Removal of Cr(VI) from Aqueous Solution Using Modified Pomegranate Peel: Equilibrium and Kinetic Studies

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Abstract: The present investigation deals with the utilization of modified pomegranate peel (MPGP) and formaldehyde modified pomegranate peel (FMPGP) as adsorbents for the removal of chromium Cr(VI) from aqueous solution. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of pH, initial Cr(VI) concentration, contact time, adsorbent dosage and temperature were considered. The optimal pH values of Cr(VI) removal by MPGP and FMPGP were 2.0 and 3.0 respectively. The time required for equilibrium was found to be about 100 minutes. The initial Cr(VI) concentration and adsorbent dosage was found to have large effect on the adsorption of Cr(VI). The maximum uptake capacities were 13.01 and 22.28 mg of Cr(VI) per gram of MPGP and FMPGP respectively. Adsorption kinetic data were tested using pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion models. Kinetic studies showed that the adsorption followed a pseudo second order reaction due to the high correlation coefficient and the agreement between the experimental and calculated values of q_e . The adsorption may follow intraparticle diffusion as well, due to the highest values of rate constants for the surface adsorption and intraparticle diffusion kinetic models, the higher values of rate constants are related to an improved bonding between Cr(VI) ions and adsorbent particle. The Dubinin-radushkevich, Freundlich and Tempkin models were the closest fit for the equilibrium data of MPGP and FMPGP.

Keywords: Adsorption, Modified Pomegranate peel, Cr(VI), kinetic, Adsorption isotherm equilibrium.

Introduction

Chromium exists in two stable oxidation states, Cr(III) and Cr(VI). The Cr(VI) state is of particular concern because this form is hazardous to health, due to its carcinogenic properties¹.

Chromium is introduced into the natural bodies of water from industries like electroplating, leather tanning, cement industries, steel industries, photography and inorganic chemicals production². Cr(VI) causes skin irradiation resulting in ulcer formation. Over exposure to Cr(VI) leads to liver damage, pulmonary congestion and oedema³. In addition, hexavalent chromium is toxic and a suspected carcinogen material and it is quite soluble in the aqueous phase almost over the entire pH range and mobile in the natural environment^{4,5}. Several species can be obtained from hexavalent chromium by change the concentration and pH of chromium solution, at pH>7, the CrO_4^{2-} from will preferably exist in the solution, while in the pH between 1 and 6, HCrO_4^- is predominant. Therefore, within the normal pH range in natural waters, the CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ ions are the expected forms of hexavalent chromium in the solution, which are quite soluble and mobile in water streams^{5,6}. The maximum permissible levels for Cr^{+3} and Cr^{+6} ions in waste water are 5 and 0.05 mgL^{-1} , respectively. The trivalent form of chromium apparently plays an important role in plant and animal metabolism, while the hexavalent form is directly toxic to bacteria, plants and animals⁷. However, the most severely chromium compounds are chromium oxide and chromium sulfate as trivalent and chromium trioxide, chromic acid and dichromates as hexavalent chromium⁸. Established methods for the removal of chromium oxyanion from wastewater include precipitation, electrochemical reduction, ion exchange, filtration, electro deposition, membrane technology, reverse osmosis, and adsorption⁹. However, most of these methods have many disadvantages including incomplete metal removal, use of expensive equipment, energy requirements, and production of toxic sludge and other disposal waste products^{10,11}. Adsorption remains the most economical and widely used process for removal of toxic pollutants from wastewater. It is by far the most widely used process for the removal of toxic metal ions from aqueous solution. Many papers have appeared on the production of low-cost adsorbent using cheaper and readily available materials¹²⁻²⁰.

The objective of the present study is to evaluate the capacity of modified pomegranate peel and formaldehyde modified pomegranate peel as adsorbents using the batch adsorption process. Several isotherm and kinetic models were used to evaluate the adsorbents. Condition parameters such as contact time, pH, initial metal ion concentrations, and adsorbent concentration were considered.

Experimental

Biomass

Pomegranate peel (PGP) was collected in the northern part of Iraq was dried, then milled and sieved to particle size of 500 μm . The biomass was divided into two parts. The first one was shaken with distilled water for overnight then filtered, this process was repeated about ten times or until we get rid off all colored or soluble materials (it was observed that more than 40% of PGP was soluble in water) then filtered and dried in an air oven at 80 $^\circ\text{C}$ for overnight and named as modified pomegranate peel MPGP. The second part was reacted with 8% formaldehyde solution in a ratio of pomegranate peel to formaldehyde solution 1:5 w/v, at 60 $^\circ\text{C}$ for 4 h^{21a}. The formaldehyde modified pomegranate peel FMPGP was filtered out, washed with deionized water to remove free formaldehyde, and then activated at 80 $^\circ\text{C}$ for 24 h in an air oven. The two parts were sieved again to 150 μm particle size.

Preparation of chromium solution and analysis

A stock solution of Cr(VI) (500 mg/L) was obtained by dissolving 1.4144 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1L of deionized water, and the solution was used for further experimental solution preparation. The pH values were adjusted with 0.13M HNO_3 or 0.1M NaOH . Analytical grade reagents were used throughout this study. The Cr(VI) content in the sorption solutions was determined by atomic absorption spectrophotometer type (Analyst 200 Perkin Elmer).

Batch biosorption studies

Effect of pH

The initial pH values were adjusted to 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 with 0.13 M HNO₃ and 0.1 M NaOH. The effect of initial pH on the chromium ions adsorption onto modified pomegranate peel MPGP and FMPGP were determined using 0.1 g of adsorbent in 50 mL of Cr(VI) solution of 10 mg/L at 20 °C for 90 minutes and 140 rpm agitation speed in case of MPGP, at 19 °C for 50 minutes using an agitation speed 240 rpm for FMPGP.

Kinetic studies

Kinetic studies were carried out at solution pH 2.0 for MPGP and pH 3 for FMPGP by mixing 0.1 g of biomass in 50 mL of Cr(VI) solution 10 mg/L and agitated at 20 °C for MPGP and 16 °C for FMPGP and samples were collected from duplicate flasks at different time intervals, filtered by whatman filter paper no. 40, the filtrate was analyzed for residual chromium concentration.

Effect of biomass dose

The effect of sorbent dose on the removal of Cr(VI) was studied using MPGP concentration of 1,2,4 and 6 g/L and FMPGP conc. of 1,2,4,8,12 g/L, shaken with Cr(VI) solution of 10 mg/L for 100 minutes for MPGP and 10 and 40 mg/L for 50 min. for FMPGP and was determined from the amount of Cr adsorbed.

Adsorption isotherm

Adsorption isotherm experiments were carried out at different temperature (20,30,40,50 °C) by shaking the biomass 0.1 g with 50 mL of Cr(VI) 10, 20, 30, 40 mg/L solution for 100 min. at pH 2 in case of MPGP and at pH 3 in case of FMPGP. The amount of Cr(VI) adsorbed onto biomass, q_e mg/g, was calculated using the following equation:

$$q_e = \frac{(C_i - C_e) \times V}{M} \quad (1)$$

where, C_i and C_e are the initial and equilibrium liquid-phase concentration (mg/L) of Cr(VI), respectively, V is the volume of the solution (L) and M is the weight of the adsorbent used. The Cr(VI) percent removal $R\%$ was calculated using the following equation:

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Results and Discussion

Effect of pH on Cr(VI) adsorption

The pH value of the solution is an important factor that controls the sorption process. Figure 1 show the extent of removal of Cr(VI) as a function of pH for initial concentration of 10 mg/L using MPGP and FMPGP as adsorbents. It can be seen that the adsorption capacity, q_e , was maximum at pH 2 and 3 for MPGP and FMPGP respectively. The predominate species^{3,21b,22} of chromium at acidic pH are $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, and $\text{Cr}_4\text{O}_{13}^{2-}$. The surface of the MPGP and FMPGP become highly protonated under acidic conditions that favoured the adsorption of Cr(VI) in the anionic form. The increase in pH value caused a decrease in protonation of the surface, which led to a decrease in the net positive surface potential of sorbent. This decreased the electrostatic forces between sorbent and sorbate, leading to reduced sorption capacity²³. Moreover, as the pH value increased, there was competition between OH^- and chromate ions, CrO_4^{2-} , which predominate in the basic solution.

Figure 1. Effect of PH on the adsorption of Cr(VI), 10 mg/L, onto MPGP and FMPGP, 0.1 g/50 mL.

Effect of contact time and initial Cr(VI) concentration

The initial concentration of metal provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases. Hence, a higher initial concentration of Cr(VI) will increase the biosorption rate as shown in Figure 2. The influence of contact time on the amounts of Cr(VI) adsorbed at equilibrium q_e is shown in Figure 3, it is clear that the rate of adsorption is so rapid at the beginning of the reaction, about 51% of Cr(VI) was removed from solution at the first five minutes, and thereafter the rate of adsorption of Cr(VI) onto MPGP and FMPGP were found to be slow, which may be attributed to the electrostatic hindrance or repulsion between the adsorbed negatively charged Cr(VI) onto the surface of MGPG or FMPGP and the available anionic Cr(VI) in solution as well as the slow pore diffusion of the Cr(VI) ion into the bulk of adsorbent¹⁶.

Figure 2. Relation between amount of Cr(VI) adsorb at equilibrium, q_e , and Its initial conc. using MPGP, 0.1 g/50 mL, at pH 2, time 80 min., and FMPGP, 0.1 g/50 mL, at pH 3, time 100 min. temperature 30 °C

Influence of adsorbent concentration

The adsorption experiments at initial chromium concentration 10 mg/L were also performed with MPGP doses (1,2,4,6 g/L) and FMPGP doses (1,4,8,12 g/L) at Cr(VI) conc. 10 and 40 mg/L, the

results are reported in Figure 4. Removal of Cr(VI) increases with an increase in the adsorbent. Dosage.

The percentage removal increases from 50.85 to 78.83% by increasing MPGP dosage from 1 to 6 g/L. while it increases from 70.67 to 80.82% at Cr(VI) conc. 10 mg/L and from 67.18 to 89.43 at Cr(VI) conc. 40 mg/L for FMPGP dosage increasing from 1 to 12 g/L. However, the adsorption capacity q_e showed a decreasing trend with increasing adsorbent dosage. If the adsorbent amount is increased by keeping the Cr(VI) concentration constant, the amount of Cr(VI) adsorbed per unit mass showed a decrease due to availability of less number of Cr(VI) ions per unit mass of the adsorbent. The adsorption capacity dropped from 5.085 to 1.314 mg/g by increasing adsorbent dosage from 1 to 6 g/L for MPGP, while, for FMPGP the q_e dropped from 2.733 to 1.918 at 10 mg/L and from 26.873 to 2.981 at 40 mg/L Cr(VI) concentration. The drop in adsorption capacity is basically due to the site remaining unsaturated during the adsorption process. The same trend was also reported by other researchers¹⁶.

Figure 3. Effect of contact time on the amount of Cr(VI) adsorbed at equilibrium, q_e , using MPGP, 0.1 g/ 50 mL, at pH 2, temp. 20⁰C and FMPGP, 0.1 g/50 mL, at pH 3 temp. 16⁰C.

Figure 4. Effect of MPGP and FMPGP dosage on Cr(VI) adsorption.

Adsorption isotherm investigation

Equilibrium data, commonly known as adsorption isotherm, are basic requirements for adsorption systems. The experimental data were fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm equations and the constant parameters of the isotherm equations were evaluated. For each isotherm, the temperature of solution and Cr(VI) concentration were varied while the adsorbent weight in each sample were held constant.

The Langmuir equation which is valid for monolayer adsorption onto a completely homogenous surface with finite number of identical sites and with negligible interaction between adsorbed molecules is represented in the following linear forms²⁴:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (3)$$

$$\text{or } \frac{1}{q_e} = \left(\frac{1}{K_L Q_m} \right) \frac{1}{C_e} + \frac{1}{Q_m} \quad (4)$$

C_e is the equilibrium concentration in solution (mg/L), q_e the amount of metal ion adsorbed (mg/L), Q_m is the maximum monolayer capacity of the adsorbent (mg/g) and K_L is an adsorption equilibrium constant (Lmg^{-1}) that related to the apparent energy of sorption. Equation (3) and (4) are the more popular linear forms of Langmuir isotherm. The values of Q_m and K_L constants and correlation coefficients for Langmuir isotherm were evaluated from a plot of $1/q_e$ versus $1/C_e$. Figure 5 and presented in Table 1, for MPGP and Table 2, for FMPGP adsorbent. Values of Q_m for the adsorption of Cr(VI) onto MPGP increases with temperature increase, confirming that the process is endothermic for both adsorbents²⁵. Although the correlation coefficients for the adsorption of Cr(VI) onto MPGP and FMPGP are high >0.99 , but the theoretical values of Q_m do not agree with the experimental values and they are higher than expected which indicate that the Langmuir model is not applicable.

Figure 5. Langmuir isotherm for the adsorption of Cr(VI) onto MPGP at different temperatures (PH 2, contact time = 80 min., MPGP dose = 2 g/L).

The Freundlich isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of sorption over the surface. It can be expressed in the linear form as follows²⁶:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F (Lmg^{-1}) and n are isotherm constants indicate the capacity and intensity of the adsorption, respectively. The linear plot of $\log q_e$ versus $\log C_e$ at each temperature indicates that the adsorption of Cr(VI) also follow Freundlich isotherm Figures 6 & 7. Table 1 & 2 show the Freundlich isotherm constants and correlation coefficients for the adsorption of Cr(VI) on to MPGP and FMPGP adsorbents. The values of n were greater than one indicating that the adsorption onto FMPGP and MPGP is favourable physical process except at 50 °C for MPGP, where its value is less than one indicating the adsorption may be chemical²⁷.

Figure 6. Freundlich isotherm for the adsorption of Cr(VI) onto MPGP at different temperature.

Figure 7. Freundlich isotherm for the adsorption of Cr(VI) onto FMPGP at different temperature.

Table 1. Comparison of the coefficients isotherm parameters from chromium (10, 20, 30, 40 mg/L) adsorption onto MPGP.

Isotherm model	Isotherm parameter	Temperature C°			
		20	30	40	50
Langmuir	$Q_m, \text{mg} / \text{g}$	20.921	26.882	47.39	47.17
	$K_L \text{L mg}^{-1}$	0.054	0.042	0.023	0.017
	R^2	0.9974	0.9997	0.9994	0.9758
Freundlich	K_F	1.514	1.377	1.262	0.9078
	n	1.506	1.339	1.183	1.979
	R^2	0.9741	0.9957	0.9974	0.9506
Tempkin	A_T	0.434	0.576	0.665	0.863
	B_T	4.02	4.789	5.742	7.002
	b_T	606	525.99	453.19	383.5
	R^2	0.9955	0.9876	0.9817	0.9827
D-R	$Q_m \text{mg/g}$	9.4669	10.133	11.182	13.0085
	$K_{D-R} \times 10^6$	3	3	3.0	4
	E, kJmol^{-1}	0.00173	0.00173	0.00173	0.002
	R^2	0.9504	0.9276	0.9285	0.9727

Table 2. Comparison of the coefficients isotherm parameters from chromium (10,20,30,40 mg/L) adsorption onto FMPGP .

Isotherm model	Isotherm parameter	Temperature C°			
		20	30	40	50
Longmuir	Q _m , mg /g	25.38	35.336	30.395	49.75
	K _L , L mg ⁻¹	0.0636	0.0507	0.0903	0.0577
	R ²	0.9908	0.9926	0.9909	0.9917
Freundlich	K _F	1.953	2.074	3.136	3.299
	n	1.452	1.333	1.524	1.361
	R ²	0.9953	0.9882	0.9739	0.9619
Tempkin	A _t	0.574	0.5844	0.887	0.881
	B _t	5.924	7.075	6.732	8.128
	b _T	411.21	356.06	386.55	330.39
	R ²	0.9654	0.9654	0.9659	0.973
D-R	Q _m , mg /g	16.928	19.595	20.156	22.28
	K _{D-R} ×10 ⁶	10	8	4	3
	E, kJmol ⁻¹	0.0032	0.0028	0.002	0.0017
	R ²	0.9946	0.9996	0.9905	0.9889

Temkin isotherm

The adsorbing species-adsorbate interactions can be explained using the tempkin isotherm equation²⁸. It is based on the following assumptions:

1. The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate repulsions.
2. The adsorption is a uniform distribution of maximum binding energy.
3. The fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. It is commonly expressed in the following linear equation.

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (6)$$

$$B_T = \frac{RT}{b} \quad (7)$$

where, T is the absolute temperature (K), and R is the universal gas constant, 8.314 Jmol⁻¹K⁻¹. b (J/mol) is a constant related to the heat of adsorption. A_T is the equilibrium binding constant (Lmg⁻¹). A plot of q_e versus lnC_e at studied temperatures for adsorption of Cr(VI) onto MPGP is given in Figure 8, while, the Tempkin constants for both adsorbents are summarized in Table 1 & 2 respectively. The correlation coefficients was relatively high, which indicate the applicability of Temkin equation. The Tempkin constant, B_T, for the adsorption of Cr(VI) onto MPGP and FMPGP show that the heat of adsorption increases with temperature increase indicating endothermic process.

The Dubinin-Radushkevich isotherm

The linear form of D-R isotherm equation can be expressed as follows²⁹.

$$\ln q_e = \ln Q_m - K_{D-R} \varepsilon^2 \quad (8)$$

where Q_m is the theoretical monolayer saturation capacity (mg g⁻¹), K_{D-R} is the D-R constant (mol²KJ⁻²). ε, is the Polanyi potential and is equal to the mean energy of adsorption, E (kJmol⁻¹) is related to K_{D-R} as³⁰:

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (9)$$

$$E = \frac{1}{\sqrt{2 K_{D-R}}} \quad (10)$$

The coefficients of D-R isotherm for adsorption onto MPGP and FMPGP adsorbents are presented in Table 1 & 2 respectively. Plot of $\ln q_e$ vs. ϵ^2 for the adsorption of Cr(VI) onto MPGP are shown in Figure 9. The values of the mean adsorption energy (E) were found to be in the range of physical adsorption²⁵ Table 1 & 2. The Q_m values were found to be increased with increase in temperature, this behavior is an indication of endothermic adsorption process Table 1 & 2. Although, the correlation coefficients of D-R isotherm for adsorption onto MPGP and FMPGP Table 1 & 2, are little bit lower than that of Langmuir isotherm, but theoretical values of Q_m are much closer to experimental values and even closer than that values obtained from Langmuir isotherm. We suggest that D-R isotherm is more applicable for the adsorption of Cr(VI) onto MPGP and FMPGP Table 1 & 2.

Figure 8. Temkin isotherm for the adsorption of Cr(VI) onto MPGP at different temperatures.

Figure 9. D-R isotherm for the adsorption of Cr(VI) onto MPGP.

Adsorption kinetic study

The dynamics of the adsorption reaction in terms of the order of the rate constant can be understood by studying the kinetic of the adsorption. Batch experiments were conducted to study the rate of Cr(10 mg/L) adsorption by MPGP and FMPGP. Several models were studied to examine the rate- controlling steps of the adsorption process such as chemical reaction, diffusion control and mass transfer. The pseudo-first order³¹, pseudo-second order³², Elovich³³, and intraparticle diffusion³⁴ kinetic models were used for the adsorption of Cr(VI) on MPGP and FMPGP.

Pseudo-first order model

The linear form of pseudo- first order kinetic model as follows³¹.

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t \quad (11)$$

where q_e and q_t are the amount of Cr adsorbed (mg g^{-1}) at equilibrium and at any time t , respectively, and $k_1(\text{min}^{-1})$ is the equilibrium rate constant of pseudo-first order adsorption. From plot of $\log(q_e - q_t)$ vs. t , the rate constant k_1 , equilibrium adsorption capacity, q_e , and correlation coefficient R^2 were calculated. The first-order kinetic model for the adsorption of Cr(VI) onto both MPGP and FMPGP is not applicable due to the low correlation coefficient values and big difference between experimental and calculated values of q_e Tables 3 & 4.

Pseudo-second-order equation

The second-order kinetic equation can be represented as follows³².

$$t / q_t = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (12)$$

Where $k_2 (\text{g mg}^{-1} \text{ min}^{-1})$ is the equilibrium rate constant of pseudo-second-order adsorption. The initial adsorption rate, $h (\text{mg g}^{-1} \text{ min}^{-1})$ is expressed by the following equation:

$$h = k_2 q_e^2 \quad (13)$$

The linear plot of t/q_t vs. t shows a good agreement for the experimental data with the pseudo-second-order kinetic model for adsorption of Cr onto MPGP and FMPGP. The correlation coefficients (R^2) are higher than 0.9989. The calculated q_e values agree very well with experimental data (Tables 3 & 4, Figures 10 & 11). These suggest that the adsorption of Cr from aqueous solution onto MPGP and FMPGP follow the pseudo-second order model. It is observed that the initial adsorption rate, h is higher for the adsorption of Cr(VI) onto FMPGP than onto MPGP Tables 3 & 4. This behavior was obvious in Figure 3.

The equilibrium between Cr(VI) in solution and that onto MPGP or FMPGP can be represented as follows:

Where k_1 and k_{-1} are the forward (adsorption) and reverse (desorption) rate constants respectively. C_e and C_a are Cr(VI) ion concentration in solution and onto adsorbent respectively. The equilibrium constant (K_o) is the ratio of Cr(VI) concentration on the MPGP and in aqueous solution ($K_o = C_a/C_e = k_1/k_{-1}$). The second order rate constant (k_2) have been calculated from the linear plots of t/q_t vs. t at different time intervals and temperatures Table 3, Figure 10.

Figure 10. Pseudo-second-order kinetics for the adsorption of Cr(VI) 10 mg/L onto MPGP MPGP 2 g/L, pH 2 .

The overall rate of adsorption (k_2) is separated into the rate of forward and reverse reaction as follows:

$$k_2 = k_1 + k_{-1} = k_1 + \left(\frac{k_1}{K_0} \right) = k_1 \left[1 + \frac{1}{K_0} \right] \quad (15)$$

These results are collected in Table 5, which indicate that at 10 mg/L Cr(VI) concentration and all temperatures studied, the forward rate constants are much higher than the reverse rate constants suggesting that the rate of adsorption is clearly dominant³⁵.

Elovich kinetic equation

Elovich equation is another kinetic model with a linear form can be expressed as follows³³:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (16)$$

Elovich constants α and β were calculated from slope and intercept of plot of q_t vs. $\ln(t)$. The correlation coefficients is some what high $R^2 > 0.92$ which reflected the applicability of the Elovich model.

Figure 12. Elovich kinetic for the adsorption of Cr(VI) onto MPGP.

Figure 11. Pseudo-second-order kinetics for the adsorption of Cr(VI), 10 mg/L, onto FMPGP. FMPGP 2 g/L, pH 3 at 16 °C.

Table 3. Comparison of the first order, second order , Elovich and intraparticle diffusion rate constants and calculated and experimental q_e values at different temperature and different time intervals at constant concentration of Cr(VI) 10 mg/L and constant dose of MPGP 2g/L.

Parameter		First-order kinetic model			Second- order kinetic model				Elovich		Intraparticle diffusion			
Temp C°	q_e (exp)	k_1 10^2	q_e (calc.)	R^2	k_2 10^2	q_e (calc.)	h $mg\ g^{-1}\ min^{-1}$	R^2	α	β	R^2	Kdiff $\times 10^2$	B_L	R^2
20	2.937	6.0	0.589	0.852	23.3	2.989	2.082	0.9997	326.587	3.694	0.9214	12.15	2.146	0.8161
30	3.059	7.9	1.077	0.9197	32.0	3.124	3.123	0.9989	672.134	3.873	0.9685	11.99	2.2227	0.9183
40	3.172	3.25	0.598	0.9684	24.6	3.111	2.381	0.9995	46424.43	5.356	0.9637	8.7	2.46	0.9209
50	3.385	2.79	0.774	0.9597	19.7	3.259	2.092	0.9997	2663.31	4.142	0.9914	11.01	2.431	0.9399

Table 4. Comparison of the first order, second order, Elovich and intraparticle diffusion rate constants and calculated and experimental q_e values for the adsorption of Cr(VI), 10 mg / L , onto FMPGP, 2g/L , at constant temperature 16 °C and different time intervals .

first order kinetic model				Second order kinetic model			
$q_e(\text{exp.}), \text{mg/g}$	$k_1, \text{min.}^{-1}$	$q_e(\text{calc.}) \text{mg/g}$	R^2	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	$h, \text{mg g}^{-1} \text{min}^{-1}$	$q_e(\text{calc.})$	R^2
3.823	0.076	0.762	0.8878	0.277	4.142	3.867	0.9995
Elovich model				intraparticle diffusion			
$B, \text{g mg}^{-1}$	$A, \text{mg g}^{-1} \text{min}^{-1}$	R^2	$K_{\text{diff.}}, \text{mg g}^{-1} \text{min}^{-1/2}$	$B_L, \text{mg/g}$	R^2		
0.361	7.54	0.9249	0.126	3.015	0.8186		

Table 5. Second order rate constants for the adsorption of chromium onto MPGP ($k_2, \text{qmg}^{-1}\text{min}^{-1}$) Equilibrium constant (K_0) , rate constants for forward (k_1) and reverse (k_{-1}) process at different temperatures .

Temperature C°	$C_e, \text{mg/L}$	K_0	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	$k_1, \text{g mg}^{-1} \text{min}^{-1}$	$k_{-1}, \text{g mg}^{-1} \text{min}^{-1}$
20	4.127	1.423	0.233	0.1368	0.0962
30	3.883	1.575	0.320	0.1425	0.0905
40	3.657	1.734	0.246	0.1477	0.0852
50	3.231	2.095	0.197	0.1577	0.0753

Intraparticle diffusion

The adsorption mechanism of adsorbent follows three steps viz. film diffusion, pore diffusion and intra-particle transport. The slowest of the three steps controls the overall rate of the process. Generally, pore diffusion and intra-particle diffusion are often rate-limiting in a batch reactor, which for continuous flow system film diffusion is more likely the rate limiting step³⁶. The linear form of intra-particle diffusion model can be expressed as follows³⁴.

$$q_t = K_{dif} t^{1/2} + B_L \quad (17)$$

where K_{dif} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion rate constant. In Figure 13 a plot of q_t versus $t^{1/2}$ are presented for MPGP. Values of B_L give an idea about the thickness of the boundary layer³⁷, which is higher in FMPGP Tables 3& 4.

Figure 13. Intraparticle diffusion plot for Cr(VI) 10 mg/L adsorption onto MPGP 2 g/L, pH 2 at different time and temperature.

The correlation coefficients of the plot range between 0.8161-0.9399 which indicate low linearity for the adsorption of Cr(VI) by MPGP or FMPGP. Moreover, it has been reported^{38, 39} that if intraparticle diffusion is the sole rate-limiting step, it is for the q_t versus $t_{1/2}$ plots to pass through the origin, which is not the case in this study. It may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during the chromium-adsorbent interactions. The evidence for such conclusion is the rate constants of second-order and intraparticle diffusion, where their values are the highest among other kinetic models, Table 3&4, large values of rate constants are related to an improved bonding between Cr(VI) ions and adsorbent particles⁴⁰.

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