

# Effective Removal of Hexavalent Chromium from Aqueous Solutions Using Ionic Liquid Modified Graphene Oxide Sorbent



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Ionic liquid modified reduced graphene oxide (IL-rGO) was prepared and examined for chromate removal. The sorbent was characterized by  $N_2$  adsorption-desorption measurement (BET), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analysis. The sorption behavior of chromate on the ionic liquid modified reduced graphene oxide sorbent from an aqueous medium was studied by varying the parameters such as contact time, initial chromate concentration, pH, and agitation speed. The results showed that sorption kinetics of chromate by IL-rGO follows the pseudo second order, which indicates that the sorption mechanism is both chemical and physical interaction. The sorption isotherm studies revealed that Langmuir model provided the best fit to all the experimental data with an adsorption capacity of 232.55 mg g<sup>-1</sup> for IL-rGO. Thermodynamic parameters, such as Gibbs free energy (−2.85 kJ mol<sup>-1</sup> at 298 K), enthalpy (55.41 kJ mol<sup>-1</sup>), and entropy (11.64 J mol<sup>-1</sup> K<sup>-1</sup>) of sorption of the chromate on ionic liquid modified reduced graphene oxide was evaluated, and it was found that the reaction was spontaneous and endothermic in nature.

*Key words:*

Langmuir isotherm, ionic liquid, reduced graphene oxide, chromate, removal

## Introduction

Chromium is one of the heavy metals present in toxic effluents released by the aerospace, electroplating, leather, mining, dyeing, fertilizer, and photography industries<sup>1,2</sup>. The Cr(VI) ion generally exists in the form of extremely soluble and highly toxic chromate ions (HCrO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), which can transfer freely to the biotic organisms prevailing in the aquatic ecosystem and food chain<sup>3</sup>. Therefore, the presence of chromium in the environment has received considerable attention. It has been found that chromium has a severe carcinogenic effect on human health, and causes cancer in the digestive system and lungs, and it may lead to other severe health hazards, such as dermatitis, bronchitis, perforation of the nasal septum<sup>4,5</sup>. Hence, the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) have set a guideline for the maximum acceptable concentrations of 50 and 100 µg L<sup>-1</sup> for total chromium in drinking water, respectively<sup>6</sup>. However, Cr(VI) concentrations in Cr(VI)-bearing wastewater and Cr(VI)-contaminated natural water resources are far

above the permitted threshold level. Therefore, it is imperative to develop new materials and effective methods for Cr(VI) remediation.

The techniques used for pollutant removal from wastewater include photodegradation<sup>7–25</sup>, adsorption<sup>24,26–45</sup>, electrocoagulation<sup>46,47</sup>, membrane filtration<sup>48,49</sup>, and reverse osmosis<sup>48</sup>. Among these methods, sorption has proved to be an attractive process because of its low cost and ease of operation. The sorption and removal of Cr(VI) has been investigated using several sorbents, including multi-walled carbon nanotubes<sup>50</sup>, Fe<sub>3</sub>O<sub>4</sub> nanoparticles<sup>51</sup>, resin<sup>52</sup>, clays<sup>53</sup>, activated carbon<sup>54</sup>, and surface-modified carbon materials<sup>55</sup>. However, there is still an increasing demand for the development of efficient and cost-effective treatment technologies for the removal of Cr(VI).

Graphene oxide, a 2D carbon material, has unique physical and chemical properties which make it an ideal candidate for extended applications such as: nanoelectronics<sup>56</sup>, supercapacitors<sup>57</sup>, sensors<sup>58</sup>, hydrogen storage<sup>59</sup>, and drug delivery<sup>60</sup>. Graphene has become a sparkling rising star on the horizon of materials science due to its extraordinary electrical, thermal, and mechanical properties<sup>59</sup>. Graphene has a large theoretical specific surface

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area of about  $2.6 \cdot 10^3 \text{ m}^2 \text{ g}^{-1}$ , high thermal conductivity ( $3 \cdot 10^3 \text{ W m}^{-1} \text{ K}^{-1}$ ), and Young's modulus ( $1.06 \cdot 10^3 \text{ GPa}$ )<sup>57</sup>. Recent research has indicated that graphene oxides and chemically modified graphene oxides have proved to be promising materials for the adsorption of metal ions due to their extraordinary mechanical strength and relatively large specific area<sup>61</sup>.

Ionic liquids (ILs) have been recently gaining widespread recognition from both research and industrial applications, such as electrochemistry, extraction, organic synthesis and catalysis for clean technology and polymerization processes<sup>62–64</sup>. This is due to their unusual properties and great potential as “green” solvents for industrial processes. Moreover, they are nonvolatile, nonflammable, thermally stable, and recyclable. However, the advantageous liquid state in most cases hinders the development of ILs in applications requiring solid shape. One way to circumvent this problem is loading ionic liquids on the surface of nanomaterials<sup>63</sup>.

In this study, reduced graphene oxide has been synthesized and modified with ionic liquid. Investigated and compared were the mechanism, isotherms, thermodynamics and kinetics of sorption of chromate by graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide. The sorption capacity and kinetics were studied using the batch method. The variables affecting the sorption process, including the agitation speed, contact time, initial concentration of chromate, solution pH, ionic strength, and temperature were optimized.

## Experimental

### Materials

Graphite powder (<20 micron) was purchased from Sigma-Aldrich, USA and used as received.  $\text{H}_2\text{SO}_4$  (>99 %), hydrochloric acid (AR grade),  $\text{H}_2\text{O}_2$  (30 % (w/v)),  $\text{KMnO}_4$  (>99 %), ammonia solution (>99 %,  $\text{NH}_4\text{OH}$ ), 1-butyl-3-methylimidazolium chloride (>99 %,  $\text{C}_8\text{H}_{15}\text{ClN}_2$ ), and cysteine (>99 %,  $\text{C}_3\text{H}_7\text{NO}_2\text{S}$ ) were all purchased from Sigma-Aldrich (St. Louis, MO, USA).

### Instrumentation

The structures of the synthesized graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide were analyzed by powder X-ray diffraction (XRD), Philips 1830 diffractometer, using graphite monochromated Cu K $\alpha$  radiation. X-ray photoemission spectroscopy (XPS) spectra were obtained with a Scienta ESCA 200 analyzer (Gammadata, Sweden) using monochromated Cu K $\alpha$  X-ray source. Adsorption-desorption isotherms of the synthesized samples were

measured at 77 K on micromeritics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method, while surface area of the sample was measured by the Brunauer-Emmet-Teller (BET) method. Transmission electron microscope (TEM) analysis was carried out with a JEOL JEM 2100 transmission electron microscope at 200 kV. The Cr(VI) concentration in the water was monitored by measuring the absorbance using an UV-vis spectrophotometer (CE 2501, CECIL instruments, Cambridge, UK) with 1.0 cm glass cuvettes at 517 nm. The pH of solutions was determined with a Metrohm 780 pH meter equipped with a combined glass calomel electrode (Metrohm Co., Herisau, Switzerland).

### Synthesis of IL-rGO

Ionic liquid modified reduced graphene oxide was obtained by the method as described by Wang *et. al.*<sup>65</sup> In a typical synthesis, 0.5 g of the ionic liquid ([Bmim][Cys]) was put into 10 mL GO aqueous suspension of  $0.5 \text{ mg mL}^{-1}$ . The mixture was kept in a tightly sealed glass bottle, and stirred for 15 h at room temperature. Firstly, the black product was isolated by centrifugation at 8000 rpm, and then the obtained black slurry was washed with deionized water. One part of the as-prepared products was then dispersed in deionized water to prepare the suspension of IL-rGO, and the other part was used to produce the powder of IL-rGO by drying at  $50^\circ\text{C}$  for 24 h under vacuum.

### Batch sorption procedure

The sorption equilibrium studies of graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide for chromate were conducted with 50 mL of a Cr(VI) solution ( $200 \text{ mg L}^{-1}$ ) and  $0.5 \text{ g L}^{-1}$  of the sorbent at 298 K, unless otherwise stated. The sorbent and sorbate was mixed on a shaking bath at 250 rpm until equilibrium was attained (typically in 5 hours). After the sorption was complete, the mixture of sorbent and sorbate was centrifuged at 3000 rpm for 3 minutes, and the amount of Cr(VI) remaining in the solution was determined by measuring its absorbance at 517 nm with a UV-Vis spectrophotometer. The amount of Cr(VI) sorbed on the sorbent was determined as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $q_e$  is the amount of Cr(VI) sorbed by the sorbent ( $\text{mg of Cr(VI)/g of the sorbent}$ ),  $C_0$  and  $C_e$  are the Cr(VI) concentrations ( $\text{mg L}^{-1}$ ) at time 0 and equilibrium, respectively,  $V$  is the volume of the solution (L), and  $W$  is the mass of the sorbent (g). Each experiment was conducted three times, and

the average and standard deviation of the results were determined.

The kinetic studies for all the five sorbents were carried out with  $250 \text{ mg L}^{-1}$  of Cr(VI) at pH 4.0. For such studies, a series of 50 mL of the Cr(VI) solution was added to 25 mg of the sorbent. The samples were shaken at 298 K and 250 rpm. The experimental data were analyzed by the most commonly used models of pseudo first-order and pseudo second-order.

## Results and discussion

### Textural characterization

The nitrogen adsorption–desorption isotherms of reduced graphene oxide and ionic liquid modified reduced graphene oxide samples are shown in Figure 1. The nitrogen adsorption–desorption isotherms of graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide show a type IV isotherm according to IUPAC classification, corresponding to mesoporous solids. The specific surface area ( $S_{\text{BET}}$ ) and specific volume of the rGO are  $2302 \text{ m}^2 \text{ g}^{-1}$  and  $0.88 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The specific surface area and specific volume of IL-rGO are reduced to  $1454 \text{ m}^2 \text{ g}^{-1}$  and  $0.62 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Therefore, it may be assumed that ionic liquids are located inside the pores or near the pore opening of reduced graphene oxide.

The XRD patterns of graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide are presented in Figure 2. Comparison of XRD pattern of IL-rGO and rGO with GO, suggested that the basal spacing between the (002) planes increased from 0.35 nm to about 0.8 nm, which was signified by a new broad peak at  $2\theta = 11.8^\circ$  replacing the peak at  $2\theta = 25.4^\circ$ . This revealed that IL-rGO, rGO, and GO were well modified and had the representative peaks of IL-rGO, rGO, and GO.

The chemical state of the carbon of the GO, rGO, and IL-rGO was examined by the XPS technique (Figure 3). The C1s XPS spectrum of GO shows that, beside the band of aromatic C-C bonds at  $\text{BE} = 284.6 \text{ eV}$ , there is a very broad peak ranging from 286 to 290 eV, indicating a considerable degree of oxidation and the presence of different oxygen-containing groups. However, C1s XPS spectra of IL-rGO show almost identical features with that of rGO, which demonstrate the aromatic nature of graphene-like material. The broadened peak shape of reduced graphene oxide and ionic liquid modified reduced graphene oxide indicates that these materials have a much more disordered structure than graphite.

The structure of the IL-rGO was further studied by transmission electron microscopy (TEM) (Figure

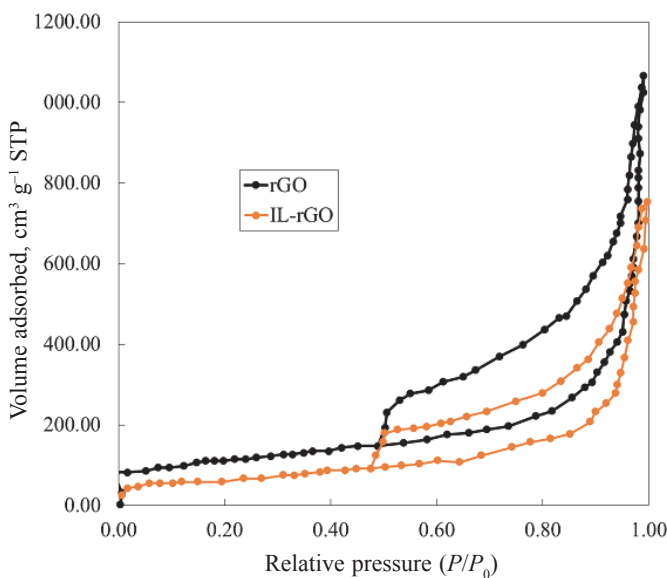


Fig. 1 –  $N_2$  sorption isotherms of graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide samples measured at 77 K

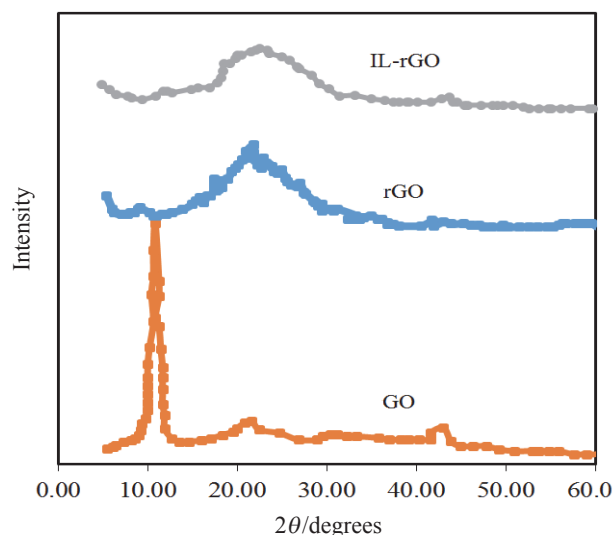


Fig. 2 – XRD patterns of graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide samples

4). The TEM image proves that IL-rGO hybrid material is formed and ionic liquids are well dispersed on the surface of reduced graphene oxide.

### Influence of contact time and initial concentration on Cr(VI) removal

The influence of contact time on Cr(VI) sorption by graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide sorbents were studied (Figure 5). The results showed that the sorption capacity increased with time and reached a constant value after 5 h. Thus, an optimum contact time of 5 h was selected for further studies.

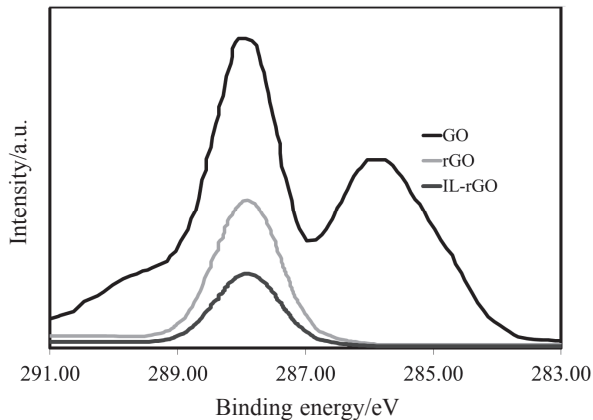


Fig. 3 – XPS patterns of graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide samples

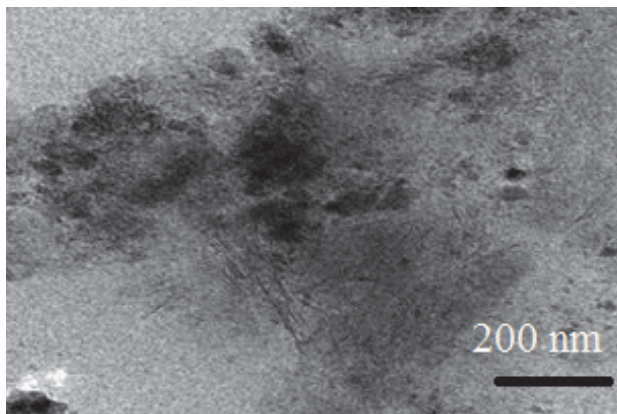


Fig. 4 – TEM image of ionic liquid modified reduced graphene oxide sample

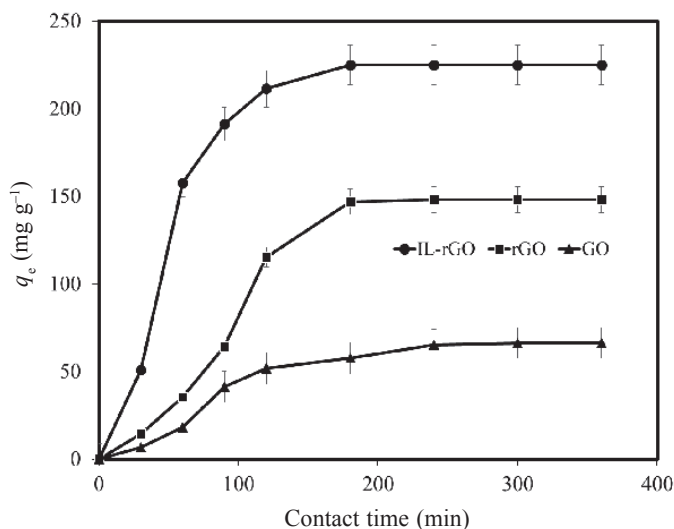


Fig. 5 – Effect of contact time on the sorption of Cr(VI) on IL-rGO, rGO, and GO (agitation speed = 250 rpm,  $[\text{Cr(VI)}] = 200 \text{ mg L}^{-1}$ , sorbent dosage =  $0.5 \text{ g L}^{-1}$ , temperature = 298 K and pH 4.0)

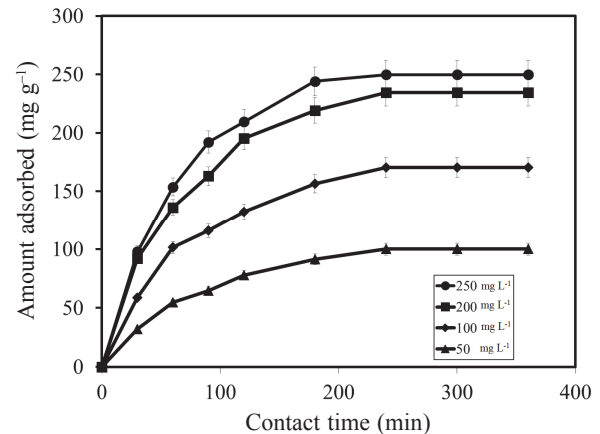


Fig. 6 – Effect of initial concentration on removal of Cr(VI) by IL-rGO (agitation speed = 250 rpm, contact time = 5 h, sorbent dosage =  $0.5 \text{ g L}^{-1}$ , temperature = 298 K and pH 4.0)

The effect of chromate ion initial concentration on its removal by IL-rGO is shown in Figure 6. The initial concentration of Cr(VI) significantly influenced the extent of Cr(VI) sorption, i.e., an increase from 50 to 250  $\text{mg L}^{-1}$  caused a significant increase in the sorbent capacity from 91.3 to 249.4  $\text{mg g}^{-1}$ , respectively. Thus, an increase in Cr(VI) initial concentration enhances the interaction between the Cr(VI) molecules and the surface of the sorbents. Therefore, the selected optimum initial concentration of Cr(VI) was 250  $\text{mg L}^{-1}$  for the rest of the experimental studies.

The higher sorption capacity of IL-rGO as compared to rGO and GO can be attributed to the fact that IL-rGO can interact more effectively than the other sorbent through complexation of chromate to ionic liquid.

#### Influence of agitation speed

The influence of agitation speed on the removal of Cr(VI) by the IL-rGO, rGO, and GO sorbents was examined by changing the agitation speed between 0 to 300 rpm, while keeping all other experimental conditions constant, as presented in Figure 7. It was found that, with a fixed stirring time, an increase in the agitation speed up to 250 rpm caused an increase in the sorbents capacity, which leveled off at a higher speed. Thus, the agitation speed of 250 rpm was chosen as the optimum agitation speed for all the sorption experiments.

#### The influence of pH

The pH is a key parameter controlling the Cr(VI) sorption process. The pH dependence of Cr(VI) sorption can largely be related to the type and ionic state of the functional groups of the sorbent surface, as well as to the Cr(VI) chemistry in the solution. The influence of pH on the sorption of Cr(VI) by IL-rGO was studied by changing the pH



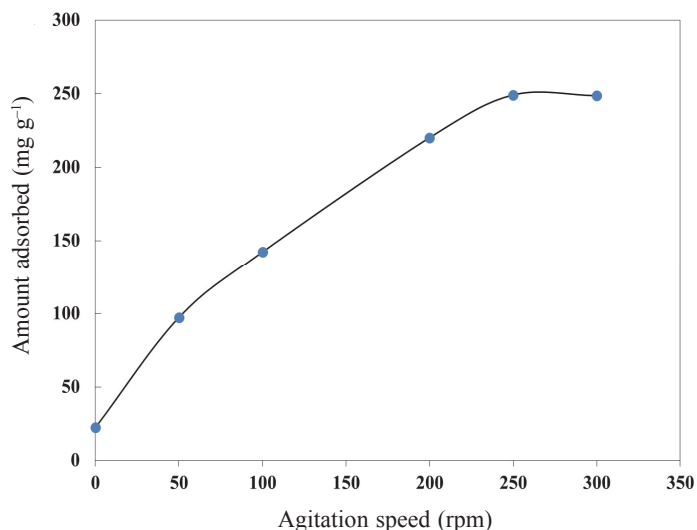


Fig. 7 – Effect of agitation speed on removal of Cr(VI) by IL-rGO (sorbent dosage = 0.5 g L<sup>-1</sup>, [Cr(VI)] = 250 mg L<sup>-1</sup>, contact time = 5 h, temperature = 298 K and pH 4.0)

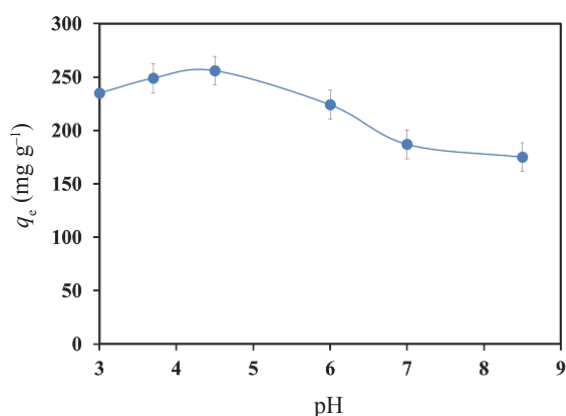


Fig. 8 – Effect of pH on the sorption of Cr(VI) onto IL-rGO (sorbent dosage = 0.5 g L<sup>-1</sup>, [Cr(VI)] = 250 mg L<sup>-1</sup>, contact time = 5 h, temperature = 298 K and [Cr(VI)] = 250 mg L<sup>-1</sup>)

from 3.0 to 8.5. The result obtained is shown in Figure 8. As the pH value increased up to 3.0, the capacity of the sorbent for removal of Cr(VI) was promoted, while the maximum removal took place in the pH range of 3.0–4.5. Further increase in pH decreased the sorption of chromium by the sorbent. The influence of pH observed on the sorption of chromate by the sorbent can be correlated to the pH-regulated distribution of Cr(VI) species and the surface charge of sorbent in the specified pH range. Maximum chromium sorption at pH 4.5 seems to be due to a net positive charge on IL-rGO surface at low pH. At low pH values, the dominant species of Cr(VI) in solution is  $\text{HCrO}_4^-$ . Therefore,  $\text{HCrO}_4^-$  easily adsorbed to the surface of positive sorbents at lower pH values. Moreover, at higher pH values,  $\text{OH}^-$  and Cr(VI) species ( $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) compete for the same sorption site on the graphene oxide, resulting in a lower removal of Cr(VI). Thus,

Table 1 – The pseudo first order and pseudo second order kinetic constants of chromate removal by IL-rGO adsorbent at different concentrations (stirring rate = 250 rpm, sorbent dosage = 0.5 g L<sup>-1</sup>, room temperature = 298 K, pH 4.0)

Initial concentration (mg L <sup>-1</sup> )	Pseudo first order model		Pseudo second order model	
	$k_1$	$R^2$	$k_2$	$R^2$
50	0.014	0.9559	$4.24 \cdot 10^{-5}$	0.9977
100	0.015	0.9426	$1.77 \cdot 10^{-5}$	0.9962
200	0.016	0.9457	$1.75 \cdot 10^{-5}$	0.9974
250	0.016	0.9638	$1.72 \cdot 10^{-5}$	0.9966

the sorption quantities of Cr(VI) at lower pH are larger than those at higher pH.

### Kinetics of sorption

The dynamics of the sorption procedure from an aqueous solution and the process of sorption of Cr(VI) on IL-rGO sorbent were considered through the fitness of the experimental data with various kinetic models. The kinetics data were fitted with pseudo first order (eq. 2) and pseudo second order (eq. 3) kinetic model, described as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $q_e$  and  $q_t$  are the sorption capacities at equilibrium and at time  $t$ , respectively, and  $k_1$  is the pseudo first order rate constant (min<sup>-1</sup>). The pseudo first order rate constant ( $k_1$ ), and the pseudo second order sorption ( $k_2$ ). The  $k_1$ ,  $k_2$  and  $R^2$  were calculated, and are provided in Table 1 and Figure 9.

The results in Table 1 and Figure 9 clearly indicate that the pseudo second order model with high calculated linear regression correlation coefficient ( $R^2$ ) can best describe the kinetics of Cr(VI) sorption for IL-rGO sorbent. Thus, these results further support the assumption that the sorption is chemisorption. The sorption on IL-rGO can also be fitted to pseudo second order model due to its high correlation coefficient. Thus, in the case of IL-rGO, sorption occurs by both chemical and physical interactions. This observation further proves the higher sorption capacity of IL-rGO sorbent as compared to the other sorbents.

### Sorption isotherm

Equilibrium sorption studies were performed to investigate the sorption capacities and mechanisms

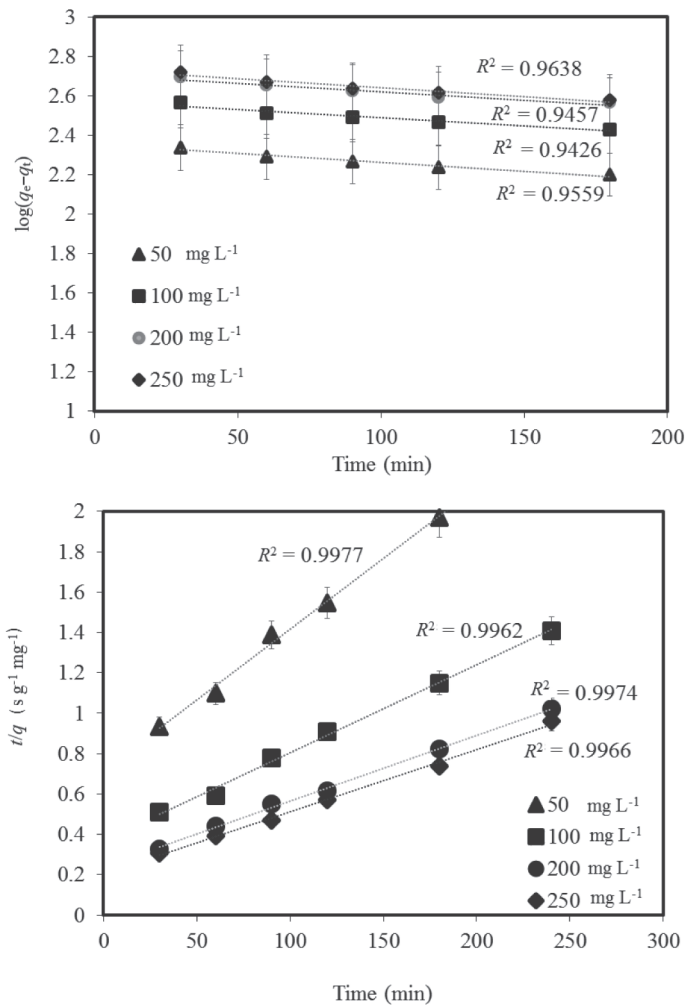


Fig. 9 – Kinetic equations (pseudo first order and pseudo second order) for chromate removal by IL-rGO sorbent at different concentrations (agitation speed = 250 rpm, sorbent dosage = 0.5 g L<sup>-1</sup>, room temperature = 298 K, pH 4.0)

of IL-rGO toward Cr(VI). The uptakes of Cr(VI) on ionic liquid modified reduced graphene oxide sorbent was quantitatively evaluated using Langmuir, Temkin and Freundlich isotherms. The Freundlich sorption isotherm is presented by the following equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (4)$$

where  $K_f$  and  $n$  are Freundlich empirical constant,  $C_e$  is the Cr(VI) equilibrium concentration in the solution (mg L<sup>-1</sup>), and  $q_e$  is the equilibrium sorption capacity (mg g<sup>-1</sup>).

The Langmuir equation is presented as follows:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m b}\right) + \left(\frac{1}{q_m}\right)C_e \quad (5)$$

where  $C_e$  is the equilibrium liquid phase concentration of Cr(VI) (mg L<sup>-1</sup>),  $q_m$  (mg g<sup>-1</sup>) is the maximum sorption capacity,  $q_e$  (mg g<sup>-1</sup>) is the equilibrium sorption capacity, and  $b$  is the Langmuir constant associated with the sorption energy.

The Temkin equation is presented as follows:

$$q_e = A \ln K_T + A \ln C_e \quad (6)$$

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

where  $A$  is the Temkin isotherm constant,  $R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $b$  is Temkin isotherm constant,  $T$  is the temperature (K), and  $K_T$  is the equilibrium binding constant (mol<sup>-1</sup>) corresponding to the maximum binding energy. The coefficient of determination ( $R^2$ ) of the linearized isotherm data of the three models at 298 K and pH of ~4.5 were calculated. The results are provided in Table 2. The comparison of the correlation coefficients values of the models suggested that the Langmuir model with a higher value of correlation was best fitted to the experimental results. Furthermore, the higher  $q_m$  values for the sorption of Cr(VI) by IL-rGO (250.0 mg g<sup>-1</sup>) indicated that its mono layer sorption capacity was very high.

#### Thermodynamics of the sorption of Cr(VI) on sorbents

Thermodynamic parameters including Gibbs free energy change ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) were calculated for sorption of Cr(VI) on ionic liquid modified reduced graphene oxide sorbent by varying the temperature in the range of 298–328 K under other optimized conditions (Table 3). As it was observed, an increase in the temperature from 298 K to 328 K caused an increase in the Cr(VI) removal by all the sorbents.

The Gibbs free energy, as well as the enthalpy process were calculated from experimental results using the following equations:

$$K_C = q_e / C_e \quad (8)$$

$$\Delta G^0 = -RT \ln K_C \quad (9)$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

Table 2 – Temkin, Langmuir and Freundlich constants for sorption of chromate on IL-rGO sorbent

Sorbent	Langmuir			Freundlich			Temkin		
	$q_m$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K_F$ (mg g <sup>-1</sup> )	$n$ (L mg <sup>-1</sup> )	$R^2$	$K_T$	$A$	$R^2$
IL-rGO	250.0	0.1176	0.9992	129.02	8.77	0.8975	1.23	114.17	0.9092

Table 3 – Thermodynamic parameters for sorption of chromate on IL-rGO sorbent (agitation speed = 250 rpm, sorbent dosage = 0.5 g L<sup>-1</sup>, temperature = 298–328 K and pH 6.0)

sorbent	T (K)	C <sub>e</sub> (mg L <sup>-1</sup> )	q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>C</sub>	ΔG <sup>0</sup> (kJ mol <sup>-1</sup> )	ΔH <sup>0</sup> (kJ mol <sup>-1</sup> )	ΔS <sup>0</sup> (J mol <sup>-1</sup> K <sup>-1</sup> )
IL-rGO	298	77.34	245.30	3.17	-2.85	55.41	11.64
	308	73.50	253.10	3.44	-3.16		
	318	67.73	264.53	3.90	-3.60		
	328	62.74	274.53	4.37	-4.02		

Table 4 – The q<sub>m</sub> values for the sorption of chromate on different sorbents

Sorbent	q <sub>m</sub> (mg g <sup>-1</sup> )	Reference
IL-rGO	250.0	This work
mesoporous carbon microspheres	165.3	66
HDTMA-zeolite	8.8	67
Aminated wheat straw	245	68
Fe <sub>3</sub> O <sub>4</sub> NP	20.2	12
Magnetotactic bacteria	70.4	69

where C<sub>e</sub> is the equilibrium concentration (mg L<sup>-1</sup>) of the Cr(VI) solution, q<sub>e</sub> is the equilibrium sorption capacity (mg g<sup>-1</sup>), R is the universal gas constant (8.314 · 10<sup>-3</sup> kJ mol<sup>-1</sup> K<sup>-1</sup>), T is the temperature in Kelvin, and K<sub>C</sub> is the equilibrium constant calculated as the surface and solution metal distribution ratio. The calculated thermodynamic parameters are listed in Table 3. As may be seen, the value of K<sub>C</sub> increased with an increase in the temperature from 298 to 328 K for all sorbents, favoring the sorption of analyte. The negative value of ΔG<sup>0</sup> and the positive value ΔH<sup>0</sup> at different temperatures indicated that the sorption of Cr(VI) by the sorbents was spontaneous and endothermic, respectively. The positive values of ΔS<sup>0</sup> suggested the increased randomness at the sorbent-solution interface during the sorption of Cr(VI) from the aqueous solution to the sorbents.

### Performance evaluation

The maximum sorption capacity (q<sub>max</sub>) of IL-rGO for Cr(VI) was calculated by the Langmuir isotherm model and compared to the other sorbents<sup>51,66–69</sup> with high capacity used for this purpose (Table 4). It is clear that IL-rGO has the advantages of higher sorption capacity.

### Conclusion

In this study, graphene oxide, reduced graphene oxide, and ionic liquid modified reduced graphene oxide were prepared. Their structural order and tex-

tural properties were studied by N<sub>2</sub> adsorption-desorption measurement (BET), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) analysis, and the potentials of these sorbents for removal of Cr(VI) were comparatively examined. The sorption kinetics of Cr(VI) by IL-rGO was found to fit the pseudo second order, indicating that the major sorption mechanism is physical. From an equilibrium study, it was found that the Langmuir model provided the best fit to the experimental data. Thus, the removal of Cr(VI) occurs through monolayer sorption. It was also found that, among the sorbents investigated for Cr(VI) removal, the IL-rGO had a higher capacity, which can be attributed to the higher sorption availability of the active sites.

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