



Adsorption of high concentration perchlorate from aqueous solution onto Mg/Fe magnetic hydrotalcite calcined product (MAG@CHT): kinetics and isotherm study

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ABSTRACT

In this study, the calcined Mg/Fe magnetic hydrotalcite (MAG@CHT) was synthesized for the first time by co-precipitation and calcination method. MAG@CHT with the destructive layered structure is effective in adsorbing perchlorate in water to recover its original layered structure by Mg/Fe magnetic hydrotalcite (MAG@HT). In addition, MAG@CHT can be quickly separated by the applied magnetic field. The pseudo-second-order kinetics model was a better description of the adsorption kinetics process. The Langmuir model was more satisfactory than the Freundlich model for fitting the isotherm experimental data. The maximum adsorption capacities obtained Langmuir model at 25°C, 30°C, and 35°C were 93.17, 103.54, and 110.88 mg/g, respectively. The detrimental effect order of co-existing anion was: $\text{Cl}^- < \text{NO}_2^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$. The Fe(III)/Fe(II) ratio of the MAG@CHT is 5.33, which is close to the theoretical value (4.70); the saturation magnetic strength value (Ms) was 9.10 emu/g, which is easy to achieve solid–liquid separation. Combined with the detailed characterization of MAG@CHT, adsorption mechanism of perchlorate on MAG@CHT likely includes: (1) adsorption on the surface of adsorbent by electrostatic interactions; (2) restoration of the layered structure by using ClO_4^- as an anion interlayer.

Keywords: Mg/Fe magnetic hydrotalcite; Perchlorate; Adsorption; Kinetics; Isotherm

1. Introduction

Perchlorate (ClO_4^-) is an emerging inorganic pollutant in the field of water treatment, and has gradually become a hot issue of concern to researchers in various countries [1]. Due to its strong oxidizing, high solubility and low reactivity, perchlorate itself is widely used in industrial fields such as rocket boosters and fireworks manufacturing [2]. Different concentrations of perchlorate have been

detected in food, soil, and water [3]. Studies have shown that perchlorate can cause great harm to human health, inhibit the normal function of the thyroid gland, and induce a series of diseases [4,5].

Commonly used techniques for removing perchlorate include adsorption [6,7], catalysis [8], and microbial degradation [9]. Catalytic and microbial degradation technologies are limited due to their relatively high cost, long microbial culture and domestication cycles, and

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slow response. However, adsorption is the most common method for removing perchlorate due to its low cost and high efficiency [10]. Common adsorbents, such as activated carbon [11], organoclay minerals [12] and hydrotalcites [13], and hydrotalcites have attracted much attention from researchers in terms of adsorbing inorganic anions.

Hydrotalcite (HT) has a large adsorption capacity for anions and belongs to anionic clay [14]. After calcination, hydrotalcite loses the interlayer water, anions, and hydroxyl groups, resulting in destruction of its layered structure and formation of a mixed metal oxide. Surprisingly, hydrotalcite itself has a “memory effect” [15,16], and the original layered structure is restored after absorbing anion in the water. For perchlorate adsorption, it has been reported that when the perchlorate initial low-concentration was 2,000 µg/L, removal efficiency could reach 91.2% at a dosage of 1.33 g/L for calcined Fe-based layered double hydroxides [17]. Although it has been reported that Mg/Al hydrotalcite could effectively adsorb high concentration perchlorate, when the initial concentration of perchlorate was 100 mg/L and the dosage was 1 g/L, the removal rate only reached 62% [18]. Moreover, Al can damage the human body and have an impact on health [19]. Herein, for all we know, Mg/Fe hydrotalcite has not been studied in adsorption of high concentrations of perchlorate. In this study, Mg/Fe hydrotalcite was prepared using Fe instead of Al to adsorb high concentrations of perchlorate.

On the other hand, it is difficult to separate the adsorbent from the solution by a conventional separation method such as centrifugation or filtration [20]. At the same time, the magnetically-adsorbed adsorbent can be effectively and quickly separated by the applied magnetic field [21]. The magnetic separation technology saves a lot of time and cost, and it has attracted the attention of researchers. Specifically, Yan et al. [22] successfully produced three kinds of composite materials of core-shell Fe₃O₄@Zn/Al, Mg/Al, and Ni/Al hydrotalcite by hydrothermal method and co-precipitation method, which can effectively remove phosphate from water. Shan et al. [23] produced magnetic Fe₃O₄@Mg/Al hydrotalcite by co-precipitation method, and the maximum adsorption capacity of Cd(II) in water at 303 K was 45.6 mg/g. However, studies toward perchlorate adsorption from water by magnetic hydrotalcite are still very limited.

This study aimed to synthesize magnetic Mg/Fe hydrotalcite calcined material (MAG@CHT) by co-precipitation and calcination method, to explore the adsorption kinetics and isotherms of MAG@CHT toward high concentration perchlorate, and to investigate the effects of pH and coexisting anions on the adsorption process. In addition, the adsorption mechanism was studied by characterization using BET, XRD, XPS, FTIR, and VSM method.

2. Materials and methods

2.1. Synthesis of magnetic substrate

The magnetic Fe₃O₄ was synthesized by chemical co-precipitation. FeCl₂·4H₂O (0.24 mol/L) and FeCl₃·6H₂O (0.48 mol/L) were weighed according to the molar ratio of Fe(II) and Fe(III) of 1:2, respectively, and then mixed into

100 mL of mixed salt solution. Under the conditions of N₂ atmosphere and controlled temperature of 45°C ± 1°C and vigorous stirring, 20% ammonia water was added dropwise to the above solution to adjust the pH to 11 ± 1. The resulting precipitate was aged at the above temperature for 30 min. The oily black precipitate obtained above was repeatedly washed to neutrality with deionized water using a magnetic separation device. The product was placed in a conical flask containing 100 mL of deionized water for use.

2.2. Synthesis of MAG@HT and MAG@CHT

A magnetic hydrotalcite having an Mg/Fe molar ratio of 3/1 was synthesized by a co-precipitation method. Solution A (200 mL) contains MgCl₂·6H₂O (1.2 mol/L) and FeCl₃·6H₂O (0.4 mol/L). Solution B (200 mL) contains 3.2 mol/L NaOH and 0.2 mol/L Na₂CO₃. The two solutions A and B were simultaneously added dropwise to the above magnetic substrate (pH 10 ± 1) under the control of a temperature of 40°C and vigorous stirring. Stirring was continued for 2 h after the titration was completed. The above precipitated product was then crystallized in a 65°C ± 1°C water bath for 18 h. The crystallized product was repeatedly washed with deionized water to a conductivity of 300 µs/cm or less. The product was dried completely at 70°C. The resulting sample was labeled as MAG@HT. The dried product was then placed in a 500°C muffle furnace, calcined for 5 h, and then taken out. The product was ground to give a powder with a particle size of <100 mesh (150 µm). The resulting product was designated as MAG@CHT.

2.3. Kinetics study

Adsorption kinetics experiments were performed in a conical flask containing 500 mL of a perchlorate solution with an initial concentration of 100 mg/L on a magnetic stirrer rotating at 200 rpm. The experimental temperature was controlled at 25°C, 30°C, and 35°C, respectively, and the dosage of MAG@CHT adsorbent was 2 g/L. Perchlorate adsorbed with MAG@CHT was calculated by the following equation:

$$q_t = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

where q_t (mg/g) stands for the perchlorate adsorption capacity for MAG@CHT at time t , V (L) stands for perchlorate solution volume, C_0 and C_t (mg/L) are the initial concentration of perchlorate and perchlorate concentration at time t , m (g) is the mass of adsorbent MAG@CHT.

2.4. Adsorption isotherm

Adsorption isotherms were obtained by adding a constant mass of MAG@CHT adsorbent to a series of different initial concentrations of perchlorate solution. One-hundred milliliters of perchlorate solution (initial concentration of 60–600 mg/L) and 0.10 g of MAG@CHT adsorbent were placed in a series of conical flasks. They were then shaken in a water bath shaker (stirring speed of 160 rpm) at 25°C, 30°C, and 35°C for 24 h to achieve adsorption equilibrium.

The pH of the solution was not adjusted during the experiment to avoid the influence of other anions on the experiment. The adsorption capacity of perchlorate by MAG@CHT at the equilibrium state was denoted as q_e (mg/g).

2.5. Effects of initial pH and coexisting anion type and strength

The initial pH of the solution was adjusted with 0.5 mol/L HCl or NaOH to investigate its effect on the adsorption capacity of MAG@CHT. A conical flask containing 100 mL of perchlorate (initial concentration of 50 mg/L, dosage of 1 g/L) was placed in a water bath shaker (stirring speed of 160 rpm) and equilibrated at 25°C with shaking for 24 h. The pH and perchlorate content of the solution before and after adsorption were measured.

To study the effect of co-existing anions, 0.10 g of MAG@CHT was added to a solution of perchlorate (concentration and volume were 0.5 mmol/L and 100 mL, respectively) containing different anions (100 mg/L). Different concentrations of Cl^- (0.1, 0.5, 1, 5 mmol/L) were evaluated as co-existing anions to explore the effect of anion strength. The experimental conditions were consistent with the initial pH influence experiments. The concentration of perchlorate after adsorption was measured.

2.6. Analysis methods

Before all samples were analyzed, 0.45 μm membrane filtration was used. The perchlorate concentration was analyzed using an ion chromatograph (ICS-2100, Thermo Fisher, CA) with an As-16 column and an AG-16 precolumn. The eluent was 25 mM KOH at a flow rate of 1.0 mL/min. The sample loop was 25 μL and the method detection limit (MDL) was 10.0 $\mu\text{g/L}$.

X-ray diffraction analysis was performed on D8 Advance with $\text{CuK}\alpha$ radiation of 5° to 80° (2 θ). The surface area, average pore volume, and pore size were measured by the Brunauer–Emmett–Teller (BET) method using TriStar II 3020 (Micromeritics, USA). Fourier transform infrared (FTIR) spectra of 4,000–600 cm^{-1} samples were recorded using a WQF-510 spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific Escalab 250SXi. The magnetic properties of the MAG@CHT were measured using a vibrating sample magnetometer (Quantum Design, USA; PPMS-9).

3. Result and discussion

3.1. Adsorption kinetics

The adsorption kinetics of perchlorate onto MAG@CHT at three different temperatures (25°C, 30°C, and 35°C) are shown in Fig. 1. To better understand the adsorption kinetics of MAG@CHT, three different kinetic adsorption models (first-order-kinetics model, pseudo-second-order kinetics model, and intraparticle diffusion model) were used to fit the adsorption kinetic data [24–26].

First-order-kinetics model:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

Pseudo-second-order kinetics model:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad (3)$$

Intraparticle diffusion model:

$$q_t = k_3 t^{0.5} \quad (4)$$

where k_1 (1/min), k_2 (g/mg min), and k_3 (mg/g min^{1/2}) are the rate constants for each kinetic model.

As shown in Fig. 1, with the reaction time running, the adsorption capacity and removal efficiency of perchlorate by MAG@CHT increased sharply in the first 120 min of the reaction, and gradually achieve equilibrium after 120 min. It can also be seen that as the temperature increases, the adsorption capacity of MAG@CHT increases continuously, from 6.65 mg/g at 25°C to 11.89 mg/g at 35°C (about 1.8 times that of 25°C).

The experimental data results and correlation coefficients (R^2) after fitting using the three kinetic models are summarized in Table 1. It can be seen from the correlation coefficient (R^2) that the pseudo-second-order kinetics model ($R^2 > 0.98$) can be more suitable to describe the adsorption process of perchlorate by MAG@CHT than the other two models. It indicates that the adsorption process of perchlorate by MAG@CHT is determined by chemical adsorption [27,28]. Furthermore, the initial adsorption rate (v_0) according to the pseudo-second-order kinetics model can be calculated by $v_0 = k_2 q_e^2$, the adsorption rates of MAG@CHT for perchlorate at 25°C, 30°C, and 35°C were 0.17, 0.25, and 0.29 mg/(g min), respectively. As the temperature increases, the adsorption rate increases correspondingly, showing the highest adsorption rate (0.29 mg/g min) and capacity (11.89 mg/g) at 35°C in the kinetics study among the three temperatures.

3.2. Adsorption isotherm and thermodynamic evaluation

Fig. 2 shows the adsorption isotherms of perchlorate by MAG@CHT at 25°C, 30°C, and 35°C. To further understand the adsorption isotherm characteristics, the commonly used Langmuir and Freundlich isotherm models were applied to fit the experimental data of the adsorption isotherms [29–31]:

Langmuir isotherm model:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (5)$$

Freundlich isotherm model:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where C_e represents the concentration (mg/L) of the perchlorate solution at equilibrium, and Q_0 represents the monolayer capacity (mg/g) of the adsorbent. K_L (L/mg) is related to the adsorption energy. K_F (mg/g)·(L/mg)^{1/n} and n represent the parameters related to the intensity of the adsorption distribution in the Freundlich adsorption model.

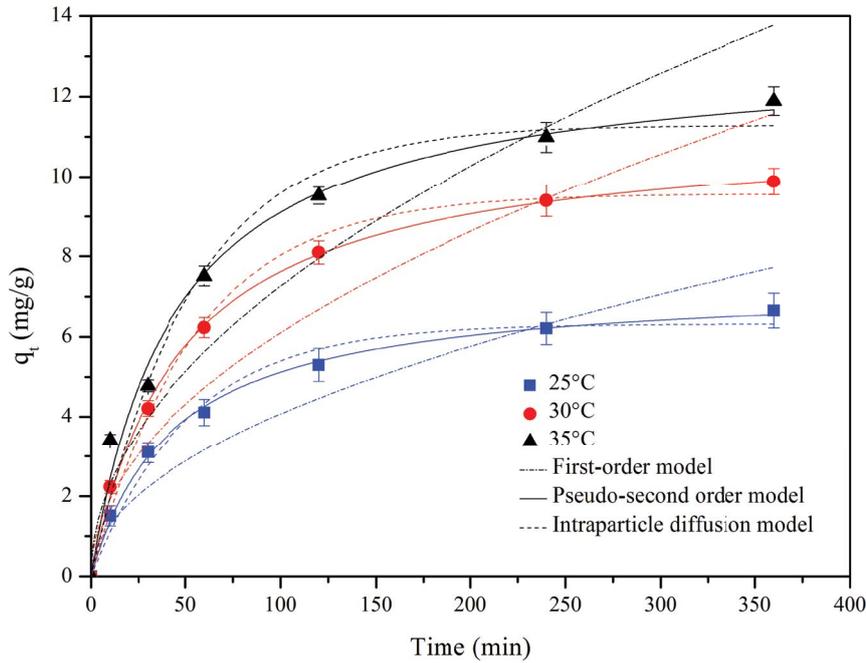


Fig. 1. Adsorption kinetics of perchlorate onto MAG@CHT at different temperatures ($V = 500$ mL, dosage = 2 g/L, $C_0 = 100$ mg/L, and 200 rpm).

Table 1
Kinetic parameters and correlation coefficients (R^2) of perchlorate adsorption by MAG@CHT

Adsorbent	T (°C)	$q_{e,exp}$ (mg/g)	First-order model				Pseudo-second-order model				Intraparticle diffusion model	
			$q_{e,cal}$ (mg/g)	k_1 (1/min)	R^2	v_0	$q_{e,cal}$ (mg/g)	k_2 (g/(mg min))	R^2	v_0	k_3 (mg/(g·min ^{1/2}))	R^2
MAG@CHT	25	6.65	6.31	0.019	0.9806	0.12	7.34	0.0031	0.9977	0.17	0.41	0.9014
	30	9.88	9.57	0.018	0.9897	0.17	11.19	0.0020	0.9986	0.25	0.61	0.9048
	35	11.89	11.30	0.018	0.9684	0.20	13.09	0.0017	0.9859	0.29	0.73	0.8979

The relevant parameters after fitting the Langmuir and Freundlich isotherm model are summarized in Table 2. According to the correlation coefficient in Table 2, the correlation coefficient of the Langmuir isotherm model fitting ($R^2 > 0.99$) is significantly higher than that of the Freundlich isotherm model, indicating that the Langmuir model is more suitable for describing the adsorption isotherm process of perchlorate by MAG@CHT. It can be concluded that the isotherm adsorption process of perchlorate onto MAG@CHT is consistent with the assumption of the monolayer adsorption [11,32].

The effect of temperature on the adsorption isothermal process is similar to that of kinetics study. As can be seen from Fig. 2, the adsorption capacity of MAG@CHT increases as the reaction temperature increases. The maximum adsorption capacities obtained by Langmuir isotherm model at 25°C, 30°C, and 35°C were 93.17, 103.54, and 110.88 mg/g, respectively.

The thermodynamic parameters of the adsorption process include the standard free energy change (ΔG° , kJ/mol), the

standard enthalpy change (ΔH° , kJ/mol), and the standard entropy change (ΔS° , kJ/mol), respectively. These parameters are calculated by the following equation [33]:

$$\Delta G^\circ = -RT \ln K_L \tag{7}$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{8}$$

where R (8.314 J/mol K) represents the ideal gas constant, T (K) represents temperature, and K_L (L/mol) represents Langmuir constant.

The thermodynamic related parameters of MAG@CHT adsorption perchlorate are listed in Table 3. It can be clearly seen that ΔG° is a negative value and continues to decrease with temperature increasing, indicating that the adsorption process is spontaneous [34]. ΔH° is a positive value, indicating that the adsorption process is endothermic. A positive value of ΔS° illustrates an increase in the randomness of the adsorption process.

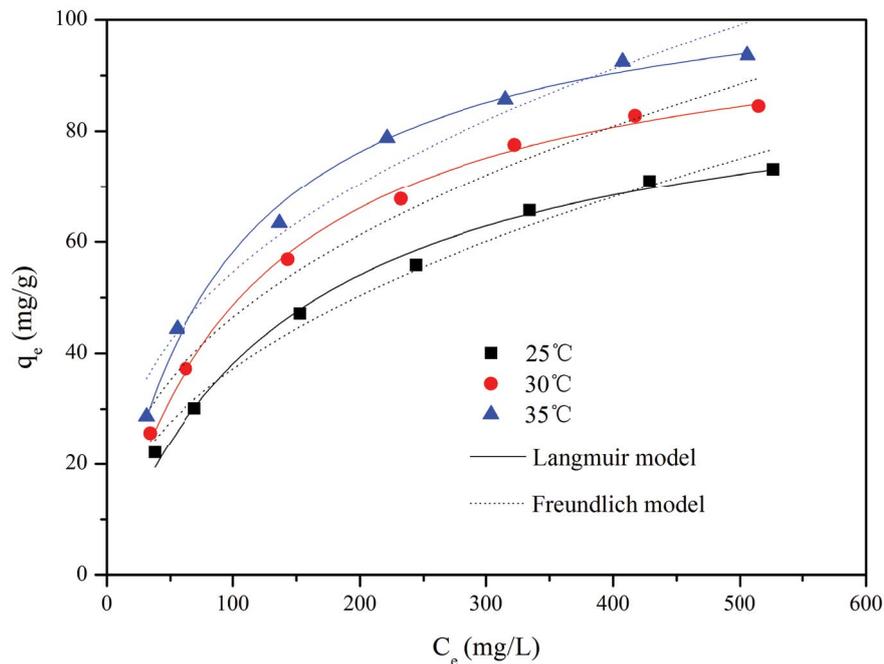


Fig. 2. Adsorption isotherm of perchlorate on MAG@CHT ($V = 100$ mL, dosage = 1 g/L, $t = 24$ h, and 160 rpm).

Table 2
Fitting parameters of perchlorate on MAG@CHT adsorption isotherm

Adsorbent	T ($^{\circ}\text{C}$)	Langmuir isotherm model			Freundlich isotherm model		
		Q (mg/g)	K_L (L/mg)	R^2	K_F (mg/g) (L/mg) $^{1/n}$	n	R^2
MAG@CHT	25	93.17	0.0069	0.9915	4.99	2.29	0.9821
	30	103.54	0.0088	0.9964	7.34	2.49	0.9706
	35	110.88	0.0110	0.9939	9.89	2.69	0.9615

Table 3
Thermodynamic parameters of perchlorate adsorption onto MAG@CHT

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
298.16	-16.20		
303.16	-17.09	36.56	0.18
308.16	-17.94		

3.3. Effects of initial pH

Solution initial pH value is one of the key factors influencing the adsorption of perchlorate onto MAG@CHT. The initial pH value will have a direct impact on the dot characteristics of the adsorbent surface. In this study, the initial pH range of the perchlorate solution was set to 2–11, which is the pH value of common water bodies. The effect of the initial pH value of the solution on the adsorption of perchlorate by MAG@CHT is shown in Fig. 3. It can be seen from Fig. 3 that the pH value of the solution

after adsorption is increased compared to the initial pH value and maintained above 9.0, possibly because MAG@CHT is a basic substance, which increases the pH of the solution after adsorption. When the initial pH increased from 2.62 to 3.87, the pH of the solution after adsorption increased from 9.10 to 10.21, while the adsorption capacity increased from 9.55 to 20.32 mg/g. It was indicated that when the initial pH of the solution was in the range of 2.62–3.87, a large amount of H^+ exist, and MAG@CHT was an alkaline material, which might cause damage of its own structure, and further influence the adsorption capacity [35,36]. However, when the initial pH of the solution increased from 3.87 to 10.28, the pH of the solution after adsorption of perchlorate was greater than 10. And the adsorption capacity of the corresponding MAG@CHT was greater than 19 mg/g. When the initial pH was 10.28, the adsorption capacity of MAG@CHT decreased slightly compared to the previous one, which may be due to the presence of more OH^- in solution, which caused competitive adsorption. To sum up, it is indicated that when the initial pH value is greater than 4, the adsorption capacity is not affected significantly, and the material can exhibit a

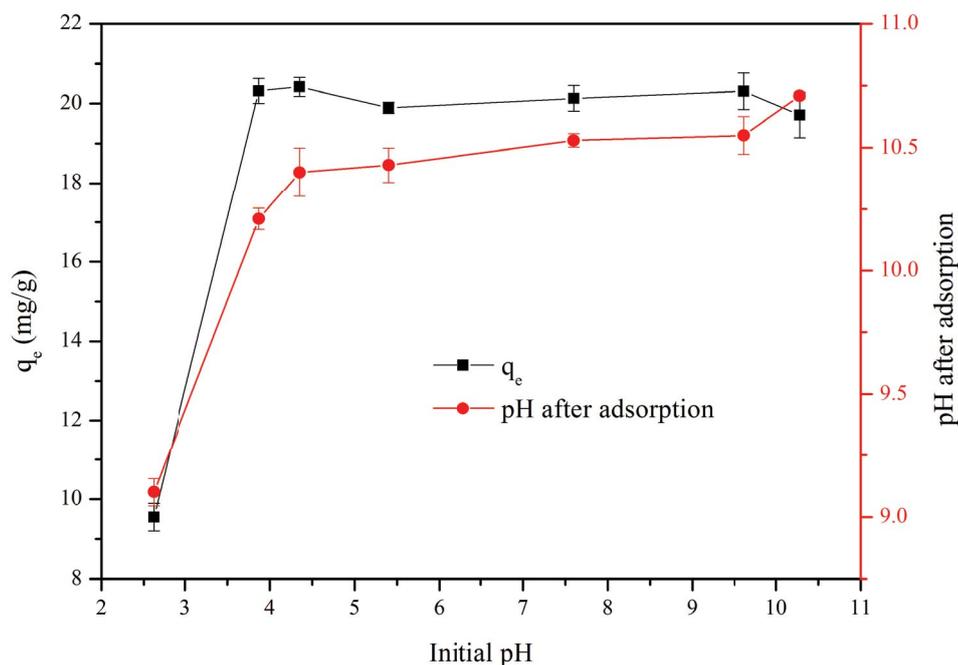


Fig. 3. Effect of initial pH of solution onto adsorption of perchlorate ($V = 100$ mL, dosage = 1 g/L, $C_0 = 50$ mg/L, $T = 25^\circ\text{C}$, $t = 24$ h, and 160 rpm).

higher adsorption capacity in a wide pH range (4–10) of the solution.

3.4. Effects of coexisting anion type and strength

There exist many other anions in perchlorate contaminated waters, which affects the adsorption of perchlorate by adsorbents. In order to investigate the effect, various anions including Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} were used to influence the adsorption capacity of MAG@CHT. The results are shown in Fig. 4a. Obviously, all the coexisting anions have a significant effect on the removal efficiency of perchlorate. The order of influence on perchlorate removal rate is: $\text{Cl}^- < \text{NO}_2^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$. The effect of oxyanions on the adsorption of perchlorate is significantly greater than that of non-oxoanions. The effect of high-valent anions is stronger than that of low-valent anions, indicating that MAG@CHT has a strong affinity for high-valent anions [37]. The coexisting anion in the solution competes with ClO_4^- for the adsorption site on the MAG@CHT, thereby inhibiting the adsorption of perchlorate.

The effect of coexisting anion strength was further explored by comparing four typical concentrations (0.1, 0.5, 1, and 5 mmol/L) of the coexisting anion Cl^- . It is apparent from Fig. 4b that as the Cl^- strength increases from 0.1 to 5 mmol/L, the capability of MAG@CHT to adsorb ClO_4^- is significantly weakened. The adsorption capacity of MAG@CHT decreased significantly from 25.43 to 3.69 mg/g. Therefore, in the presence of high concentration of Cl^- , it will have a higher competitive effect on the adsorption site with ClO_4^- , resulting in a decrease in the adsorption capacity of MAG@CHT.

3.5. Characterization

3.5.1. BET analysis

The physical properties of the adsorbent have an effect on the adsorption capacity, so it is necessary to analyze the physical properties of the adsorbent. By analyzing the BET analysis results, the specific surface area of MAG@CHT was 70.89 m^2/g , and the pore volume and average pore diameter were 0.63 mL/g and 31.73 nm, respectively. Therefore, MAG@CHT is a typical mesoporous material [38].

3.5.2. XRD analysis

In order to better understand the structure of the adsorbent, the XRD patterns of MAG@HT, MAG@CHT, and MAG@CHT-A (after perchlorate adsorption) are compared, and the results are shown in Fig. 5. From the XRD pattern of MAG@HT, it can be clearly seen that the seven main characteristic diffraction peaks appear in the symmetrical reflection of the 2θ (003, 006, 110, and 113) plane and the wide asymmetric reflection of the (012, 015, and 018) plane. These are all characteristic peaks of hydrotalcite [39]. In addition, the peak of Fe_3O_4 crystal phase can be clearly observed at 30° , indicating that the magnetic substrate has been successfully loaded on the hydrotalcite. In the Fig., there are no other peaks other than the above peaks. It is indicated that the MAG@HT exhibited clear crystal phase with low impurity content, and the introduction of the magnetic substrate does not affect the basic structure of the hydrotalcite.

After being calcined, it was found that the significant hydrotalcite characteristic peaks (003, 006, 110, 113, 012, 015, and 018) of MAG@HT disappeared, indicating that the layer

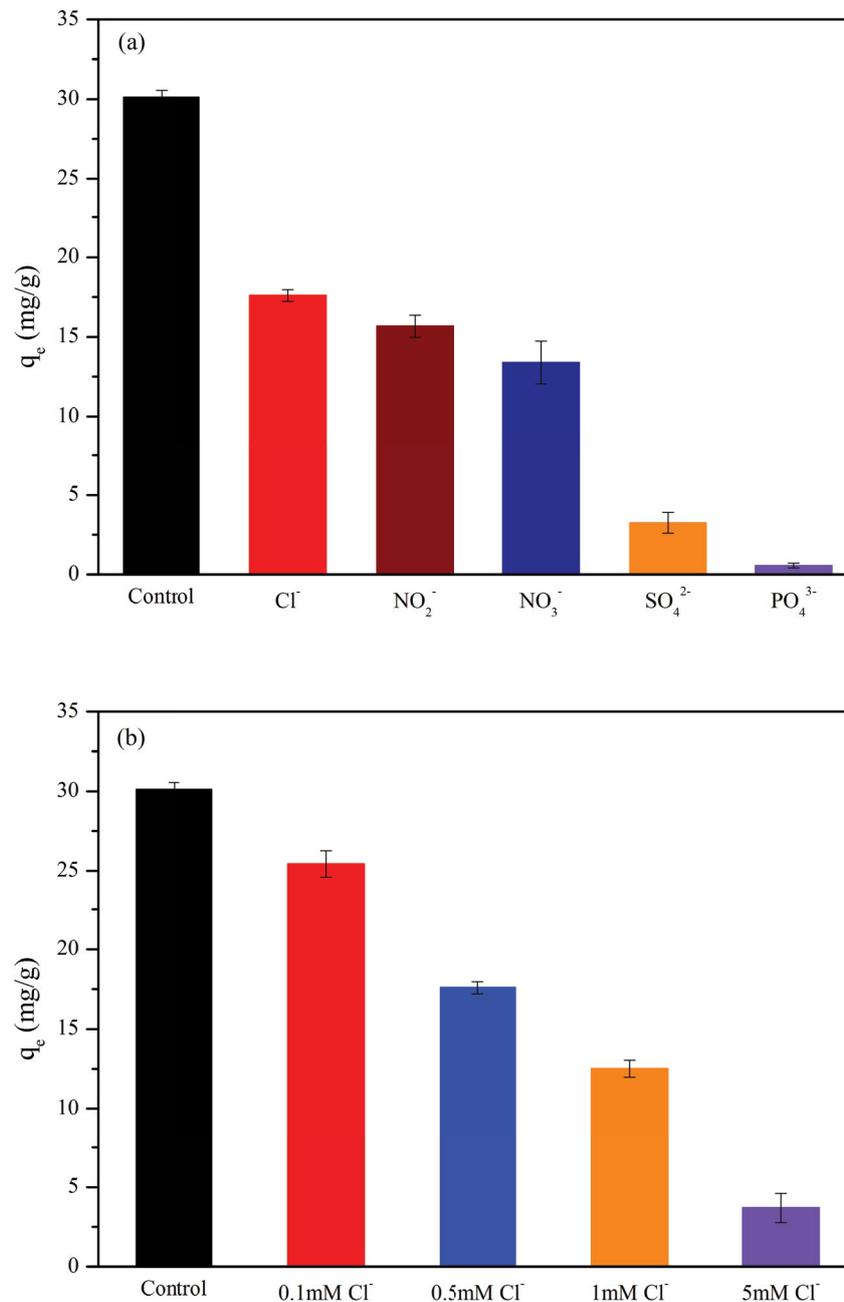


Fig. 4. Effects of coexisting anion type and strength on adsorption of perchlorate by MAG@CHT ($V = 100$ mL, dosage = 1 g/L, $C_0 = 100$ mg/L, $C_{\text{coexisting anions}} = 0.05$ mmol/L, $T = 25^\circ\text{C}$, $t = 24$ h, and 160 rpm).

structure of MAG@CHT was destroyed. At the same time, significant peaks at 43° and 62° were observed, belonging to magnesium iron oxide ($\text{Mg}(\text{Fe}_3\text{O}_4)$) [19]. In addition, the Fe_3O_4 crystal phase peak can still be clearly observed at 30° . All of the above indicate that the MAG@CHT after calcination was a mixed metal oxide, and the calcination process did not affect the structure of Fe_3O_4 . After the perchlorate was adsorbed by MAG@CHT, the layer structure of hydrocalcite was restored, which is the “structural memory effect” [40]. It indicated that the negative charged layer was formed after adsorption of perchlorate on the positive layer of

MAG@CHT [28]. Before and after the adsorption of perchlorate by MAG@CHT, the peak of Fe_3O_4 crystal phase can be clearly observed at 30° . It shows that the adsorption process does not affect the structure of Fe_3O_4 .

3.5.3. FTIR analysis

To further understand the functional groups of the adsorbent, the FTIR spectra of MAG@HT, MAG@CHT, and MAG@CHT-A are compared and the results are shown in Fig. 6. FTIR spectrum in the figure shows that $-\text{OH}$ bending

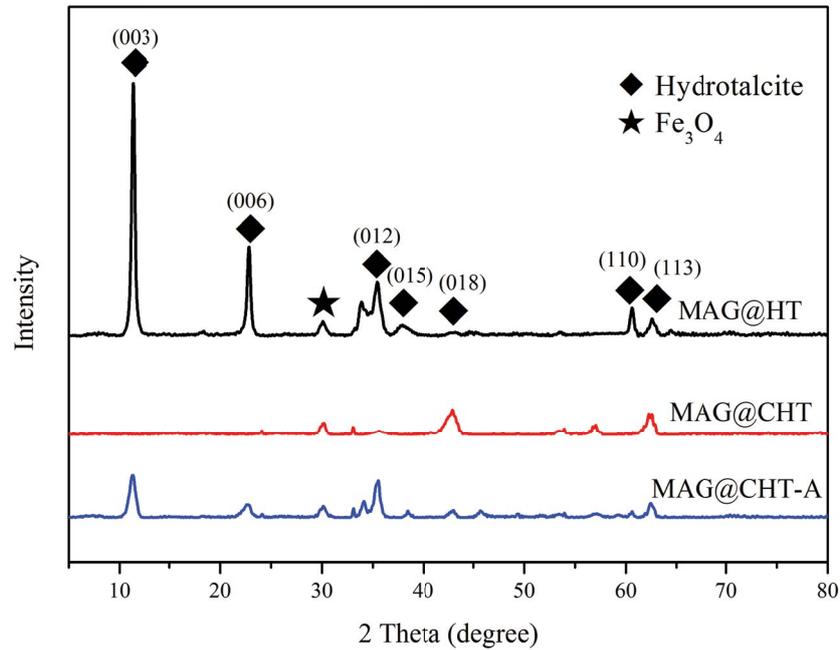


Fig. 5. XRD patterns of MAG@HT, MAG@CHT, and MAG@CHT-A (after perchlorate adsorption).

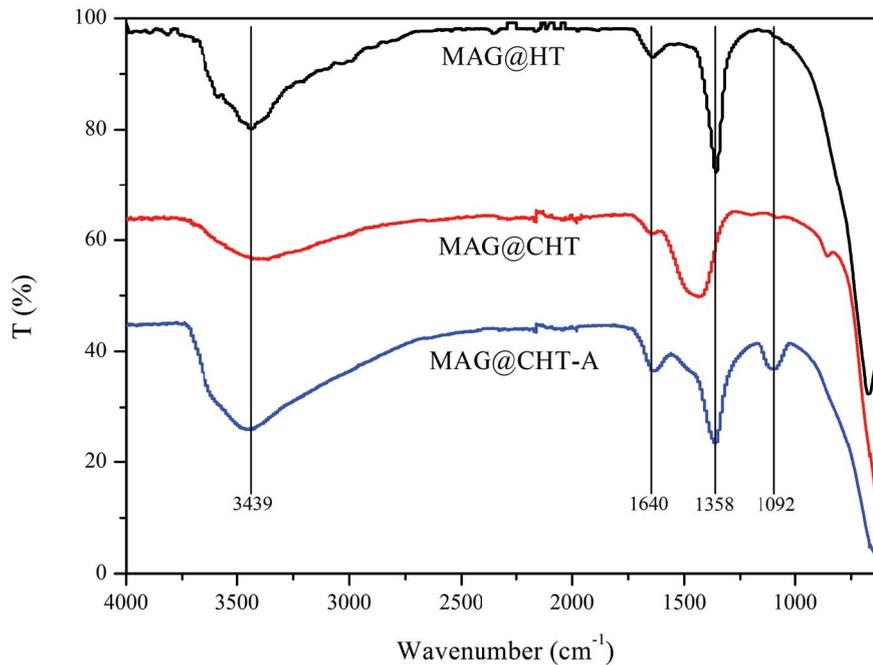


Fig. 6. FTIR spectra of MAG@HT, MAG@CHT, and MAG@CHT-A (after perchlorate adsorption).

vibration [41] derived from interlayer water and hydroxyl groups was observed at a wavelength of $3,439\text{ cm}^{-1}$. The bending vibration of the interlayer water was observed at $1,640\text{ cm}^{-1}$ [42]. The oscillation peak of CO_3^{2-} was observed at $1,358\text{ cm}^{-1}$ [16,43]. At the same time, the characteristic peak of $600\text{--}800\text{ cm}^{-1}$ is attributed to the vibration peak of the magnesium iron skeleton. It is indicated that the introduction

of the magnetic substrate into the hydrotalcite substrate does not change the properties of its functional groups.

After the MAG@HT was calcined at 500°C for 5 h, the above characteristic peak ($3,439$ and $1,640\text{ cm}^{-1}$) in the FTIR spectrum of MAG@CHT was significantly weakened, and the oscillation peak of CO_3^{2-} was blue shifted from $1,358$ to $1,410\text{ cm}^{-1}$. This phenomenon is caused by the disappearance

of large amount of interlayer water, hydroxyl, and CO_3^{2-} after calcination [44]. After adsorption of perchlorate, the characteristic peak of hydrotalcite significantly enhanced. Meanwhile, the oscillation peak of CO_3^{2-} shifted from $1,410$ to $1,358\text{ cm}^{-1}$. It is indicated that the layered structure is restored after adsorption of perchlorate by MAG@CHT. In addition, the characteristic peak of O–Cl was observed at $1,092\text{ cm}^{-1}$ in the spectrum of MAG@CHT-A [45], indicating that ClO_4^- was successfully adsorbed onto MAG@CHT.

3.5.4. XPS analysis

The adsorbent was characterized by X-ray photoelectron spectroscopy (XPS) to further determine the surface composition of the MAG@CHT. The XPS spectrum of MAG@CHT is shown in Fig. 7. Fig. 7a shows a comprehensive analysis of the XPS full spectrum of MAG@CHT, and the binding energies at 49.08 , 530.08 , 710 , and 725 eV represent the characteristic diffraction peaks of $\text{Mg}2p$, $\text{O}1s$, $\text{Fe}2p_{3/2}$,

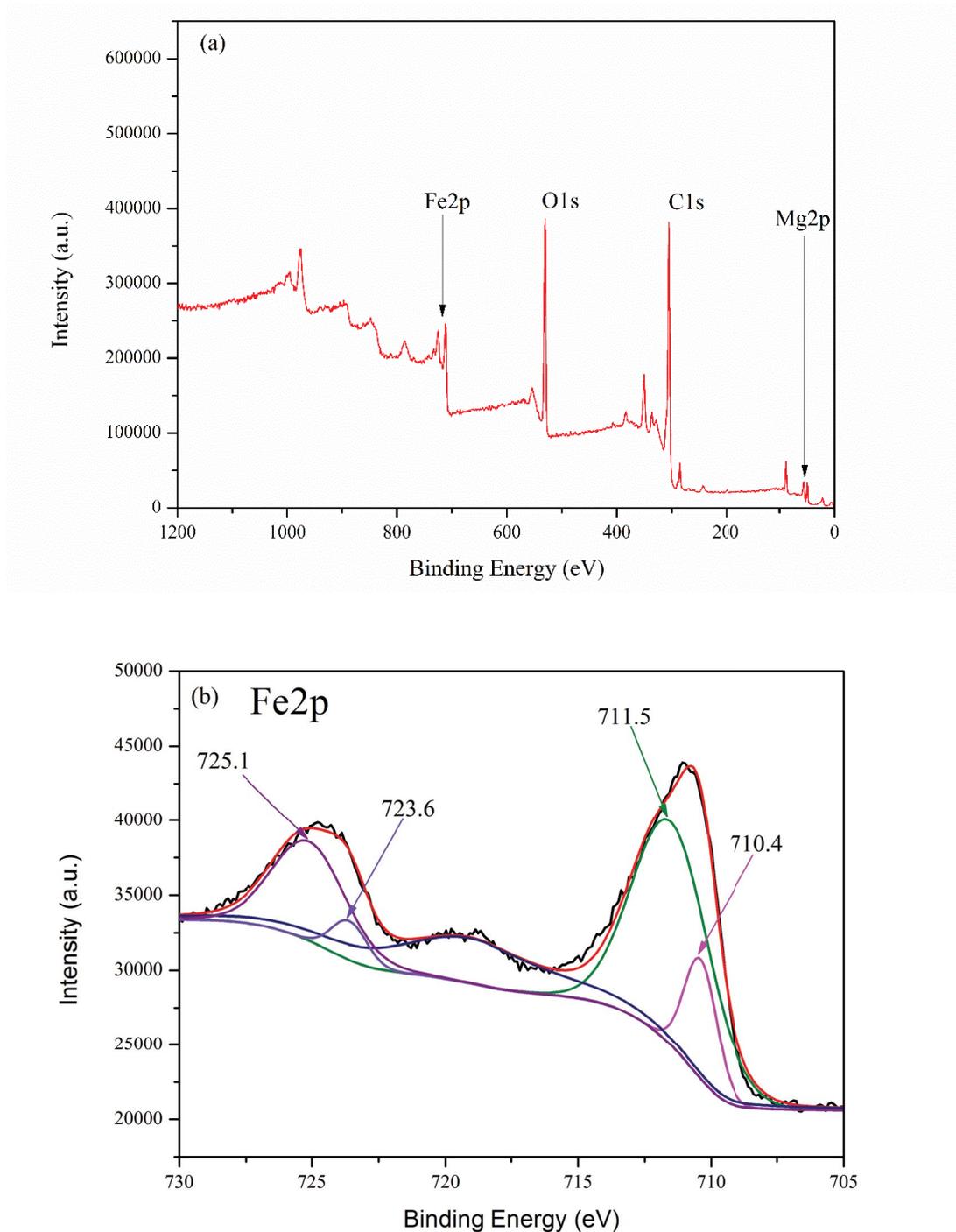


Fig. 7. XPS spectrum of: (a) full spectrum of MAG@CHT and (b) $\text{Fe}2p$ region spectrum of MAG@CHT.

and Fe2p_{1/2'}, respectively. It is indicated that the synthesized MAG@CHT adsorbent contains C, O, Fe, and Mg, which are consistent with the main constituent elements [46].

In addition, the Fe2p peak fitting fit in Fig. 7b was analyzed. The results of the analysis are summarized in Table 4. The results show that the characteristic diffraction peaks at the binding energies of 711.5 and 725.1 eV belong to the characteristic peaks of Fe(III), while the characteristic diffraction peaks at the binding energies of 710.4 and 723.6 eV belong to the characteristic peaks of Fe(II), respectively [47]. By calculating the peak areas of Fe(III) and Fe(II), the ratio is 4.70:1. Since the Fe(III) in the initial magnetic substrate was 0.048 mol, while the Fe(III) in the hydrotalcite co-precipitation precursor salt solution (A) was 0.08 mol, hence the total Fe(III) was 0.128 mol. Meantime, the Fe(II) in the initial magnetic substrate was 0.024 mol. Therefore, the theoretical Fe(III)/Fe(II) ratio should be 0.128/0.024, that is 5.33:1, which is close to the XPS testing result. Based on the above analysis, the results indicate that Fe₃O₄ is present in MAG@CHT, and the co-precipitation such as iron salt is sufficient, and magnetic hydrotalcite is successfully obtained, which is consistent with the XRD results.

3.5.5. VSM analysis

The magnetic hysteresis loop of the MAG@CHT obtained by the VSM test is shown in Fig. 8. The saturation magnetic strength value (M_s) of the MAG@CHT adsorbent prepared by the co-precipitation method was 9.10 emu/g. In addition, the coercivity and remanence of MAG@CHT are close to zero, indicating that MAG@CHT is a superparamagnetic material [48]. As can be seen from the inset in Fig. 8, the MAG@CHT can achieve rapid solid–liquid separation after 30 s when there is an external magnet.

3.6. Mechanism analysis

According to the BET results in section 3.5.1 (BET analysis), MAG@CHT with positive charges possesses a large specific surface area, providing more adsorption sites for perchlorate with negative charges based on electrostatic interactions.

According to the XRD analysis results of MAG@HT and MAG@CHT before and after adsorption, MAG@HT contains the obvious characteristic peaks of hydrotalcite,

Table 4
Form, peak area, and content of Fe element in XPS analysis

Fe2p	Binding Energy (eV)									
	725.1	Fe(III)	723.6	Fe(II)	711.5	Fe(III)	710.4	Fe(II)	Total	
	Area	%	Area	%	Area	%	Area	%	Area	%
MAG@CHT	23,812.47	25.00	4,330.03	4.55	54,731.31	57.45	12,391.01	13.01	95,264.82	100

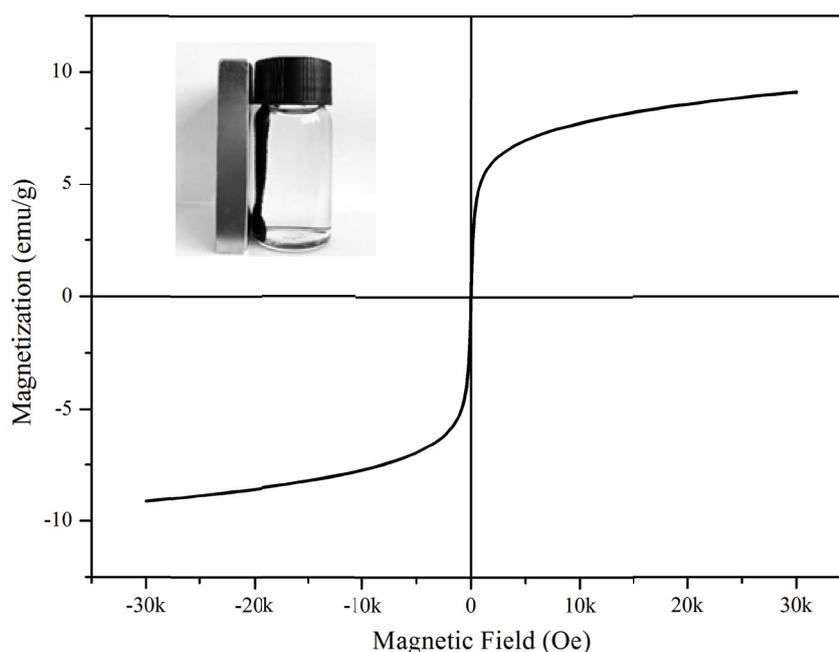


Fig. 8. Magnetic hysteresis loops of MAG@CHT and the photograph of 30 s when MAG@CHT attracted by a permanent magnet (inset).

indicating that it has a layered structure. Due to the loss of a large amount of interlayer water and hydroxyl groups in MAG@CHT, the original negative electrode layer was destroyed and thus the layered structure was destroyed. After adsorbing perchlorate in water, the perchlorate is fixed on positive layer of MAG@CHT through weak hydrogen bonding and electrostatic interactions to form the new negative layer. It indicates that MAG@CHT restored layered structure after adsorbing perchlorate, which is consistent with the FTIR pattern results. The successful adsorption of perchlorate was observed in FTIR spectrum of MAG@CHT after adsorption. The results show that the restoration of the layered structure through the “memory effect” can effectively adsorb perchlorate. In summary, the adsorption mechanism of perchlorate on MAG@CHT mainly includes: (1) adsorption on the surface of adsorbent by electrostatic interactions; (2) restoration of the layered structure by using ClO_4^- as an anion interlayer.

4. Conclusion

In this study, a magnetic Mg/Fe hydrotalcite calcined material (MAG@CHT) was synthesized by co-precipitation and calcination to effectively adsorb perchlorate from aqueous solution. The pseudo-second-order kinetic model better describes the kinetics of adsorption of perchlorate on MAG@CHT. The Langmuir model is more satisfactory for fitting isotherm experimental data. The order of influence of coexisting ions on perchlorate removal rate is: $\text{Cl}^- < \text{NO}_2^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{PO}_4^{3-}$. It was confirmed by XRD and FTIR analysis that after the magnetic Mg/Fe hydrotalcite was calcined at 500°C, the layered structure of the hydrotalcite was destroyed. The original layered structure is restored after adsorption of perchlorate. It was confirmed by XRD and XPS analysis that Fe_3O_4 did not affect the hydrotalcite structure during the preparation of MAG@CHT, and was successfully loaded on hydrotalcite. VSM analysis shows that MAG@CHT is a superparamagnetic material. This study shows that MAG@CHT is a novel adsorbent that has both magnetic properties and adsorption capacity for perchlorate.

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