



Potential of pomegranate husk carbon for Cr(VI) removal from wastewater: Kinetic and isotherm studies

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ABSTRACT

Pomegranate husk was converted into activated carbon and tested for its ability to remove hexavalent chromium from wastewater. The new activated carbon was obtained from pomegranate husk by dehydration process using concentrated sulfuric acid. The important parameters for the adsorption process such as pH, metal concentration and sorbent weight were investigated. Batch equilibrium experiments exhibited that a maximum chromium uptake was obtained at pH 1.0. The maximum adsorption capacity for pomegranate husk activated carbon was 35.2 mg g^{-1} as calculated by Langmuir model. The ability of activated carbon to remove chromium from synthetic sea water, natural sea water and wastewater was investigated as well. Different isotherm models were used to analyze the experimental data and the models parameters were evaluated. This study showed that the removal of toxic chromium by activated carbon developed from pomegranate husk is a promising technique.

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1. Introduction

Wastewater effluents from most industries in Alexandria city in Egypt contain high levels of heavy metal concentrations and thus create serious environmental pollution hazards especially for the coastal water [1–4]. Heavy metals are toxic and non-biodegradable and probably have health effect [5]. Chromium is an important pollutant introduced into natural waters by a variety of industrial wastewaters including those from paint and pigment manufacturing, stainless steel production, corrosion control, textile, leather tanning, chrome electroplating, metal finishing industries, wood preservation, and photography. 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 [5,6]. Several species can be obtained from hexavalent chromium by change the concentration and pH of chromium solution. At $\text{pH} > 7$, the CrO_4^{2-} form 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 [6,7]. The maximum permissible levels for Cr^{3+} and Cr^{6+} ions in wastewater are 5 and 0.05 mg L^{-1} , respectively. The trivalent form

of chromium apparently plays an essential role in plant and animal metabolism, while the hexavalent form is directly toxic to bacteria, plants and animals [8]. However, the most severely chromium compounds are chromium oxide and chromium sulfate as trivalent and chromium trioxide, chromic acid and dichromates as hexavalent chromium [9].

Adsorption process has been extensively used to remove toxic metals from aquatic medium using low cost adsorbents such as agriculture wastes and activated carbon developed from agriculture wastes [10–17].

The main objective of this study was to develop new activated carbon from pomegranate husk (PGHC) and evaluate the possibility of its power as sorbents for the elimination of Cr^{6+} from polluted waters. A systematic evaluation of the parameters involved such as pH, sorbents mass, initial chromium concentration and time have been investigated. The interference of the real wastewater and saline water on the Cr^{6+} adsorption was additionally investigated.

2. Materials and methods

2.1. Preparation of activated carbon

Pomegranate husk was collected from the local market and washed with tap water, distilled water and oven dried at 150°C for 3 days. The dried material was mechanically milled, sieved and the particles of $\sim 1.0 \text{ mm}$ size were used for dehydration. The dried pomegranate husk 2.0 kg was added in small portion to 1500 mL

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of 98% H₂SO₄ in an efficient fume hood and the resulting reaction mixture was kept for overnight at room temperature (25 ± 2 °C) followed by refluxing for 10 h. After cooling to room temperature, the reaction mixture was poured onto 6 L of cold water and filtered. The resulting material was soaked in 1% NaHCO₃ solution to remove any remaining acid. The obtained carbon was then washed with distilled water until pH of the activated carbon reached 6, dried in an oven at 150 °C for 48 h in the absence of oxygen and sieved to the particle size ≤0.063 mm and kept in a glass bottle until used.

2.2. Preparation of synthetic solution

All the chemicals used throughout this study were of analytical-grade. All the adsorption experiments were carried out at room temperature (25 ± 2 °C). A stock solution of Cr⁶⁺ (1000 mg L⁻¹) was obtained by dissolving K₂Cr₂O₇ salt (2.8289 g) in distilled water (1000 mL) and the concentration of Cr⁶⁺ in the stock solution was measured, and the solution was used for further experimental solution preparation. Concentrations ranged between 5 and 100 mg L⁻¹ were prepared from the stock solution and the concentration of each Cr⁶⁺ solution was measured to have the standard curve. Before mixing the carbon and chromium solution, the initial pH of each test solution was adjusted to the required value with 0.1 M HCl or 0.1 M NaOH. The concentration of free chromium ions in the stock solutions and unadsorbed Cr⁶⁺ in the reaction medium was determined spectrophotometrically at λ 540 nm in a spectrophotometer (Milton Roy, Spectronic 21D) using diphenyl carbazide which forms a red-violet colored complex [18,19].

2.3. Simulation studies

Different weights of K₂Cr₂O₇ were dissolved in synthetic sea water, obtained by dissolving 35 g of NaCl in 1.0 L distilled water, to have different concentrations of Cr⁶⁺.

A specific weight of Cr⁶⁺ metal ion was added to 1 L of coastal water (salinity 37 ± 1 g L⁻¹) in a glass jar in order to obtain a known concentration of the metal.

A known weight of Cr⁶⁺ metal ion was dissolved in 1 L of filtered wastewater, which was collected from El-Emoum drain that contains several industrial effluents and agriculture drain near Lake Maruit, in order to obtain a known concentration of the metal.

2.4. Batch adsorption studies

2.4.1. Effect of pH on metal adsorption

The effect of pH on the equilibrium uptake of Cr⁶⁺ ions was studied using 75 mg L⁻¹ chromium concentration onto 3.0 g L⁻¹ of PGHC at different initial pH values (1.0–10). The suspensions were shaken at room temperature (25 ± 2 °C) using agitation speed (200 rpm) for the minimum contact time required to reach the equilibrium (180 min) and the amount of chromium adsorbed was determined.

2.4.2. Effect of carbon dose

The effect of PGHC dose on the equilibrium uptake of chromium ions was performed by shaking of PGHC (0.2, 0.3, 0.4, 0.5 and 0.6 g) with 100 mL of known chromium concentration (25, 50, 75, 100, 125 and 150 mg L⁻¹, individually, which means, every Cr concentration should test by shaking with all the above weights of PGHC) to the equilibrium uptake (180 min) and the amount of chromium adsorbed determined.

2.4.3. Kinetics studies

Kinetic studies were achieved by shaking of PGHC (0.2, 0.3, 0.4, 0.5 and 0.6 g) individually with 100 mL of chromium solution (25, 50, 75, 100, 125 and 150 mg L⁻¹) at room temperature (25 ± 2 °C)

and solution pH (1.0). Samples of 0.5 mL were collected from the duplicate flasks at required time intervals and centrifuged for 5 min. The clear solutions were analyzed for residual chromium concentration in the solution.

2.4.4. Adsorption isotherm

Adsorption isotherm experiments were carried out in 300 mL conical flasks at 25 °C on a shaker for 180 min. The PGHC (0.2, 0.3, 0.4, 0.5 and 0.6 g) were thoroughly mixed with 100 mL of chromium solutions. The isotherm studies were performed by varying the initial chromium concentrations from 25 to 150 mg L⁻¹ at pH 1.0. The pH value was adjusted using 0.1 M HCl or 0.1 M NaOH before addition of biomass and was maintained throughout the experiment. After shaking the flasks for 180 min, the reaction mixture was analyzed for the residual chromium concentration. All the experiments are duplicated and only the mean values are reported. The maximum deviation observed was less than ±5%.

3. Results and discussion

3.1. Effect of pH on Cr⁶⁺ uptake

Earlier studies on heavy metal adsorption have shown that pH is the most important parameter affecting the adsorption process. To find the optimum pH for the effective adsorption of chromium ions by PGHC, experiments were performed at different initial pH values (1.0–10.2). The variation of Cr⁶⁺ removal with initial pH is given in Fig. 1. As seen from the figure, the lowest uptake value was found at pH 8.2 and the highest uptake occurred at pH 1.0 and the uptake values decreased significantly with further increase in pH. At pH < 1, no more adsorption has mentioned than adsorption at pH 1. At optimum sorption pH, the dominant species of Cr⁶⁺ ions in solution are HCrO₄⁻, Cr₂O₇²⁻, Cr₄O₁₃²⁻ and Cr₃O₁₀²⁻, which could be adsorbed primarily by electrostatical nature. At very low pH values, the surface of sorbent would also be surrounded by the hydromium ions which enhance the Cr⁶⁺ interaction with binding sites of PGHC by greater attractive forces. As the pH increased, the overall surface charge on PGHC became negative and adsorption of chromium decreased. Also, it has been known that in the case of high chromium concentration, the Cr₂O₇²⁻ ions precipitate at higher pH values [20]. PGHC surface would be positively charged up to pH < 4, and heterogeneous in the pH range 4–6. Thereafter, it should be negatively charged. Also, it should be mentioned that the form and valency of chromium ion are pH dependent and the

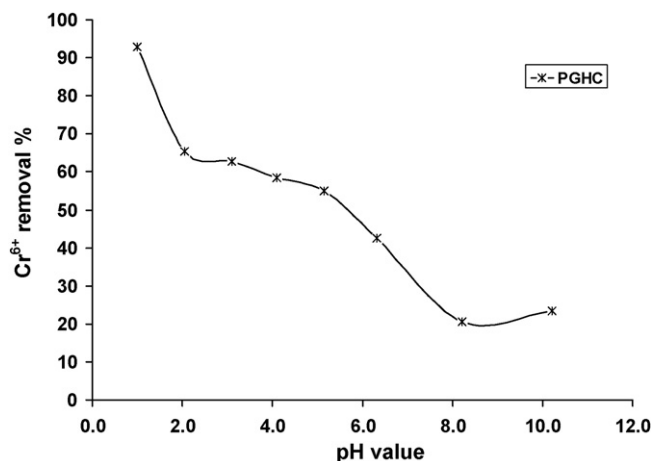


Fig. 1. Effect of system pH on adsorption of chromium (75 mg L⁻¹) onto PGHC (0.3 g/100 mL) at 25 ± 2 °C.

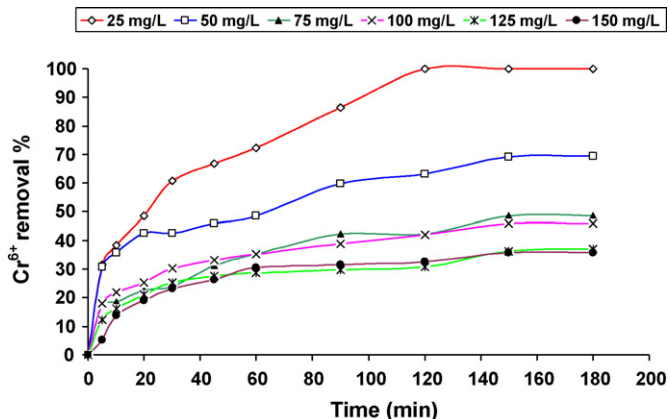


Fig. 2. Effect of contact time on the removal of different initial concentrations of chromium using PGHC (0.2 g/100 mL) at pH 1.0.

adsorption process is chromium ion form dependent, therefore, the adsorption capacity is highly pH dependent.

3.2. Effect of contact time and initial Cr⁶⁺ 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 Cr⁶⁺ will increase the biosorption rate. The results of percentage removal of Cr⁶⁺ at pH 1.0 with increasing of contact time using PGHC are presented in Fig. 2 and the relation between amounts of Cr⁶⁺ adsorbed at equilibrium (*q_e*) and its initial concentration using different doses of PGHC are shown in Fig. 3. The percentage of Cr⁶⁺ removal was increased with increasing time and PGHC concentrations. Above 20% of Cr⁶⁺ adsorption occurred in the first 5–20 min, and thereafter the rate of adsorption of Cr⁶⁺ onto PGHC was found to be slow. The slow rate of chromium adsorption is probably occurred due to the electrostatic hindrance or repulsion between the adsorbed negatively charged Cr⁶⁺ onto the surface of PGHC and the available anionic Cr⁶⁺ in solution as well as the slow pore diffusion of the Cr⁶⁺ ion into the bulk of PGHC. The electrostatic interactions will be the major effect on the adsorption due to the presence of highly acidic solution (pH 1), which may control the adsorption via the attraction and repulsion between surface

functions and chromium ions. The equilibrium was found to be nearly 180 min when the maximum Cr⁶⁺ adsorption onto PGHC was reached. In addition, the effect of initial Cr⁶⁺ concentration on the capacity of adsorption onto PGHC is shown in Figs. 2 and 3, where percentage removal of Cr⁶⁺ determined at 180 min of contact time for six different initial chromium concentrations is shown. The percentage of removal of the chromium ions decreased with the increasing of the initial chromium concentration and it can be concluded that the adsorption process may occur through electrostatic interactions.

3.3. Effect of adsorbent dose on metal adsorption

The effect of PGHC dosage on the adsorption of Cr⁶⁺ from aqueous solutions was investigated using five different adsorbent concentrations and six different initial chromium concentration. The extent of adsorption is proportional to specific area, which can be defined as that portion of the total area that is available for adsorption. Concentrations of PGHC were varied from 2 to 6 g L⁻¹ and 25–150 mg L⁻¹ initial chromium concentrations at pH 1.0. The results are presented in Fig. 4, which indicate that the equilibrium concentration (*C_e*) of Cr⁶⁺ ion decreases with increasing PGHC concentration for a given initial Cr⁶⁺ ion concentration. This result may be attributed to the fact that the higher sorbent doses provide the more sorbent surface area and pores volume which will be available for adsorption.

3.4. Isotherm data analysis

The adsorption of chromium ions was carried out at different initial chromium ion concentrations ranging from 75 to 150 mg L⁻¹, at optimum pH (1.0), at 200 rpm with the optimum agitation period. Analysis of the isotherm data is important in order to develop an equation which accurately represents the results of the column and which could be used for column design purposes. In addition, adsorption isotherm can be used to describe how solute interacts with adsorbent and so is critical in optimizing the use of adsorbent. Langmuir and Freundlich models are the most widely accepted surface adsorption models for the single-solute systems. The data obtained were analyzed with the Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich (D–R) and generalized isotherm equations. The best-fitting isotherm was tested by determination of the linear regression, and the parameters of the isotherms have been obtained

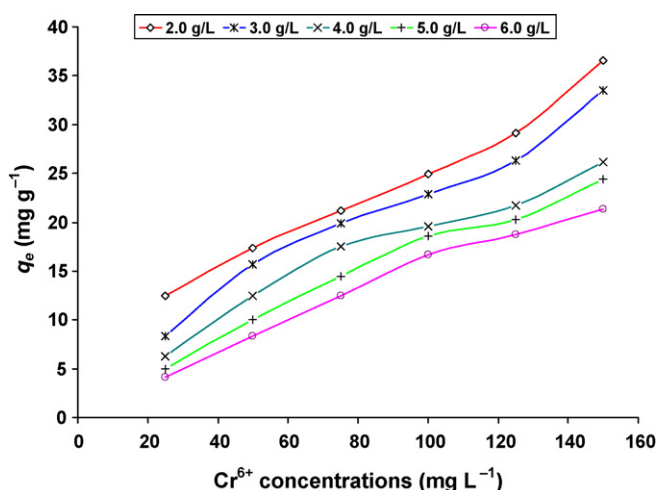


Fig. 3. Relation between amounts of chromium (Cr⁶⁺) adsorbed at equilibrium (*q_e*) and its initial concentration using different doses of PGHC.

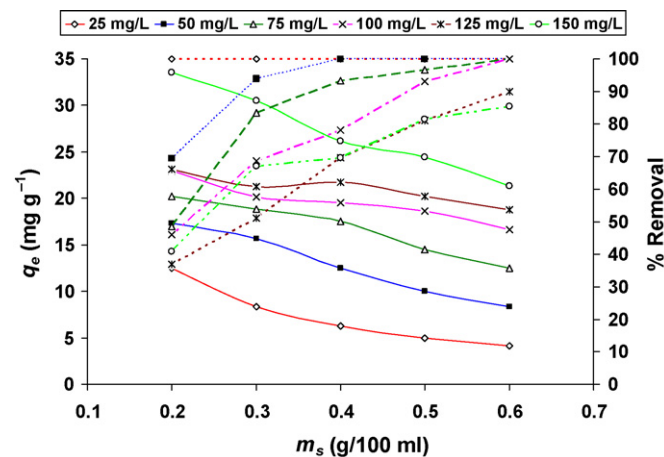


Fig. 4. Effect of PGHC dose on Cr⁶⁺ removal and *q_e* (*C₀*: 25–150 mg L⁻¹, pH 1.0, agitation speed: 200 rpm, temperature: 25 ± 2 °C), dotted lines are for the relation between *m_s* and % removal while solid lines are for the relation between *m_s* and *q_e*.

Table 1
The four linear forms of Langmuir isotherm model

Name	Linear form	Plot	Slope	Intercept
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} \times C_e$ (2)	C_e/q_e versus C_e	$1/Q_m$	$1/(K_L Q_m)$
Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{K_L Q_m}\right) \frac{1}{C_e} + \frac{1}{Q_m}$ (3)	$1/q_e$ versus $1/C_e$	$1/(K_L Q_m)$	$1/Q_m$
Langmuir-3	$q_e = Q_m - \left(\frac{1}{K_L}\right) \frac{q_e}{C_e}$ (4)	q_e versus q_e/C_e	$1/K_L$	Q_m
Langmuir-4	$\frac{q_e}{C_e} = K_L Q_m - K_L q_e$ (5)	q_e/C_e versus q_e	K_L	$K_L Q_m$

from the intercept and slope of the linear plots of the different isotherm models.

3.4.1. Langmuir isotherm

At room temperature ($25 \pm 2^\circ\text{C}$), Cr^{6+} ions adsorbed onto the PGHC are in equilibrium with Cr^{6+} ions in aqueous solution after 180 min contact time. The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. Estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the PGHC was calculated using the Langmuir isotherm model since the saturated monolayer isotherm can be explained by the non-linear equation of Langmuir Eq. (1) [21].

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

where C_e is the equilibrium concentration (mg L^{-1}), q_e the amount of metal ion adsorbed (mg g^{-1}), Q_m a complete monolayer (mg g^{-1}) and K_L is an adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption. Eq. (1) can be linearized into four different forms in Table 1 (Eqs. (2)–(5)), which give different parameter estimates [22,23].

The more popular linear forms used are Langmuir-1 and Langmuir-2, and the results obtained from the four forms of Langmuir model for the adsorption of Cr^{6+} onto PGHC are shown in Table 2. The results given in Table 2 shows the strong positive evidence that the adsorption of chromium ions onto PGHC follows the Langmuir-1 form and not follow the other three forms. The applicability of the Langmuir-1 form to the adsorption of Cr^{6+} ions onto PGHC was proved by the high correlation coefficients $R^2 > 0.999$ for all initial chromium concentration tested. Fig. 5 shows the comparison between Langmuir equilibrium isotherms calculated q_e obtained from Langmuir-1 form and the experimental

data of Cr^{6+} ($75\text{--}150 \text{ mg g}^{-1}$) adsorption on various doses of PGHC ($0.2\text{--}0.6 \text{ g}/100 \text{ mL}$). Table 2 and Fig. 5 explain the high applicability of Langmuir-1 form to the adsorption of chromium onto PGHC. The maximum monolayer capacity, Q_m , obtained from the Langmuir isotherm was 35.21 mg g^{-1} , which is lower than that obtained from our previous work on the activated carbon obtained from seed husk of *Casuarina equisetifolia* ($Q_m 172.4 \text{ mg g}^{-1}$) but the pomegranate husk is much more available than the seed husk of *C. equisetifolia*.

3.4.2. The Freundlich isotherm

The Freundlich model was chosen to estimate the adsorption intensity of the Cr^{6+} on the PGHC surface based on sorption heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. It can be derived assuming a logarithmic decrease in the enthalpy of sorption with the

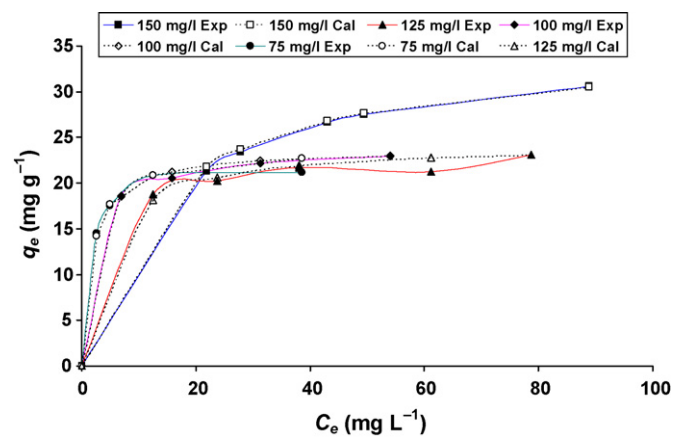


Fig. 5. Comparison between Langmuir equilibrium isotherms (q_e) plots and the experimental data of Cr^{6+} ($75\text{--}150 \text{ mg g}^{-1}$) adsorption on various doses of PGHC ($0.2\text{--}0.6 \text{ g}/100 \text{ mL}$).

Table 2
Isotherm parameters obtained from the four linear forms of Langmuir model for the adsorption of chromium onto PGHC

Isotherm model	Isotherm parameters	Cr concentrations (mg L^{-1})			
		150	125	100	75
Langmuir-1	Q_m (mg g^{-1})	35.21	24.30	23.87	23.70
	$K_L \times 10^3$ (L mg^{-1})	73.82	234.11	506.04	589.39
	R^2	0.999	1.000	1.000	1.000
Langmuir-2	Q_m (mg g^{-1})	34.72	23.15	22.99	20.45
	$K_L \times 10^3$ (L mg^{-1})	75.77	332.56	62.69	1023.01
	R^2	0.960	0.891	0.694	0.783
Langmuir-3	Q_m (mg g^{-1})	34.56	23.20	23.10	20.34
	$K_L \times 10^3$ (L mg^{-1})	77.50	328.75	567.83	1098.66
	R^2	0.931	0.850	0.640	0.625
Langmuir-4	Q_m (mg g^{-1})	35.24	23.58	24.27	21.88
	$K_L \times 10^3$ (L mg^{-1})	72.10	279.40	363.10	686.80
	R^2	0.931	0.850	0.640	0.625

Table 3
Comparison of the coefficients isotherm parameters for chromium adsorption onto PGHC

Isotherm model	Isotherm parameter	Cr concentrations (mg L ⁻¹)			
		150	125	100	75
Freundlich	n	4.33	10.00	9.01	11.77
	K_F (mg g ⁻¹)	10.67	14.71	14.82	14.65
	R^2	0.962	0.996	0.962	0.996
Tempkin	A_T (L g ⁻¹)	1.66	748.16	387.23	30827.92
	B_T (mg L ⁻¹)	6.12	2.07	2.29	1.419
	R^2	0.967	0.880	0.785	0.409
Dubinin–Radushkevich	Q_m (mg g ⁻¹)	32.01	22.07	22.03	19.50
	$K_{D-R} \times 10^3$ (mol ² kJ ⁻²)	33.80	4.70	1.60	0.40
	E (kJ mol ⁻¹)	0.380	0.402	0.402	0.410
	R^2	0.898	0.898	0.898	0.898
Generalized isotherm	N_b	0.46	0.26	0.28	1.04
	K_G (mg L ⁻¹)	2.17	1.45	1.80	15.86
	R^2	0.996	0.996	0.996	0.996

increase in the fraction of occupied sites and is given by the following non-linear equation [24]:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F (mg g⁻¹) stands for adsorption capacity and n for adsorption intensity of metal ions on the sorbent. Eq. (6) can be linearized in logarithmic form Eq. (7) and the Freundlich constants can be determined from the linear plot of $\log(q_e)$ versus $\log(C_e)$.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

The linear Freundlich isotherm plots for the adsorption of the Cr⁶⁺ ions onto PGHC are presented in Fig. 6. Examination of the correlation coefficients reported in Table 3 shows that the Freundlich model is less applicable to PGHC than the Langmuir-1 linear form while it is more applicable than the other three forms of Langmuir model. The correlation coefficient obtained for activated carbon is ranged between 0.962 and 0.996, which indicates that the experimental data fitted well to Freundlich model. The n values (4.33–11.77) are higher than 1.0, indicating that Cr⁶⁺ is favorably adsorbed by PGHC at 25 °C. Moreover, the magnitude of K_F ranged between 10.67 and 14.82, which indicates high adsorptive capacity and easy uptake of Cr⁶⁺ from aqueous solution by PGHC.

3.4.3. The Tempkin isotherm

Tempkin isotherm model considered the effects of indirect adsorbate–adsorbate interaction isotherms which explained that

the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage due to adsorbate–adsorbate interactions. Therefore, the adsorption potentials of the adsorbent for adsorbates can be evaluated using Tempkin adsorption isotherm model, which assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has generally been applied in the following form Eq. (8) [25–27]:

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad (8)$$

The Tempkin isotherm Eq. (8) can be simplified to the following equation (9):

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (9)$$

where $B_T = (RT)/b$ and A_T (L g⁻¹) are the Tempkin constant and can be determined by a plot of q_e versus $\ln C_e$. Also, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J mol⁻¹ K⁻¹. The constant b is related to the heat of adsorption [28,29].

The linear plots of the Tempkin isotherm Eq. (9) for the adsorption data are shown in Fig. 7. Examination of the data shows that the Tempkin isotherm is not applicable to the adsorption of Cr⁶⁺ onto PGHC due to the low correlation coefficients (Table 3).

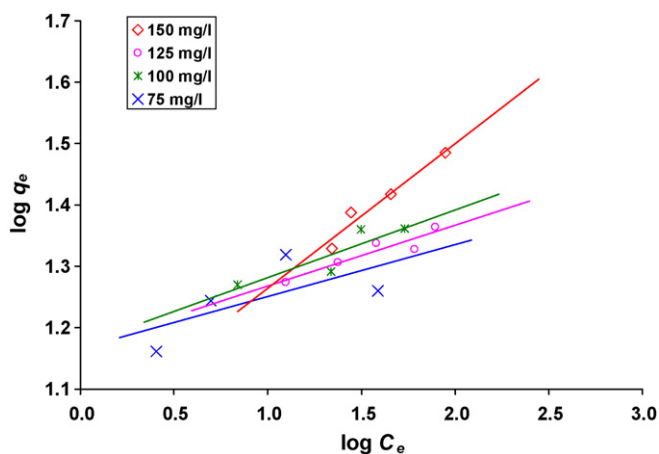


Fig. 6. Freundlich isotherm of Cr⁶⁺ (75–150 mg L⁻¹) adsorbed onto PGHC (0.2–0.6 g/100 mL).

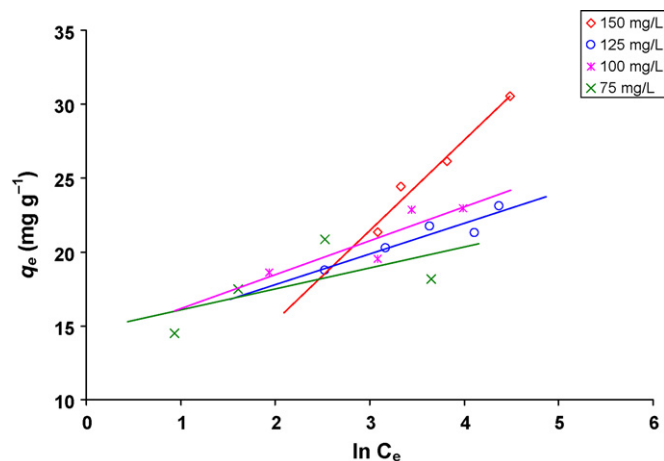


Fig. 7. Tempkin equilibrium isotherm model for the adsorption of Cr⁶⁺ (75–150 mg L⁻¹) onto PGHC (0.2–0.6 g/100 mL).

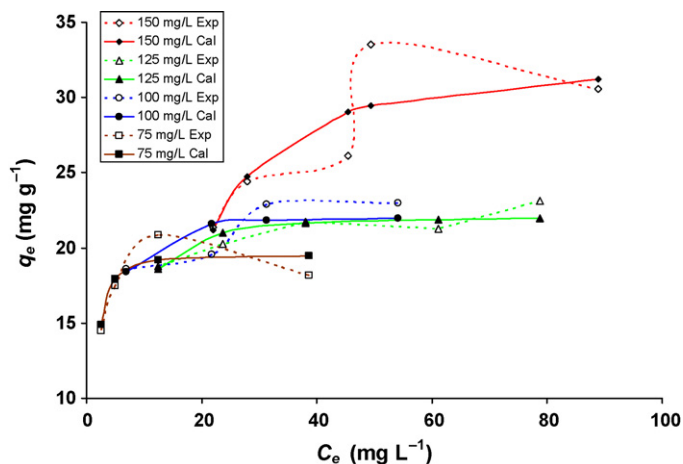


Fig. 8. Comparison between Dubinin and Radushkevich equilibrium isotherms (q_e) plots and the experimental data of Cr^{6+} (75–150 mg g^{-1}) adsorption on various dose of PGHC (0.2–0.6 g/100 mL).

3.4.4. The Dubinin–Radushkevich isotherm

Another equation that has been used to determine useful thermodynamic adsorption parameters is the Dubinin–Radushkevich (D–R) equation. It does not assume a homogeneous surface or a constant sorption potential [30]. The Dubinin–Radushkevich (D–R) model was chosen to estimate the characteristic porosity and the apparent free energy of adsorption [31–33]. The D–R model has been generally applied in the following form Eq. (10) and its linear form can be shown in Eq. (11):

$$q_e = Q_m \exp(-K_{D-R}\varepsilon^2) \quad (10)$$

$$\ln q_e = \ln Q_m - K_{D-R}\varepsilon^2 \quad (11)$$

where K_{D-R} is a constant related to the adsorption energy, Q_m the theoretical monolayer saturation capacity (mg g^{-1}) and ε is the Polanyi potential, calculated from Eq. (12).

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

The slope of the plot of $\ln q_e$ versus ε^2 gives K_{D-R} ($\text{mol}^2 \text{kJ}^{-2}$) and the intercept yields the adsorption capacity, Q_m (mg g^{-1}). The mean free energy of adsorption (E), defined as the free energy change when 1 mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation Eq. (13) [34]:

$$E = \sqrt{(2K)} \quad (13)$$

The calculated value of E is given in Table 3. The maximum adsorption capacity Q_m obtained using D–R isotherm model for adsorption of Cr^{6+} over PGHC was 32.01 mg g^{-1} (Table 3), which is very close to that obtained from Langmuir isotherm model (Table 2). However, the correlation coefficients obtained from D–R isotherm model are lower than those obtained for Langmuir and Freundlich isotherm models reflecting the inapplicability of D–R isotherm model which is clearly proved by comparing the experimental and calculated q_e as shown in Fig. 8. The values of E calculated using Eq. (13) are ranged between 0.380 and $0.410 \text{ kJ mol}^{-1}$ for PGHC that are lower than the typical range of bonding energy for ion-exchange mechanisms ($8\text{--}16 \text{ kJ mol}^{-1}$), indicating that physisorption plays a significant role in the adsorption process of Cr^{6+} ion onto PGHC, which is in agreement with the result obtained from pH study.

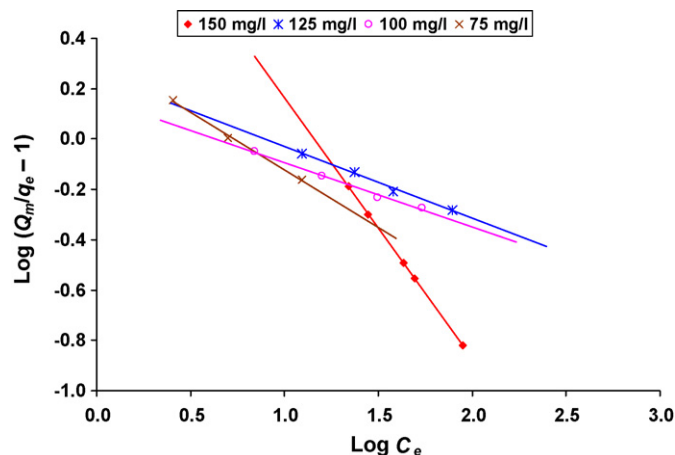


Fig. 9. Generalized isotherm model.

3.4.5. Generalized isotherm equation

A generalized isotherm equation was tested for correlation of the equilibrium data [35–37]. Linear form of the generalized isotherm is given by:

$$\log \left[\frac{Q_m}{q_e} - 1 \right] = \log K_G - N_b \log C_e \quad (14)$$

where K_G is the saturation constant (mg L^{-1}), N_b the cooperative binding constant, Q_m the maximum adsorption capacity of the adsorbent (mg g^{-1}) (obtained from Langmuir isotherm model), and q_e (mg g^{-1}) and C_e (mg L^{-1}) are the equilibrium chromium concentrations in the solid and liquid phases, respectively. From plot of $\log[(Q_m/q_e) - 1]$ versus $\log C_e$; the intercept gave $\log K_G$ and the slope gave N_b constants. Parameters related to each isotherm were determined by using linear regression analysis and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is given in Table 3. Apparently, the generalized adsorption isotherm represents the equilibrium data reasonably well (Fig. 9). The saturation constant (K_G) were ranged between 1.45 and 15.86 mg L^{-1} and the correlation coefficient are comparable to that obtained from Langmuir-1 form, but much higher than that obtained from other three linear forms of Langmuir model (Tables 2 and 3).

3.5. Kinetic studies

Batch experiments were conducted to explore the rate of chromium adsorption by PGHC at pH 1.0 and different chromium and PGHC concentrations. The kinetic adsorption data can be processed to understand the dynamics of the adsorption reaction in terms of the order of the rate constant. The kinetic of Cr^{6+} adsorption PGHC is required for selecting optimum operating conditions for the full-scale batch process. Moreover, it is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes. Thus, the process of chromium removal from aqueous phase by PGHC may be represented by pseudo first-order [38], pseudo second-order [39], Elovich [40–42] and intraparticle diffusion [43,44] kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of Cr^{6+} adsorption.

3.5.1. Pseudo first-order kinetic model

The kinetic data were treated with the Lagergren first-order model [38], which is the earliest known one describing the adsorption rate based on the adsorption capacity. It is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (15)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g^{-1}), and k_1 is the rate constant of pseudo first-order adsorption (min^{-1}). Eq. (15) was integrated with the boundary conditions of $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ and rearranged to the following linear equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (16)$$

If the pseudo first-order kinetics is applicable, a plot of $\log(q_e - q_t)$ versus t should provide a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively (Fig. 10). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed from Fig. 10 that the Lagergren model does not fit the experimental data. On the other hand, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots even when the correlation coefficient R^2 are relatively high (Table 4). This shows that the adsorption of Cr^{6+} onto PGHC is not appropriate to describe the entire process and not a first-order reaction.

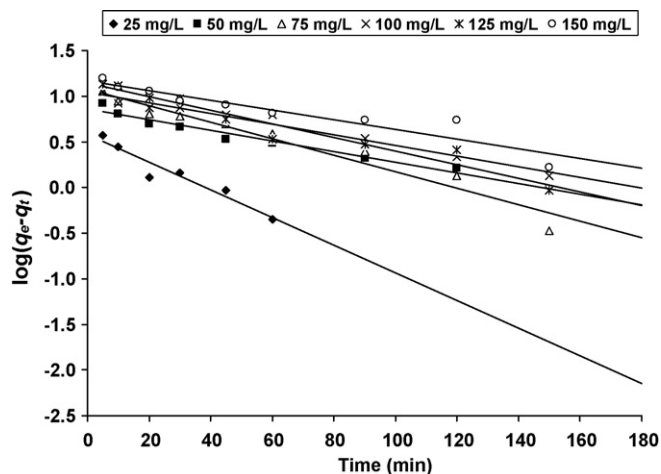


Fig. 10. Pseudo first-order kinetics for Cr^{6+} (25–150 mg L^{-1}) adsorption onto PGHC (0.4 $\text{g}/100 \text{ mL}$) at pH 1.0 and temperature $25 \pm 2 \text{ }^\circ\text{C}$.

3.5.2. Pseudo second-order kinetic model

Adsorption kinetic was explained by the pseudo second-order model given by Ho et al. [39] as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (17)$$

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the second-order rate constant of adsorption. Integrating Eq. (17) for the boundary conditions $q=0$ to $q=q_t$ at $t=0$ to $t=t$ is linearized to obtain the following equation:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (18)$$

Table 4

Comparison of the first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial chromium and PGHC

Parameter		First-order kinetic model				Second-order kinetic model			
Carbon concentration (g L^{-1})	Cr^{6+} (mg L^{-1})	q_e (exp.) (mg g^{-1})	$k_1 \times 10^3$ (min^{-1})	q_e (calc.) (mg g^{-1})	R^2	$k_2 \times 10^3$ ($\text{g mg}^{-1} \text{ min}^{-1}$)	q_e (calc.) (mg g^{-1})	h ($\text{mg g}^{-1} \text{ min}^{-1}$)	R^2
2.0	50	17.34	10.44	15.43	0.966	4.25	17.04	1.23	0.986
	75	18.19	14.38	19.35	0.991	1.95	20.12	0.79	0.983
	100	22.97	7.39	28.10	0.941	10.02	25.38	6.46	1.000
	125	23.11	16.83	27.41	0.979	2.50	25.32	1.60	0.998
	150	30.57	26.22	20.73	0.979	2.22	26.39	1.54	0.989
3.0	50	15.65	9.11	12.44	0.961	3.50	16.10	0.91	0.991
	75	20.85	15.00	17.96	0.989	1.97	22.83	1.03	0.994
	100	22.89	10.87	8.75	0.788	2.41	23.87	1.37	0.986
	125	21.28	12.26	8.75	0.866	2.33	21.14	1.04	0.971
	150	33.52	20.56	11.05	0.904	1.47	33.90	1.69	0.999
4.0	50	12.50	7.18	13.36	0.975	4.66	12.94	0.78	0.992
	75	17.50	12.00	20.73	0.951	3.29	18.66	1.15	0.994
	100	19.55	11.09	13.36	0.972	2.91	20.24	1.19	0.983
	125	21.74	13.80	17.04	0.944	2.38	23.20	1.28	0.993
	150	26.13	14.79	12.21	0.884	2.30	26.46	1.61	0.978
5.0	50	10.00	5.15	32.93	0.999	13.87	10.41	1.50	1.000
	75	14.49	8.63	18.88	0.989	4.51	15.31	1.06	0.997
	100	18.62	10.20	12.44	0.987	2.91	19.69	1.13	0.985
	125	20.25	12.93	14.74	0.993	2.41	21.37	1.10	0.988
	150	24.43	15.36	16.58	0.983	1.58	25.64	1.04	0.990
6.0	50	8.33	3.27	42.61	0.990	32.56	8.53	2.37	1.000
	75	12.50	7.08	25.33	0.994	7.17	13.23	1.26	0.999
	100	16.67	7.98	21.42	0.991	6.03	17.42	1.83	0.998
	125	18.76	10.83	16.35	0.974	3.27	19.80	1.28	0.995
	150	21.35	12.36	16.35	0.995	2.90	22.47	1.47	0.994

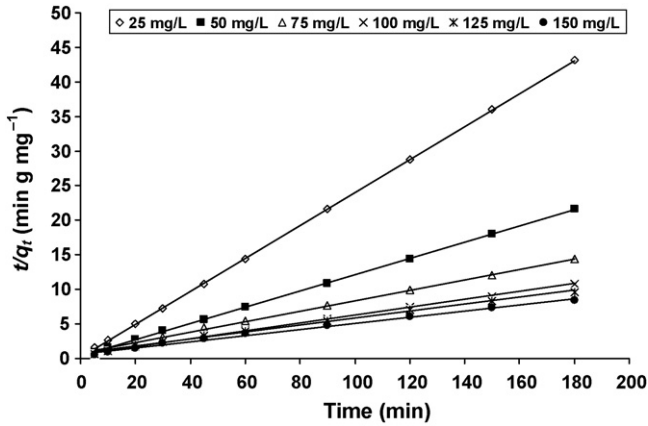


Fig. 11. Plot of the pseudo second-order model at different initial Cr⁶⁺ concentrations (25–150 mg L⁻¹), PGHC (0.6 g/100 mL), pH 1.0 and temperature 25 ± 2 °C.

The second-order rate constants were used to calculate the initial sorption rate (*h*), given by the following Eq. (19):

$$h = k_2 q_e^2 \tag{19}$$

The plot of *t/q_t* versus *t* should show a linear relationship if the second-order kinetics is applicable. Values of *k₂* and *q_e* were calculated from the intercept and slope of the plots of *t/q_t* versus *t* (Fig. 11). The linear plots of *t/q_t* versus *t* show good agreement between experimental and calculated *q_e* values at different initial Cr⁶⁺ and adsorbent concentrations (Table 4) with correlation coefficients *R*² ≥ 0.983, which indicated that the pseudo second-order kinetic model provided good correlation for the adsorption of Cr⁶⁺ onto PGHC for all studied initial Cr⁶⁺ and adsorbent concentrations in contrast to the pseudo first-order model. Moreover, values for the rate of initial adsorption, *h*, have no specific role, while the pseudo second-order rate constant (*k₂*) decreases with increase the initial Cr⁶⁺ concentration for all studied doses of PGHC.

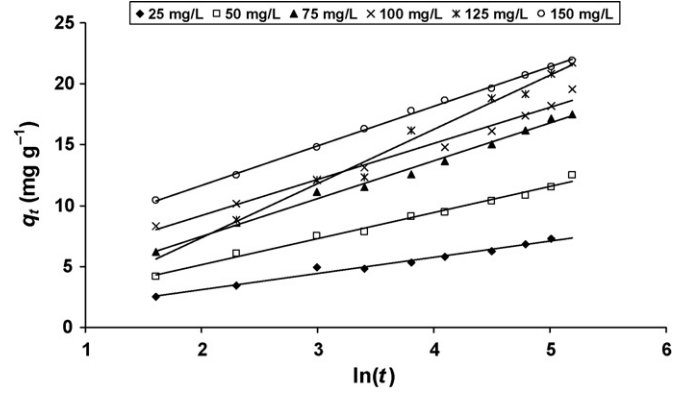


Fig. 12. Elovich model plot for the adsorption of Cr⁶⁺ (25–150 mg L⁻¹) onto PGHC (0.4 g/100 mL).

3.5.3. Elovich kinetic model

Elovich kinetic equation is another rate equation based on the adsorption capacity, which is generally expressed as [40–42]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{20}$$

where α is the initial adsorption rate (mg g⁻¹ min⁻¹) and β is the desorption constant (g mg⁻¹) during any one experiment. It is simplified by assuming $\alpha\beta t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (21) becomes form as followed:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{21}$$

If Cr⁶⁺ adsorption by PGHC fits the Elovich model, a plot of *q_t* versus ln(*t*) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) × ln(αβ) (Fig. 12). Thus, the constants can be obtained from the slope and the intercept of the straight line (Table 5). Correlation coefficients obtained by Elovich model were

Table 5

The parameters obtained from Elovich kinetics model and intraparticle diffusion model using different initial Cr⁶⁺ concentrations and PGHC doses

Sorbent dose (g L ⁻¹)	Cr ⁶⁺ conc. (mg L ⁻¹)	Elovich			Intraparticle diffusion		
		β (g mg ⁻¹)	α (mg g ⁻¹ min ⁻¹)	R ²	K _{dif} (mg g ⁻¹ min ^{-0.5})	C (mg g ⁻¹)	R ²
1.0	50	0.37	6.44	0.993	0.83	6.23	0.976
	75	0.23	1.66	0.984	1.13	3.80	0.974
	100	0.59	28294.83	0.973	0.85	16.04	0.716
	125	0.21	4.57	0.982	1.39	7.00	0.904
	150	0.14	2.75	0.989	2.08	3.97	0.928
2.0	50	0.41	4.95	0.977	0.79	4.98	0.966
	75	0.25	3.66	0.996	1.30	4.60	0.951
	100	0.27	8.19	0.970	1.02	8.95	0.953
	125	0.32	5.90	0.983	1.11	5.56	0.879
	150	0.17	6.51	0.995	1.73	9.37	0.952
3.0	50	0.47	3.20	0.990	0.65	4.02	0.949
	75	0.32	4.68	0.992	0.94	5.84	0.951
	100	0.34	8.87	0.986	0.90	7.33	0.967
	125	0.22	3.13	0.982	1.24	6.27	0.933
	150	0.31	16.07	0.999	1.22	9.26	0.954
4.0	50	0.71	14.44	0.983	0.40	5.49	0.854
	75	0.40	4.51	0.992	0.76	5.18	0.944
	100	0.30	4.40	0.991	0.91	6.66	0.989
	125	0.26	3.45	0.991	1.09	5.96	0.987
	150	0.25	6.59	0.993	1.32	7.40	0.951
5.0	50	1.03	51.22	0.972	0.25	5.55	0.805
	75	0.49	6.34	0.989	0.60	5.47	0.894
	100	0.44	20.11	0.991	0.69	8.41	0.933
	125	0.32	6.50	0.992	0.97	6.58	0.962
	150	0.28	6.98	0.996	1.06	7.83	0.979

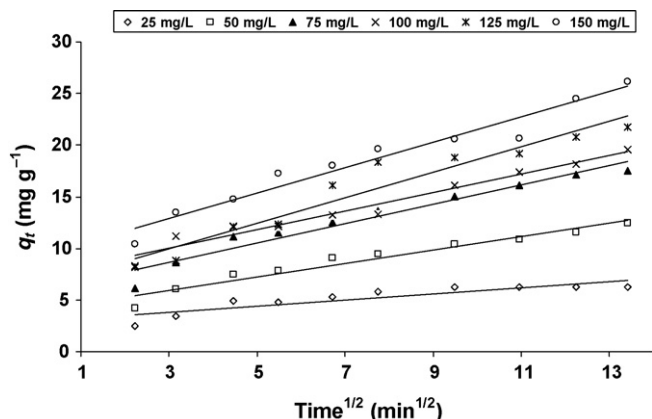


Fig. 13. Intraparticle diffusion model plot for the adsorption of Cr^{6+} (25–150 mg L^{-1}) onto PGHC (0.4 g/100 mL) at room temperature ($25 \pm 2^\circ\text{C}$).

higher than that obtained from pseudo first-order model and comparable to that obtained from pseudo second-order model.

3.5.4. The intraparticle diffusion model

The adsorption process required a multi-step involving the transport of solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process, and is therefore, rate-determining step. The intraparticle diffusion model is explored by using the following equation [43,44]:

$$q_t = K_{\text{dif}} t^{0.5} + C \quad (22)$$

where C is the intercept and K_{dif} ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intra-particle diffusion rate constant. The plot of q_t against $t^{0.5}$ may present a multi-linearity correlation, which indicates that two or more steps occur during adsorption process (Fig. 13). The rate constant K_{dif} directly evaluated from the slope of the regression line and the intercept is C and is reported in Table 5.

The values C provide information about the thickness of the boundary layer, since the resistance to the external mass transfer increases as the intercept increases. R^2 values given in Table 5 are ranged between 0.716 and 0.979, confirming that the rate-limiting step is actually the intra-particle diffusion process for some of the data analyzed when the R^2 values become close to 1.000. The linearity of the plots demonstrated that intra-particle diffusion played a significant role in the uptake of the chromium by sorbent. The intra-particle diffusion rate constants, K_{dif} , were in the range of (0.25–2.08 $\text{mg g}^{-1} \text{min}^{-0.5}$). However, Fig. 13 shows low linearity for the adsorption of chromium by PGHC which indicates that both of surface adsorption and intra-particle diffusion are involved in the rate-limiting step. However, still there is no sufficient indication about which of the two steps was the rate-limiting step. It has been reported [45,46] that if the intraparticle diffusion is the sole rate-limiting step, it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin, which is not the case in this study. It

Table 6

Data obtained for the adsorption of chromium (150 mg L^{-1}) from different solution using PGHC (5.0 g L^{-1})

Solution of chromium used	PGHC	
	Removal %	Maximum capacity (mg g^{-1})
Distilled water	85.39	35.71
Artificial sea water	84.02	35.21
Natural sea water	83.15	34.85
Wastewater	82.50	33.95

may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during the chromium-PGHC interactions.

3.6. Effect of saline water and real wastewater on the adsorption process

The studies of the effects of salinity and real wastewater on the capability of the PGHC to remove Cr^{6+} ions from solution were investigated. The above work was achieved using synthetic sea water, natural sea water and real wastewater and the results are reported in Table 6. Salt concentration is directly proportional to the ionic strength of aqueous solutions. Ionic strength is also one of the important factors that influence the equilibrium uptake. However, the percentage of Cr^{6+} removal from aqueous solution prepared by dissolving of the Cr^{6+} into distilled water, synthetic sea, natural sea water and wastewater were 85.39%, 84.02%, 83.15% and 82.50% for PGHC, respectively, which indicates that the removal percentage of Cr^{6+} adsorption were not affecting by the changing of the type of chromium ion solution. The slightly decrease in removal percentages and maximum capacities occurred by the presence of salt ions (Na^+Cl^-) may be due to the inhibition effect of salt on the active centers of carbon. These results indicate that the PGHC is applicable material for removal of Cr^{6+} ions from different types of aqueous solutions including wastewater.

3.7. Desorption of Cr^{6+} from sorbent

Desorption studies will help to elucidate the nature of adsorption process and to recover the Cr^{6+} from sorbent. Moreover, it also will help to regenerate the sorbents so that it can be used again to adsorb metal ions, and to develop the successful sorption process [47]. Desorption experiments were carried out at 25°C by using 0.1N NaOH giving 95% desorption after 120 min contact time. Activation of the washed PGHC after desorption process was achieved by agitation with 1N HCl for 120 min followed by washing with distilled water.

4. Conclusion

The PGHC has been identified as an effective adsorbent to remove Cr^{6+} ions from various aqueous solutions. The adsorption process is pH dependent and the optimum pH was 1.0. The kinetic studies proved that the second-order kinetic was the applicable model. Furthermore, the isotherm equilibrium studies confirmed that the Langmuir-1 form and generalized models are the highest fitted models for the adsorption process of Cr^{6+} by PGHC. The PGHC exhibited high adsorption capacity under several initial chromium and sorbent dose concentrations. The adsorption process was found to be controlled by more than one mechanism such as the film diffusion and particle diffusion. The proposed sorbents are efficient, environment friendly and can reduce the huge amount of toxic chromium ions from effluent discharges by the industries around the big cities.

References

- [1] A. El Nemr, Assessment of heavy metal pollution in surface muddy sediments of Lake Burullus, southeastern Mediterranean, Egypt, Egypt. J. Aquat. Biol. Fish. 7 (4) (2003) 67–90.
- [2] A. El Nemr, A. El-Sikaily, A. Khaled, Heavy metals concentration in some fish tissues from south Mediterranean waters, Egypt, Egypt. J. Aquat. Biol. Fish. 7 (3) (2003) 155–172.
- [3] A. El-Sikaily, A. Khaled, A. El Nemr, Heavy metals monitoring using bivalves from Mediterranean Sea and Red Sea, Environ. Monit. Assess. 98 (1–3) (2004) 41–58.

- [4] A. El Nemr, A. El Sikaily, A. Khaled, Total and leachable heavy metals in muddy and sandy sediments of Egyptian coast along Mediterranean Sea, *Environ. Mon. Assess.* 129 (2007) 151–168.
- [5] C. Pellerin, S.M. Booker, Reflection on hexavalent chromium, health hazards of an industrial heavyweight, *Environ. Health Perspect.* 108 (9) (2000) 402–407.
- [6] F. Gode, E. Pehlivan, Removal of Cr(VI) from aqueous solution by two Lewatitanion exchange resins, *J. Hazard. Mater.* B119 (2005) 175–182.
- [7] Y.G. Ko, U.S. Choi, T.Y. Kim, D.J. Ahn, Y.J. Chn, FT-IR and isotherm study on anion adsorption onto novel chelating fibers, *Macromol. Rapid Commun.* 23 (2002) 535–539.
- [8] F.C. Richard, A.C.M. Bourg, Aqueous geochemistry of chromium: a review, *Water Res.* 25 (7) (1991) 807–816.
- [9] R.L. Ramos, A.J. Martinez, R.M.G. Coronado, Adsorption of chromium(VI) from aqueous solutions on activated carbon, *Water Sci. Technol.* 30 (9) (1994) 191–197.
- [10] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* B97 (2003) 219–243.
- [11] E. Demirbas, M. Koby, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on activated carbons prepared from agricultural wastes, *Water SA* 30 (4) (2004) 533–539.
- [12] N. Ahalya, R.D. Kanamadi, T.V. Ramachandra, Biosorption of chromium(VI) from aqueous solutions by the husk of Bengal gram (*Cicer arietinum*), *Electron. J. Biotech.* 8 (3) (2005) 258–264.
- [13] A. El Nemr, A. Khaled, A. El Sikaily, O. Abdelwahab, Removal of toxic chromium (VI) from aqueous solution by activated carbon developed from *Casuarina equisetifolia*, *Chem. Ecol.* 23 (2) (2007) 119–129.
- [14] A. Abdelwahab, A. El Nemr, A. El-Sikaily, A. Khaled, Biosorption of direct yellow 12 from aqueous solution by marine green algae *Ulva lactuca*, *Chem. Ecol.* 22 (2006) 253–266.
- [15] O. Abdelwahab, A. El Sikaily, A. Khaled, A. El Nemr, Mass transfer processes of chromium (VI) adsorption onto guava seeds, *Chem. Ecol.* 23 (1) (2007) 73–85.
- [16] O. Abdelwahab, A. El-Sikaily, A. El Nemr, A. Khaled, Biosorption of toxic chromium from aqueous solutions, saline water and wastewater by inactivated biomass of green alga *Ulva lactuca* and its activated carbon, in: International Conference on Aquatic Resources: Needs and Benefits NIOF, Alexandria, Egypt, 18–21st September, 2006, p. 54.
- [17] A. El-Sikaily, A. Khaled, A. El Nemr, O. Abdelwahab, Removal of methylene blue from aqueous solution by marine green alga *Ulva lactuca*, *Chem. Ecol.* 22 (2006) 149–157.
- [18] F.D. Snell, C.T. Snell, *Colorimetric Method of Analysis*, vol. 2, third ed., D. Van Nostrand Company, New York, Toronto, 1959.
- [19] F.W. Gilcreas, M.J. Tarars, R.S. Ingols, *Standard Methods for the Examination of Water and Wastewater*, 12th ed., American Public Health Association (APHA) Inc., New York, 1965, 213 pp.
- [20] E. Malkoç, Y. Nuhoglu, The removal of chromium(VI) from synthetic wastewater by *Ulothrix zonata*, *Fresenius Environ. Bull.* 12 (4) (2003) 361–376.
- [21] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [22] D.G. Kinniburgh, General purpose adsorption isotherms, *Environ. Sci. Technol.* 20 (1986) 895–904.
- [23] E. Longhinotti, F. Pozza, L. Furlan, M.D.N.D. Sanchez, M. Klug, M.C.M. Laranjeira, V.T. Favere, Adsorption of anionic dyes on the biopolymer chitin, *J. Brazil. Chem. Soc.* 9 (1998) 435–440.
- [24] H.M.F. Freundlich, Über die adsorption in lösungen, *Zeitschrift für Physikalische Chemie (Leipzig)* 57A (1906) 385–470.
- [25] C. Aharoni, D.L. Sparks, Kinetics of soil chemical reactions—a theoretical treatment, in: D.L. Sparks, D.L. Suarez (Eds.), *Rate of Soil Chemical Processes*, Soil Science Society of America, Madison, WI, 1991, pp. 1–18.
- [26] C. Aharoni, M. Ungarish, Kinetics of activated chemisorption. Part 2. Theoretical models, *J. Chem. Soc. Faraday Trans.* 73 (1977) 456–464.
- [27] X.S. Wang, Y. Qin, Equilibrium sorption isotherms for of Cu²⁺ on rice bran, *Process Biochem.* 40 (2005) 677–680.
- [28] C.I. Pearce, J.R. Lloyd, J.T. Guthrie, The removal of color from textile wastewater using whole bacterial cells: a review, *Dyes Pigments* 58 (2003) 179–196.
- [29] G. Akkaya, A. Ozer, Adsorption of acid red 274 (AR 274) on *Dicranella varia*: determination of equilibrium and kinetic model parameters, *Process Biochem.* 40 (11) (2005) 3559–3568.
- [30] A.H. Gemeay, A.S. El-Sherbiny, A.B. Zaki, Adsorption and kinetic studies of the intercalation of some organic compounds onto Na⁺-montmorillonite, *J. Colloid Interface Sci.* 245 (2002) 116–125.
- [31] L.V. Radushkevich, Potential theory of sorption and structure of carbons, *Zhurnal Fizicheskoi Khimii* 23 (1949) 1410–1420.
- [32] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, *Chem. Rev.* 60 (1960) 235–266.
- [33] M.M. Dubinin, Modern state of the theory of volume filling of micropore adsorbents during adsorption of gases and steams on carbon adsorbents, *Zhurnal Fizicheskoi Khimii* 39 (1965) 1305–1317.
- [34] S. Kundu, A.K. Gupta, Investigation on the adsorption efficiency of iron oxide coated cement (IOCC) towards As(V)—kinetics, equilibrium and thermodynamic studies, *Colloids Surf. A Physicochem. Eng. Aspects* 273 (2006) 121–128.
- [35] F. Kargi, S. Ozmichi, Biosorption performance of powdered activated sludge for removal of different dyestuffs, *Enzyme Microb. Technol.* 35 (2004) 267–271.
- [36] S. Ozmihci, F. Kargi, Utilization of powdered waste sludge (PWS) for removal of textile dyestuffs from wastewater by adsorption, *J. Environ. Manage.* 81 (2006) 307–314.
- [37] F. Kargi, S. Cikla, Biosorption of zinc(II) ions onto powdered waste sludge (PWS): kinetics and isotherms, *Enzyme Microb. Technol.* 38 (2006) 705–710.
- [38] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, *Kungliga Svenska Vetenskapsakademiens, Handlingar* 24 (1898) 1–39.
- [39] Y.S. Ho, G. McKay, D.A.J. Wase, C.F. Foster, Study of the sorption of divalent metal ions on to peat, *Adsorpt. Sci. Technol.* 18 (2000) 639–650.
- [40] J. Zeldowitsch, Über den mechanismus der katalytischen oxidation von CO an MnO₂, *Acta Physicochim. URSS* 1 (1934) 364–449.
- [41] S.H. Chien, W.R. Clayton, Application of Elovich equation to the kinetics of phosphate release and sorption on soils, *Soil Sci. Soc. Am. J.* 44 (1980) 265–268.
- [42] D.L. Sparks, Kinetics of reaction in Pure and Mixed Systems, in *Soil Physical Chemistry*, CRC Press, Boca Raton, 1986.
- [43] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–60.
- [44] K. Srinivasan, N. Balasubramanian, T.V. Ramakrishan, Studies on chromium removal by rice husk carbon, *Ind. J. Environ. Health* 30 (1988) 376–387.
- [45] Y.S. Ho, Removal of copper ions from aqueous solution by tree fern, *Water Res.* 37 (2003) 2323–2330.
- [46] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, *Sep. Purif. Technol.* 53 (2007) 97–110.
- [47] A. Baran, E. Bicak, S.H. Baysal, S. Onal, Comparative studies on the adsorption of Cr⁶⁺ ions on to various sorbents, *Bioresour. Technol.* 98 (2006) 661–665.