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A novel process for bromate removal from water using calcined Zn–Al layered double hydroxides

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ABSTRACT

Zn–Al layered double hydroxides (Zn–Al LDHs) and their calcined products (Zn–Al CLDHs) were synthesized and used to remove bromate. The factors influencing the bromate adsorption were discussed. The process of bromate adsorption by Zn–Al CLDHs samples is rapid. As much as 98% of the bromate can be effectively removed under the reaction condition of Zn–Al CLDHs dosage of 0.8 g/L, neutral pH, reaction temperature of 293 K, and initial bromate concentration of 100 μg/L. Moreover, the adsorption isotherms of bromate adsorption on CLDHs are well fitted by the Freundlich equation, and the process of bromate adsorption by Zn–Al CLDHs can be regarded as an exothermic reaction. The regenerated Zn–Al CLDHs samples are also effective in bromate adsorption, which suggests that Zn–Al CLDHs have the potential for reuse. The results of this study suggest that Zn–Al CLDHs show potential for developing a simple process for a field application to remove bromate from water.

Keywords: Bromate; Isotherms model; Regeneration; Thermodynamics; Zn–Al layered double hydroxides

1. Introduction

Bromate is rarely present in natural water but may be formed during the oxidation of source water containing the bromide ion [1,2]. Wu and his coworkers have detected bromate in tap water, groundwater, and bottled water in China, with concentrations ranging <0.35–28.4 μg/L [3]. Related studies have also been conducted on bottled water and drinking water in Canada, France, and the USA [4–6].

To remove bromate from drinking water, increasing approaches have been employed, such as activated carbon reduction [7–9], zero-valent iron reduction [10,11], metal oxides or metal hydroxides adsorption [12–14], and catalytic hydrogenation [15,16]. However, the release of biomass and excessive organic compounds during the activated carbon reduction process limits its practical application. Although zero-valent iron reduction provides a more efficient and cost–effective approach to reduce bromate, additional

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treatment processes are generally necessary for the removal of Fe^{2+} formed in the reaction process.

Layered double hydroxides (LDHs), which consist of positively charged sheets of brucite-like hydroxides and numerous charge-balancing anions located in the hydrated interlayer regions, have recently proved to be excellent and effective adsorbents for capturing anions such as phosphate [17], arsenate [18], nitrate [19,20], and terephthalate anions [21]. In contrast to other adsorbents, calcined layered double hydroxides (CLDHs) adsorb anions from aqueous solutions by structural reconstruction, also known as the "memory effect," which makes it possible to be reused. These LDHs and CLDHs have been studied as promising materials for the sorption of harmful anions. However, to the best of our knowledge, the literature on bromate removal by LDHs is very limited. Only Mg/Al CLDHs [22–24] and Fe–Al LDHs [25–27] have been found to be used for bromate removal from water. In addition, no information on bromate removal using carbonate $\left(CO_3^{2-}\right)$intercalated Zn–Al CLDHs is available.

In this study, we synthesized and characterized a series of Zn–Al CLDHs, and investigated the influencing factors of bromate removal, such as pH, reaction temperature, and the amount of CLDHs and coexisting anions in the solution. We also studied an adsorption isotherm model and the thermodynamics involved in bromate removal. Moreover, the stability and regenerative ability of Zn–Al CLDHs were also examined. The objective of this study was to achieve the optimal conditions and factors influencing the bromate removal by Zn–Al CLDHs, which can provide a basic guidance for the further application of Zn–Al CLDHs in bromate removal.

2. Experimental

2.1. Zn–Al CLDHS preparation and characterization

A series of Zn–Al LDHs samples were prepared by a co-precipitation method and subsequent hydrothermal treatment. The samples were designated as Zn–Al αLDHs, where *α* represents the starting molar ratios of Zn/Al (α = 2, 3, and 4). To obtain CLDHs, the Zn–Al αLDHs samples were further calcined at 500℃ for 4 h in a muffle furnace. Both Zn–Al αLDHs samples and αCLDHs samples were stored in capped bottles for further use.

Zn–Al LDHs and CLDHs samples were characterized using an X'Pert PRO X-ray diffraction (XRD) instrument. XRD analysis was conducted in ambient air with Cu Kα (1.540598 Å) using a wide-angle goniometer operated at 40 kV and 40 mA. Patterns were collected in the range of 10.0–70.0° (2θ), and the XRD data were matched with Joint Committee on Powder Diffraction Standards data files.

2.2. Chemical analysis

Samples were periodically taken from the suspension and analyzed for bromate using an ICS-2000 ion chromatograph (IC, Dionex, USA). The concentrations of the Zn and Al ions were measured using a NexIon 300Q inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, USA). The solution pH was periodically monitored with a pH electrode and a pH meter (Orion 3 Star, USA).

2.3. Adsorption study

The batch adsorption experiments were carried out in a 500 mL reactor at constant temperature. A bromate solution with a predetermined concentration and Zn–Al 2CLDHs were added to the reactor. This solution was stirred for 24 h to achieve complete equilibrium. Before the experiments, the pH was adjusted by adding NaOH or HCl solution, and no buffer was added during the experiments. The solution temperature was controlled using a pot-style water bath (DFY-5). Samples were periodically extracted and then analyzed for bromate, Zn, and Al. All experiments were performed in triplicate.

Unless otherwise specified, all experiments were carried out at room temperature and a pH value of 6.9. The equilibrium bromate adsorption capacity q_e (μmol/g) was calculated by $q_e = (C_0 - C_e)\ V/m$, where C_0 (μmol/L) and C_e (μmol/L) represent the initial and equilibrium bromate concentrations, respectively; m is the mass of Zn–Al αCLDH(T); and V is the volume of solution, in L.

2.4. Regeneration study

To evaluate the regeneration ability of CLDHs, Zn–Al 2CLDH+ samples (obtained after adsorption of bromate with Zn–Al 2CLDHs) were regenerated by the calcination process at 500℃. The bromate adsorption experiments performed by the regenerated materials followed the steps described in 2.3. The concentrations of BrO_3^-, Zn, and Al were determined, and the bromate removal efficiency by the regenerated materials was calculated.

3. Results and discussion

The effect of the Zn/Al αLDHs calcination temperature and Zn/Al molar ratio has been examined in our previous work [28]. The appropriate Zn/Al molar ratio and calcination temperature were determined as 2 and 500℃, respectively. Therefore, Zn–Al 2CLDHs was chosen as the adsorbent to evaluate its performance in bromate removal in this study. A typical profile of bromate adsorption by 2CLDHs is presented in Fig. 1.

It can be seen that Zn–Al 2CLDHs samples have good adsorption ability and can effectively decrease bromate concentration from an initial concentration of 100 μg/L to less than 0.5 μg/L within 3 h. Moreover, the concentration of Zn and Al ions was below 1.0 and 0.2 mg/L, respectively, which suggests that Zn–Al CLDHs are stable materials in aqueous media.

3.1. XRD characteristic of Zn–Al LDHs and CLDHs

The XRD patterns of Zn–Al 2LDHs, Zn–Al 2CLDHs, and Zn–Al 2CLDH+ (obtained after adsorption of bromate with Zn–Al 2CLDHs) are shown in Fig. 2. As shown in Fig. 2, the XRD patterns of Zn–Al 2LDHs exhibited symmetric and sharp peaks at low 2υ values, which were characteristic diffraction peaks of hydrotalcite-like compounds. However, some extremely weak diffraction peaks ascribed to the phase of ZnO appeared in the 2CLDHs sample. In addition, the XRD pattern of the 2CLDH+ sample exhibited the same peaks as those of 2LDHs. This means the reconstruction of the hydrotalcite-like structure has been further verified on 2CLDHs after the adsorption of bromate, which owes to its unique property of "memory effect."

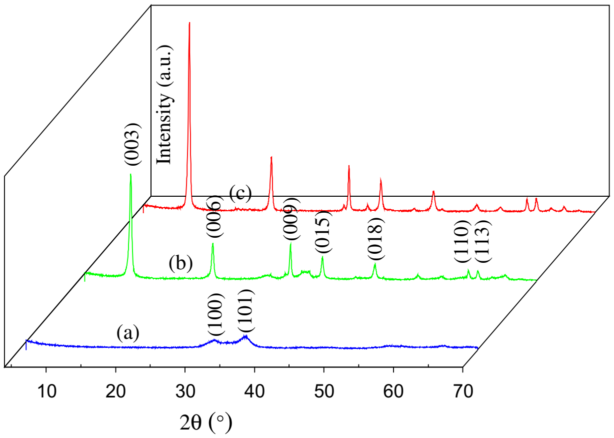

Fig. 2. XRD patterns of Zn–Al 2LDHs, 2CLDHs, and 2CLDH+ samples: (a) 2CLDHs, (b) 2CLDH+, and (c) 2LDHs.

3.2. Effect of dosage on bromate removal

To examine the effect of dosage on bromate removal, different dosage of 2CLDHs ranging 0.2–1.0 g/L was dispersed in a bromate solution (100 μg/L) with stirring for 3 h at room temperature. The results are shown in Fig. 3.

It can be seen that bromate removal efficiency increased with the increasing dosage of 2CLDHs. Bromate removal efficiency increased 88.8–100% with the dosage of 2CLDHs increasing 0.2–1.0 g/L, respectively. However, when the dosage was over 0.6 g/L, no significant improvement in bromate removal efficiency can be seen. Meanwhile, the adsorption capacity of the material decreased with the increasing dosage 0.2–1.0 g/L. This can be explained by the

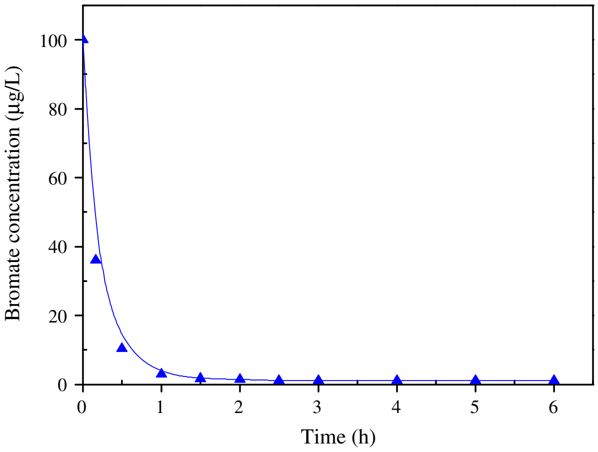

Fig. 1. Effect of contact time on bromate adsorption by Zn–Al 2CLDHs (initial $BrO_3^- = 100$ μg/L, 2CLDHs = 0.8 g/L, temperature = 293 K, pH 6.9).

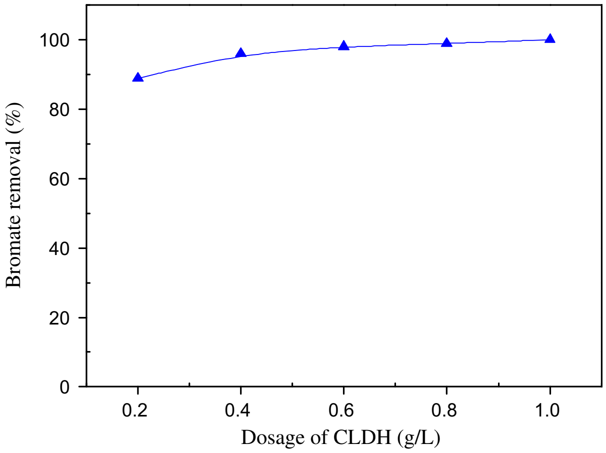

Fig. 3. Effect of dosage of Zn–Al 2CLDHs on bromate removal (initial $BrO_3^- = 100$ μg/L, temperature = 293 K, pH 6.9).

surface sites heterogeneity theory [29], in which the surface is composed of many active sites with a spectrum of binding energies. With the low adsorbent dosage, all types of surface-active sites are involved in adsorption and the surfaces are saturated quickly, thus showing a high adsorption capacity. However, with the high adsorbent dosage, the availability of higher energy sites decreases with the increasing amounts of lower energy sites involved in adsorption, thereby resulting in a lower adsorption capacity.

3.3. Effect of pH on bromate removal

Fig. 4 summarizes the results of the effect of pH value on bromate removal. It indicates that no significant effect of pH was observed on bromate removal at pH values 4.5–9.5, with a bromate removal efficiency of 91–98% under the specified experimental conditions. A similar influence of pH on bromate adsorption was observed for Mg–Al LDH (OH or Cl) in a previous report [24].

However, a remarkable drop of 40% in the bromate removal efficiency was observed when the pH value increased 9.5–10.5. This can be explained by the decrease in electrostatic interactions between the Zn–Al CLDH and bromate due to the negatively charged hydrated surface of 2CLDHs, when pH values were higher than the isoelectric point (IEP) [30]. The zeta potentials of Zn–Al 2CLDHs samples at different pH values were also analyzed in this study by a Zetasizer Nano ZS90 (Malvern Instruments Inc, England). The IEP for Zn–Al 2CLDHs samples was found to be at a pH of approximately 10.8. In addition, the initial pH of this working solution (6.9) is lower than the IEP of Zn–Al 2CLDHs. A high zeta potential of +40 mV was observed for this material corresponding to the working solution pH of 6.9, which indicates that the positively charged Zn–Al 2CLDHs have a strong electrostatic attraction toward bromate.

Furthermore, a significant release of aluminum ion was detected at high pH values (10.5, 11.5). The concentration of aluminum ion in solution exceeded 0.2 mg/L, which indicated that the Zn–Al CLDHs had partly dissolved. This might also lead to a decrease in bromate removal efficiency.

In addition, the concentration of Zn and Al ions can meet standards for drinking water quality (GB5749-2006) at a pH value less than 9.5. This can be explained by the fact that the equilibrium pH was approximately 8.0, which indicated that the layered materials were a type of amphoteric compound, and no Zn–Al CLDHs samples were dissolved at this pH value. Moreover, the 2CLDHs exhibited the maximum bromate removal efficiency at a pH value of 6.5 or 7.5, which means that the 2CLDHs have a high adsorption activity under neutral conditions. This feature will provide a strong incentive for its application in water treatment, because the pH value of most water sources remains neutral to slightly alkaline.

3.4. Effect of reaction temperature and the initial bromate concentration

The effect of the reaction temperature on bromate removal is shown in Fig. 5. The results illustrate that bromate adsorption decreases 98–84% with an increase in temperature 293–323 K at the initial bromate concentration of 100 μg/L. That is, the interaction between bromate and Zn–Al CLDHs is an exothermic reaction,

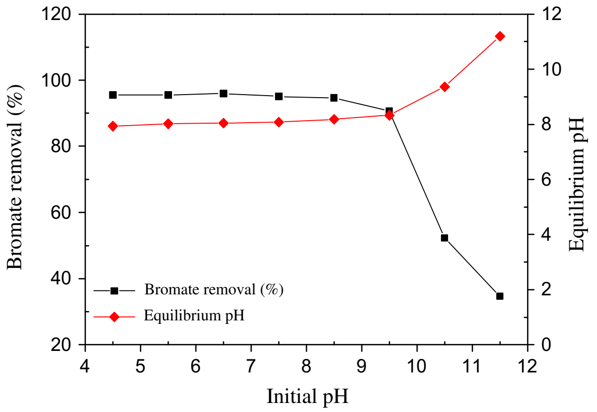

Fig. 4. Effect of initial pH on bromate removal by 2CLDHs and equilibrium pH (2CLDHs = 0.8 g/L, initial BrO_3^- = 100 μg/L, temperature = 293 K).

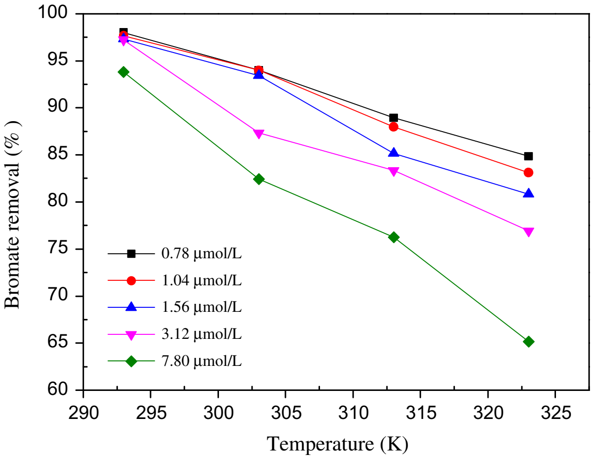

Fig. 5. Effect of temperature on bromate removal by 2CLDHs (initial BrO_3^- = 100 μg/L, 2CLDHs = 0.8 g/L, pH 6.9).

and the rise of reaction temperature may result in reducing the bromate adsorption.

In addition, when initial bromate concentration increased 100–1,000 µg/L (0.78–7.8 µmol/L) bromate removal efficiency showed no significant decrease at the reaction temperature of 293 K, while when the reaction temperature was 323 K, the bromate removal rate decreased by approximately 30%. This means that the initial bromate concentration has little influence on bromate removal at room temperature.

3.5. Adsorption isotherms

The popular adsorption isotherm models including the Langmuir and Freundlich models have been used to analyze the adsorption data [31].

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \tag{1}$$

$$\log q_e = \log K_F + n \log C_e \tag{2}$$

where K_L (L/µmol) is the Langmuir constant related to the binding energy; K_F (L/µmol) and n are the Freundlich temperature-dependent constants: K_F represents a measure of adsorption capacity and n is a constant related to energy and intensity of sorption; q_m (mmol/g) is the maximum adsorption capacity of the adsorbent; q_e (mmol/g) is the equilibrium adsorption capacity of adsorbent; and C_e (mmol/L) is the equilibrium bromate concentration in the solution. The parameters of Langmuir and Freundlich isotherm models are given in Table 1 and Fig. 6.

The values of R^2 for both the Langmuir and Freundlich isotherm models are very close to 1, indicating that the experimental data of bromate adsorption on Zn–Al CLDHs can be described well using the Langmuir and Freundlich isotherm models. The data are slightly better fitted by the Freundlich equation than the Langmuir equation, which suggests a heterogeneous distribution of surface-active sites and multilayer sorption of 2CLDHs.

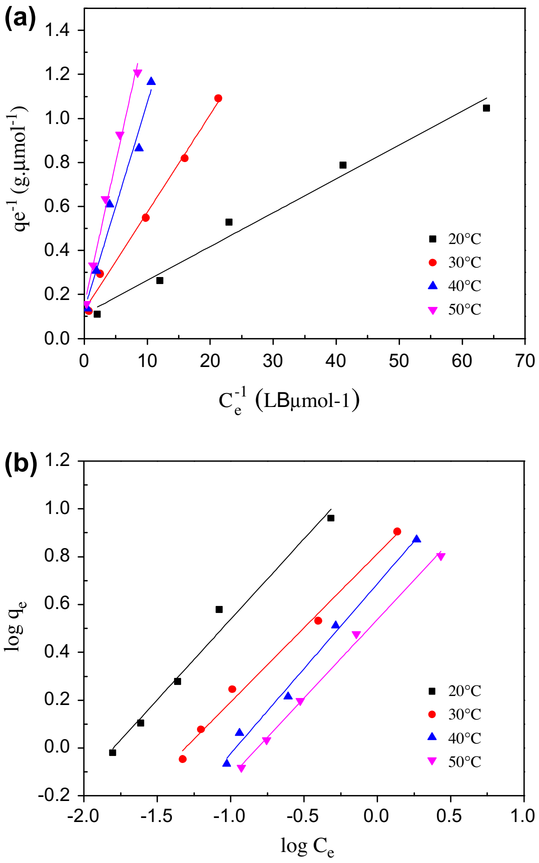

Fig. 6. Adsorption isotherm models for bromate removal by 2CLDHs (a) Langmuir isotherm models and (b) Freundlich isotherm models.

3.6. Adsorption thermodynamics

The thermodynamic parameters of Gibbs free energy (ΔG°), standard enthalpy changes (ΔH°), and standard entropy changes (ΔS°) of bromate adsorption

Table 1
Langmuir and Freundlich isotherm constants for bromate adsorption on 2CLDHs

	Langmuir isotherm model			Freundlich isotherm model		
Temperature (K)	q_m (mmol/g)	K_L (L/µmol)	R^2	n	K_F (L/µmol)	R^2
293	9.05	7.18	0.982	0.672	16.26	0.982
303	7.82	2.87	0.991	0.602	6.50	0.992
313	7.72	1.38	0.971	0.709	4.86	0.991
323	6.56	1.17	0.990	0.657	3.45	0.997

Notes: q_m is the maximum adsorption capacity of Zn–Al 2CLDHs; K_L is the Langmuir adsorption constant; K_F is the Freundlich adsorption constant; n is a constant related to energy and intensity of adsorption; R^2 is correlation coefficient.

by CLDHs were calculated using the following equations [32]:

$$\Delta G^\circ = -RT \ln K_L \tag{3}$$

$$\ln K_L = \Delta S^\circ / R - \Delta H^\circ / RT \tag{4}$$

where R represents the universal gas constant, $R = 8.314$ J/(K mol), T (K) and K_L denote the temperature and the Langmuir constant, respectively.

The results are listed in Table 2. The negative values of ΔG° indicate that bromate removal by Zn–Al CLDHs is a spontaneous adsorption process. According to the Van't Hoff equation (Eq. (4)), Fig. 7 shows a good linear relationship between $\ln K_L$ and $1/T$. The negative value of ΔH° further confirms the exothermic property of adsorption process, implying that the reaction occurs more easily at low temperature. Moreover, the negative value of ΔS° reveals a decrease in randomness at the solid–solution interface during the adsorption of free bromate ions on 2CLDHs. The decreased disorderliness of the material may be attributed to the reconstruction of CLDHs to LDHs.

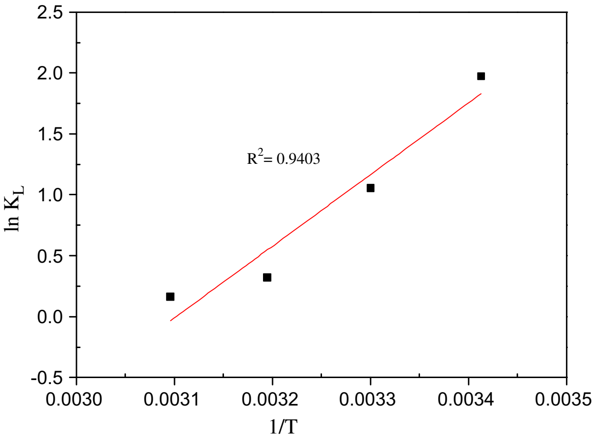

Fig. 7. Van't Hoff plot for bromate adsorption on 2CLDHs.

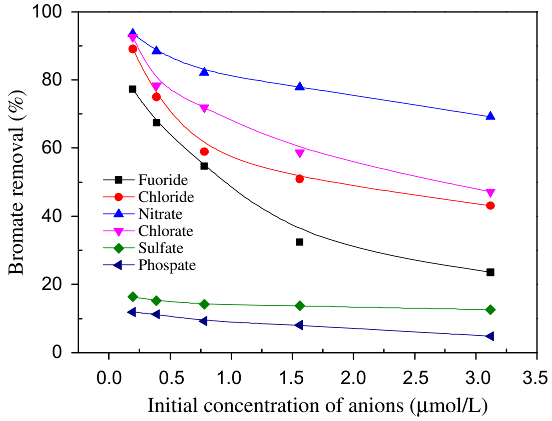

Fig. 8. Effect of coexisting anions on bromate removal by 2CLDHs.

3.7. Effect of coexisting anions on bromate removal

To investigate the effect of coexisting anions, such as fluoride, chloride, nitrate, chlorate, sulfate, and phosphate, on the bromate adsorption by Zn–Al CLDHs, experiments were conducted with the various concentrations (0.2–3.0 μmol/L) of coexisting anions on bromate removal with an initial bromate concentration of 0.78 μmol/L. Fig. 8 shows that the bromate removal efficiency obviously decreased with an increase in coexisting anion concentration, and the effect of competing anions on bromate removal followed the order of $PO_4^{3-} > SO_4^{2-} > F^- > Cl^- > ClO_3^- > NO_3^-$. Nitrate presented the minimum adverse impact on bromate removal, especially when its concentration was as low as 0.2 μmol/L. This represented a decrease of less than 5% in the removal rate compared with the original value of 98%, which was obtained without the presence of nitrate. In contrast, a significantly adverse effect was induced by phosphate, and less than 12% bromate removal was observed when the solution contained phosphate.

The effect of coexisting anions on bromate removal may depend on their affinity toward 2CLDHs, and a higher affinity of the competing anion toward 2CLDHs may result in a lower bromate removal. In addition, as shown in previous studies, oxyanions with higher ionic potential (Z/r, charge/radius) are

Table 2
Thermodynamic parameters for bromate adsorption on 2CLDHs

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/(mol K))
293	−4.800	−48.860	−0.152
303	−2.659		
313	−0.831		
323	−0.433		

preferentially adsorbed by LDHs [22,23]. The *Z*/*r* of the studied anions varies in the order of $PO_4^{3-} > SO_4^{2-} > F^- > Cl^- > ClO_3^- > NO_3^-$. That is to say, multivalent anions have a greater interfering effect than monovalent anions. Among the monovalent anions, F^- has an especially significant influence on bromate removal because of the relatively smaller radius than the other monovalent anions.

3.8. Regeneration of Zn–Al CLDHs

From an environmental and financial point of view, the performance of the good regeneration for adsorbents can largely promote their widespread application in drinking water treatment. For this reason, a batch of cyclic adsorption–regeneration experiments were conducted, and the results are presented in Fig. 9. After a series of thermal regeneration processes, bromate removal efficiency decreased by 2, 7.6, 12, and 19% for the first, second, third, and fourth regeneration cycle, respectively, compared with the original removal efficiency of 98%. This may be due to the decrease of crystallinity of 2CLDHs caused by mechanical agitation or recrystallization during each round of this cyclic adsorption–regeneration process. Moreover, the hypothesis of recrystallization was supported by XRD (Fig. 2). However, no significant decrease in bromate removal within four cycles of thermal regeneration suggests that Zn–Al CLDHs have the potential for reuse.

In addition, the leakage of metal ions including Zn and Al was also detected. The concentration of Zn and Al increased with the increasing of recycle times. By the third regeneration cycle, the concentration of Zn in solution exceeded 1 mg/L. This may result from the Zn–Al CLDHs with a lower degree of crystallinity being more vulnerable to dissolution than others. Therefore, the crystallinity of Zn–Al CLDHs needs to be further enhanced to improve its stability for application in future research.

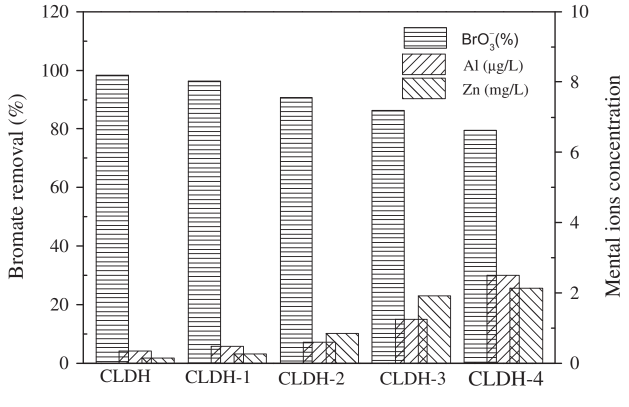

Fig. 9. Effect of regeneration times on bromate removal and the leakage of Zn and Al.

4. Conclusions

In this paper, Zn–Al CLDHs were synthesized by a co-precipitation method and subsequent hydrothermal treatment and used to remove bromate from aqueous solution. Appropriate reaction conditions for maximizing the removal efficiency of bromate were investigated. The results show that Zn–Al 2CLDHs can effectively reduce bromate in solution from 100 μg/L to less than 5 μg/L within 3 h, with a bromate removal efficiency of 98%. A wide range of pH (4.5–9.5) is suitable for bromate removal. Furthermore, bromate removal decreases with an increase in reaction temperature, which indicates the adsorption process is an exothermic reaction. The equilibrium bromate adsorption data on 2CLDHs are well fitted by the Freundlich isotherm model. The crystallinity and the adsorption ability of Zn–Al CLDH need to be further enhanced to improve its stability for application in future research.

Acknowledgements

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