

Characterization of radioactive cobalt on graphene oxide by macroscopic and spectroscopic techniques

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Abstract Graphene oxide (GO) was synthesized using the modified Hummers method and characterized by XRD and FTIR. The sorption of $^{60}\text{Co}(\text{II})$ on GO as a function of contact time, pH, polyacrylic acid, ionic strength, temperature and solution concentration was studied by batch technique. The sorption kinetics indicated that the sorption of $^{60}\text{Co}(\text{II})$ on GO could be simulated by the pseudo-second-order model very well. The maximum sorption capacities of GO for $^{60}\text{Co}(\text{II})$ calculated from Langmuir model at pH 6.40 and $T = 300\text{ K}$ was $\sim 62.0\text{ mg/g}$. The thermodynamic parameters from the temperature-dependent sorption isotherms indicated that the $^{60}\text{Co}(\text{II})$ sorption on GO was an endothermic and spontaneous process. The interaction mechanism between GO and $\text{Co}(\text{II})$ were outer-sphere surface complexation or ion exchange at $\text{pH} < 7$, whereas the inner-sphere surface complexation was observed at $\text{pH} 7\text{--}9$ in terms of the analysis of XPS spectra.

Keywords Sorption · $^{60}\text{Co}(\text{II})$ · Graphene oxide · Interaction mechanism

Introduction

With the rapid development of nuclear energy, kinds of radioactive pollutants are discharged into environment in

recent years. A large number of the radionuclides ^{60}Co and ^{58}Co are observed in the waste waters of nuclear reactor, medical treatment and food industries. It is determined that the radioactive ^{60}Co can be bio-accumulated through food chain, which could damage people health. Excess intake ^{60}Co may be caused human neuron toxicological disorders, genotoxicity, blood disease and even death [1]. Therefore, it is great important to remove ^{60}Co from the waste waters [2].

The removal of ^{60}Co from the waste waters has been paid more attention in recent years. Sorption technique has been demonstrated an efficient method to remove radionuclides due to the low cost and simple operation. Various sorbents such as organic materials, metal oxide, silicate and clay minerals have been investigated to remove $\text{Co}(\text{II})$ from aqueous solutions [3–9]. In these studies, the low sorption capacity of these sorbents was observed. For example, only 0.23 and 0.92 mg $\text{Co}(\text{II})$ was absorbed by per gram scolecite [3] and kaolinite [6], respectively. However, it has been demonstrated that graphene oxide (GO) presented high efficient adsorption performance due to its large specific surface area and massive oxygen-containing functional groups [10–12]. Herein, GO has been extensively applied as a promising material for the removal of radionuclides and heavy metals in the waste waters [13–16]. Zhao et al. [13] found that the maximum adsorption capacity of GO for $\text{Co}(\text{II})$ at $\text{pH} 6.0$ and $T = 303\text{ K}$ were about 68.2 mg/g, whereas the details on interaction mechanism between GO and $\text{Co}(\text{II})$ isn't observed by spectroscopic technique.

The aims of this study is (1) to characterize the microscopic properties of GO by using the X-ray powder diffraction (XRD) and the Fourier transform infrared (FT-IR) spectroscopy; (2) to elaborate the sorption of $\text{Co}(\text{II})$ on GO as a function of contact time, pH, ionic strength, natural

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organic matters and temperature and solution concentration; (3) to determine the interaction mechanism between GO and Co(II) by XPS measurement. Owing to the similar chemical properties, the stable Co(II) cation was employed instead of ^{60}Co in this study. This paper highlights the interaction mechanism between GO and bivalent radionuclides from aqueous solution in the environmental contaminant cleanup.

Experimental

Materials

The GO was prepared from the flake graphite in accordance with the modified Hummers method [17]. Briefly, the graphite was added into the concentrated H_2SO_4 solution, then KMnO_4 was slowly added over 2 h under ice-bath conditions, then the residual MnO_4^- was removed by adding 30 % H_2O_2 into the suspension. The oxidized graphite layers were exfoliated from each other by continuous ultrasonic and centrifugation treatment several times. The more details on the synthesis of GO can be found in our previous literatures [13, 16].

The Co(II) stock solution (1.0 mol/L) was prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent, Sinopharm, China) in Milli-Q water. The Co(II) solution used in this study was made by diluting the stock solution with Milli-Q water. All other reagents (analytical grade, Sinopharm, China) were used directly in this study.

Characterization

The XRD pattern of GO was characterized by the MAC Science Co. M18XHF diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The scanning rate was $2^\circ/\text{min}$. The structure of GO was identified by comparison to the JCPD standards. The FT-IR spectra of the samples were recorded by the Nicolet 8700 FT-IR spectrometer at room temperature. The X-ray photoelectron spectra (XPS) were characterized by the thermo ESCALAB 250 electron spectrometer with multidetection analyzer using Al $K\alpha$ X-ray source (1486.6 eV) at 10 kV and 5 mA under 10^{-8} Pa residual pressure. Surface charging effects were corrected with C 1s peak at 284.4 eV as a reference. The recorded lines (O 1s, C 1s and Co 2p) were fitted by using XPSPEAK41 program after subtraction of the background (Shirley baseline correction).

Sorption experiment

The sorption of Co(II) on GO was carried out under ambient condition by using the batch technique. The

mixture of GO suspension and NaClO_4 electrolyte solution was pre-equilibrated for 24 h, and then the desired concentration of Co(II) solution was added. The negligible amount of 0.01 or 0.1 mol/L HClO_4 or NaOH solution were added in the mixtures to obtain the appropriate pH values. After the mixtures were shaken for 24 h, the GO was separated from the solution by centrifugation at 15,000 rpm for 20 min. The concentrations of Co(II) in the solution were detected by atomic absorption spectroscopy (AAS6300C, Shimadzu, Japan). All the experimental data were represented by the average of triple determination data. The relative errors were showed $\pm 2\%$. The Co(II) sorption percentage on GO ($R\%$) and distribution coefficients (K_d) could be defined as Eqs. (1) and (2), respectively:

$$R\% = (C_0 - C_e)/C_0 \times 100\% \quad (1)$$

$$K_d = (C_0 - C_e)V/C_e m \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) were the initial concentration and equilibration concentration, respectively. The V (mL) and m (g) were the volume and the mass, respectively.

Results and discussion

Characterization of GO

The synthetic GO was characterized by using XRD and FTIR. The XRD pattern of GO is shown in Fig. 1a. The sharp diffraction peak of GO appears at $2\theta = 10.03^\circ$, which is corresponding to the (002) plane. The interplanar spacing of GO was calculated to be 0.88 nm, which is consistent with previous works [13, 18]. Figure 1b shows the FTIR spectrum of GO at high and low-frequency region. The absorption peak at $3,420\text{ cm}^{-1}$ is attributed to the O–H stretching vibration of COOH groups. The peaks at $1,734\text{ cm}^{-1}$ and at $1,620\text{ cm}^{-1}$ are assigned to C=O group and C=C group respectively. The adsorption peaks at $1,224$ and $1,100\text{ cm}^{-1}$ refer to the C–O group. The results from FTIR spectrum indicated that the plentiful oxygen-containing functional groups such as hydroxyl (OH), epoxy (C–O) and carboxyl (COOH) are observed on GO surfaces, which are easy to combine with radionuclides and heavy metals in aqueous solution.

Sorption kinetics

Figure 2a shows the sorption of Co(II) on GO under varying time interval. As illustrated in Fig. 2a, the sorption of Co(II) on GO increases sharply within 5 h, then slightly reaches equilibrium in 10 h. The sorption of Co(II) on GO surface achieves the balance in such a short time, which

shows that the sorption of Co(II) on the GO surface may be due to chemical sorption [19]. It is observed that 24 h is enough to reach the sorption equilibrium, which is adopted in latter experiments. The pseudo-first-order and pseudo-second order kinetic models are adopted to fit the sorption kinetics of Co(II) on GO. The pseudo-first and pseudo-second order equation are written as Eq. (3) [20] and Eq. (4) [21], respectively:

$$\log(q_e - q_t) = \log q_e - k_f t / 2.303 \tag{3}$$

$$t/q_t = 1/k_s q_e^2 + t/q_e \tag{4}$$

where q_e and q_t (mg/g) are the amount of Co(II) sorption on GO at equilibrium and t , respectively. k_f and k_s are the pseudo-first and pseudo-second rate constant, respectively.

The calculated parameters of two kinetic models are listed in Table 1. As shown in Table 1, it can be seen that

the sorption kinetics of Co(II) on GO by pseudo-second order kinetic model ($R^2 = 0.999$) is better than the pseudo-first order kinetic model ($R^2 = 0.976$).

Effect of sorbent content

The effect of sorbent content on the Co(II) sorption onto GO is given in Fig. 2b. The sorption of Co(II) on GO increases quickly from 34.8 to 50.7 % with increasing sorbent content from 0.12 to 0.48 g/L at pH 6.40, whereas the little change in K_d values is observed with increasing sorbent content. The more reactive sites of GO surface can be available to combine metal ions when the amount of sorbent content increases. The similar phenomena is also described by Xu et al. [22] that the sorption of Co(II) on bentonite increased with improving sorbent content. The

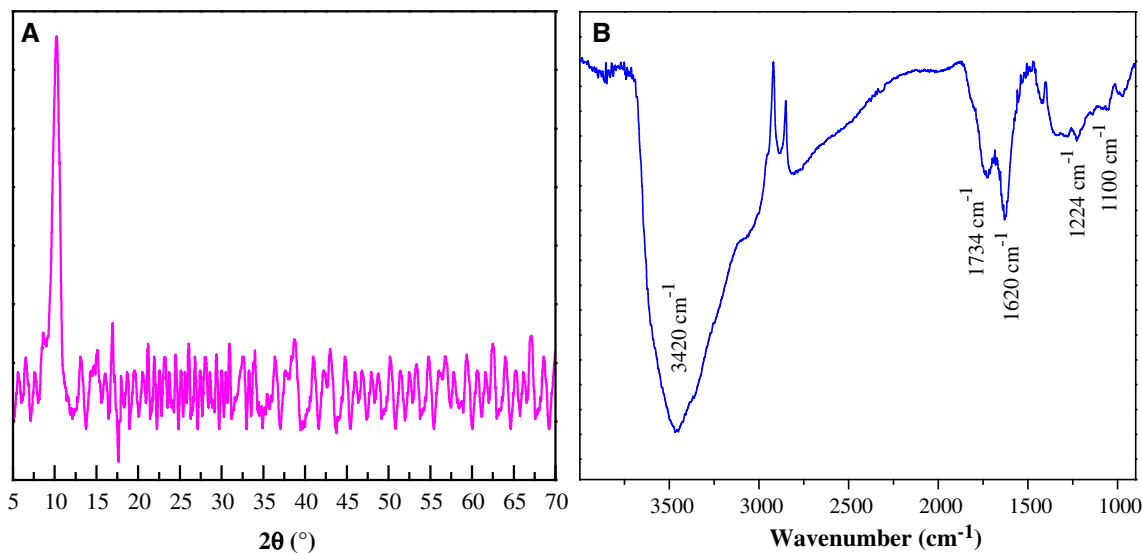


Fig. 1 The characterization of GO. a XRD pattern. b FTIR spectrum

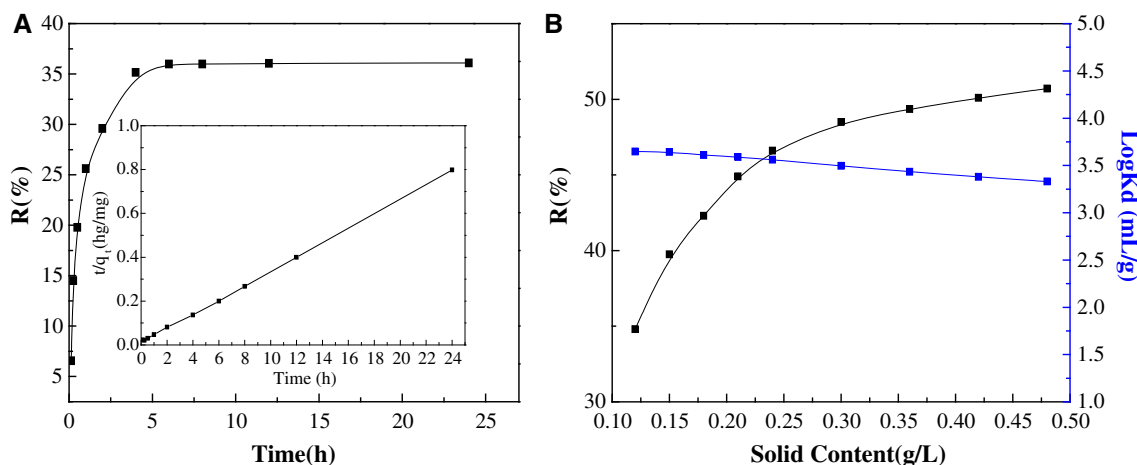


Fig. 2 a sorption kinetics of Co(II) on GO, $C_0 = 10$ mg/L, $I = 0.01$ mol/L NaClO_4 , $m/V = 0.12$ g/L, $T = 300$ K, solid line pseudo-second order kinetic model; b the effect of sorbent content on Co(II) sorption onto GO, $C_0 = 10$ mg/L, $\text{pH} = 6.4$, $I = 0.01$ mol/L NaClO_4 , $T = 300$ K

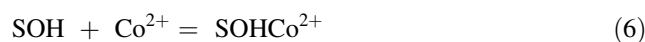
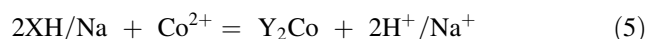
K_d values reduce with improving sorbent content, which is due to the aggregation of GO particles. The collision and overcrowding of GO particles at higher sorbent content increase the aggregation of GO particles, which may decrease the specific surface area and prolong Co(II) diffusion path on GO [23].

Effect of pH and ionic strength

Figure 3a shows the effect of pH on Co(II) sorption on GO in the presence of 0.01, 0.1 and 1 mol/L NaClO₄ solutions. According to Fig. 3, it is shown that the sorption of Co(II) on GO strongly depend on the pH values. The sorption of Co(II) on GO rises slowly at pH 2.0–4.0, then rises quickly at pH between 4.0 and 9.0, finally keeps the plateau at pH >9.0. The increment of Co(II) sorption may partly be due to the electrostatic interaction. It is found that the pH_{ZPC} (pH at zero point of charge) of GO is ~ 4.0 [13], therefore the surface of GO presents the positive charge at $pH < pH_{ZPC}$. According to the calculation of Co(II) speciation ($\log K_1 = -9.65$, $\log K_2 = -18.8$, and $\log K_3 = -31.5$), the main species of Co(II) is Co^{2+} at $pH \leq 8.0$, Co^{2+} , $Co(OH)^+$ and $Co(OH)_2$ at $pH 8.0-9.0$ (Fig. 3b). Therefore, the slight change of Co(II) sorption on GO at $pH < 4.0$ is attributed to the electrostatic repulsion. With

the pH value increasing, the surface of GO is negative, thereby the enhanced sorption of Co(II) on GO at pH 4.0–9.0 may be partly due to the electrostatic attraction. According to the calculation of solubility product of $Co(OH)_2(s)$ ($K_{sp} = 2.50 \times 10^{-16}$), the precipitate ($Co(OH)_2(s)$) is observed at pH 8.6 at $C_0 = 1.70 \times 10^{-4}$ mol/L. Thereby, the high-level sorption of Co(II) on GO at $pH > 9.0$ can be ascribed to the co-precipitation of Co(II) on GO surface.

The effect of ionic strength on the sorption is also shown in Fig. 3a. The sorption of Co(II) on GO strongly depends on ionic strength at $pH < 7.0$, whereas the sorption of Co(II) is independent of ionic strength at $pH > 7.0$. It is reported that the outer-sphere complexation and ion exchange are effected by ionic strength, but inner-sphere complexation is not effected by ionic strength [24, 25]. Therefore, it can be induced that the Co(II) sorption on GO may be due to outer-sphere complexation or ion exchange with H^+/Na^+ at $pH < 7.0$ and inner-sphere surface complexation at $pH > 7.0$. The ion exchange and outer-sphere surface complexation can be described by Eqs. (5) and (6), respectively:



where XH/Na and SOH refer to ion exchange sites and amphoteric surface groups, respectively. The inner-sphere complex between Co(II) and the electron donating oxygen of surface of GO is formed through covalent bond at pH between 7.0 and 9.0. This main reactions of the Co(II) sorption on GO can be described by the Eq. (7):

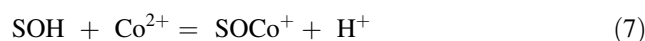


Table 1 The calculated parameters of pseudo-first and pseudo-second order kinetic models

kinetic models	q_e (mg/g)	K_f (h^{-1})	K_s (g/(mg h))	R^2
pseudo-first order	15.8	0.622	–	0.976
pseudo-second order	30.8	–	0.0880	0.999

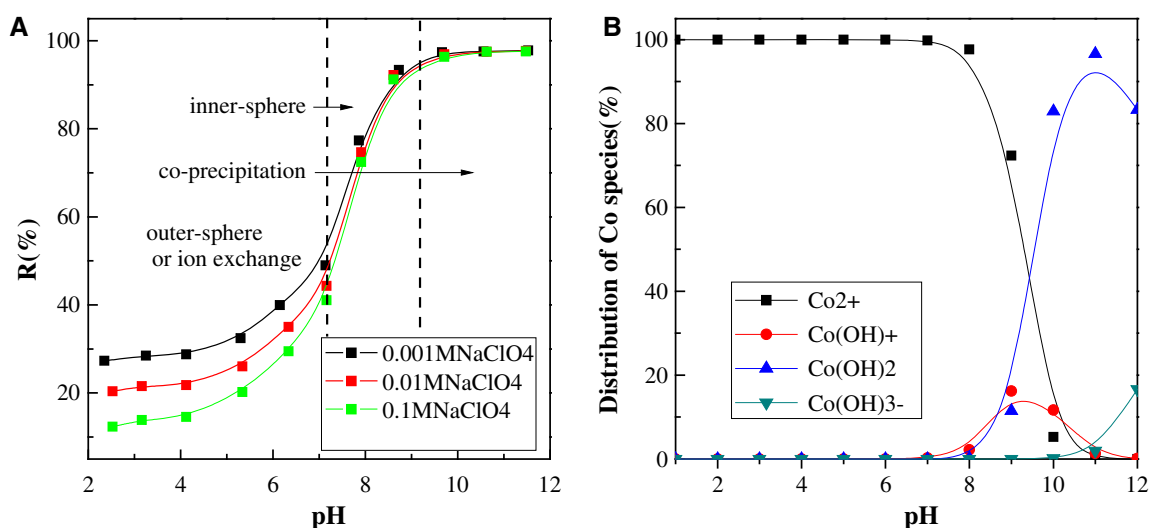
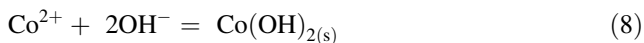


Fig. 3 a Effect of pH on Co(II) sorption onto GO in presence of 0.01, 0.1 and 1 mol/L NaClO₄ solutions, $C_0 = 10$ mg/L, $m/V = 0.12$ g/L, and $T = 300$ K. b Distribution of Co(II) species as a function of pH, $C_0 = 10$ mg/L, $I = 0.01$ mol/L NaClO₄, and $T = 300$ K

Based on the above paragraph, the high-level sorption of Co(II) on GO at pH >9.0 can ascribe the co-precipitation of Co(II) on GO surface. The co-precipitation reaction may be expressed by Eq. (8):



Therefore, the sorption mechanism of Co(II) on GO is ion exchange or outer-sphere surface complexation at pH <7.0, and the inner-sphere surface complexation predominates the sorption of Co(II) on GO at pH 7.0–9.0. The co-precipitation is observed at pH >9.0.

Effect of foreign ions

The sorption of Co(II) on GO as a function of 0.01 mol/L LiClO₄, NaClO₄, KClO₄ and Mn(ClO₄)₂ solutions is shown in Fig. 4a. The sorption of Co(II) on GO obviously decreases in the order of LiClO₄ > NaClO₄ > KClO₄ at pH < 7.0, which is consistent with their hydrated radius. It is found that the cation radius of hydration of Li⁺ and K⁺ is 3.40 and 2.32 Å, respectively. Therefore, the bigger hydrated radius, the lower repulsion is observed. In our experiments, the GO has been equilibrated with alkali ions before the addition of Co(II) ions. The results demonstrate that foreign cation may alter surface charge of GO. It is noted that the inhibited adsorption of Co(II) on GO is observed in the presence of bivalent cations such as Mn(II), which could be due to the competitive adsorption between Co(II) and Mn(II) on GO nanosheets.

As one of the representatives for natural organic matters, polyacrylic acid (PAA) has been widely used to simulate the effect of natural organic matters on heavy metals

sorption due to the occurrence of carboxylic group. The influence of PAA on Co(II) sorption onto GO was investigated in this study. As shown in Fig. 4b, the sorption of Co(II) on GO rises at pH < 7.5, then the sorption of Co(II) on GO is suppressed at pH > 7.5 in the presence of 10.0 mg/L PAA. The enhanced sorption at low pH can be interpreted by the high sorption of PAA on the GO through π - π interactions [26]. The occurrence of carboxylic group on the surface of GO-coated PAA contributes to stronger electrostatic attraction and/or high chemical ability for Co(II). However, the adsorbed PAA on the surface of GO can be dissolved with increasing pH, which is easy to combine with Co(II) ion in aqueous solution. Therefore, the suppressed sorption of Co(II) on GO at high pH conditions is attributed to the combination of PAA with Co(II) in aqueous solution, which inhibit the sorption of Co(II) on the surface of GO.

Effect of temperature

The sorption isotherms of Co(II) on GO at 300, 313 and 333 K are shown in Fig. 5. The sorption of Co(II) on GO rises with increasing the temperature. The experimental data are matched with the Langmuir and Freundlich models. The Langmuir model assumes identical sites on solid surface, no interaction among the adsorbate molecules and monolayer adsorption [27]. The Freundlich model is an empirical relationship describing the sorption on the heterogeneous solid surface, which assumes that the surface sites of solid have a spectrum of different binding energies [28]. The Langmuir and Freundlich model is described by the Eqs. (9) and (10), respectively:

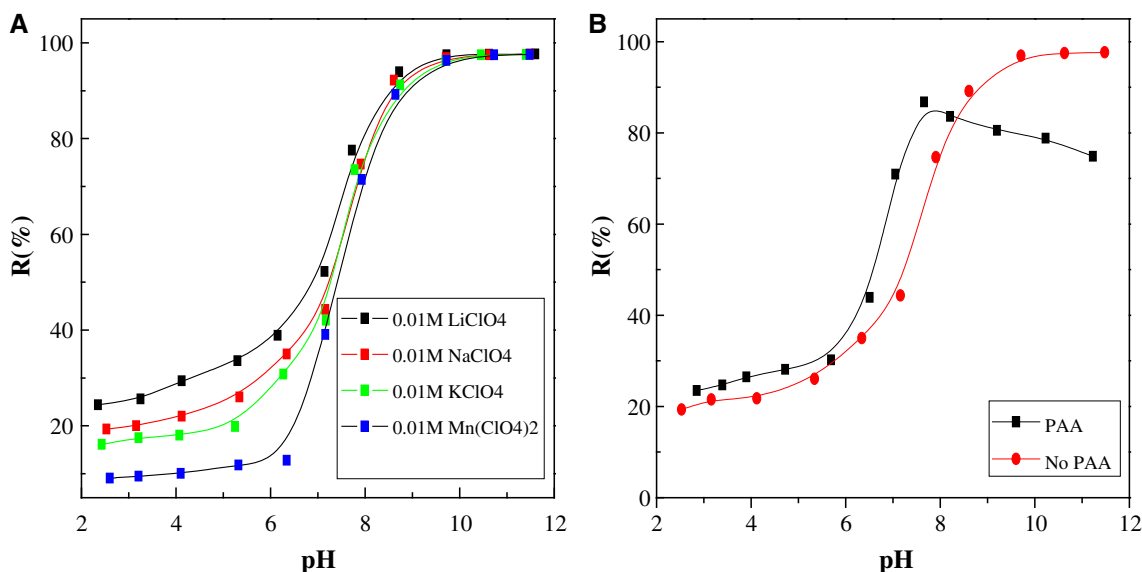


Fig. 4 Effect of foreign ions on the sorption of Co(II) on GO, **a** $I = 0.01$ mol/L LiClO₄, NaClO₄, Mn(ClO₄)₂ and KClO₄, $C_o = 10$ mg/L, $m/V = 0.12$ g/L, $T = 300$ K. **b** $C_{PAA} = 10$ mg/L, $C_o = 10$ mg/L, $I = 0.01$ mol/L NaClO₄, $m/V = 0.12$ g/L, $T = 300$ K

$$C_s = Q_{\max} \times K_L \times C_e / (1 + K_L C_e) \quad (9)$$

$$C_s = K_F C_e^n \quad (10)$$

where C_s (mg/g) and C_e (mg/L) are the amount of Co(II) sorption on GO and concentration of Co(II) at solution after equilibrium, respectively. K_L and K_F are the Langmuir constant and Freundlich constant, respectively. Q_{\max} (mg/g) is the maximum adsorption capacity, and n is the degree of dependence of sorption capacity with equilibrium concentration in aqueous solution (Table 2).

The relevant parameters calculated from the two models are listed in Table 2. The fitting results show that the sorption behaviors of Co(II) on GO are simulated by Langmuir model very well ($R^2 > 0.97$), indicating that monolayer sorption was dominated between Co(II) and GO.

The thermodynamic parameters (standard enthalpy change- ΔH° , standard entropy change- ΔS° , and Gibbs free energy changes- ΔG°) for Co(II) sorption on GO can be calculated from the sorption isotherms at three temperatures. The values of ΔG° , ΔH° and ΔS° can be calculated by the following Eqs. (11) and (12), respectively:

$$\Delta G^\circ = RT \ln K = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

$$\ln K^\circ = \Delta S^\circ / R - \Delta H^\circ / RT \quad (12)$$

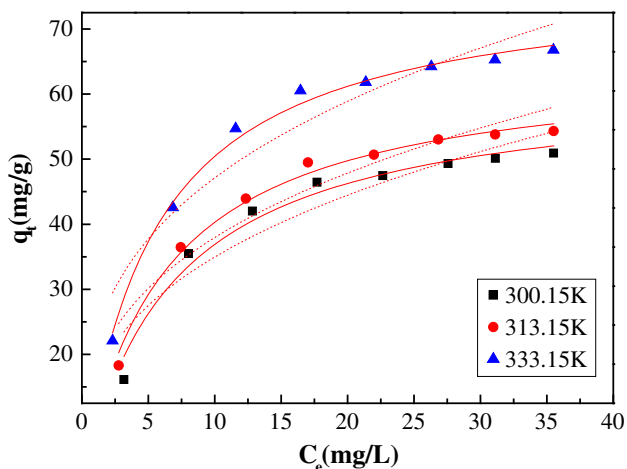


Fig. 5 Sorption isotherms of Co(II) on GO at different temperatures. $I = 0.01$ mol/L NaClO_4 , $C_o = 10$ mg/L, $m/V = 0.12$ g/L, $T = 300$ K, $\text{pH} = 6.4$. The *solid lines* are Langmuir model simulation, and the *dashed lines* are Freundlich model simulation

Table 2 Parameters of the Langmuir and Freundlich models of Co(II) sorption onto GO

Conditions	Langmuir constants			Freundlich constants		
	Q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F ($\text{mg}^{1-n} \text{L}^n/\text{g}$)	$1/n$	R^2
$T = 300.15$ K	62.0	0.147	0.972	15.8	0.346	0.868
$T = 313.15$ K	65.0	0.163	0.989	17.6	0.334	0.900
$T = 333.15$ K	77.8	0.184	0.992	22.5	0.321	0.903

Table 3 Thermodynamic parameters for Co(II) sorption onto GO

ΔH° (kJ/mol)	ΔS° (kJ/mol/K)	ΔG° (kJ/mol)		
		$T = 300$ K	$T = 313$ K	$T = 333$ K
11.08	0.11	-21.94	-23.37	-25.57

where R (8.314 J/mol/K) and T (K) are the universal gas constant and temperature in Kelvin, respectively. The sorption equilibrium constant, K° , can be calculated by plotting $\ln Kd$ versus C_e and extrapolating C_e to zero (Fig. 6a). The values of ΔH° and ΔS° can be obtained by the slope and intercept of the plot of $\ln K^\circ$ versus $1/T$ (Fig. 6b). The values of ΔG° , ΔH° and ΔS° are tabulated in Table 3. As listed in Table 3, the positive values of ΔH° (11.08 kJ/mol) is observed, which may be concluded that the sorption of Co(II) on GO is an endothermic process. It is well known that the dehydration from hydrous Co(II) is an endothermic process, whereas the combination of dehydrated Co(II) with the functional group of GO is an exothermic process. It is assumed that the endothermic energy of dehydration may surpass the exothermic energy of the dehydrated Co(II) ions combining with the surface of GO. The negative ΔG° (i.e., -21.94 kJ/mol at $T = 300$ K) is observed, showing that the sorption process is a spontaneous process. The decline of ΔG° value is observed with the increase of temperature, indicating that an increase in the temperature could contribute to the sorption Co(II) on GO. The value of ΔS° is 0.11 kJ/mol/K, which reflects that the randomness degree increases at the solid-liquid interface during the sorption process. The thermodynamic results reveal that the sorption of Co(II) on GO is an spontaneous and endothermic process.

Interaction mechanism

A complementary description about the interaction mechanism between Co(II) and GO is obtained by XPS analysis. The XPS spectra is used to analyze the samples of GO after Co(II) sorption at pH 5.0 and pH 8.0 (Fig. 7). As shown in Fig. 7a, the characteristic peak of cobalt appears at 782.38 and 781.48 eV (assigned to Co2p3/2) at pH 5.0 and 8.0, respectively, which is consistent with the results reported by Dillard and Koppelman [29] who found that binding energy

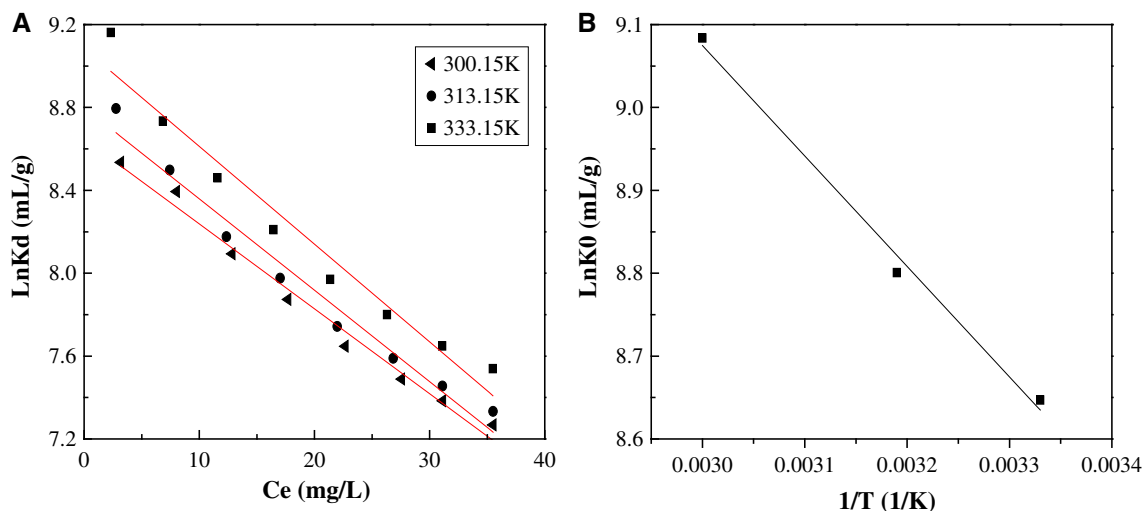


Fig. 6 Plots of $\text{Ln } K_d$ & C_e (a) and $\text{Ln } K^0$ & $1/T$ (b), $\text{pH} = 6.4$, $C_0 = 10 \text{ mg/L}$, $I = 0.01 \text{ mol/L NaClO}_4$, $m/V = 0.12 \text{ g/L}$

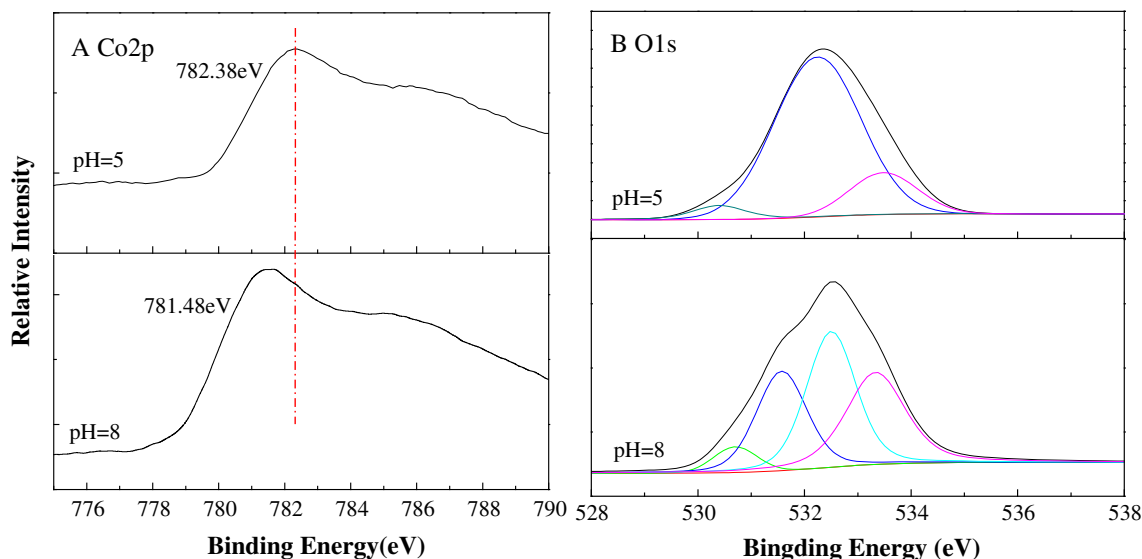


Fig. 7 The XPS spectra of GO after Co(II) sorption at pH 5.0 and pH 8.0. **a** Co 2p; **b** O 1s

of Co(2p_{3/2}) on kaolinite increased with decreasing pH. Figure 7b show the high resolution scans of O 1s XPS spectra. The peaks centered at 530.38, 532.28 and 533.48 eV at pH 5.0, which are assigned to the C=O, C–OH and C–O–C, respectively. However, one new peak appears at the position (~531.58 eV) and relative intensity of C–OH peak decreases at pH 8.0, which are assumed that the C–OH group may be displaced by inner-sphere complex between GO and Co(II). The above results indicate that the C–OH functional groups on GO take part in the Co(II) sorption onto GO, and Co(II) ion might happen sorption on GO as different surface complex at different pH condition. The shifts of binding energy can be attributed to forming strong covalent bond [30, 31]. This XPS feature was accordance with the results of the ionic strength effect. Therefore, the sorption of Co(II) on

GO is the outer-sphere surface complex or ion exchange at $\text{pH} < 7.0$ and the inner-sphere surface complex at $\text{pH} 7.0\text{--}9.0$. Future studies on the proposed mechanism between Co(II) and GO need to demonstrate by other spectroscopic techniques such as the extended X-ray absorption fine structures.

Conclusions

The GO was synthesized and characterized by XRD and FTIR. The characterization results reveal a large number of oxygen-containing functional groups on the surface of GO. According to the results of macroscopic sorption, the following conclusions can be obtained:

- (1) The sorption kinetics and isothermal sorption of Co(II) on GO could be satisfactorily described by the pseudo-second order kinetic and Langmuir model, respectively.
- (2) Sorption of Co(II) on the GO is strongly influenced by various environmental factors such as pH and ionic strength, PAA, alkali ions and temperature.
- (3) The thermodynamic parameters calculated from the isotherms at different temperatures indicate that the sorption Co(II) on GO is an spontaneous and endothermic process.
- (4) The XPS spectra show that the sorption of Co(II) on GO is the outer-sphere surface complex or ion exchange at pH < 7.0 and the inner-sphere surface complex 7.0–9.0, respectively.

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