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Effects of background electrolytes and ionic strength on enrichment of Cd(II) ions with magnetic graphene oxide–supported sulfanilic acid



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ABSTRACT

To elucidate the influence mechanisms of background electrolytes and ionic strength on Cd(II) removal, the adsorption of Cd(II) onto magnetic graphene oxide–supported sulfanilic acid (MGO–SA) in aqueous solutions containing different types and concentrations of background electrolytes was studied. The results indicate that Cd(II) adsorption was strongly dependent on pH and could be strongly affected by background electrolytes and ionic strength. The Cd(II) removal was decreased with the presence of background electrolyte cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and Ni²⁺), and the divalent cations exerted more obvious influences on the Cd(II) uptake than the monovalent cations at pH 6. Both Cl⁻ and No₃⁻ had negative effects on Cd(II) adsorption because they can form water-soluble metal–anion complexes with Cd(II) ions. The presence of 0.01 mol L⁻¹ Na₃PO₄ reduced the removal percentage of Cd(II) at pH < 5 but extremely enhanced the Cd(II) removal when the pH > 5. The Cd(II) adsorption was sensitive to changes in the concentration of NaCl, NaNO₃, NaClO₄, and Na₃PO₄. Besides, the adsorption isotherm of Cd(II) onto MGO–SA could be well described by the Freundlich model and was also influenced by the type of background electrolyte ions and the ionic strength.

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1. Introduction

Cadmium (Cd) and its compounds were classified as "carcinogenic to humans (Group 1)" by IARC (International Agency for Research on Cancer) [1]. For environmental protection, it is desirable to eliminate Cd(II) ions from wastewater prior to their discharge to the environment. Adsorption is a popular method for the removal of toxic metal ions from wastewater as it is simple and economically viable [2]. It is well known that the effectiveness of an adsorption reaction is determined by a number of variables, including pH, temperature, adsorbate concentration, background electrolyte, and ionic strength [3]. The effects of pH, temperature and adsorbate concentration on adsorption have been fully investigated [3–8]. While in natural water or wastewater systems, several types of background electrolyte ion, such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Cl⁻, NO₃⁻, SO₄²⁻, and PO₄³⁻, are present at various concentrations, which will affect the removal of pollutants [9]. Thus, these conditions should be considered when evaluating Cd(II) adsorption

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capacity of adsorbent or when applying laboratory results to practical projects [10].

The effects of background electrolyte and ionic strength on adsorption of heavy metals are very complicated and this issue has been studied by several authors [6–9.11]. Yang et al. [9] found that type of background anion $(ClO_4^-, Cl^-, NO_2^-, NO_3^-, SO_3^{2-})$, and PO₄³⁻) could not affect adsorption trends and adsorption amounts of Cu(II) onto TiO₂. However, Liu et al. [8] studied the effects of foreign cations and anions on the adsorption of Co(II) to magnetite/ graphene oxide composite (M/GO) and reported that the Co(II) adsorption was reduced due to the influence of foreign ions. Li et al. [7] investigated the effect of ionic strength on the adsorption of Cu(II) to graphene oxide/Fe₃O₄ composites in NaNO₃ solutions and found that Cu(II) adsorption was nearly independent of ionic strength. Yang et al. [6] reported that the adsorption of Pb(II) on carbon nanotubes/polyacrylamide multiwalled composites decreased when the NaClO₄ concentration increased from 0.001 to 0.1 mol L⁻¹. In contrast, the Cu(II) adsorption onto NH₂-MCM-41 was found to increase with the increase of Na₂SO₄ concentration [11]. According to these studies, we can get that background electrolyte ions and ionic strength in the adsorption system have different effects (no impact, improvement, and reduction) on the heavy

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metal adsorption, and these effects depend on a number of factors [12], including (i) the intrinsic nature of adsorbent surfaces, (ii) the chemical properties of adsorbates in aqueous solution, (iii) the chemical properties of cations and anions of background electrolytes, (iv) the pH of aqueous solution, (v) the concentration range of adsorbates. Although many previous studies have given some insights into the influences of background electrolytes and ionic strength on heavy metal adsorption, more researches are still needed in order to have a better understanding of the influence mechanism.

The background cations and anions and their concentrations (ionic strength) in solution may affect the adsorption of heavy metals in several ways [13,14]: (i) the background cations may compete with heavy metal ions for available adsorption sites; (ii) the anions of background electrolytes may form water-soluble metal-anion complexes or precipitates with metal ions. Different background cations have different influences on the heavy metal adsorption due to the different physicochemical properties. Besides, the extent of complexation is different from one anion to another anion, and different metal-anion complexes have the corresponding charges, sizes and affinities to adsorbent surface [12]. Thus, the identification of the chemical species in solution (speciation of the metal ions and the background cations and anions) is very important for understanding the influence mechanism of background electrolytes and ionic strength on heavy metal adsorption.

In a previous study, we reported a method to synthesize a magnetic graphene oxide–supported sulfanilic acid composite (MGO–SA) by reacting aryl diazonium salt of sulfanilic acid with magnetic graphene oxide sheets [3]. This composite was found to be an ideal adsorbent for Cd(II) ions removal because it had a lot of hydroxyl and sulfo groups and could be easily separated by magnetic separation from the medium [15]. The objectives of this study were to: (i) evaluate the influences of background cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and Ni²⁺), background anions (Cl⁻, NO₃⁻, ClO₄⁻, and PO₄³⁻), and ionic strength of four background electrolytes (NaCl, NaNO₃, NaClO₄, and Na₃PO₄) on the adsorption of Cd(II) onto MGO–SA in aqueous solution; (ii) discuss the influence mechanism by analyzing the speciation of the metal ions and the background ions in aqueous solution.

2. Materials and methods

2.1. Materials

All the chemicals used in the experiments were analytical grade. The stock solution (1 g L^{-1}) of Cd(II) was prepared by dissolving pure cadmium powder (1.000 g of pure cadmium powder was dissolved into 20 mL HNO₃ solution (20%) in a 1000 mL flask and Milli-Q water was added up to the mark). The solutions of

different concentrations used in various experiments were obtained by diluting the stock solution.

MGO–SA was synthesized by the procedure reported earlier [3,15]. The first step is to prepare graphene oxide (GO) using a modified Hummers method [4,16,17]. Then, magnetic graphene oxide (MGO) was synthesized by loading magnetic nanoparticles on the GO surface through chemical coprecipitation method [8]. Finally, MGO–SA was prepared by grafting sulfanilic acid on the MGO surface [16].

2.2. Adsorption experiments

All the adsorption experiments were performed according to the batch method in conical flasks on an orbital shaker with a shaking speed of 180 rpm. The stock solution of Cd(II) and the stock suspension of the MGO-SA were added to achieve the desired concentrations of the different components. To investigate the adsorption efficiency of MGO-SA for Cd(II) in the presence of various background electrolyte ions, NaCl, KCl, CaCl₂, MgCl₂, MnCl₂, ZnCl₂, NiCl₂, NaNO₃, NaClO₄ and Na₃PO₄ were added into the conical flasks. Effect of ionic strength on the adsorption was studied by using NaCl, NaNO₃, NaClO₄ and Na₃PO₄ as background electrolytes with variation of concentrations. After mixed for 24 h, the mixture was separated by a magnetic process using a permanent magnet. The Cd(II) concentration in the supernatant was analyzed using flame atomic absorption spectrometry (PerkinElmer AA700, USA). The adsorption capacity (q_e) and the adsorption percentage (R_e) of Cd(II) adsorbed on MGOs/SA were calculated from the difference between the initial concentration (C_0) and the equilibrium concentration (*C_e*) [18].

2.3. Speciation modeling methods

In order to analyze the effects of background electrolyte type and concentrations on cadmium speciation in aqueous solution under different pH conditions, Visual MINTEQ (ver. 3.0) was used for the chemical speciation calculations. The parameters were set as follows: pH was fixed at different values; temperature was 30 °C; ionic strength was to be calculated depending on components added; different concentrations of Cd(NO₃)₂ and background electrolytes were added as components.

3. Results and discussion

3.1. Effects of pH and background electrolyte cations on Cd(II) adsorption

The effects of pH and background electrolyte cations on Cd(II) adsorption as a function of pH were examined by using two monovalent (Na⁺ and K⁺) and five divalent (Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and



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Fig. 1. (a) Effects of different cations (Na⁺, K⁺, and Ca²⁺) in background solution (concentration = 0.01 mol L⁻¹) on Cd(II) adsorption onto the MGO–SA at different pH; (b) effects of Na⁺, K⁺, Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and Ni²⁺ (concentration = 0.01 mol L⁻¹) on Cd(II) adsorption at pH 6: $C_{0(Cd)}$ = 10 mg L⁻¹, m/V = 0.34 g L⁻¹, T = 30 °C, t = 24 h.

Ni²⁺) cations. The adsorption percentages of Cd(II) as a function of pH in 0.01 mol L^{-1} NaCl, KCl, and CaCl₂ solutions are shown in Fig. 1a. The adsorption of Cd(II) on MGO-SA increased with the increase of pH values from 2 to 11 both in the absence and presence of background electrolytes. It is well known that the solution pH affects the speciation of ions and the surface charge of adsorbent [19]. Percentages of Cd(II) species in aqueous solution without background electrolyte were computed by the program Visual MINTEQ, and the results are demonstrated in Table S1 (Supplementary data). We can see that the predominant Cd(II) species is Cd²⁺ when the pH < 8, and the main Cd(II) species are Cd^{2+} , $Cd(OH)^+$, $Cd(OH)_2(aq)$ and $Cd(OH)_{\overline{3}}$ in the pH range of 8–11. The pH_{pzc} value obtained from the zeta potential for MGO-SA is 4.22. The uptake of Cd(II) was small at pH < 4.22, which may be due to that the positive Cd^{2+} was difficult to be adsorbed by the positively charged surface of MGO-SA because of the electrostatic repulsion [5]. Coordination and ion exchange may be the two main mechanisms for the Cd(II) adsorption onto the MGO-SA in this pH range. As the pH increased from 4.22 to 8, the deprotonated sites (negatively charged) of the MGO-SA surface were more available to capture the positively charged Cd(II) ions (Cd²⁺) by electrostatic attraction, thereby resulting in the increase of Cd(II) adsorption. At pH > 8, the high removal percentage was mainly due to the cooperating role of precipitation of Cd(OH)₂ and adsorption of Cd²⁺, Cd(OH)⁺, Cd(OH)₃ on MGO–SA by electrostatic attraction.

From Fig. 1a, we can also find that the Cd(II) adsorption was strongly affected by the background cations. At pH < 9.5, the

influences background cations on the Cd(II) adsorption under the same pH value were in the following sequence: $CaCl_2 > KCl > NaCl$. However, the influence of NaCl on the Cd(II) adsorption was similar to KCl at pH > 9.5. Yang et al. [14] investigated the influences of background cations on radionuclide ⁶³Ni(II) adsorption onto mordenite and also found a similar result. Distributions of Cd(II), Na, K, and Ca species in solution with the addition of 0.01 mol L^{-1} NaCl, KCl, and CaCl₂ as a function of solution pH were obtained by using the program Visual MINTEQ and the results are shown in Fig. 2. As shown in Fig. 2a-c, the main Cd(II) species in the two solutions were Cd^{2+} and $CdCl^{+}$ at pH < 8, while Cd^{2+} , $CdCl^{+}$, $Cd(OH)^{+}$ and $Cd(OH)_{2}(aq)$ were the predominant species in the pH range of 8–11. The Na⁺, K⁺ and Ca²⁺ were the main background electrolyte cations species in the three solutions at pH < 11 (Fig. 2d-f). There are two possible reasons for the reduction of Cd(II) removal in the presence of NaCl. KCl. and CaCl₂: (i) The ion with higher valence is more easily and strongly adsorbed onto adsorbent by electrostatic attraction [18]. In the solution with background electrolytes (NaCl, KCl, and CaCl₂), the metal chloride (CdCl⁺), which was one of the main Cd(II) species, had lower affinity to the negatively charged MGO–SA surface than the Cd²⁺, leading to the reduction in the adsorption capacity of MGO-SA for Cd(II) ions. (ii) The competition of Na⁺, K⁺, and Ca²⁺ with the Cd(II) ions for adsorption sites of MGO-SA resulted in the decrease of Cd(II) adsorption [20]. We can see that the distributions of Cd(II) and Na⁺ species in 0.01 mol L^{-1} NaCl solution (Fig. 2a and d) were quiet similar to the distributions of Cd(II) and K⁺ species in 0.01 mol L⁻¹ KCl solution (Fig. 2b and e). However, the influence of KCl on Cd(II)



Fig. 2. Distribution of Cd(II) species [(a) NaCl, (b) KCl, and (c) CaCl₂] and background electrolyte cations species [(d) Na, (e) K, and (f) Ca] in solution with the addition of 0.01 mol L⁻¹ NaCl, KCl, and CaCl₂ as predicted by Visual MINTEQ: $C_{0(Cd)} = 10 \text{ mg L}^{-1}$, $T = 30 \degree$ C.

Table 1

Percentages of Cd(II) species and electrolyte cations species (computed by the program Visual MINTEQ) in aqueous solution with different background electrolytes (0.01 mol L⁻¹) at pH 6: C_{0(Cd)} = 10 mg L⁻¹, T = 30 °C.

Background electrolytes	Percentage of Cd(II) species (%)				Percentage of electrolyte cations species		
	Cd ²⁺	CdCl⁺	$CdCl_2(aq)$	CdNO ₃ ⁺			
NaCl	60.50	38.18	1.30	0.02	99.62% Na ⁺ , 0.38% NaCl (aq)		
KCl	60.50	38.18	1.30	0.02	99.60% K ⁺ , 0.40% KCl (aq)		
CaCl ₂	48.79	48.31	2.89	0.01	97.40% Ca ²⁺ , 2.57% CaCl ⁺ , 0.03% CaNO ₃ ⁺		
MgCl ₂	48.92	48.20	2.87	0.01	96.00% Mg ²⁺ , 4.00% MgCl ⁺		
MnCl ₂	48.65	48.42	2.91	0.01	98.94% Mn ²⁺ , 1.02% MnCl ⁺ , 0.01% MnNO ⁺ ₃ , 0.03% MnCl ₂ (aq)		
ZnCl ₂	48.83	48.27	2.88	0.01	96.88% Zn ²⁺ , 2.96% ZnCl ⁺ , 0.09% ZnOH ⁺ , 0.02% ZnNO ₃ ⁺ , 0.05% ZnCl ₂ (aq)		
NiCl ₂	48.59	48.47	2.93	0.01	99.58% Ni ²⁺ , 0.39% NiCl ⁺ , 0.02% NiNO ₃ ⁺ , 0.01% NiOH ⁺		

adsorption was stronger than that of NaCl at pH < 9.5 (Fig. 1a). This may be due to the less competitive nature of Na^+ with Cd(II) ions for adsorption sites as compared to K⁺ [21]. The radii of hydration for Na^+ and K^+ are 2.76 Å and 2.32 Å, respectively [22]. The Na^+ formed only outer-sphere complex with MGO-SA surface due to its large hydrated ionic size, whereas K⁺ was able to form inner-sphere complexes [21]. At higher pH values (pH > 9.5), no drastic difference of Cd(II) adsorption onto MGO-SA in the NaCl and KCl solutions was observed, which may be due to the surface precipitates at high pH values [8]. The influence of CaCl₂ on Cd(II) adsorption was stronger than those of NaCl and KCl. There are three possible reasons: (i) The percentage of CdCl⁺ in CaCl₂ solution is higher than those in NaCl and KCl solutions, which reduced the electrostatic attraction and resulted in the more reduction of Cd(II) adsorption. (ii) The bivalent Ca²⁺ was much more easily to be adsorbed on the adsorbent surface than monovalent Na^+ and K^+ due to the strong electrostatic attraction [8]. (iii) One Na⁺ or K⁺ adsorbed on the MGO–SA surface only occupied one adsorption site, while Ca²⁺ could take up two sites, which resulted in a larger decrease in the Cd(II) removal in the presence of CaCl₂ [14]. From Fig. 1b, we can also see that the divalent cations (Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and Ni²⁺) had bigger influence on the Cd(II) uptake than the monovalent cations (Na⁺ and K⁺) at pH 6, and only slight differences of Cd(II) adsorption onto MGO-SA in the CaCl₂, MgCl₂, MnCl₂, ZnCl₂, and NiCl₂ solutions were observed. The percentages of Cd(II) species and electrolyte cation species in aqueous solution with different background electrolytes at pH 6 were calculated by the program Visual MINTEQ and the results are demonstrated in Table 1. The distributions of Cd(II) species in CaCl₂, MgCl₂, MnCl₂, ZnCl₂, and NiCl₂ solutions were quiet similar. The adsorption capacity of MGO-SA for Cd(II) ions showed very little variation as the divalent background cation changed (Fig. 1b), which may be attributed to the different distributions of Ca, Mg, Mn, Zn, and Ni species in aqueous solution (Table 1) and the various physicochemical properties of these species.

3.2. Effects of background electrolyte anions on Cd(II) adsorption

Fig. 3 shows the effect of background electrolyte anions on the Cd(II) adsorption onto MGO-SA as a function of pH value in 0.01 mol L⁻¹ NaCl, NaNO₃, NaClO₄ and Na₃PO₄ solutions, respectively. As can be observed, different background electrolyte anions had different influences on the Cd(II) removal. The presence of NaCl, NaNO₃ and NaClO₄ in the aqueous solution had significant inhibitory effects on the uptake of Cd(II) by MGO-SA at various pH values, and the adsorption of Cd(II) under the same pH value was in the following sequence: NaCl < NaNO₃ < NaClO₄. A similar trend for the adsorption of Co(II) onto Magnetite/Graphene oxide composite was also reported [8]. These phenomena may be mainly attributed to the formation of water-soluble metal-anion complexes and the competition of Na⁺ with the Cd(II) ions for available adsorption sites on the MGO-SA surface [23]. The Cd(II) species at various pH values in the presence of NaCl, NaNO₃ and NaClO₄ were calculated by Visual MINTEQ and the results are shown in Tables S1, S2 and S3 (SD), respectively. As shown in Tables S1 and S2, CI^- and NO_3^- could form water-soluble metal-anion complexes with Cd(II) ions (e.g., CdCl⁺ and CdNO₃⁺), which resulted in the decrease of electrostatic attraction between the positively charged Cd(II) ions and the negatively charged surface of MGO–SA, thereby inhibiting the adsorption of Cd(II). The Cl⁻ had a larger influence on the Cd(II) uptake than NO_3^- , mainly due to the more significant tendency of Cl⁻ to complex Cd(II) ions. What's more, the competition of Na⁺ with the Cd(II) ions for adsorption sites also leaded to the decrease of the removal percentage of Cd(II). Thus, the inhibition of Cd(II) adsorption by the NaClO₄ may be mainly due to the competition of Na⁺ with the Cd(II) ions for adsorption sites.

The influence of 0.01 mol L^{-1} Na₃PO₄ on the Cd(II) removal was complicated (Fig. 3). The removal percentage of Cd(II) ions was reduced by the Na_3PO_4 at pH < 5 but extremely enhanced when the pH > 5. This phenomenon can be explained by the competition of high concentration of Na⁺ ions with the Cd(II) ions for adsorption sites in low pH environment and the formation of precipitates in higher pH environment. As seen from Table S4 (SD), the main Cd(II) species in the solution was Cd^{2+} (>85%) at pH < 5, while the CdHPO₄(aq) was the predominant Cd(II) species at higher pH values (5 < pH < 10), and Cd(II) mainly existed in the species of CdHPO₄(ag) and Cd(OH)₂ at pH > 10. Therefore, in low pH environment, the PO₄³⁻ had slight influence on the adsorption process, while the concentration of Na^+ (0.03 mol L^{-1}) was very high, and these positively charged ions could compete with the Cd²⁺ for the available adsorption sites. The formation of CdHPO₄ and Cd(OH)₂ may be the reasons for explaining the enhanced adsorption of Cd(II) onto MGO-SA in the presence of Na_3PO_4 at pH > 5 [13].

3.3. Effect of ionic strength on Cd(II) adsorption

The ionic strength of an aqueous solution is a very important variable that affects the adsorption of heavy metal ions at the solid–liquid interface [24]. The effect of ionic strength on Cd(II)



Fig. 3. Cd(II) adsorption on MGO–SA at different pH without and with addition of 0.01 mol L⁻¹ NaCl, NaNO₃, NaClO₄, and Na₃PO₄: $C_{0(Cd)} = 10 \text{ mg L}^{-1}$, $m/V = 0.34 \text{ g L}^{-1}$, $T = 30 \degree$ C, t = 24 h.



Fig. 4. Effects of concentrations of (a) NaCl (0, 0.001, 0.01, and 0.1 mol L^{-1}), (b) NaNO₃ (0, 0.001, 0.01, and 0.1 mol L^{-1}), (c) NaClO₄ (0, 0.001, 0.01, and 0.1 mol L^{-1}), and (d) Na₃PO₄ (0, 0.001, 0.005, and 0.01 mol L^{-1}) on Cd(II) adsorption onto MGO–SA as a function of pH: $C_{0(Cd)} = 10 \text{ mg } L^{-1}$, $m/V = 0.34 \text{ g } L^{-1}$, $T = 30 \degree$ C, t = 24 h.

uptake was studied by conducting batch experiments at different concentrations of NaCl, NaNO₃, NaClO₄ and Na₃PO₄, and the obtained results are shown in Fig. 4. The increases in the concentrations of NaCl, NaNO₃ and NaClO₄ from 0 to 0.1 mol L⁻¹ resulted in a significant decrease of the Cd(II) adsorption onto MGO-SA, which may be attributed to the following four possible reasons: (i) When the concentrations of NaCl, NaNO₃ and NaClO₄ were increased from 0 to 0.1 mol L⁻¹, the solution contained more positively charged Na⁺, which competed with more Cd(II) ions for the available adsorption sites of MGO-SA, thereby resulting in the decrease of the Cd(II) uptake. (ii) As seen from Tables S1-3 (SD), the proportion of Cd²⁺ species and water-soluble metal-anion complexes (CdOH⁺, CdCl⁺, and CdNO₃⁺) decreased when the concentration of background electrolytes increased, which indicated that there were more CdOH⁺, CdCl⁺, and CdNO₃⁺ species in the solution with higher concentration of background electrolytes. However, these species were more difficult than the bivalent Cd²⁺ to be attracted by the negatively charged MGO-SA surface, which reduced the removal percentage of Cd(II). (iii) The percentage of the $Cd(OH)_2$ (aq) decreased with the increase of NaCl (Table S1), NaNO₃ (Table S2) and NaClO₄ (Table S3) concentrations, which may be one of the reasons for the decrease of Cd(II) adsorption at high ionic strength in high pH environment. (iv) The particle aggregation of MGO-SA increased when the concentrations of the NaCl, NaNO₃ and NaClO₄ were increased from 0 to 0.1 mol L^{-1} due to the enhancement of electrostatic repulsion, which then reduced the available adsorption sites, thereby decreasing the uptake percentage of Cd(II) [5,25].

As seen from Fig. 4d, the adsorption of Cd(II) was significantly influenced by the Na₃PO₄ in the adsorption system at various pH values, particularly in the high pH environment. There was a decrease in Cd(II) adsorption when the Na₃PO₄ concentration increased from 0.001 to 0.1 mol L⁻¹ at pH < 7.5, while in the system with different concentrations of Na₃PO₄ (0.001, 0.005, and 0.01 mol L⁻¹), nearly all the Cd(II) ions were removed by the MGO–SA at pH > 7.5. The presence of 0.001 mol L⁻¹ Na₃PO₄ improved the adsorption in a wide pH range. However, the presence of 0.005 and 0.01 mol L⁻¹ Na₃PO₄ slightly inhibited the Cd(II)

uptake at low pH values but significantly enhanced the adsorption of Cd(II) at higher pH values. The Cd(II) species predicted by Visual MINTEQ in the presence of 0.001, 0.005, and 0.01 mol L⁻¹ Na₃PO₄ are presented in Table S4. The percentage of CdHPO₄(aq) increased with the increase of Na₃PO₄ concentration. However, the percentage of Cd²⁺ and Cd(OH)₂(aq) decreased as the Na₃PO₄ concentration increased. Moreover, the concentration of Na⁺ in the solutions increased from 0.003 to 0.03 mol L⁻¹ when the Na₃PO₄ concentration increased from 0.001 to 0.01 mol L⁻¹, which leaded to an increase in the competition of Na⁺ with Cd(II) ions for the adsorption sites. Because of the above reasons, the adsorption of



Fig. 5. Effects of (a) background electrolytes and (b) NaCl concentration on the Freundlich adsorption isotherms for Cd(II) adsorption onto MGO–SA: m/V = 0.34 g L⁻¹, T = 30 °C, t = 24 h, pH = 6.00 ± 0.01 .

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Background electrolytes	$0 \text{ mol } L^{-1} \text{ NaCl}$	$0.001 \text{ mol } \text{L}^{-1} \text{ NaCl}$	$0.01 \text{ mol } \text{L}^{-1} \text{ NaCl}$	$0.01 \text{ mol } \text{L}^{-1} \text{ NaNO}_3$	$0.01 \text{ mol } \text{L}^{-1} \text{ KCl}$
Langmuir isotherm					
$q_{max} (\mathrm{mg}\mathrm{g}^{-1})$	54.83	58.22	47.11	55.35	51.64
$K_L (L mg^{-1})$	0.081	0.049	0.033	0.028	0.020
R^2	0.910	0.933	0.980	0.952	0.976
Freundlich isotherm					
K _F	9.97	6.91	3.84	3.99	2.52
n	2.69	2.24	1.98	1.90	1.72
R^2	0.992	0.977	0.983	0.985	0.986
Temkin isotherm					
$a_T (L g^{-1})$	1.81	0.815	0.463	0.521	0.369
b_T (k[mol ⁻¹)	0.267	0.232	0.275	0.257	0.285
R^2	0.929	0.933	0.960	0.918	0.925

 Table 2

 Isotherm parameters for adsorption of Cd(II) onto MGO–SA in the presence of different concentration of NaCl and different kind of background electrolytes.

Cd(II) in 0.005 and 0.01 mol L⁻¹ Na₃PO₄ solutions was lower than that in 0.001 mol L⁻¹ Na₃PO₄ solution at pH < 7.5. The Cd(II) adsorption in 0.001, 0.005, and 0.01 mol L⁻¹ Na₃PO₄ solutions was similar at pH > 7.5, which may be due to the formation of large amount of CdHPO₄ and Cd(OH)₂ [8].

3.4. Effects of background electrolytes and ionic strength on adsorption isotherms

The adsorption isotherm indicates how the adsorption ions distribute between the liquid phase and the solid phase after the adsorption process reaches an equilibrium state. The experimental data for Cd(II) adsorption onto MGO-SA in the presence of different background electrolytes (0.01 mol L^{-1} NaCl, NaNO₃ and KCl) and different ionic strength (0, 0.001 and 0.01 mol L⁻¹ NaCl) at 30 °C were analyzed by using the Langmuir [26,27], Freundlich [28] and Temkin [29] isotherm models. These adsorption isotherms obtained by the nonlinear method are shown in Figs. S1, 5, and S2, respectively, and the relative parameters calculated from the three models are listed in Table 2. We can see that all the correlation coefficient R^2 values of Freundlich model are higher than those of Langmuir model and Temkin model, which indicated that Freundlich model was more suitable for the adsorption process. Gong et al. [30] also reported that Freundlich adsorption model better explained the adsorption of Cu²⁺ on LDH-NCs@CNs. The better fitting of the Freundlich isotherm model may be due to the heterogeneous distribution of active adsorption sites on the MGO-SA surface [30,31]. All the values of Freundlich constant n (Table 2) were within the beneficial range from 1 to 10, indicating the beneficial adsorption [30,32]. The Freundlich constant K_F indicates the adsorption capacity of the adsorbent [33]. The values of K_F increased as the concentration of NaCl increased, which indicated a negative effect of ionic strength on the adsorption process of Cd(II) onto MGO–SA. From Table 2, we can also see that the K_F value was the highest in 0.01 mol L⁻¹ NaNO₃ solution, and was the lowest in 0.01 mol L⁻¹ KCl solution, indicating that the influence of KCl on Cd(II) uptake was stronger than those of NaNO₃ and NaCl.

4. Conclusions

The MGO–SA can be used as an adsorbent for Cd(II) ion removal from aqueous solution, and the adsorption capacity of MGO–SA for Cd(II) increases as the pH value increases from 2 to 11. The possible sequestration mechanisms of Cd(II) ions at different pH values include coordination, ion exchange, electrostatic attraction, and precipitation. The divalent background electrolyte cations (Ca²⁺, Mg²⁺, Mn²⁺, Zn²⁺, and Ni²⁺) have bigger influence on Cd(II) adsorption than the monovalent cations (Na⁺ and K⁺) at pH 6. The inhibitory effect of NaCl, NaNO₃, and NaClO₄ on Cd(II) uptake is in the following order: NaCl > NaNO₃ > NaClO₄. The removal of Cd(II) ions is inhibited by the presence of 0.01 mol L⁻¹ Na₃PO₄ at low pH values due to competition of high concentration of Na⁺ with the Cd(II) ions for adsorption sites, but it is improved at high pH values because of the formation of CdHPO₄ and Cd(OH)₂ precipitates. Besides, the Cd(II) adsorption onto MGO–SA decreases with the increase in the ionic strength of NaCl, NaNO₃ and NaClO₄. The presence of different Na₃PO₄ concentrations has different impacts (improve or reduce) on the Cd(II) adsorption at various pH values. The adsorption isotherms are fitted better by the Freundlich model, suggesting that Cd(II) adsorption on MGO–SA is heterogeneous coverage. What's more, the adsorption isotherms can be affected by background electrolytes and ionic strength.

These results reinforce the fact that water quality conditions play a critical role in MGO-SA adsorption performance. The program Visual MINTEQ is a useful tool for analyzing the speciation of the heavy metal ions and the background ions, which provides valuable information for investigating the influence mechanism of foreign ions on the adsorption process. The background electrolyte cations affect the Cd(II) removal mainly by competing for available adsorption sites. The background electrolyte anions can form metal-anion complexes with Cd(II) ions, which limits the transfer rate of Cd(II) ions from solution to the adsorbent surface. Previous studies have shown that the presence of various concentrations of background electrolytes in aqueous solution could affect the adsorption characteristics of heavy metals on different materials [6,8,9,11,14,18]. The findings of this research amplify the understanding of the influence mechanism of background electrolyte ions and ionic strength on the adsorption of heavy metals. This work is important for the application of adsorption technology in wastewater treatment projects. However, further studies should be performed to investigate the effect of organic ligands on the adsorption of heavy metals and to reduce the preparation cost of MGO-SA.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2014.08.054.

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