



## Regular Article

# Synthesis and application of magnetic chlorapatite nanoparticles for zinc (II), cadmium (II) and lead (II) removal from water solutions

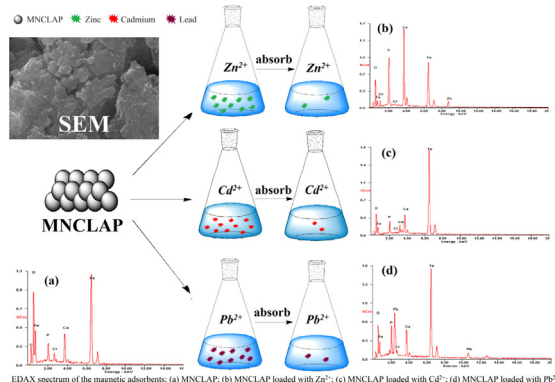


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Magnetic chlorapatite nanoparticles (MNCLAP) was synthesized and used as adsorbent to remove Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from aqueous solutions. The synthesized MNCLAP was characterized by scanning electron microscopy (SEM), energy dispersive analysis system of X-ray (EDAX), transmission electron microscopy (TEM) X-ray powder diffraction (XRD) and magnetization curves. Influence of different sorption parameters, such as equilibration time, initial heavy metal concentration, the amount of MNCLAP, pH values and competition adsorption were investigated in this study. Moreover, the desorption experiment was also carried out to explore the adsorption property of MNCLAP. The adsorption kinetic data has a very high correlation coefficient ( $R^2 = 0.9999$ ) with the pseudo-second-order kinetic model, and the Langmuir model was used in describing adsorption isotherms. The maximum adsorption capacities of MNCLAP adsorbent towards Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> were 1.1769, 1.1022 and 1.1546 mmol g<sup>-1</sup>, respectively. EDTA solution was the best efficient eluant for heavy metal desorption with 25.94%, 22.95% and 32.84% released rate of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>, respectively. Experimental results revealed that the prepared MNCLAP combined both the properties of chlorapatite and magnetic material and it showed remarkable advantages in heavy metal removal from aqueous solutions.

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## 1. Introduction

Heavy metals like zinc (Zn), cadmium (Cd) and lead (Pb) in environments are harmful to animals, plants, and humans because of their toxicity properties [1–5]. For example, Pb could cause toxicant on aquatic organisms by multiple channels directly or indirectly through food chains, drinking water, and skin contact [6,7]. So the removal of heavy metals such as Zn, Cd and Pb from natural environment has attracted wide attentions [8–10]. Many techniques were used to remove toxic heavy metals from polluted water, such as adsorption, chemical precipitation, filtration, complexing, and electrochemical treatment [11,12]. Adsorption technologies have gained the most attention owing to its simple operation, economy and merits of efficiency [13,14]. The commonly used prevalent adsorbents includes hydroxyapatite, zeolites, clays, activated carbons, polymeric materials and biomass [15,16]. At present, many papers have investigated the functions of environmental mineral material for the treatment of heavy metal in wastewater. It has been reported that zeolites [17,18], montmorillonite [19,20], rectorite [21,22], graphene [23–26], diatomite [27,28] and other minerals were effective to remove heavy metals from wastewater [29,30] with low cost. However, these adsorbents have low separation inconvenience and low absorption capacity; therefore, efforts are still needed to find new promising adsorbents.

Phosphate (P) amendments have been widely recognized as a low-cost, effective and non-disruptive material for the treatment of heavy metals. Apatite materials [ $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ , X = F, Cl, Br, OH] with special crystal chemistry characteristics are becoming the most promising P-based materials for the heavy metal removal from wastewater [31,32]. As a kind of apatite, chlorapatite [ $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$  (CLAP)] is an ideal material for heavy metal removal since the complexes of CLAP and heavy metal were highly stable under oxidizing and reducing conditions, and CLAP has a high adsorption capacity for heavy metals [33–36]. On the other hand, CLAP can be easily synthesized and even has no toxicity to organism, thus it is possible to regulate the concentrations of Pb, Cd, Zn, and other heavy metals in environment [37,38]. Additionally, it has also been confirmed that CLAP could transfer the metals from unstable fraction to stable fraction and reduce the toxicity by precipitation, ion exchange and adsorption effect [39–42]. In our previous study, we found that the modified CLAP could immobilize heavy metals in polluted sediment with a high efficiency through precipitation and adsorption effect [43]. However, the modified CLAP could not be applied in aquatic environment since it is difficult to remove the loaded-nanoparticles from polluted water with the only use of CLAP. In consideration of the potential eutrophication risk induced by the application of P-materials, CLAP is almost banned in wastewater treatment. As a fast, efficient and economical way to separate materials from aquatic environment, magnetic separation technology has been widely used in wastewater treatment and gained extensively attention [44,45]. Therefore, the combination of CLAP and magnetic separation technology may be a promising way to make the possible use of CLAP in removal of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from water solution without posing secondary pollution to the environment [46].

In this study, we propose to synthesize a new class of magnetic chlorapatite nanoparticles (MNCLAP) and explore the possibility of using it as an adsorbent to remove  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from water solution. The MNCLAP was expected to combine both the properties of chlorapatite and magnetic material, in which the chlorapatite may act as an adsorption agent with a high adsorption capacity and the magnetic material plays as an assistant for the separation of loaded-nanoparticles from polluted water. In addition, using MNCLAP as an adsorbent to remove heavy metals from water solution has never been reported in the literature before. The

characterization and the adsorption experiments of the MNCLAP adsorbents were also investigated in details below.

## 2. Experimental materials and methods

### 2.1. Materials

Cadmium chloride hemidihydrate ( $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ ), zinc chloride ( $\text{ZnCl}_2$ ), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), iron (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ammonia (25%), trisodium phosphate dodecahydrate ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ) and calcium chloride dehydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). All solutions were prepared from their nitrate salts (AR) with ultra-pure water.

### 2.2. Synthesis of MNCLAP

The synthesis of MNCLAP was carried out according to the earlier reported literature with some modifications [47]. The specific steps were as follows: at room temperature, reasonable amount of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (3.7 mmol) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (1.85 mmol) were dissolved in 30 mL deoxygenated water under a nitrogen atmosphere and then solicated for 10 min. After that, 10 mL of 25% ammonia solution was added to the above solution under mechanical stirring with the formation of black precipitate. After 15 min, an amount of 50 mL of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  ( $6.08 \text{ g L}^{-1}$ , pH = 11) and an amount of 50 mL of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  ( $3.9369 \text{ g L}^{-1}$ , pH = 11) solutions were added to the resulted precipitate solution drop wisely under mechanical stirring. After 30 min, the solution was heated at  $90^\circ\text{C}$  for 2 h and then cooled without stirring for 12–24 h at room temperature. Then used magnet to separate precipitate and washed the precipitate repeatedly with deionized water till neutrality. The products were dried in the oven at  $90^\circ\text{C}$  for 4 h then grinded them into powder. Finally, the products were the prepared MNCLAP.

### 2.3. Adsorbent characterization

The morphology of synthesized MNCLAP was characterized using a scanning electron microscope (SEM) (Quanta TM-250, USA). Transmission electron microscopy (TEM, FEI Titan 300-kV FEG) attached with energy dispersive analysis system of X-ray (EDAX) system was employed to investigate the nanoparticle structure. Images of the materials were obtained at an accelerating voltage of 20 kV. X-ray diffraction (XRD) patterns of MNCLAP samples were studied using AXS D8 Advance, LynxEye array detector equipped with Cu-K $\alpha$  radioactive source ( $\lambda = 0.154 \text{ nm}$ ). The angle of diffraction was varied from  $10^\circ$  to  $80^\circ$  at the speed of  $2^\circ/\text{min}$ . The magnetic properties were characterized by magnetization curves using a HH-50 vibrating sample magnetometer under the condition of sensitivity 20 mV.

### 2.4. Adsorption experiments

At room temperature ( $25 \pm 1^\circ\text{C}$ ), the experimental adsorption of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were carried out according to the batch method. The initial concentration of three heavy metals in conical flasks was  $2 \times 10^{-3} \text{ mol L}^{-1}$  (20 mL, pH =  $5 \pm 0.1$ ) and the dosage of MNCLAP adsorbent was  $0.1 \text{ g L}^{-1}$ . The mixture sample was placed in the constant temperature water bath oscillator and shaken for a period of time. After that, we used a magnet to separate MNCLAP from the solutions. The initial and final heavy metal concentrations were detected by atomic absorption spectrophotometer (AAS, Agilent 3510, and USA).

#### 2.4.1. Effect of equilibration time

The effect of contact time on metal sorption was investigated in different time intervals from 15 min to 48 h with the initial concentration of  $2 \times 10^{-3} \text{ mol L}^{-1}$  (20 mL, pH =  $5 \pm 0.1$ ). After the completely reaction, the samples were taken out and the MNCLAP adsorbent was separated by a magnet while the residual heavy metal concentrations were measured by AAS.

#### 2.4.2. Effect of initial metal concentration

Sorption isotherms were studied by equilibrating MNCLAP adsorbent with metal solutions of different initial concentrations ranging from  $10^{-4}$  to  $10^{-2} \text{ mol L}^{-1}$  for 24 h. After the completely reaction, the samples were taken out and the MNCLAP adsorbent was separated by a magnet while the final heavy metal concentrations were measured by AAS.

#### 2.4.3. Effect of MNCLAP amount

The conical flasks containing different amount (0.05, 0.07, 0.1, 0.2, 0.3 and  $0.5 \text{ g L}^{-1}$ ) of MNCLAP adsorbent and  $2 \times 10^{-3} \text{ mol L}^{-1}$  of metal solution were shaken on a constant temperature water bath oscillator for 24 h. After the completely reaction, the samples were taken out and the MNCLAP adsorbent was separated by a magnet while the final heavy metal concentrations were measured by AAS.

#### 2.4.4. Effect of pH

To evaluation the sorption behavior of different metals, the initial pH of the heavy metal solutions was adjusted to 4–10 (using  $\text{HNO}_3$  or  $\text{NaOH}$ ) with the same metal initial concentrations, equilibration time and adsorbent amount. After the completely reaction for 24 h, the samples were taken out and the MNCLAP adsorbent was separated by a magnet while the final heavy metal concentrations were measured by AAS.

#### 2.4.5. Competitive adsorption

In the competitive adsorption experiment, one heavy metal ion concentration was fixed to  $2 \times 10^{-3} \text{ mol L}^{-1}$  with other heavy metal ions concentration varying from  $10^{-4}$  to  $10^{-2} \text{ mol L}^{-1}$  to study the effect of three metal ions coexistence on the total adsorptive capacity of MNCLAP. To make the comparison more accurately, the initial metal concentrations ranging from  $10^{-4}$  to  $10^{-2} \text{ mol L}^{-1}$  were selected, which was in consistent with isotherm experiment. Other conditions were the same with the process we mentioned above.

#### 2.5. Desorption experiments

In this part, in order to assess the reversibility of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  sorption, the desorption experiments were conducted in solutions with different initial pH. Specific methods are as follows: Firstly, an amount of MNCLAP adsorbent was loaded with  $2 \times 10^{-2} \text{ mol L}^{-1}$  of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  to reach the equilibration. After that, the mixture was separated by a magnet and the residual heavy metal concentrations were measured by AAS. Then the heavy metal-loaded MNCLAP adsorbent separated from the mixture was extensively washed by ultra-pure water with several times and dried at  $90^\circ\text{C}$  in an oven. Secondly, 0.10 g of dried MNCLAP adsorbent was added into four kinds of eluants (20 mL) separately, which includes  $\text{Ca}(\text{NO}_3)_2$ , EDTA, HCl and NaOH. The samples were placed in a constant temperature water bath oscillator and shaken for 24 h. At last, the samples were taken out and the MNCLAP adsorbent was separated by a magnet while the final heavy metal concentrations were measured by AAS.

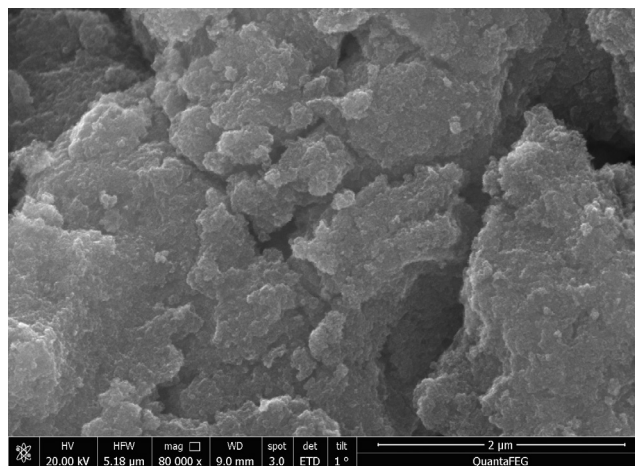


Fig. 1. SEM micrograph of the synthesized MNCLAP adsorbents.

### 3. Results and discussion

#### 3.1. Characterization of MNCLAP

Fig. 1 was the SEM micrograph of MNCLAP. As can be seen from in Fig. 1, the synthesized MNCLAP was in spherical shape with a rough surface. Fig. 2 was the TEM image of synthesized MNCLAP. From the TEM image, we can see that the average diameter of these particles was estimated at approximately 20 nm. Fig. 3 showed the EDAX spectra of MNCLAP adsorbents unloaded and loaded with  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , respectively. Fig. 3 showed the MNCLAP adsorbents were consisted of calcium, phosphorus, iron and oxygen and the composition of each element were shown in Table 1. From Table 1 we can see that iron and oxygen were successfully presented in MNCLAP adsorbents with a remarkable content. Comparing the spectras of loaded MNCLAP (Fig. 3b–d) with unloaded MNCLAP (Fig. 3a), the zinc peak, cadmium peak and lead peak could be observed in Fig. 3b, c and d, respectively, which suggested

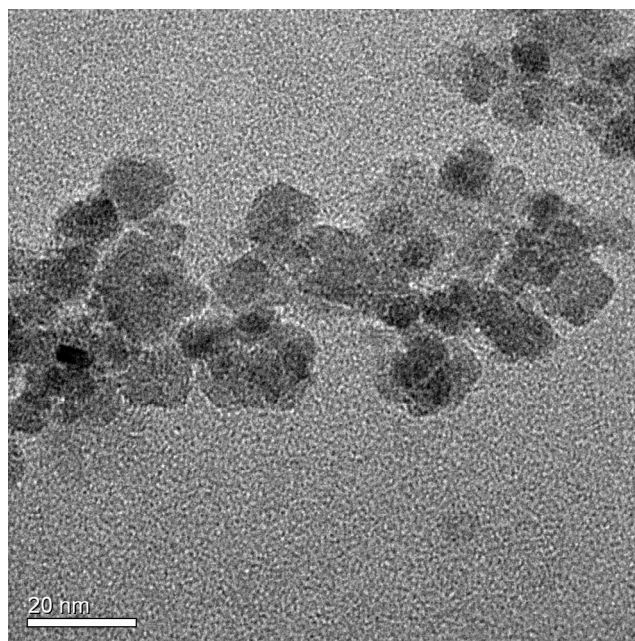


Fig. 2. TEM micrograph of the synthesized MNCLAP adsorbents.

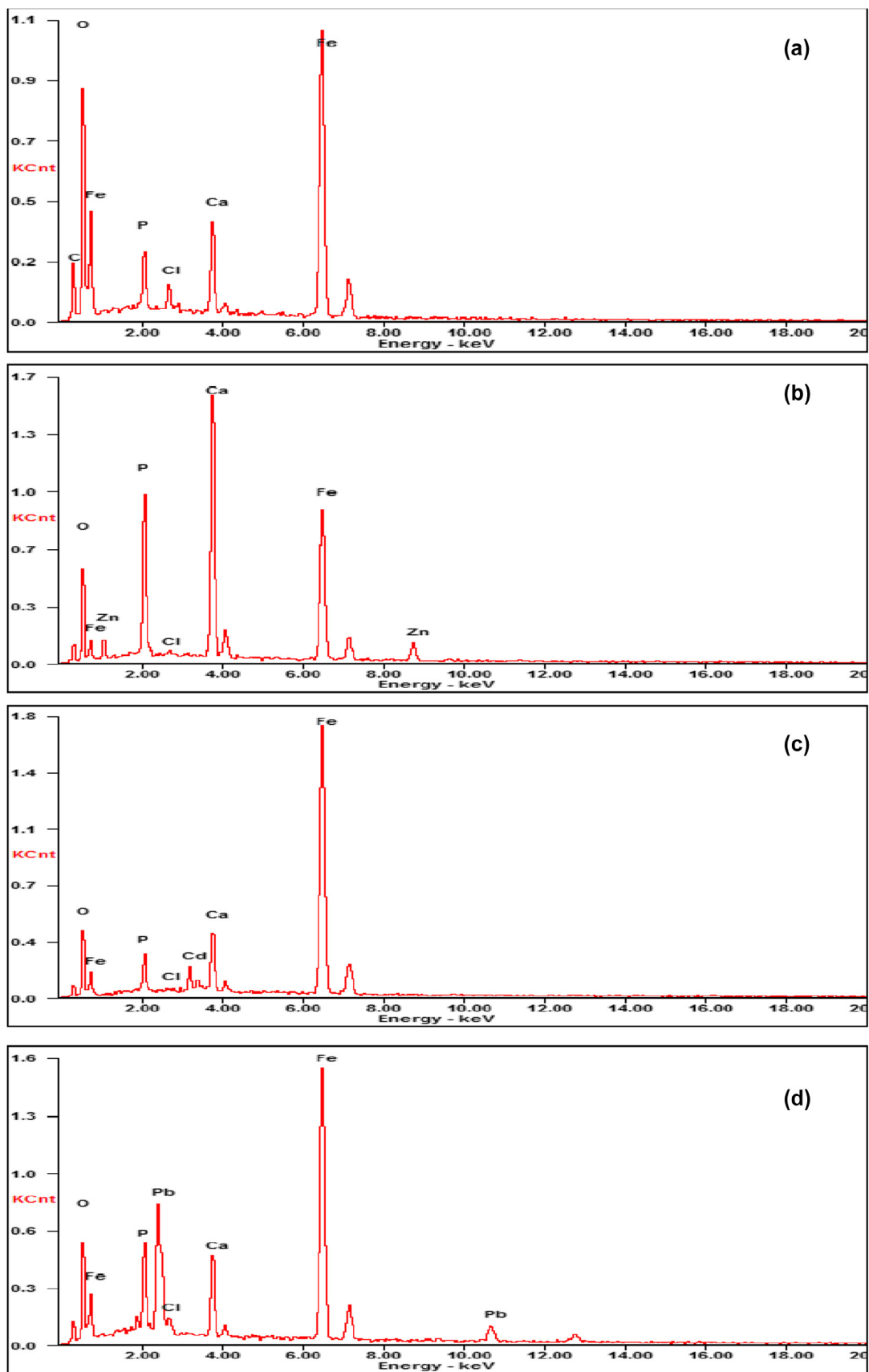


Fig. 3. EDAX spectrum of the magnetic adsorbents: (a) MNCLAP; (b) MNCLAP loaded with Zn<sup>2+</sup>; (c) MNCLAP loaded with Cd<sup>2+</sup>; (d) MNCLAP loaded with Pb<sup>2+</sup>.

**Table 1**The chemical composition of before and after loaded Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>.

Substance (At%)	Ca	P	O	Fe	Zn	Cd	Pb
MNCLAP	4.1	2.85	40.22	24.17	0	0	0
MNCLAP loaded with Zn	14.16	11.99	59.07	12.47	2.02	0	0
MNCLAP loaded with Cd	6.33	5.64	48.93	36.66	0	2.05	0
MNCLAP loaded with Pb	6.26	8.21	56.11	24.84	0	0	3.54

that Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> had been adsorbed on the surface of MNCLAP successfully.

Fig. 4 showed the XRD pattern of prepared MNCLAP adsorbent. It can be seen in Fig. 4 that the main components of MNCLAP were apatite (chlorapatite), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (Fe<sub>2</sub>O<sub>3</sub>). It suggested that the MNCLAP was successfully synthesized and magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (Fe<sub>2</sub>O<sub>3</sub>) acted as magnetic material in it. The magnetization curve of the MNCLAP was measured under room conditions and results were shown in Fig. 5. It can be seen from the Fig. 5 that the saturation magnetization was 40.68 emu g<sup>-1</sup>, suggesting that there was a strong magnetic response to a magnetic field. It has been known that the saturation magnetization, which indicated the maximum magnetic strength, is a most important parameter magnetic separation. Previous study has reported that 16.3 emu g<sup>-1</sup> of saturation magnetization was enough for magnetic separations with a conventional magnet [48]. Therefore, in our study, the synthesized MNCLAP has the enough ability to be separated from solutions. Fig. S1 showed the separation process of the MNCLAP adsorbent from the mixture solution, which we can see that the MNCLAP adsorbent can be successfully separated from the solutions by an external magnetic field. Thus, sufficient evidences confirmed that the MNCLAP adsorbent synthesized in this experiment can be used as magnetic adsorbents to remove Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from the solution.

### 3.2. Adsorption experiment

#### 3.2.1. Sorption kinetics

The sorption kinetics experiments were conducted in this study and results were presented in Fig. 6. Fig. 6 showed that the adsorption of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> by MNCLAP was separated into two dis-

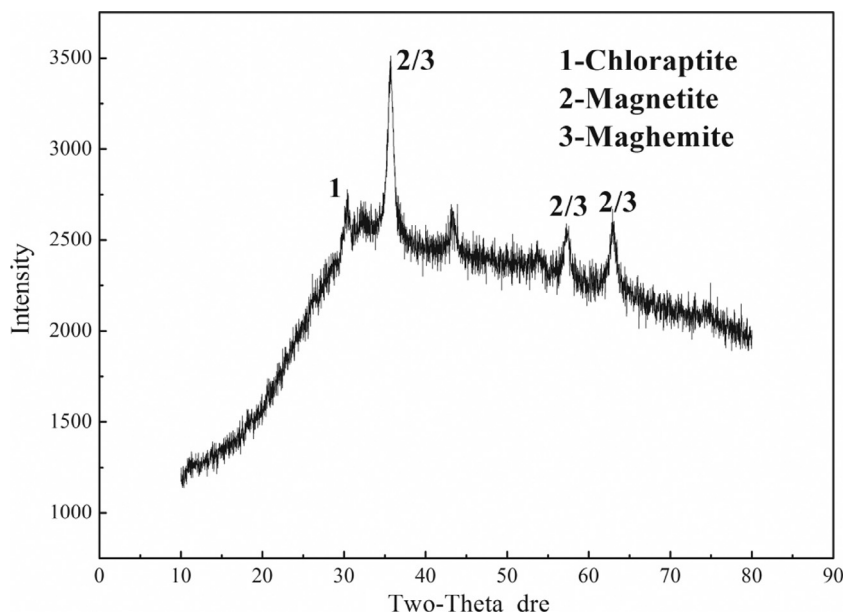
tinct stages: the adsorption of metal was increased quickly in the first two hours and then slowed down until reached to the adsorption equilibrium. The time for adsorption equilibrium was estimated to 24 h since there was only a slight increase of adsorption quantity after 24 h and it could almost be neglected in consideration of the sorption system. Therefore, the contact time we chosen in this study was 24 h.

In this experiment, we choose the pseudo-second-order kinetic model to determine the adsorption rate constants. The expression of linear form of pseudo-second-order kinetic model as follows:

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

where  $q_t$  (mmol g<sup>-1</sup>) represented the amount of heavy metal ions adsorbed on MNCLAP at  $t$  time (h) and  $q_e$  (mmol g<sup>-1</sup>) indicated the amounts of heavy metal ions adsorbed on MNCLAP at equilibrium time,  $k$  (g mmol<sup>-1</sup> h<sup>-1</sup>) is the rate constant of pseudo-second-order kinetics. Second-order rate constant  $k$  and  $q_e$  can be obtained from the intercept and slope of the plot by plotting the  $t/q_t$  versus  $t$ , respectively.

Table 2 listed the results of pseudo second-order model data in our experiment. As can be seen from the table, the correlation coefficients of linear relationship between  $t/q_t$  and  $t$  were 0.9999 for Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>, respectively, which indicated that the sorption process of the present experiment was in consistent with the pseudo second-order kinetic model. According to previous studies [49], the pseudo-second-order kinetic model was found to be suitable to describe the kinetics of metal sorption by different apatite materials: Chojnacka et al. studied the equilibrium and kinetic modeling of chromium (III) sorption by animal bones using the pseudo-second-order kinetic model [50]; Cheung et al. used the

**Fig. 4.** XRD pattern of the MNCLAP.

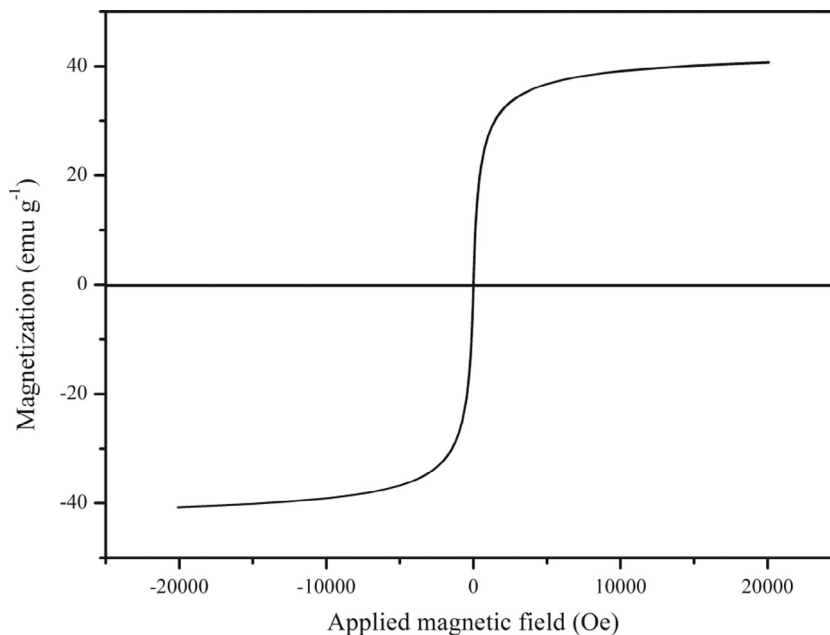


Fig. 5. The magnetic hysteresis loop diagram of the MNCLAP.

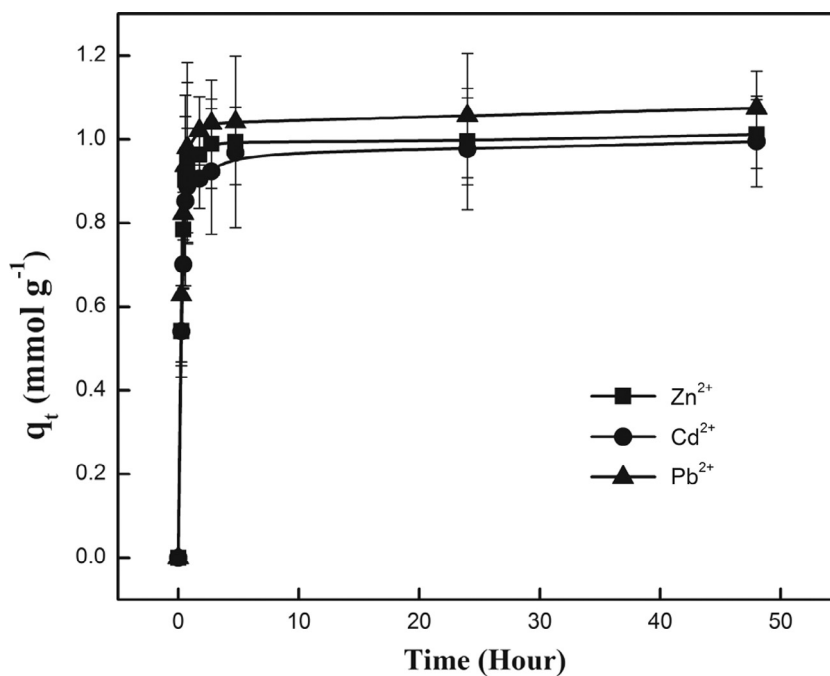


Fig. 6. Adsorption kinetic curves of heavy metals by MNCLAP adsorbents.

Table 2  
MNCLAP of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> of adsorption kinetic parameters.

Substance	$q_e$	$k$	$R^2$
Zn <sup>2+</sup>	0.9881	0.1200	0.9999
Cd <sup>2+</sup>	1.0045	0.1782	0.9999
Pb <sup>2+</sup>	0.9304	0.1264	0.9999

pseudo-second-order kinetic model to investigate the sorption kinetic for the removal of cadmium ions from effluents using bone char [51]; Chaturvedi et al. also studied sorption kinetics and leach ability of heavy metal from the contaminated soil amended with

immobilizing agent (humus soil and hydroxyapatite) using the pseudo-second-order kinetic model [52] and the pseudo-second-order kinetic model was also used in Saxena et al. study to analyze the sorption of uranium by low-cost rock phosphate [53].

### 3.2.2. Sorption isotherms

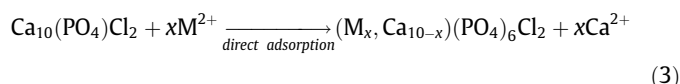
To obtain the adsorption capacity of the MNCLAP adsorbents on heavy metal ions, sorption experiment was conducted with the initial concentrations of examined metals ranging from 10<sup>-4</sup> to 10<sup>-2</sup> mol L<sup>-1</sup>. The maximum adsorption capacities for heavy metals by MNCLAP adsorbents were assessed by the adsorption isotherms. In order to describe the adsorption behavior of MNCLAP in this

experiment, the Langmuir adsorption isotherm was used. The linear form of Langmuir isotherm equation can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{C_e}{q_m b} \quad (2)$$

where  $q_e$  ( $\text{mmol g}^{-1}$ ) was the amount of metal ions adsorbed on MNCLAP at equilibrium time,  $q_m$  ( $\text{mmol g}^{-1}$ ) was the maximum adsorption capacity of MNCLAP,  $C_e$  ( $\text{mol L}^{-1}$ ) was the amount of metal ions in the liquid at equilibrium time,  $b$  ( $\text{L mol}^{-1}$ ) was the Langmuir constant and it was related to the energy of adsorption. By plotting  $C_e/q_e$  versus  $C_e$  of the plot the constants  $b$  and  $q_m$  can be obtained from the intercept and slope of the linear plot, respectively. The results from Fig. 7 showed that the correlation coefficients for the adsorption of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on MNCLAP were 0.9998, 0.9997 and 0.9996, respectively, indicating that the Langmuir adsorption isotherm was appropriate for describing the experimental data. The Langmuir constants for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were  $0.3047 \times 10^3$ ,  $0.3215 \times 10^3$  and  $0.4098 \times 10^3 \text{ L mol}^{-1}$ , respectively, demonstrating that the MNCLAP had better adsorption affinity for  $\text{Pb}^{2+}$  than  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  since the Langmuir constant has a positive relationship with the binding energy. The maximum adsorption capacities of MNCLAP for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were 1.1769, 1.1022 and  $1.1546 \text{ mmol g}^{-1}$ , respectively. In previous studies, researchers

have demonstrated the maximum adsorption capacities of hydroxyapatite for  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  were  $0.592$  and  $0.568 \text{ mmol g}^{-1}$ , respectively [54]. Reddad et al. investigated the adsorption behaviors of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by using the sugar beet pulp as adsorbent and found that the maximum adsorption capacities of sugar beet pulp for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were  $0.2706$ ,  $0.2161$  and  $0.3556 \text{ mmol g}^{-1}$ , respectively. Some literatures about the heavy metal adsorption by other adsorbents were summarized in Table 3. From Table 3 we can see that prepared MNCLAP has an absolute advantage in the adsorption of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  with much higher adsorption capacity than other adsorbents. That may attribute to the special crystal chemistry characteristics of nano-chlorapatite since the chlorapatite could scavenge heavy metals through precipitation, ion-exchange and adsorption effects [55]. The related equations were shown as below:



where  $\text{M}^{2+}$  represented the heavy metal ions.

### 3.2.3. Effect of MNCLAP amount

In order to determine relationship between MNCLAP amount and the heavy metals adsorption quantities, sorption experiment

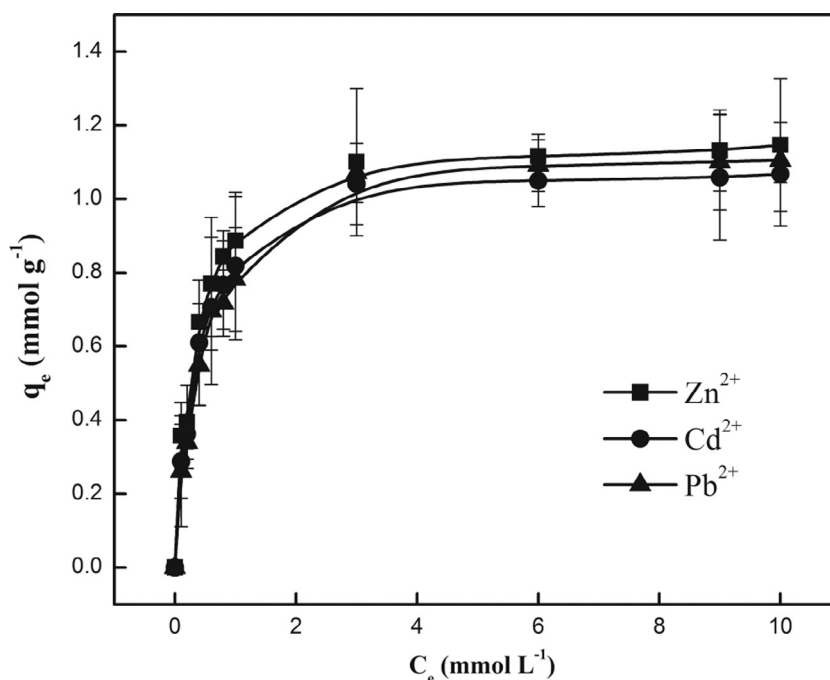


Fig. 7. Adsorption isotherms curves of heavy metals by MNCLAP adsorbents.

Table 3  
Comparison of adsorption capacities of various adsorbents towards  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ .

Type of adsorbent	Adsorption capacities ( $\text{mmol g}^{-1}$ )			References
	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$	
Hydroxyapatite	0.592	0.568	–	[54]
Hydroxyapatite	0.336	0.371	0.384	[56]
Sugar beet pulp	0.2706	0.2161	0.3556	[57]
Silica-supported dithiocarbamate	–	0.3587	0.3397	[58]
Fungal biomass immobilized within a loofa sponge (FBILS)	0.7477	–	0.6472	[59]
Salicylic acid type chelate adsorbent	0.477	0.508	0.4194	[60]
Polymer-modified magnetic nanoparticles	0.6636	0.2633	0.8016	[61]
MNCLAP	1.1769	1.1022	1.1546	This work

was conducted with the MNCLAP amount ranging from 0.05 to 0.5 g L<sup>-1</sup> and results were shown in Fig. 8. Results demonstrated that the adsorbed heavy metals, including Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>, were increased with the increasing of MNCLAP amount at the beginning. Then the adsorption amount reached to the maximum at the MNCLAP dosage of 0.1 g L<sup>-1</sup>. After that, the adsorption amount was experienced a sharply decrease with the increasing of MNCLAP amount. The possible explanation was that at the initial stage with a quantitative amount of heavy metals, the adsorption

process was accelerated by providing more adsorption sites through increasing the dosage of MNCLAP before reached to the maximum (saturation). However, when the adsorption reached to the equilibrium, the heavy metal retained in solutions cannot adsorb on the available adsorption sites of added MNCLAP since the same cations were distributed on greater amount of surface. Thus the optimum adsorption amount of MNCLAP for three metal ions removal was 0.1 g L<sup>-1</sup>, which was used in the following experiment.

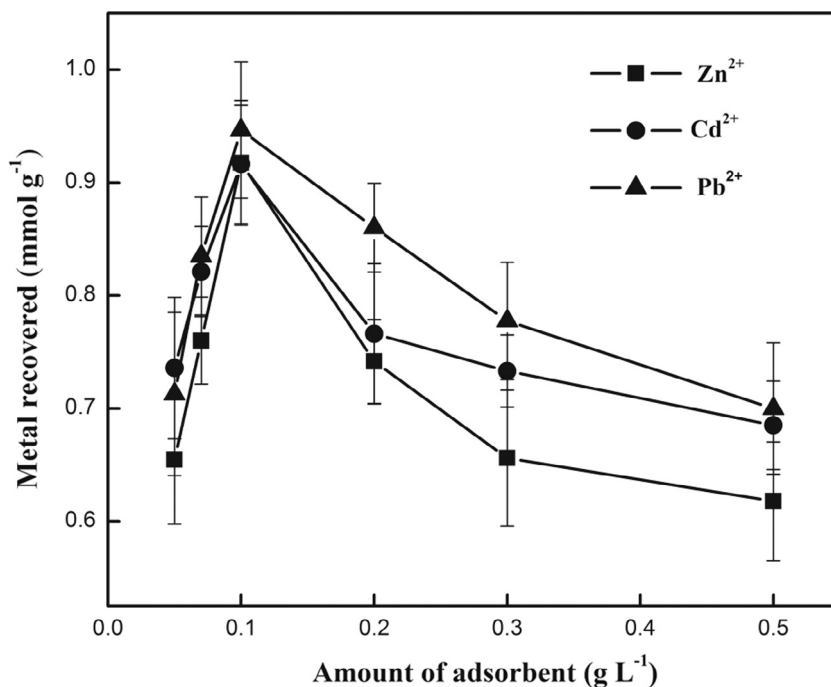


Fig. 8. The effect of MNCLAP amount.

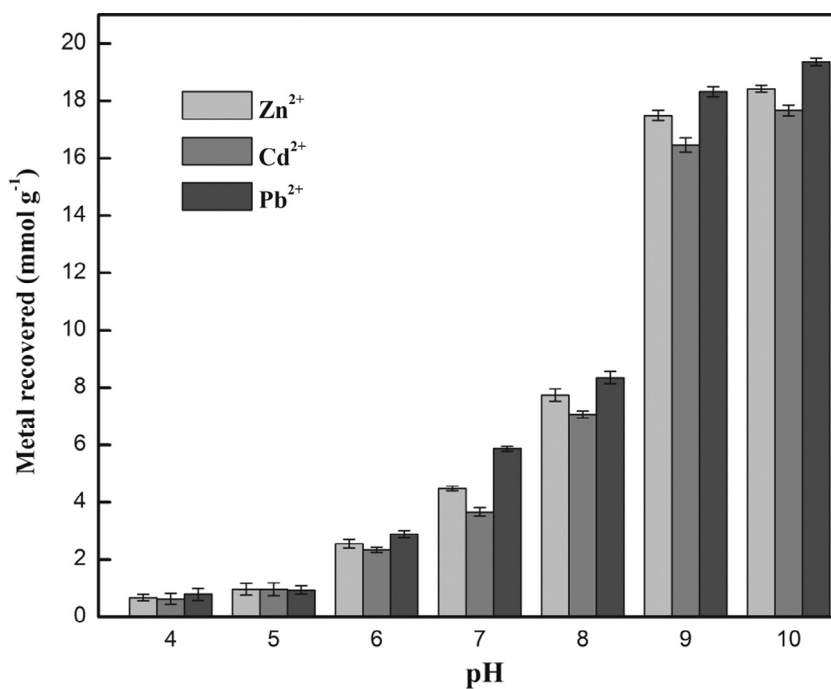
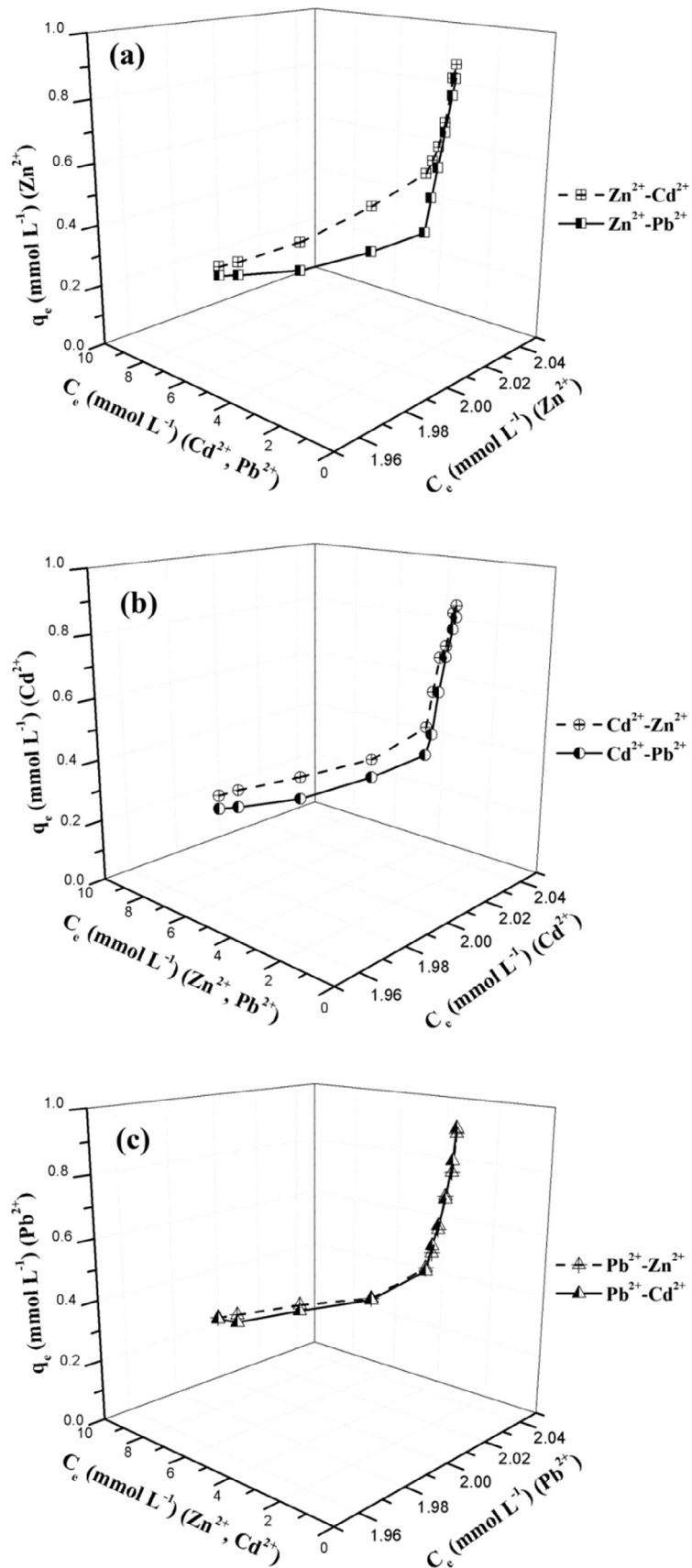


Fig. 9. The effect of initial pH values on the amount of the heavy metals adsorbed on MNCLAP adsorbents.





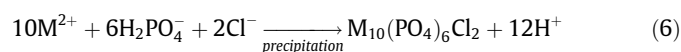
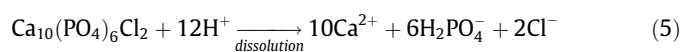
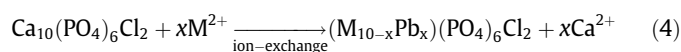
**Fig. 10.** The competitive of adsorption behavior of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>: (a) the relationship between the adsorption capacity of Zn<sup>2+</sup> and the equilibrium concentrations of Zn<sup>2+</sup>-Cd<sup>2+</sup> and Zn<sup>2+</sup>-Pb<sup>2+</sup>; (b) the relationship between the adsorption capacity of Cd<sup>2+</sup> and the equilibrium concentrations of Cd<sup>2+</sup>-Zn<sup>2+</sup> and Cd<sup>2+</sup>-Pb<sup>2+</sup>; (c) the relationship between the adsorption capacity of Pb<sup>2+</sup> and the equilibrium concentrations of Pb<sup>2+</sup>-Zn<sup>2+</sup> and Pb<sup>2+</sup>-Cd<sup>2+</sup>.

**Table 4**  
Desorption of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from loaded MNCLAP adsorbents.

Eluants	Initial pH	Final pH			Desorbed (%)		
		Zn <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>
EDTA (0.003 mol L <sup>-1</sup> )	2.64	5.25	5.64	5.77	25.94	22.95	32.84
HCl (0.01 mol L <sup>-1</sup> )	2.22	4.92	4.08	3.82	5.98	5.99	8.42
NaOH (0.01 mol L <sup>-1</sup> )	11.94	9.17	9.59	9.43	0.99	0.76	4.38
Ca(NO <sub>3</sub> ) <sub>2</sub> (0.01 mol L <sup>-1</sup> )	5.71	6.31	6.74	6.63	15.96	14.15	15.13

### 3.2.4. Effect of pH

To investigate the influence of initial pH on heavy metal adsorption, the initial pH ranging from 4 to 10 were selected for the pH experiment. The relationship between the adsorbed amount of heavy metals by MNCLAP and pH values was shown in Fig. 9. As can be seen from the Fig. 9, with the increase of pH value, the amount of adsorbed metal ions (including Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>) was gradually increased. A remarkable increase can be noticed when pH exceeded 8, after which the adsorption amount increased dramatically. The possible explanation for this phenomenon may be that the heavy metal ions started to precipitate under extremely alkaline conditions, leading to the reduction of metal ions in solution. In the early study of Chen et al., they also found that the initial solution pH could greatly affect the metal sorption mechanism by apatite, along with the changes of metal-apatite reaction products [62]. Pyromorphite-type minerals such as ZnO, CdCO<sub>3</sub> or Cd(OH)<sub>2</sub>, and Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> were confirmed to be apatite-induced adsorption products of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> under alkaline condition, respectively [62]. Additionally, Smičiklas et al. also reported that the sorption of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> by hydroxyapatite was increased with an increase of pH, they demonstrated that the ion exchange, specific cation sorption, dissolution-precipitation were the mechanisms involved [56]. Related equations were shown in below:



where M<sup>2+</sup> represented the heavy metal ions.

### 3.2.5. Competition adsorption behavior

The relationship between the adsorption capacity of MNCLAP and the initial concentration of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> with the total metal concentration unchanged was shown in Fig. 10. It can be seen from Fig. 10 that the adsorption capacity of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> experienced some reductions with the coexistence of other heavy metal ions. An interesting phenomenon was found in the competition adsorption behaviors among the estimated metal ions: the adsorption capacity of MNCLAP on Zn<sup>2+</sup> was reduced from 0.9556 to 0.1326 mmol g<sup>-1</sup> and from 0.9168 to 0.0976 mmol g<sup>-1</sup> with the initial concentration of Cd<sup>2+</sup> and Pb<sup>2+</sup> varying from 10<sup>-4</sup>–10<sup>-2</sup> mol L<sup>-1</sup> to 10<sup>-2</sup> mol L<sup>-1</sup> (Fig. 10a), respectively; the adsorption amount of Cd<sup>2+</sup> on MNCLAP was reduced from 0.9386 to 0.1535 mmol g<sup>-1</sup> and from 0.9071 to 0.1053 mmol g<sup>-1</sup> with the initial concentration of Zn<sup>2+</sup> and Pb<sup>2+</sup> varying from 10<sup>-4</sup> mol L<sup>-1</sup> to 10<sup>-2</sup> mol L<sup>-1</sup> (Fig. 10b), respectively; the adsorption capacity of MNCLAP on Pb<sup>2+</sup> was reduced from 0.9725 to 0.2219 mmol g<sup>-1</sup>, and from 0.9872 to 0.2168 mmol g<sup>-1</sup> with the initial concentration of Zn<sup>2+</sup> and Cd<sup>2+</sup> varying from 10<sup>-4</sup> mol L<sup>-1</sup> to 10<sup>-2</sup> mol L<sup>-1</sup> (Fig. 10c), respectively, that was to say, the coexistence of other heavy metal ions may greatly reduce the one type metal adsorp-

tion by MNCLAP since the maximum adsorption capacities of MNCLAP adsorbent towards single Zn<sup>2+</sup>, Cd<sup>2+</sup> or Pb<sup>2+</sup> are 1.1769, 1.1022 and 1.1546 mmol g<sup>-1</sup>, respectively. This fact indicated that Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> were adsorbed in the same sites and they would compete for the adsorption sites on MNCLAP adsorbent in the binary system. Results also indicated that the adsorption capacity of Zn<sup>2+</sup> and Cd<sup>2+</sup> were reduced more apparently with the presence of Pb<sup>2+</sup> in the binary system. That may attribute to the higher Langmuir constant of Pb<sup>2+</sup> than Zn<sup>2+</sup> and Cd<sup>2+</sup> during the adsorption, which was in consistent with the study of Corami et al. [63]. Consequently, owing to the higher Langmuir constant, effects of the coexistence of Zn<sup>2+</sup> and Cd<sup>2+</sup> on Pb<sup>2+</sup> adsorption were more slightly and the reduction of Pb<sup>2+</sup> adsorption capacity induced by Cd<sup>2+</sup> was more apparent than Zn<sup>2+</sup>. It confirmed that the adsorption affinity of MNCLAP was in the order of: Pb<sup>2+</sup> > Cd<sup>2+</sup> > Zn<sup>2+</sup>.

### 3.3. Desorption experiment

The results of desorption experiment were shown in Table 4. Results showed that the EDTA solution may induce the biggest heavy metal ions desorption amount from the metal-loaded MNCLAP adsorbent. This phenomenon may attribute to the complex formed by EDTA and metal ions which possesses lower sorption affinity for MNCLAP adsorbents [64]. It can be found that whether under the extreme acid or alkaline conditions, only trace amounts of metal ions can be desorbed, and the desorbed Zn<sup>2+</sup> and Cd<sup>2+</sup> were almost negligible under the alkaline condition. Additionally, the desorption rates of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> in Ca(NO<sub>3</sub>)<sub>2</sub> solutions were 15.96%, 14.15%, and 15.13%, respectively. This may due to the reversible process of ion-exchange [shown in Eq. (4)] between the MNCLAP adsorbents and the solution: Ca<sup>2+</sup> may concentrate on the surface of MNCLAP adsorbents while the concentration of Ca<sup>2+</sup> in solutions was higher than that of MNCLAP adsorbents, leading to the desorption of heavy metals.

## 4. Conclusions

In this study, a new class of magnetic chlorapatite nanoparticles was synthesized and its possibility to remove Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from water solution was investigated. The product MNCLAP was characterized by SEM, EDAX, TEM, XRD and magnetization curves, and these results demonstrated that the MNCLAP was in spherical shape within about 20 nm. Laboratory tests showed that prepared MNCLAP could not only remove the heavy metal ions from water solutions but also can be easily separated from the solutions by using an external magnetic field. The maximum adsorption capacities of MNCLAP adsorbent towards Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> were 1.1769, 1.1022 and 1.1546 mmol g<sup>-1</sup>, respectively, which showed a much higher adsorption capacity than other adsorbents reported before. It also can be obtained that the optimum dosage of MNCLAP adsorbent for Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> was 0.1 g L<sup>-1</sup> and the adsorption amount was increased with the pH ranging from 4 to 8. In the binary component system, MNCLAP adsorbent showed a better adsorption affinity for Pb<sup>2+</sup> than for Zn<sup>2+</sup> and Cd<sup>2+</sup>. The EDTA solu-

tion was confirmed to be the most efficient eluant for desorption of metals from MNCLAP. These experimental results showed that in MNCLAP adsorbent the chlorapatite may act as an adsorption agent with a high adsorption capacity and the magnetic material played as an assistant for the separation of loaded-nanoparticles from polluted water. It was the first time to combine both the properties of chlorapatite and magnetic material and the MNCLAP showed remarkable advantages in heavy metal removal from aqueous solutions. The prominent advantage of prepared MNCLAP adsorbents with paramagnetism and high adsorption capacity was particularly important for its possible practical application and the mechanisms involved in the adsorption should be studied in future.

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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.2017.06.056>.

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