

# Efficient removal of cobalt from aqueous solution using $\beta$ -cyclodextrin modified graphene oxide

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$\beta$ -Cyclodextrin modified graphene oxide (denoted as  $\beta$ -CD-GO) was synthesized and applied as a sorbent to remove Co(II) from aqueous solution. The synthesized  $\beta$ -CD-GO was characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) in detail, and the results of the characterization indicated that  $\beta$ -CD was successfully grafted onto the surface of GO. The effects of pH, ionic strength, competing ions and solid content on the sorption of Co(II) onto the  $\beta$ -CD-GO nanocomposites were investigated. The results indicated that Co(II) sorption on  $\beta$ -CD-GO was strongly dependent on pH and independent of ionic strength under the experimental uncertainties. The sorption isotherms of Co(II) on  $\beta$ -CD-GO could be described well by the Langmuir model. The thermodynamic data ( $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$ ) calculated from the temperature-dependent sorption isotherms suggest that the sorption of Co(II) on  $\beta$ -CD-GO is a spontaneous and endothermic process. The maximum sorption capacity of Co(II) on  $\beta$ -CD-GO ( $72.4 \text{ mg g}^{-1}$ ) at  $\text{pH} = 6.0 \pm 0.1$  and  $T = 303 \text{ K}$  was much higher than that of Co(II) on GO ( $47.39 \text{ mg g}^{-1}$ ) and other sorbents. The abundant oxygen-containing functional groups of modified  $\beta$ -CD on the GO surface can improve the sorption capacity of  $\beta$ -CD-GO for Co(II). The results indicate that  $\beta$ -CD-GO is a promising material for the removal and enrichment of Co(II) from wastewater.

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## 1 Introduction

Radionuclides  $^{60}\text{Co}$  and  $^{58}\text{Co}$  are abundant in the nuclear waste released from pressurized water nuclear reactors, and  $^{60}\text{Co}$  is also widely used in research and medical applications.<sup>1</sup> The release of Co(II) into the environment could result in defects, diarrhea, low blood pressure, lung irritation or paralysis, and may also cause mutations (genetic changes) in living cells.<sup>2</sup> Therefore, the removal of Co(II) from aqueous solution is important for public health. Over the past decades, various methods such as precipitation, ion-exchange, and sorption have been employed to remove Co(II) from large volumes of aqueous solution.<sup>3–5</sup> Sorption technology is widely regarded as one of the most effective choices for the removal of heavy metal ions from aqueous solution because it is simple and cost-effective.<sup>6,7</sup> However, most of the common sorbents, such as clay minerals (*i.e.* maximum sorption capacity  $\sim 13.2 \text{ mg g}^{-1}$  Co(II) on sludge<sup>8</sup>), metallic oxides (*i.e.* maximum  $\sim 28.3 \text{ mg g}^{-1}$  Co(II) on  $\gamma\text{-Fe}_2\text{O}_3$ <sup>9</sup>) and carbon materials (*i.e.* maximum  $\sim 4.1 \text{ mg g}^{-1}$  Co(II) on poly(acrylonitrile-*g*-starch)<sup>10</sup> and  $\sim 12.4 \text{ mg g}^{-1}$  Co(II) on bis(imidazole)-modified glycidyl methacrylate copolymer<sup>11</sup>), usually suffer from either low

sorption capacities or sorption efficiencies in the removal of heavy metal ions from aqueous solution. Therefore, the design and development of special sorbents with high sorption capacities for contaminants is critical for pollution management and related applications.

Graphene has a large specific surface area (theoretical value is  $2620 \text{ m}^2 \text{ g}^{-1}$ ),<sup>12</sup> which gives it the potential for application in the removal of pollutants in environmental pollution management.<sup>13–15</sup> However, the strong aggregation of graphene nanosheets, the absence of effective methods of dispersing graphene in aqueous solution<sup>16</sup> and the presence of less effective functional groups for sorption applications on its surface greatly restrict the application of graphene in environmental management. Therefore, it is necessary to modify the surface of graphene to enhance its sorption capacity and dispersion properties in aqueous solution.

Cyclodextrins (CDs) are cyclic oligosaccharides with a characteristic truncated cone shape which forms a well-defined cylindrical cavity.<sup>17</sup>  $\beta$ -CD, the most common CD, is characterized by a hydrophilic exterior and a hydrophobic interior,<sup>18</sup> and has the tendency to form inclusion complexes with contaminants such as organic pollutants and heavy metal ions.<sup>19,20</sup> Therefore, the modification of  $\beta$ -CD on the graphene oxide (GO) surface can effectively enhance the sorption capacity of GO.

In this study,  $\beta$ -CD modified GO (denoted as  $\beta$ -CD-GO) was synthesized by an *in situ* polymerization technique and

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characterized by scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM/EDX), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The batch sorption technique was adopted to evaluate the effect of different experimental conditions on the sorption performance of  $\beta$ -CD-GO in the removal of Co(II) from aqueous solution.

## 2 Experimental section

### 2.1. Preparation of GO

GO was synthesized from flake graphite by a modified Hummers method.<sup>21,22</sup> Under mechanical stirring and in an ice–water bath, 98% H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub> were slowly added into a three-necked flask containing graphite powder and NaNO<sub>3</sub>, and then the mixture reacted at room temperature for 5 days. After dilution with Milli-Q water at 98 °C, and cooling to 60 °C, H<sub>2</sub>O<sub>2</sub> (30%) was added to the mixture to reduce the residual KMnO<sub>4</sub>. Finally, the solid GO was obtained after the black deposit was filtered and thoroughly washed with Milli-Q water and alcohol.

### 2.2. Preparation of $\beta$ -CD-GO

$\beta$ -CD-GO was synthesized according to previous work by Guo.<sup>23</sup> After a 50 mL mixture of GO (0.05 g L<sup>-1</sup>) and  $\beta$ -CD (18 g L<sup>-1</sup>) was adjusted to pH 11 by ammonia solution, the solution was placed in a water bath (60 °C) and 2 mL hydrazine solution was added to initiate the modification reaction. After reaction at 60 °C for 4 h, a stable black dispersion was obtained. After filtration with a nylon membrane (0.22  $\mu$ m) and being washed thoroughly with Milli-Q water, the dispersion was dried at 60 °C for 24 h in a vacuum oven. Thus  $\beta$ -CD-GO was obtained and used in the following experiments.

### 2.3. Characterization

The synthesized  $\beta$ -CD-GO and GO were characterized by SEM/EDX, FT-IR, Raman spectroscopy and XPS. The SEM/EDX investigations were carried out on a JSM-6320F field emission scanning electron microscopy (FESEM) instrument coupled with an EDX unit (INCA). FT-IR spectroscopy was carried out on Perki Elmer 100 spectrometer in a KBr pellet. The Raman spectrum was carried out on a LabRam HR Raman spectrometer at an excitation wavelength of 514.5 nm by an Ar<sup>+</sup> laser. The XPS measurements were performed with an ESCALab220i-XL surface microanalysis system (VG Scientific) equipped with an Al K $\alpha$  ( $h\nu = 1486.6$  eV) source.

### 2.4. Sorption experiments

The sorption experiments were carried out using the batch sorption technique in polyethylene centrifuge tubes. The sorbents, NaCl and Co(II) were added to achieve the desired concentrations of the different components. The pH was adjusted to the desired values by adding negligible amounts of 0.1 or 0.01 M HCl or NaOH. The test tubes were shaken for 24 h to achieve sorption equilibrium and then centrifuged for 20 min at 8000 r min<sup>-1</sup>. The concentration of Co(II) was analyzed with an atomic absorption spectrophotometer. All of the

experimental data were the averages of triplicate determinations. The relative errors of the data were about 5%. The amount of Co(II) adsorbed on the  $\beta$ -CD-GO or GO surface was calculated from the difference between the initial concentration and the final concentration. The sorption percentage and the distribution coefficient ( $K_d$ ) were calculated from the following equations:

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \quad (1)$$

$$\text{Sorption\%} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where  $C_0$  (mg L<sup>-1</sup>) is the initial concentration,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentration,  $m$  (g) is the mass of  $\beta$ -CD-GO and  $V$  (L) is the volume of the suspension.

## 3 Results and discussion

### 3.1. Characterization of $\beta$ -CD-GO and GO

The microstructures of GO and  $\beta$ -CD-GO can be observed by SEM imaging (Fig. 1). Differences in the surface morphology between GO and  $\beta$ -CD-GO can be observed. Fig. 1a shows that the surface of GO is smooth and there are few wrinkles, whereas the surface of  $\beta$ -CD-GO is rougher and features more wrinkles (Fig. 1b), which is important for preventing the aggregation of GO. Additionally, there are many packed nanoparticles which suggests that  $\beta$ -CD molecules have been successfully attached to the GO surface. This was also confirmed by EDX characterization. The atomic percentages of used graphite, prepared GO and  $\beta$ -CD-GO were 99.33% C and 0.67% O, 88.96% C and 11.03% O, and 94.49% C and 5.52% O respectively (Table 1).

The FT-IR spectra of GO,  $\beta$ -CD and  $\beta$ -CD-GO are shown in Fig. 2. The peak at  $\sim 3400$  cm<sup>-1</sup> is due to the O–H stretching vibration of hydroxyl groups on the sorbent surface. In the GO spectrum, a C–O group ( $\sim 1220$  cm<sup>-1</sup> and  $\sim 1100$  cm<sup>-1</sup>), C=O group ( $\sim 1730$  cm<sup>-1</sup>) and C=C bond ( $\sim 1620$  cm<sup>-1</sup>) can be seen, which indicates that large amounts of oxygen-containing functional groups exist on the GO surface. In the  $\beta$ -CD-GO spectrum, a significant increase in band intensity is visible at  $\sim 1030$  cm<sup>-1</sup> and  $\sim 2920$  cm<sup>-1</sup>, which can be attributed to the surface modified  $\beta$ -CD. It further confirms the successful modification of GO with  $\beta$ -CD.

In the Raman spectra (Fig. 3), the G band at  $<1580$  cm<sup>-1</sup> is associated with the vibration of sp<sup>2</sup> carbon atoms in a

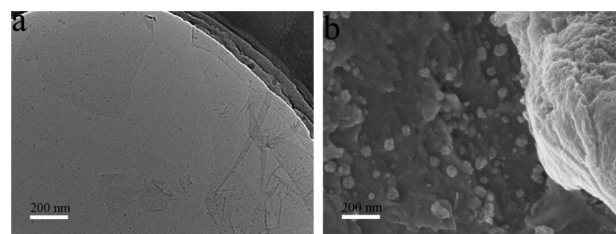


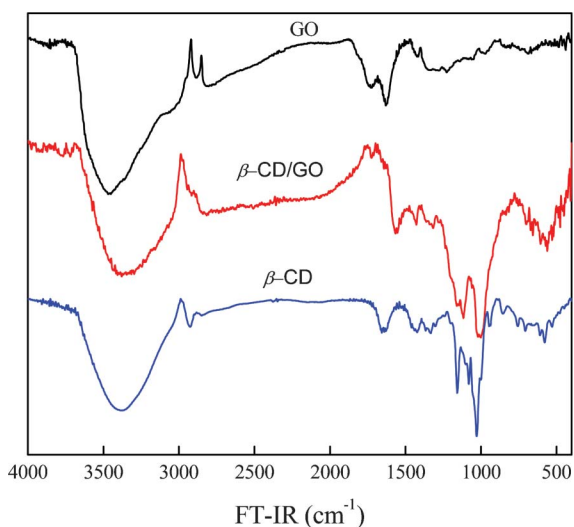
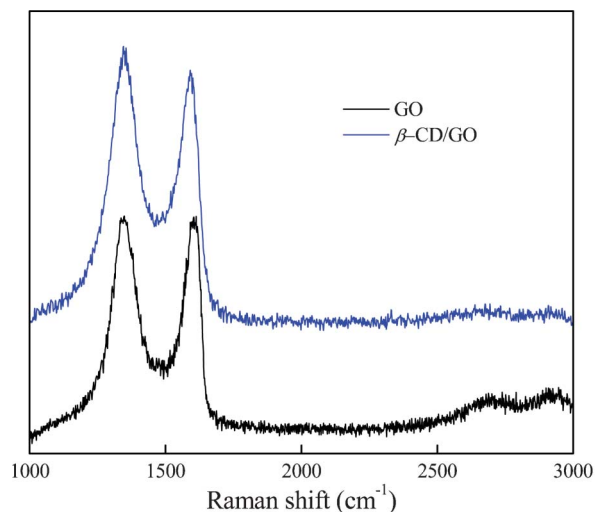
Fig. 1 SEM images of (a) GO and (b)  $\beta$ -CD-GO.

**Table 1** Elemental composition of used graphite, GO and  $\beta$ -CD-GO, obtained by EDX

	C (at%)	O (at%)
Used graphite	99.33	0.67
GO	88.96	11.03
$\beta$ -CD-GO	94.49	5.52

graphitic 2D hexagonal lattice, and the D band at  $<1350\text{ cm}^{-1}$  is related to the vibrations of the  $\text{sp}^3$  carbon atoms in defects and disorders. The value of the  $I_G/I_D$  ratio can be used to study the relative extent of GO structural graphite. The  $I_G/I_D$  ratios are 0.93 for GO and 0.87 for  $\beta$ -CD-GO. The  $I_G/I_D$  ratio of GO decreases markedly after modification with  $\beta$ -CD, which could be due to the effect of the modified  $\beta$ -CD on the GO surface, because the modified  $\beta$ -CD on the GO surface would exist in a disordered form.

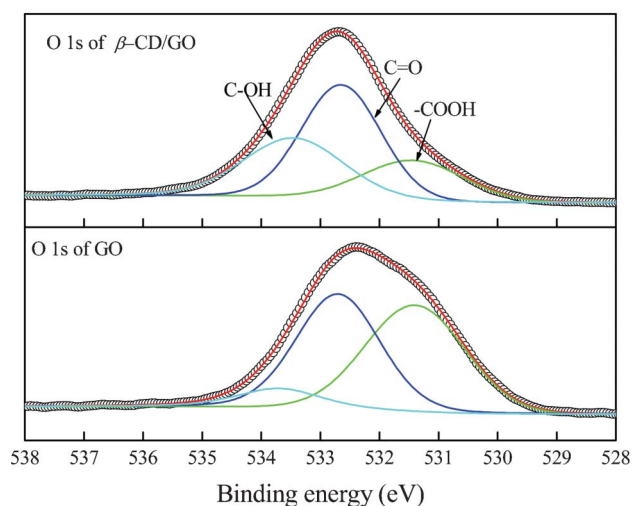
XPS (Fig. 4) is an effective technique for the analysis and identification of surface groups. The O 1s spectrum of  $\beta$ -CD-GO can be deconvoluted into three peaks at  $531.4 \pm 0.2$ ,  $532.7 \pm 0.2$ , and  $533.7 \pm 0.2$  eV, which correspond to  $-\text{COOH}$ ,  $>\text{C}=\text{O}$  and  $-\text{C}-\text{OH}$  species, respectively. The quantitative analysis of the O 1s spectrum of GO gives peak fractions of 46.7% for  $-\text{COOH}$ , 44.9% for  $>\text{C}=\text{O}$  and 8.38% for  $-\text{C}-\text{OH}$ , whereas those of the O 1s spectrum of  $\beta$ -CD-GO are 35.8% for  $-\text{COOH}$ , 28.2% for  $>\text{C}=\text{O}$  and 36.0% for  $-\text{C}-\text{OH}$  (Table 2). One can see that the peak fractions of  $-\text{COOH}$  and  $>\text{C}=\text{O}$  decrease, whereas the peak fraction of  $-\text{C}-\text{OH}$  increases after GO was modified with  $\beta$ -CD. This is reasonable because  $\beta$ -CD is a cyclic oligosaccharide which contains many hydroxyl groups. The modified  $\beta$ -CD molecules on GO increase the peak fraction of  $-\text{C}-\text{OH}$  and thereby decrease the other peak fractions.<sup>24,25</sup>

**Fig. 2** FT-IR spectra of GO,  $\beta$ -CD and  $\beta$ -CD-GO.**Fig. 3** Raman spectra of GO and  $\beta$ -CD-GO.

### 3.2. Effect of pH and ionic strength

The pH of aqueous solution (Fig. 5A) is an important factor which affects the sorption of  $\text{Co}(\text{II})$  because a change in the solution pH can influence the surface properties of the sorbents and the hydrolysis, precipitation and complexation of  $\text{Co}(\text{II})$ .<sup>26</sup> The sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO as a function of pH in 0.1, 0.01, and 0.001 M NaCl solutions is shown in Fig. 5A. It can be seen that the sorption of  $\text{Co}(\text{II})$  increases slowly at  $\text{pH} < 6$ , then quickly at  $\text{pH} 6-9$ , and maintains high level of sorption at  $\text{pH} > 9$ . This strong pH-dependent sorption suggests that the sorption of  $\text{Co}(\text{II})$  is mainly dominated by surface complexation.<sup>27</sup>

The relative distribution of  $\text{Co}(\text{II})$  species in aqueous solution can be calculated from the hydrolysis constants of  $\text{Co}(\text{II})$  ( $\log K_1 = -9.6$ ,  $\log K_2 = -9.2$ , and  $\log K_3 = -12.7$ ).<sup>28</sup> The distribution of different  $\text{Co}(\text{II})$  species in aqueous solution as a function of solution pH is shown in Fig. 5B.  $\text{Co}(\text{II})$  exists as the

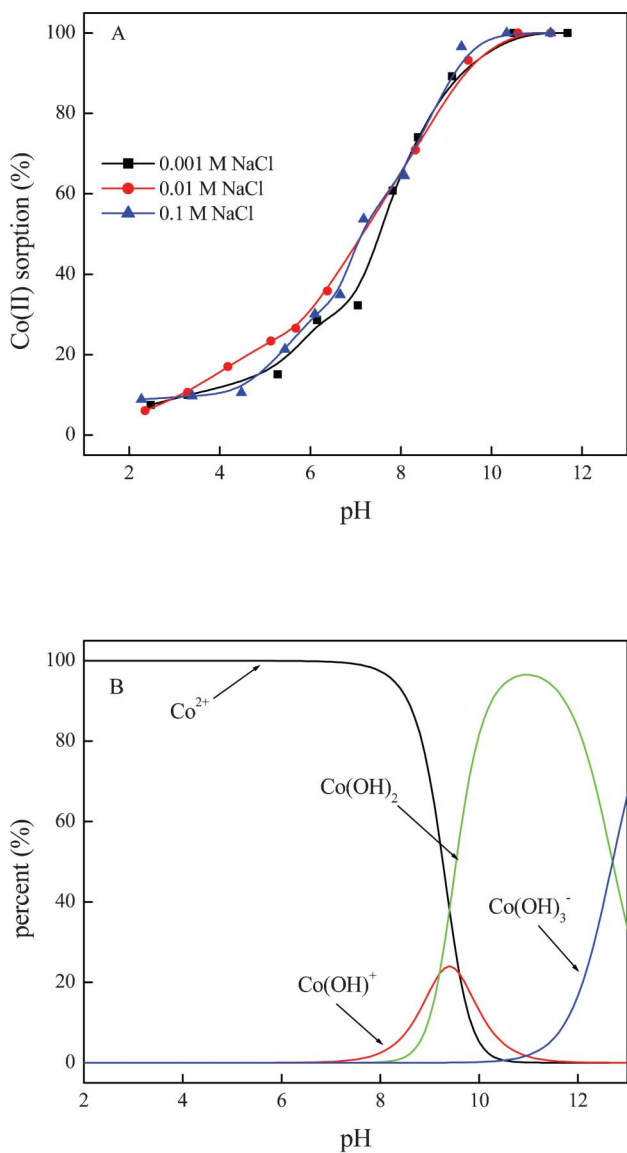
**Fig. 4** XPS spectra of GO and  $\beta$ -CD-GO.

**Table 2** Curve fitting results of the XPS O 1s spectra

	Peak	BE <sup>a</sup> (eV)	FWHM <sup>b</sup> (eV)	%
GO	-COOH	531.40	1.98	46.7
	>C=O	532.70	1.67	44.9
	-C-OH	533.70	1.67	8.38
$\beta$ -CD-GO	-COOH	531.44	2.02	35.8
	>C=O	532.65	1.58	28.2
	-C-OH	533.66	2.03	36.0

<sup>a</sup> Binding energy. <sup>b</sup> Full width at half-maximum.

prevailing species of  $\text{Co}^{2+}$  up to pH 8.0, and then the proportions of  $\text{Co}(\text{OH})^+$  and  $\text{Co}(\text{OH})_2$  become more important. When the pH value is higher than that for the formation of



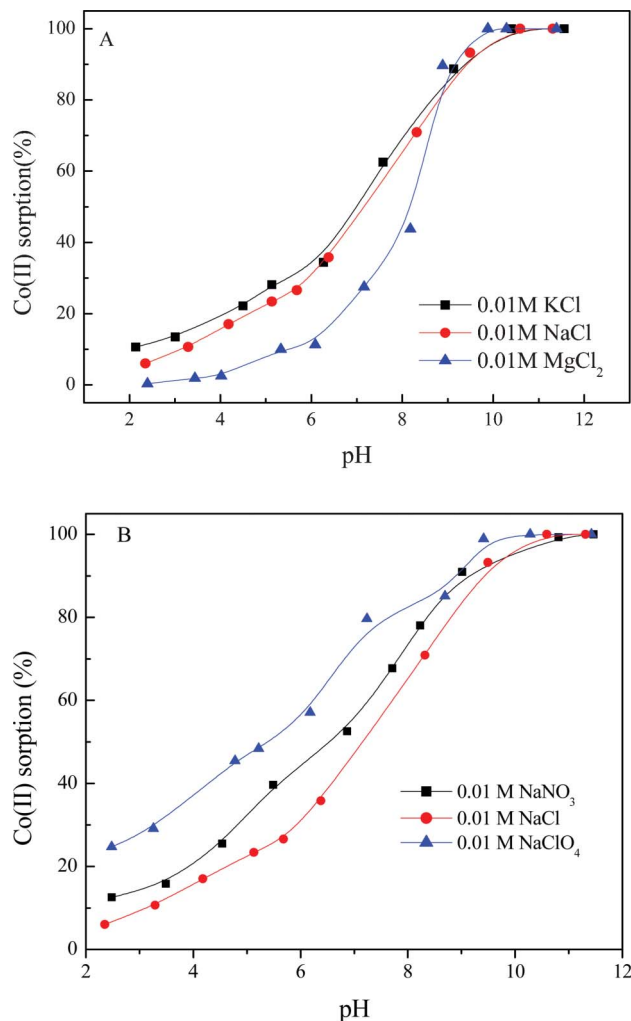
**Fig. 5** Effect of pH on (A) the sorption of Co(II) to  $\beta$ -CD-GO and (B) the relative distribution of Co(II) species. A:  $T = 303$  K,  $m/V = 0.1$  g  $\text{L}^{-1}$ ,  $I = 0.01$  M, NaCl,  $C_{[\text{Co}(\text{II})]} = 10$  mg  $\text{L}^{-1}$ .

$\text{Co}(\text{OH})_2$ ,  $\text{Co}(\text{II})$  is removed from the solution by sorption as well as by precipitation. At very low pH values, electrostatic interactions can hinder the sorption of  $\text{Co}(\text{II})$  because both the  $\text{Co}(\text{II})$  ions and the sorbent surface are positively charged, which explains the poor sorption of  $\text{Co}(\text{II})$  ions on the  $\beta$ -CD-GO surface at low pH values. With increasing pH, the surface charge becomes more negative and the electrostatic interactions between  $\text{Co}(\text{II})$  ions and  $\beta$ -CD-GO decrease, thereby resulting in an increase in  $\text{Co}(\text{II})$  sorption.

The influence of ionic strength on the sorption of  $\text{Co}(\text{II})$  onto  $\beta$ -CD-GO was investigated by a series of experiments using solutions containing different concentrations of NaCl. As shown in Fig. 5A, for all of the ionic strengths which were tested,  $\text{Co}(\text{II})$  displays a weak affinity for  $\beta$ -CD-GO at low pH, suggesting that  $\text{Co}(\text{II})$  does not easily form complexes with protonated carboxylic acid groups on the surface of  $\beta$ -CD-GO. No differences can be found at high pH under the experimental uncertainties, indicates that inner-sphere surface complexation is the main sorption mechanism. It is noteworthy that the sorption decreases significantly with increasing ionic strength at pH 6–9. The ionic strength dependence of  $\text{Co}(\text{II})$  sorption onto  $\beta$ -CD-GO could be for two reasons: (1) metal ions form electrical double layer complexes with  $\beta$ -CD-GO, which favors a low ionic strength. This may indicate that the sorption interactions between the carboxylic acids on the surface of  $\beta$ -CD-GO and the  $\text{Co}(\text{II})$  ions are partially ionic in nature; (2) the ionic strength of the solution influences the activity coefficient of the  $\text{Co}(\text{II})$  ions, which limits their transfer to the surface of  $\beta$ -CD-GO.<sup>29</sup>

### 3.3. Effect of competing ions

To investigate the influence of competing ions on  $\text{Co}(\text{II})$  sorption, the sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO was studied as a function of pH in 0.01 mol  $\text{L}^{-1}$  NaCl,  $\text{MgCl}_2$ , KCl,  $\text{NaNO}_3$  and  $\text{NaClO}_4$  solutions, respectively. As can be seen from Fig. 6A, the sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO is strongly affected by the competing cations at pH < 9. The sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO under the same pH values is in the following sequence:  $\text{K}^+ > \text{Na}^+ > \text{Mg}^{2+}$ , indicating that cations can alter the surface properties of  $\beta$ -CD-GO and thus can affect the sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO. The sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO can be considered as the competition of  $\text{Co}(\text{II})$  with competing cations ( $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$ ) at the  $\beta$ -CD-GO surface. The higher valence ion is much more readily sorbed onto the sorbent surface. Therefore, the influence of  $\text{Mg}^{2+}$  on  $\text{Co}(\text{II})$  sorption is stronger than that of  $\text{Na}^+$  and  $\text{K}^+$ . Because the radius of  $\text{Na}^+$  is smaller than that of  $\text{K}^+$ ,  $\text{Na}^+$  has a higher affinity to the surface of  $\beta$ -CD-GO. The higher tendency for counterion complexation with the surface groups of  $\beta$ -CD-GO reduces the number of ion interaction sites on the surface of  $\beta$ -CD-GO for  $\text{Co}(\text{II})$  to interact with. In this work, the concentration of the competing cations ( $1.00 \times 10^{-2}$  mol  $\text{L}^{-1}$ ) is much higher than that of  $\text{Co}(\text{II})$  ( $1.7 \times 10^{-4}$  mol  $\text{L}^{-1}$ ), and the influence of alkali metal cations and alkaline earth cations on the sorption of bivalent  $\text{Co}(\text{II})$  is obvious. At pH < 9, the sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO can be attributed to the exchange of  $\text{Co}(\text{II})$  with alkali metal cations or alkaline earth cations. It is reasonable that the coexisting competing cations can affect the sorption of  $\text{Co}(\text{II})$  on  $\beta$ -CD-GO. One can also see that the sorption of  $\text{Co}(\text{II})$  on



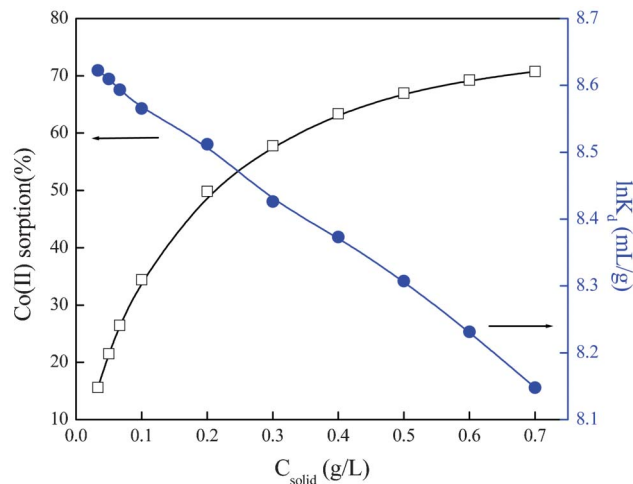
**Fig. 6** Effect of ionic strength on the sorption of Co(II) to  $\beta$ -CD-GO.  $T = 303$  K,  $m/V = 0.1$  g L<sup>-1</sup>,  $C_{[Co(II)]initial} = 10$  mg L<sup>-1</sup>. A: effect of cations, B: effect of anions.

$\beta$ -CD-GO at  $pH > 9$  is not affected by competing cations, which may be due to the formation of surface precipitates at high pH values.<sup>26,30</sup>

From Fig. 6B, one can see that the sorption of Co(II) on  $\beta$ -CD-GO is highest in 0.01 mol L<sup>-1</sup> NaClO<sub>4</sub> solution and is the lowest in 0.01 mol L<sup>-1</sup> NaCl solution at  $pH < 9$ . Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> can form soluble complexes with Co(II), whereas ClO<sub>4</sub><sup>-</sup> cannot. Moreover, the acid radical radius order is Cl<sup>-</sup> < NO<sub>3</sub><sup>-</sup> < ClO<sub>4</sub><sup>-</sup>. The smaller radicals take up more ion exchange sites which leads to a decrease in Co(II) sorption.<sup>31</sup>

### 3.4. Effect of solid content

The effect of solid content on the sorption of Co(II) on  $\beta$ -CD-GO is shown in Fig. 7. The sorption of Co(II) increases with increasing solid content. This trend is expected because the number of functional sites which participate in the sorption of Co(II) increase with an increasing solid content. The distribution coefficient ( $K_d$ ) decreases a little with an increasing solid content (Fig. 7). The decrease of  $K_d$  with an increasing solid content may be attributed to the competition with  $\beta$ -CD-GO.

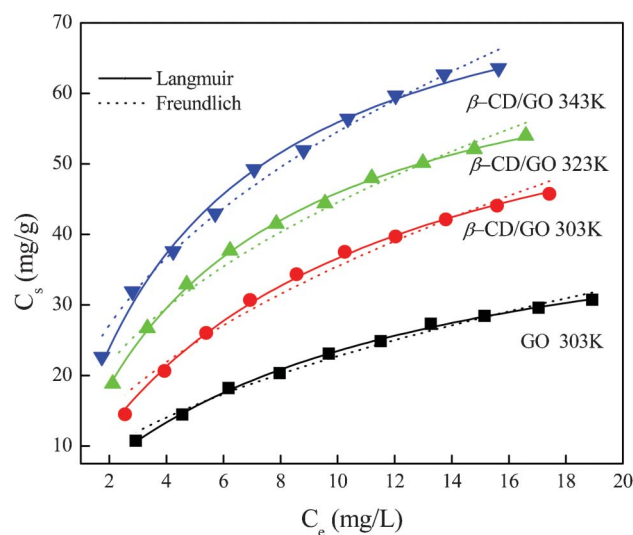


**Fig. 7** The effect of solid content on the sorption of Co(II) to  $\beta$ -CD-GO.  $T = 303$  K,  $C_{[Co(II)]initial} = 10$  mg L<sup>-1</sup>,  $I = 0.01$  M NaCl,  $pH = 6.0 \pm 0.1$ .

Such competition reduces the effective functional group sites at the surface of  $\beta$ -CD-GO and results in a decrease of the sorption and complexation ability of  $\beta$ -CD-GO with an increasing solid content.

### 3.5. Sorption isotherms

The sorption isotherms obtained at 303, 323 and 343 K are shown in Fig. 8. With an increase in Co(II) concentration, the sorption initially increases rapidly and then increases more slowly. The sorption isotherms increase in the order 303, 323, and 343 K. This means that the process of sorption is favored at high temperatures. To gain a better understanding of the sorption mechanism and to quantify the sorption data, the



**Fig. 8** Sorption isotherms of Co(II) on GO and  $\beta$ -CD-GO at three different temperatures. The solid line represents the Langmuir model and the dashed line represents the Freundlich model.  $pH = 6.0 \pm 0.1$ ,  $m/V = 0.1$  g L<sup>-1</sup>,  $I = 0.01$  M NaCl.

Langmuir and Freundlich models were used to simulate the experimental data (Fig. 9).

The Langmuir isotherm model was applied to describe the monolayer sorption process. It can be expressed by the following equation:

$$C_s = \frac{bC_{s\max}C_e}{1 + bC_e} \quad (3)$$

Eqn (3) can be expressed in the linear form:

$$\frac{C_e}{C_s} = \frac{1}{bC_{s\max}} + \frac{C_e}{C_{s\max}} \quad (4)$$

where  $C_e$  is the equilibrium concentration of Co(II) remaining in solution ( $\text{mg g}^{-1}$ ),  $C_{s\max}$  ( $\text{mg g}^{-1}$ ), the maximum sorption

capacity, represents the amount of Co(II) adsorbed at a complete monolayer coverage, and  $b$  ( $\text{L mg}^{-1}$ ) is a Langmuir constant which is related to the sorption heat.

The Freundlich isotherm model is applicable to several kinds of sorption on solid surfaces, which fits the sorption data at low and medium concentrations on heterogeneous surfaces. The model has the following form:

$$C_s = K_F C_e^n \quad (5)$$

Eqn (5) can be expressed in linear form:

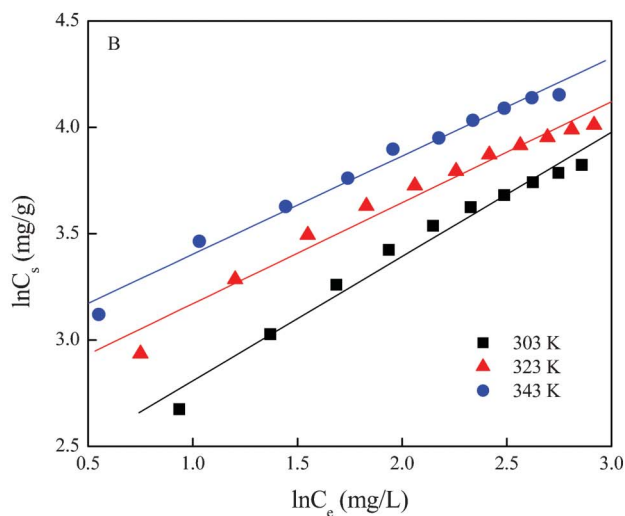
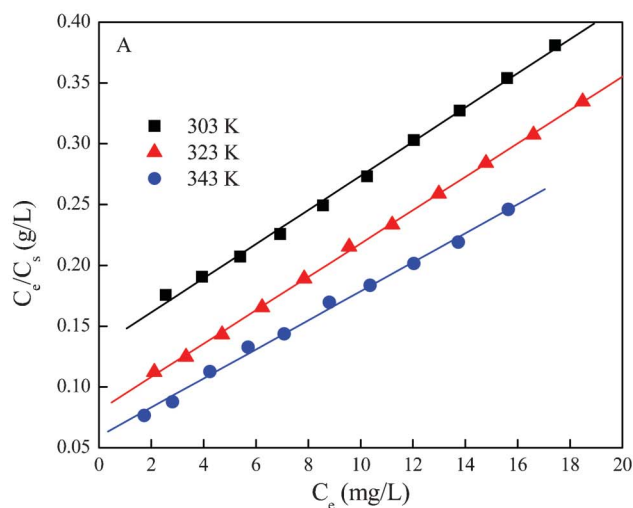
$$\ln C_s = \ln K_F + n \ln C_e \quad (6)$$

where  $K_F$  ( $\text{mg}^{1-n} \text{L}^n \text{g}^{-1}$ ) represents the sorption capacity when the equilibrium concentration of the metal ions is equal to 1, and  $n$  represents the degree of the dependence of sorption with the equilibrium concentration.

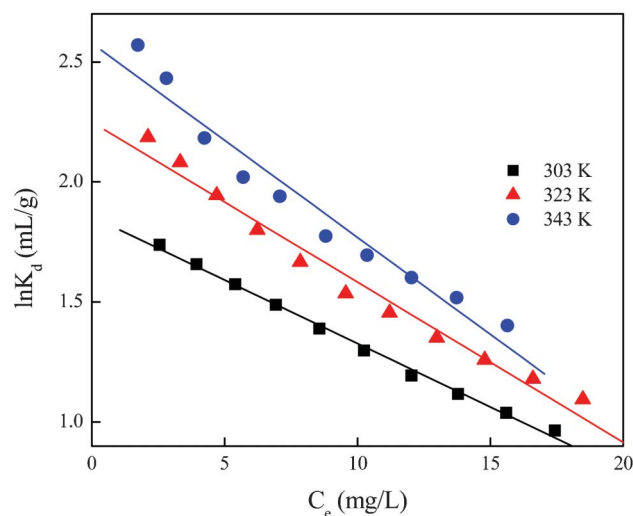
Thermodynamic parameters were helpful for practical application. In order to investigate the impact of temperature, the sorption isotherms of  $\beta$ -CD-GO at different temperatures were obtained and shown in Fig. 8. The sorption of Co(II) increases with an increase in the reaction temperature. The highest sorption isotherm is obtained at  $T = 343 \text{ K}$ , while the lowest sorption isotherm is obtained at  $T = 303 \text{ K}$ , which illustrates that the sorption of Co(II) on  $\beta$ -CD-GO is promoted at higher temperatures. The thermodynamic parameters ( $\Delta G^0$ ,  $\Delta S^0$  and  $\Delta H^0$ ) are calculated from the temperature-dependent sorption isotherms. The value of the free energy change is derived from the function:

$$\Delta G^0 = -RT \ln K^0 \quad (7)$$

where  $K^0$  is the sorption equilibrium constant. The values of  $\ln K^0$  represent the sorption ability of  $\beta$ -CD-GO towards Co(II).  $K^0$  can be calculated by plotting  $\ln K_d$  versus  $C_e$  and extrapolating  $C_e$  to zero (see Fig. 10). The standard enthalpy change ( $\Delta H^0$ )



**Fig. 9** Langmuir (A) and Freundlich (B) isotherms of the sorption of Co(II) on  $\beta$ -CD-GO at three different temperatures.  $\text{pH} = 6.0 \pm 0.1$ ,  $m/V = 0.1 \text{ g L}^{-1}$ ,  $I = 0.01 \text{ M NaCl}$ .



**Fig. 10** Linear plots of  $\ln K_d$  versus  $C_e$ .  $\text{pH} = 6.0 \pm 0.1$ ,  $m/V = 0.1 \text{ g L}^{-1}$ ,  $I = 0.01 \text{ M NaCl}$ .

and the standard entropy change ( $\Delta S^0$ ) are calculated from the following equation:

$$\ln K^0 = \frac{\Delta H^0}{R} - \frac{\Delta S^0}{RT} \quad (8)$$

Linear plots of  $\ln K^0$  vs.  $1/T$  for Co(II) sorption on  $\beta$ -CD-GO are shown in Fig. 11.  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the ideal gas constant and  $T$  (K) is the temperature.

The change of Gibbs free energy ( $\Delta G$ ) was calculated from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad (9)$$

The values calculated from the thermodynamic equations are listed in Table 3. The positive value of  $\Delta H^0$  indicates that the sorption is endothermic, which is in accordance with the fact that the sorption increases as the reaction temperature increases. A probable interpretation for the positive enthalpy is that the Co(II) ions are completely solvated in water, the hydration sheath of Co(II) is supposed to be destroyed before the ions adsorb onto the  $\beta$ -CD-GO surface, and the energy required for this dehydration process exceeds the energy released when the cations are attached to the solid surface,<sup>32</sup> meaning a high temperature is favored. The negative value of the change in Gibbs free energy ( $\Delta G^0$ ) indicates that the sorption is a spontaneous process under the applied experimental conditions.<sup>33</sup>

As the reaction temperature increases, the values of  $\Delta G^0$  become even more negative, which illustrates that sorption is more efficient at higher temperature. At high temperature, cations are likely to be more desolvated, which favors the sorption reaction.<sup>34</sup> The positive value of the entropy change ( $\Delta S^0$ ) may be attributed to the structure change of the composite complex.<sup>35</sup> It can be concluded that the sorption of Co(II) on  $\beta$ -CD-GO is an endothermic and spontaneous

**Table 3** Thermodynamic parameters of Co(II) sorption on  $\beta$ -CD-GO

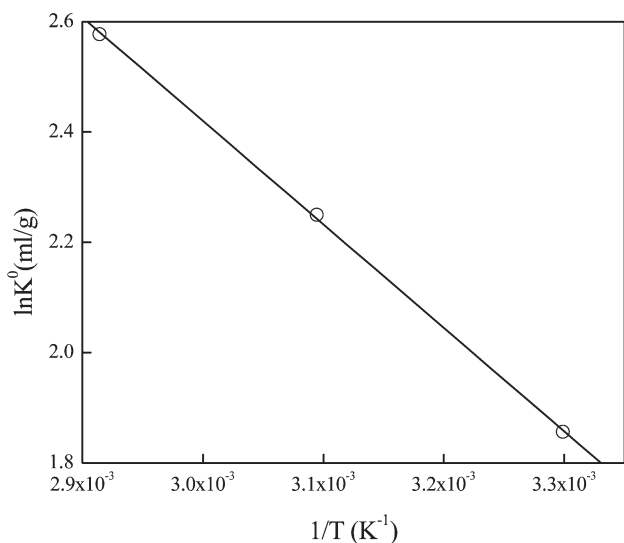
$T$ (K)	$\Delta G^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )
303	-4.68	66.93	15.61
323	-6.04	66.93	15.58
343	-7.35	66.93	15.61

process according to the thermodynamic data of the sorption isotherms.

From the fitting curves and the correlation coefficients listed in Table 4, it is clear that the Langmuir model simulates the experimental data better than the Freundlich model, which indicates that monolayer sorption occurs and the interaction between the ions is weak and can be neglected.<sup>36</sup> The  $C_{s \text{ max}}$  of Co(II) sorption on  $\beta$ -CD-GO at pH  $6.0 \pm 0.1$  and  $T = 303 \text{ K}$  was about  $72.43 \text{ mg g}^{-1}$ , which is much higher than that of Co(II) on GO ( $47.39 \text{ mg g}^{-1}$ ). This means that under the same experimental uncertainties, in comparison to GO, the modified  $\beta$ -cyclodextrins on GO can reduce the amount of sorbent that is needed by  $\sim 35 \text{ wt\%}$ . Moreover, in comparison to the  $C_{s \text{ max}}$  values of Co(II) sorption on common sorbents, such as Al-pillared bentonite ( $38.6 \text{ mg g}^{-1} \text{ Co(II)}$  at pH 6 and  $T = 303 \text{ K}$ ),<sup>37</sup> lemon peel ( $25.6 \text{ mg g}^{-1} \text{ Co(II)}$  at pH 6 and  $T = 298 \text{ K}$ ),<sup>38</sup> activated carbon ( $1.2 \text{ mg g}^{-1} \text{ Co(II)}$  at pH 6 and  $T = 303 \text{ K}$ ),<sup>39</sup> and magnetite-GO ( $12.98 \text{ mg g}^{-1} \text{ Co(II)}$  at pH 6.8 and  $T = 303 \text{ K}$ ),<sup>40</sup> one can see that  $\beta$ -CD-GO has a much higher sorption capacity than other commonly used sorbents. It indicates that  $\beta$ -CD-GO may be a high-efficiency material in the clean-up of heavy metal ion-based pollution.

## 4 Conclusions

The results of SEM, FT-IR, Raman and XPS analysis indicated that  $\beta$ -CD was successfully modified onto the surface of GO. The ionic strength-independent and pH-dependent Co(II) sorption on  $\beta$ -CD-GO indicated that the sorption mechanism of Co(II) featured outer-sphere surface complexation at low pH values, whereas the removal of Co(II) was accomplished by simultaneous precipitation and inner-sphere surface complexation at high pH values. The sorption of Co(II) on  $\beta$ -CD-GO was also influenced by competing ions. The thermodynamic parameters indicated that the interaction of Co(II) with  $\beta$ -CD-GO was an endothermic and spontaneous process. The main sorption mechanism for Co(II) adsorbed onto  $\beta$ -CD-GO was the surface complexation of Co(II) with abundant oxygen-containing functional groups on the surface of  $\beta$ -CD-GO. The maximum sorption capacities ( $C_{s \text{ max}}$ ) of Co(II) on  $\beta$ -CD-GO at pH  $6.0 \pm 0.1$  and  $T = 303 \text{ K}$  was about  $72.43 \text{ mg g}^{-1}$ , which is much higher than that of Co(II) on GO.  $\beta$ -CD-GO exhibits the potential for application as a sorbent in the clean-up of environmental pollution.



**Fig. 11** Linear plots of  $\ln K^0$  vs.  $1/T$  for Co(II) sorption on  $\beta$ -CD-GO.

**Table 4** Parameters of the Langmuir and Freundlich isotherms at different temperatures

Sorbent	<i>T</i> (K)	Langmuir			Freundlich		
		$C_s \text{ max}$ (mg g <sup>-1</sup> )	<i>b</i> (L mg <sup>-1</sup> )	<i>R</i> <sup>2</sup>	$k_F$ (mg <sup>1-<i>n</i></sup> L <sup><i>n</i></sup> g <sup>-1</sup> )	<i>n</i>	$R^2$ (mg <sup>1-<i>n</i></sup> L <sup><i>n</i></sup> g <sup>-1</sup> )
GO	303	47.39	0.983	0.998	6.28	0.562	0.988
β-CD-GO	303	72.43	0.1051	0.997	9.24	0.585	0.977
	323	72.99	0.1696	0.999	14.81	0.475	0.971
	343	84.03	0.2010	0.996	18.95	0.462	0.985

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