/m), q, mg/g				
			Adsorbent Dose (g/L)				
			2.0	4.0	6.0	8.0	10.0
1	30	5.4772	15.3	7.8	4.4	5.5	3.5
2	60	7.7459	15.7	8.3	5.0	5.9	4.0
3	90	9.4868	17.6	8.8	5.5	6.5	4.6
4	120	10.9544	19.9	9.8	5.6	7.4	4.9
5	150	12.2474	20.6	10.5	5.8	7.5	4.9
6	180	13.4164	21.2	10.8	5.8	7.6	4.9
7	210	14.4913	21.3	11.1	5.8	7.6	4.9
8	240	15.4919	21.5	11.1	5.8	7.6	4.9
9	270	16.4316	21.6				
10	300	17.3205	21.6				

Table 13: Effect of Intraparticle diffusion rate constant on the removal of Cr(VI)

S. No.	Dose of the adsorbent m, g/ L	K _p
1	2.0	0.6061
2	4.0	0.3755
3	6.0	0.2355
4	8.0	0.1355
5	10.0	0.1392

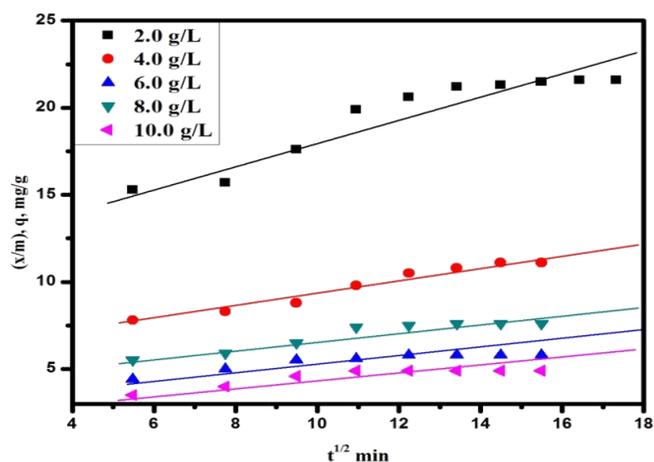


Fig. 9: The data for intra particle diffusion plot for different doses

3.10. Thermodynamic Studies

The percentage of adsorption of Cr(VI) increases as the temperature of the system increases from 35-50°C presented in table-14. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined. $K_o = C_{solid} / C_{liquid}$, $\Delta G^\circ = -RT \ln$,

$\log K_o = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT)$ where K_o is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium, C_{liquid} is the liquid phase concentration at equilibrium, T is the temperature in Kelvin and R is the gas constant.

Since equilibrium constant increases (table 15) with increasing temperature, suggesting the adsorption of Cr(VI) is purely endothermic. Increase in temperature leads to increase both in adsorption rate and the amount of adsorbed materials [29, 34-36].

Thermodynamically, the value of ΔG° is negative, and the value of ΔH° is positive, suggesting the adsorption is spontaneous at higher temperature [30]. The positive values of ΔS° showed the increasing randomness at the solid/liquid interface during the process [37]. Since this trend was observed in the present study, adsorption of

Cr(VI) on AZSC is probably a physical adsorption process.

3.11. Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ion. If the adsorbed metal ion can be desorbed using neutral pH water or by very dilute acids, then the attachment of the metal ions onto the surface the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorbs the metal ions, then the

adsorption is by ion exchange. If organic acids like acetic acid can desorb the metal ion, then the metal ion is held on the adsorbent through chemisorption [20]. The effect of various reagents used for desorption studies reveals that hydrochloric acid is a better reagent for desorption, because we could get more than 87% removal of adsorbed metal ions. The desorption of metal ions by dilute mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through physisorption [38, 39].

Table 14: Equilibrium parameters for the adsorption of Cr(VI) onto AZSC

S. No.	[Cr(VI)] _{ini.} C ₀ , mg/L	Temperature, °C											
		C _e (mg/L)				q _e (mg/g)				(% of removal of Cr(VI))			
		35	40	45	50	35	40	45	50	35	40	45	50
1	50	7.5	4.2	2.2	0.8	21.25	22.9	23.9	24.6	85	91.6	95.6	98.4
2	100	55.2	47.2	42.8	37.6	22.4	26.4	28.6	31.2	44.8	52.8	57.2	62.4
3	150	100.8	90.5	83.2	75.2	24.6	29.75	33.4	37.4	32.8	39.6	44.5	49.86
4	200	146.6	134.2	124.6	114.6	26.7	32.9	37.7	42.7	26.7	32.9	37.7	42.7
5	250	193.2	178.4	168.8	155.8	28.4	35.8	40.6	47.1	22.72	28.64	32.48	37.68
6	300	240.6	222.2	208.2	194.8	29.7	38.9	45.9	52.6	19.8	25.93	30.6	35.06
7	400	337.2	316.5	302.8	283.8	31.4	41.75	48.6	58.1	15.7	27.83	24.3	29.05
8	500	434.6	409.8	394.8	374.5	32.7	45.1	52.6	62.6	13.08	18.04	21.04	25.1

Table 15: Equilibrium constant and thermodynamic parameters for the adsorption of Cr(VI) onto AZSC

S. No	[Cr(VI)] _{ini.} C ₀ , mg/L	Temperature, °C										ΔH°	ΔS°
		K ₀				ΔG°							
		35	40	45	50	35	40	45	50				
1	50	5.666	10.90	21.72	61.5	-4.44	-6.216	-8.101	-1.106	13.033	0.4361		
2	100	0.81159	1.1186	1.336	1.6595	0.534	-0.291	-0.765	-1.3602	38.627	0.1237		
3	150	0.4880	0.6574	0.8028	0.9946	1.837	1.091	0.5857	0.1454	38.838	0.120		
4	200	0.3642	0.4903	0.6051	0.7452	2.586	1.854	1.328	0.3376	39.217	0.118		
5	250	0.2939	0.4013	0.4810	0.6046	3.1356	2.376	1.935	1.351	39.003	0.1164		
6	300	0.2468	0.3501	0.4409	0.5400	3.5820	2.731	2.165	1.6547	42.897	0.127		
7	400	0.1862	0.2638	0.3210	0.4094	4.304	3.467	3.004	2.398	42.579	0.1242		
8	500	0.1504	0.2201	0.2664	0.3351	5.087	3.876	3.441	2.795	43.146	0.1244		

4. CONCLUSION

The equilibrium time, 180 min appears to be sufficient for the maximum adsorption of Cr(VI) species by AZSC, under the given set of experimental conditions and the maximum amount of Cr(VI) adsorbed is found to be 84.9%, for a concentration of 50 mg/L with the dose of AZSC 2 g/L, at 35°C with the optimum pH 1.5 and adsorbent of size 75-125 μ. The percentage removal of Cr(VI) increases with the increase of the dose of the adsorbent and decreases with the increase of the concentration of adsorbate solutions. Similarly, the minimum time required to achieve maximum adsorption also increases with the increase of the dose of the adsorbent. The optimal pH to be fixed for further experimental work has been found to be 1.5. The

Lagergren and Bhattacharya-Venkobachar results confirmed that the adsorption process follows first order kinetic nature and the formation of monolayer coverage of Cr(VI) onto AZSC.

The equilibrium data were found to be well represented by Langmuir and Freundlich isotherms and the results of thermodynamic studies have confirmed the adsorption is found to be an endothermic process

The R_L values have confirmed the favorability of adsorption process. Studies pertaining to FT-IR, SEM, effect of temperature and desorption studies reveal the existence of physisorption. Kinetic studies and adsorption isotherm studies reveal the monolayer adsorption. All the above information reveals that the selected AZSC may be used as an adsorbent for the

removal of Cr (VI) from waste water.

Conflict of interests

The Authors declares that there is no conflict of interest.

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