Adsorption kinetics, isotherms and thermodynamics of Cr(III) on graphene oxide

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HIGHLIGHTS

- The adsorption capacity of GO for Cr(III) is high.
- The adsorption of Cr(III) on GO is spontaneous and endothermic.
- Cr(III) is adsorbed on the O-containing functional groups of GO.

GRAPHICAL ABSTRACT

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ABSTRACT

The adsorption kinetics, isotherms and thermodynamics of Cr(III) on graphene oxide (GO) were studied. The adsorption kinetic data were well described with pseudo-second-order model and the equilibrium data were well fitted by Langmuir model. The calculated thermodynamic parameters indicated that the adsorption of Cr(III) on GO was spontaneous and endothermic. The maximum adsorption capacity of Cr(III) on GO at pH 5.0 and $T=296\text{ K}$ was about 92.65 mg g^{-1} , which was higher than other reported adsorbents. It was found that the adsorption of Cr(III) on GO was strongly dependent on solution pH, but weakly dependent on ionic strength. Fourier transform infrared (FTIR) spectra suggested that Cr(III) was adsorbed on GO mainly through the formation of inner-sphere complexes with the O-containing functional groups on GO surface. Results in this study suggested that GO was a suitable material for the preconcentration and removal of Cr(III) from water.

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1. Introduction

Chromium (Cr) compounds are widely used in many modern industries, such as tanning, metallurgy, textiles, wood protection, electroplating and the manufacture of dyes and pigments etc.,

which results in a large quantity of this element being discharged with industrial wastewater [1]. Water containing a high concentration of Cr can cause serious environmental problems and induce toxic and carcinogenic health effects on humans [2]. To reduce human exposure to chromium, the US Environmental Protection Agency has set a maximum contaminant level of 0.1 mg L^{-1} for total Cr in drinking water [3]. And the industrial discharge of Cr(VI) and total Cr in China are limited below 0.5 and 1.5 mg L^{-1} , respectively [4]. In natural environment, Cr predominantly exists in two

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oxidation states, the trivalent form Cr(III), and hexavalent form Cr(VI). Although Cr(III) is less toxic than Cr(VI) [5], prolonged contact with high concentrations of Cr(III) can cause allergic skin reactions, cancer and DNA damage [6–8]. In addition, it is possible that Cr(III) can also be transformed to highly toxic Cr(VI) under some oxidizing conditions. Thus, removal of Cr(III) from wastewater is necessary. The conventional removal methods of heavy metals from water include chemical oxidation or reduction, chemical precipitation, ion exchange, membrane technology, filtration, electrochemical treatment and adsorption etc. [9–11]. Among these approaches, adsorption has been found to be superior to other techniques due to its low-cost, high efficiency and easy operation [12,13].

Graphene (G) is a two-dimensional structure with only one atomic thickness, and has attracted considerable attention due to its distinctive and unique physicochemical properties [14]. Graphene oxide (GO) is the oxidized form of G, consisting of abundant surface O-containing functional groups such as carboxyl, hydroxyl, and epoxy groups on its edges and surfaces. Previous studies had revealed that GO was one of the most effective adsorbents for Co(II), Cd(II), Pb(II), Cu(II) and Eu(III) [15–18], where the amount of O-containing functional groups on GO is an important factor influencing the adsorption of heavy metal ions. In addition, electron donor–acceptor interaction between the delocalized π electron of graphene layer (electron donors) and heavy metals (electron acceptors) is also considered to be responsible for the adsorption. Although much information has been available on Cr(III) adsorption on ion exchange resin, lignin, activated carbon and brown coal [19–24], very little is known about the adsorption of Cr(III) on GO. Understanding of the kinetics and thermodynamics of Cr(III) adsorption on GO is critical for the design and operation of adsorption equipment.

The aim of this study is to investigate the adsorption kinetics, thermodynamics and isotherms of Cr(III) on GO and factors that influence the adsorption of Cr(III) on GO such as solution pH and ionic strength. The adsorption rates are evaluated with the pseudo-first-order, pseudo-second-order and intra-particle diffusion equations. The effect of temperature on the adsorption isotherms is determined and the thermodynamic parameters of free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) during adsorption at different temperatures are calculated. The adsorption mechanism of Cr(III) on GO is probed by FTIR technique.

2. Experimental

2.1. Materials

All reagents are analytical grade and are used as received. GO was synthesized by a modified Hummers method [25]. Detailed processes are described in the Supplementary data.

2.2. Characterization of GO

GO and graphite were characterized by transmission electron microscopy (TEM), scanning electron microscope (SEM), Raman spectroscopy and X-ray diffraction (XRD). The TEM image was obtained with a H-7500 (Hitachi, Japan). The SEM image was obtained on a field emission scanning electron microscope (SU-8020). Raman spectrum was recorded with a Renishaw Via Raman spectrometer (Renishawplc, UK). The laser excitation was provided by a regular model laser operated at wavelength of 532 nm. The elemental compositions (C, H, O) of GO were determined with a high-temperature combustion method (PE 2400 SERIES II analyzer, Pekin-Elmer, Inc., USA). The crystallographic

structures of GO and graphite were determined by XRD patterns on an X' Pert PRO diffractometer (PANalytical, Holland) with Cu $K\alpha$ radiations generated at 40 kV, 40 mA. Scattering angles were ranged from 5° to 40° with a scanning speed at 1° per minute.

2.3. Adsorption kinetics

The adsorption kinetics experiments were carried out at 296 ± 0.5 K by mixing 5.0 mg GO with 20 mL of 0.01 M NaNO_3 solution containing 13.0 mg L^{-1} Cr(III) in 40 mL of polyethylene centrifuge tubes at pH 5.0 ± 0.1 . After the samples were shaken end-over-end for predefined time intervals, the suspensions were centrifuged and filtered. The concentrations of Cr(III) in the filtrate were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (IRIS Advantage, Thermo Elemental). The quantity of Cr(III) adsorbed at time t , q_t (mg g^{-1}), was deduced from the mass balance between initial concentration and concentration at time t in solution.

2.4. Adsorption experiments

A batch technique was utilized for all adsorption experiments with 5.0 mg GO and 20 mL of 0.01 M NaNO_3 solution in 40 mL of polyethylene centrifuge tubes. The initial concentrations of Cr(III) ranged from 2.6 to 104.0 mg L^{-1} . In all cases, the pH of the equilibrium solutions was maintained at 5.0 ± 0.1 by addition of 0.1 M HNO_3 or NaOH. The suspensions were rotated continuously for 12 h at different temperatures (296 ± 0.5 , 306 ± 0.5 and 316 ± 0.5 K). After equilibrium, the suspensions were centrifuged and filtered. The concentrations of Cr(III) in the filtrate were determined by ICP-OES.

The pH effect was conducted using a batch adsorption approach as mentioned above. Initial concentration of Cr(III) was 13.0 mg L^{-1} . And two background electrolyte concentrations (0.01 M and 0.1 M NaNO_3) were used in the adsorption reaction. The pH was adjusted from 3.0 to 8.0 by addition of 0.1 M HNO_3 or NaOH. After equilibrium, the suspensions were centrifuged and filtered to separate the liquid and solid phases. The concentrations of Cr(III) in the filtrate were determined by ICP-OES.

2.5. Electrophoretic mobilities (EPMs) measurement

The suspension for EPMs measurement was prepared by mixing a certain amount of GO with 20.0 mL 0.01 M NaNO_3 solution. The solution pH was adjusted using 0.1 M HNO_3 or NaOH. The suspension was rotated continuously for 12 h at room temperature ($23.0 \pm 1^\circ\text{C}$). The EPMs were determined on a ZetaSizer Nano ZS (Malvern Instruments, Worcester-shire, U.K.). Three independent EPMs measurements were collected for each sample to ensure accurate and reproducible data.

2.6. Micro-Fourier transform infrared spectroscopy (μ -FTIR)

μ -FTIR spectra were recorded on NICOLET iN 10 MX (Thermo Scientific). Samples for μ -FTIR analysis were prepared by mixing a certain amount of GO with 20.0 mL Cr(III) solution in polyethylene centrifuge tubes. After equilibrium and centrifugation, the supernatant is discarded, and the residual sample is freeze-dried overnight. Microsamples (Cr(III)-adsorbed GO or pure GO) were pressed on a diamond bracket and μ -FTIR spectra were measured. The resolution for FTIR spectra was 4 cm^{-1} , and a total of 100 scans were collected for each spectrum.

Fig. 1. Characterization of graphite and GO: (a) and (c) TEM image; (b) and (d) SEM image; (e) Raman spectrum; (f) XRD spectrum.

3. Result and discussion

3.1. Characterization of GO

The results of TEM, SEM, Raman and XRD of graphite and the prepared GO are shown in Fig. 1. Compared to graphite (Fig. 1a and b), it was found that GO is closely agglomerated together by thin and randomly aggregated nanosheets (Fig. 1c), and has typically wrinkled, sheet-like structure (Fig. 1d). Elemental analysis result suggests that the prepared GO includes numerous O-containing functional groups (Table S1).

Fig. 1e shows Raman spectra of graphite and GO, which is used to monitor the structural changes during oxidation of graphite to GO. Raman spectrum of graphite displays two prominent peaks at 1328 and 1574 cm^{-1} , which correspond to the well documented D band and G band, respectively. It is well known that the G band corresponds to the in-plane vibrations of the graphitic structure, and the D band is related to structural defects, amorphous carbon, or

edges that can break symmetry and selection rule. When graphite is oxidized to GO, it is found that the D band and G band broadens and the intensity of D band increases significantly, suggesting some modification of graphite into amorphous carbon containing a certain fraction of sp^3 carbons. Defect content is given by the ratio of D band to G band intensity (I_D/I_G). Compared to graphite, the I_D/I_G of GO increases from 0.29 to 0.75, indicating the increase of amorphous carbon and structural defects. The weak and broad 2D peak at $\sim 2830 \text{ cm}^{-1}$ is another indication of disorder as the result of an out-of-plane vibration mode.

Fig. 1f shows the XRD patterns of graphite and GO. The very intense and narrow peak at 26.5° corresponds to the graphite spacing (002) of graphite plane. After oxidation, the peak of graphite (002) disappears and an additional peak at 10.6° is observed, which corresponds to the typical diffraction peak of GO. This suggests that oxidation treatment creates abundant O-containing functional groups on the surfaces of GO nanosheets.

Fig. 2. (a) Effect of contact time on Cr(III) adsorption rate (pH = 5.0, $T = 296$ K); (b) test of pseudo first-order rate equation for the adsorption of Cr(III) by GO; (c) test of pseudo second-order rate equation for the adsorption of Cr(III) by GO; (d) test of intra-particle diffusion equation for the adsorption of Cr(III) by GO.

3.2. Adsorption kinetics

The adsorption of Cr(III) on GO versus equilibrium time is presented in Fig. 2a. It is found that the adsorption kinetics of Cr(III) onto GO included two steps: a fast initial adsorption followed by a slow gradual adsorption. The initial rapid phase (first 0.25 h) accounted for a considerable portion of the adsorption. During this stage, about 85.0% of Cr(III) was adsorbed, which can be attributed to the rapid diffusion of Cr(III) ion from solution to the external surface of GO [21]. Adsorption in the subsequent time was slower and probably resulted from the diffusion of metal ions into the porous structures of the adsorbent [22]. Although the adsorption reached equilibrium in 2 h, a 12 h period was used for the following adsorption experiment to ensure complete equilibrium.

To evaluate the differences in the adsorption kinetic rates, the pseudo-first-order Eq. (1), pseudo-second-order Eq. (2) and intra-particle diffusion Eq. (3) models were used to fit the results.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

$$q_t = k_{\text{dif}} t^{1/2} + C \quad (3)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the concentrations of Cr(III) adsorbed on GO at equilibrium and at time t , k_1 (h⁻¹) is the rate constant of Eq. (1) for the adsorption, k_2 (g mg⁻¹ h⁻¹) is the rate

constant of Eq. (2) for the adsorption, k_{dif} (mg g⁻¹ h^{-0.5}) is the diffusion rate constant of Eq. (3). C is the intercept and relates to the thickness of the boundary layer.

It was shown that the pseudo-second-order kinetic model can better describe the experimental data than the pseudo-first-order kinetic model with a higher correlation coefficient (R^2) of 0.99 (Fig. 2b and c). Successful fitting of the data with the pseudo-second-order kinetic model suggests that chemisorption was the rate-controlling step [17,18]. Kinetic constants, including k and q_e were calculated from the slopes and intercepts of the plots, which are presented in Table 1. It is shown that the values of q_e of the pseudo-second-order 43.72 mg g⁻¹ are more close to the experimental adsorption capacity, 44.04 mg g⁻¹, than that of the pseudo-first-order 42.64 mg g⁻¹.

Fig. 2d shows the kinetic data fitted by the intra-particle diffusion model. It is found that the curve is nonlinear over the whole time range and includes two linear regions. For the first portion the correlation coefficient (R^2), k_{dif} and C values are 0.71, 39.11 and 21.90, which is attributed to the fast mass transfer of Cr(III) from the bulk solution to the adsorbent surface. While for the second portion the correlation coefficient (R^2), k_{dif} and C values are 0.88, 1.26 and 40.12, which means the occurrence of the intra-particle diffusion on GO. According to Weber and Morris [26], if intra-particle diffusion is the rate-controlling factor, the regression of q_t versus $t^{1/2}$ should be linear and passes through the origin. Significantly, the multi-linearity and the deviation of the straight line

Table 1
Coefficients of kinetic model regression (Cr(III) concentration of 13.0 mg L⁻¹, pH = 5.0).

Pseudo-first order model			Pseudo-second order model		
q_e (mg g ⁻¹)	k_1 (h ⁻¹)	R^2	q_e (mg g ⁻¹)	k_2 (mg g ⁻¹ h ⁻¹)	R^2
42.64	0.36	0.92	43.72	0.71	0.99
Intra-particle diffusion model					
$k_{\text{dif},1}$ (mg g ⁻¹ h ^{-0.5})	C_1	R_1^2	$k_{\text{dif},2}$ (mg g ⁻¹ h ^{-0.5})	C_2	R_2^2
39.11	21.90	0.71	1.26	40.12	0.88

Fig. 3. Adsorption of Cr(III) on GO as a function of pH in different NaNO_3 concentrations. Data are means of three separate experiments. Error bars represent standard deviation.

from the origin in this study indicate that intra-particle diffusion is not the sole rate-controlling step and boundary layer diffusion controls the adsorption to some degree. Similar results were found for methyl green on graphene [27] and Zn adsorption on GO [28], respectively.

3.3. Effect of pH and ionic strength

Solution pH plays a critical important role in the adsorption of metal ions onto various adsorbents because it may affect the surface charge of the adsorbent and the ionic species of metals. Therefore, the adsorption of Cr(III) on GO at different equilibrium solution pH is examined (Fig. 3). Result indicates that Cr(III) adsorption by GO was highly pH-dependent and increases with increasing solution pH. At $\text{pH} < 4.0$, The adsorption of Cr(III) increased slowly, followed an abrupt increase at $\text{pH} 4.0\text{--}5.5$, and then reached a plateau at $\text{pH} > 6.0$. At low pH, the low adsorption capacity of Cr(III) can be attributed, in part, to the competition between the excess proton in solution and Cr(III) for the same binding sites on GO surface [29]. An increase of solution pH increased the number of negatively charged sites on GO surface, which further facilitated the adsorption of cationic Cr(III). Fig. S1 shows the EMPs of GO as a function of solution pH, where the EMPs of GO were more negative with increasing solution pH, suggesting more negative charged sites available on GO. Undoubtedly, the increased negative charged sites on GO promoted the adsorption of Cr(III) through electrostatic attraction and/or complexation. When solution pH increased, the percentage of free Cr ion decreased, while the percentage of hydrolyzed Cr(III) species increased [29]. According to Mclean and Bledsoe [30], hydrolyzed Cr(III) species more tended to be adsorbed on GO than that of free Cr(III) ion. This may be another reason about the pH dependence of Cr(III) adsorption on GO. Increasing

Table 2
Parameters for Langmuir and Freundlich models of Cr(III) adsorption on GO.

Experimental conditions	Langmuir model			Freundlich model		
	q_m	K_L	R^2	K_F	n	R^2
$T = 296\text{ K}$	92.65	0.11	0.98	19.44	0.35	0.97
$T = 306\text{ K}$	101.58	0.25	0.98	29.10	0.30	0.96
$T = 316\text{ K}$	119.78	0.36	0.98	38.62	0.28	0.95

solution pH above 6.0, Cr(III) can precipitate from aqueous solution as $\text{Cr}(\text{OH})_3$ [29]. In this study, to make sure the maximum adsorption efficiency as well as to avoid precipitation of Cr(III), all the following experiments were conducted at pH 5.0.

The effect of ionic strength on Cr(III) adsorption on GO at different pH is also shown in Fig. 3. It is found that the increase of NaNO_3 concentrations from 0.01 to 0.1 M had little effects on the adsorption of Cr(III) on GO throughout the examined pH range. Generally, the ions in background electrolyte can compete with the metal adsorbed on the outer-sphere sorption sites, whereas it does not compete for the inner-sphere sites. Thus, the lack of an ionic strength effect on Cr(III) adsorption suggested that Cr(III) is adsorbed on GO mainly through the coordination with the O-containing functional groups of GO to form inner-sphere complexes. In previous studies, the adsorption of Eu(III) and Pb(II) on GO were also independence of ionic strength [13,31], which was consistent with the result in this paper.

3.4. Adsorption isotherms

Fig. 4a shows the adsorption isotherms of Cr(III) on GO at three different temperatures. Langmuir Eq. (4) and Freundlich Eq. (5) models were applied to fit the adsorption data.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_L is the Langmuir constant; q_m is the maximum adsorption capacity (mg g^{-1}) and q_e is the amount of Cr(III) adsorbed at equilibrium (mg g^{-1}), K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The relative parameters calculated from the two models are listed in Table 2. It is found that the adsorption isotherms were fitted better by the Langmuir model than that by the Freundlich model, suggesting that Cr(III) adsorption on GO was monolayer coverage. As shown in Table 2, the q_m values of Cr(III) adsorption on GO at 296 K is 92.65 mg g^{-1} , which was much higher than the maximum adsorption capacity of Cr(III) on other adsorbents, such as lignin (17.97 mg g^{-1}), bagasse fly ash (4.35 mg g^{-1}), sawdust (5.52 mg g^{-1}), ion-exchange resin (20.28 mg g^{-1}), and activated

Fig. 4. Adsorption isotherms of Cr(III) on GO at different temperatures (a); plots of $\ln(C_s/C_e)$ vs. C_s at different temperatures (b).

Table 3

Thermodynamic parameters on the adsorption of Cr(III) by GO.

Temperature (K)	296	306	316
$\ln K_0$	3.44	4.17	4.77
ΔG^0 (kJ mol ⁻¹)	-8.46	-10.61	-12.53
ΔH^0 (kJ mol ⁻¹)	51.71	51.71	51.71
ΔS^0 (J mol ⁻¹ K ⁻¹)	203.27	203.66	203.29

carbon (39.56 mg g⁻¹) [2,9,19,21,22]. Thus, it is believed that GO is a very effective adsorbent for the removal of Cr(III) from wastewater.

3.5. Thermodynamic analysis

Fig. 4a shows the effect of temperature on Cr(III) adsorption on GO. It is observed that the adsorption of Cr(III) is temperature dependence. An increase in temperature results in a corresponding increase in the adsorption of Cr(III). The standard free energy change, ΔG^0 , is evaluated using the following equation:

$$\Delta G^0 = -RT \ln K_0 \quad (6)$$

where R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), and T is the temperature in Kelvin. K_0 can be evaluated using a method described by Niwas et al. [32] in the following equation:

$$K_0 = \frac{\alpha_s}{\alpha_e} = \frac{\nu_s C_s}{\nu_e C_e} \quad (7)$$

where α_s and α_e are the activities of adsorbed Cr(III) and Cr(III) in solution at equilibrium, while ν_s and ν_e are the activity coefficients of the adsorbed Cr(III) and Cr(III) in solution. C_s (mg g⁻¹) and C_e (mg L⁻¹) are the amount of Cr(III) adsorbed by per mass of GO and Cr(III) in solution at equilibrium, respectively. When the concentration of Cr(III) in solution decreases and approaches to zero, the activity coefficient approaches unity, and K_0 can be obtained by plotting $\ln(C_s/C_e)$ against C_s , and extrapolating C_s to zero (Fig. 4b). The straight line obtained is fitted to the points based on a least-squares analysis. Its intercept with the vertical axis gives the values of $\ln K_0$.

The average standard enthalpy change (ΔH^0) is calculated from Van't Hoff equation (Eq. (8)):

$$\ln K_0(T_3) - \ln K_0(T_1) = \frac{-\Delta H^0}{R} \left(\frac{1}{T_3} - \frac{1}{T_1} \right) \quad (8)$$

where T_3 and T_1 are two different temperatures. Standard entropy change (ΔS^0) is calculated by the equation below

$$\Delta S^0 = -\frac{\Delta G^0 - \Delta H^0}{T} \quad (9)$$

The thermodynamic parameters are listed in Table 3. Three ΔG^0 values at different temperatures are negative thereby implying that the adsorption of Cr(III) by GO is spontaneous process. The values of ΔG^0 becomes more negative with increasing temperature, demonstrating the higher temperatures facilitate the adsorption of Cr(III) on GO. The observed positive ΔH^0 suggests that the interaction of Cr(III) on GO is an endothermic process, which is supported by the increased adsorption of Cr(III) with the increase of temperature. In the adsorption process, hydrated Cr(III) ions firstly need energy to denude water molecules from their hydrated shell to some extent. Thus, at higher temperature, Cr(III) are readily dehydrated, and the adsorption on GO more favorable. Similarly, the positive ΔS^0 is also attributed to the dehydration of Cr(III) ion caused by the interaction between Cr(III) and the functional groups of GO [33–35].

3.6. μ -FTIR analysis

To reveal the adsorption mechanisms of Cr(III) on GO, a μ -FTIR study was performed. Fig. 5 shows the μ -FTIR spectra of

Fig. 5. μ -FTIR spectra of GO before and after the adsorption of Cr(III).

GO and GO with adsorbed Cr(III). For GO, the spectrum indicated that GO includes numerous O-containing functional groups on its outermost surface and defect sites. The broad peak at 3418 cm⁻¹ is dominated by -OH stretching vibration. The peak at 1631 and 1389 cm⁻¹ are assigned to the aromatic C=C stretching vibration and carboxyl O=C-O stretching vibration, respectively. When Cr(III) was adsorbed on GO, it was found that the peak attributable to the hydroxyl group broadened and shifted from 3418 to 3387 cm⁻¹. In addition, the peak of carboxyl O=C-O stretching vibration (1389 cm⁻¹) also split into two peaks at 1396 and 1363 cm⁻¹ after the adsorption of Cr(III). These results suggested that O-containing functional groups on GO played an important role in the adsorption of Cr(III), i.e., Cr(III) was adsorbed mainly through the interaction with these O-containing groups on GO. An attempt also was made to reveal the occurrence of electron donor-acceptor interaction between Cr(III) and GO surface. As shown in Fig. 5, the band of C=C stretching vibration shift from 1631 to 1628 cm⁻¹ when Cr(III) was adsorbed. However, the slight shift cannot be considered as the solid evidence for the formation of electron donor-acceptor interaction between Cr(III) and aromatic C=C bond because it was caused not only by the formation of electron donor-acceptor interaction, but also by the conjugate effect between aromatic C=C bond and coordinated O-containing functional groups. Combined the ionic strength independence of Cr(III) adsorption, we speculate that electron donor-acceptor interaction should not be the main adsorption mechanism of Cr(III).

4. Conclusions

The present study showed the adsorption of Cr(III) on GO was spontaneous and endothermic. The process of adsorption follows pseudo-second-order model and the equilibrium data can be well fitted with Langmuir model. The increase of solution pH facilitated the adsorption of Cr(III). The independence of ionic strength and FTIR suggested that Cr(III) was adsorbed on GO through the formation of inner-sphere complexes with the O-containing functional groups on GO.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.05.062>.

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