- 1 Synthesis and application of magnetic chlorapatite nanoparticles for
- 2 Zinc (II), Cadmium (II) and Lead (II) removal from water solutions
- 3 Bounmy Keochaiyom ^{a,b}, Jia Wan ^{a,b}, Guangming Zeng ^{a,b,*}, Danlian Huang ^{a,b,*},
- 4 Wenjing Xue^{*a,b*}, Liang Hu^{*a,b*}, Chao Huang^{*a,b*}, Chen Zhang^{*a,b*}, Min Cheng^{*a,b*}
- ^a College of Environmental Science and Engineering, Hunan University, Changsha, 410082, PR
- 6 China
- 7 ^b Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry
- 8 of Education, Hunan University, Changsha, 410082, PR China
- 9

^{*} Corresponding author at: College of Environmental Science and Engineering, Hunan University, Changsha, Hunan410082, PR China

Tel: +86 731 88822754; fax: +86 731 88823701

E-mail address: zgming@hnu.edu.cn (G Zeng) and huangdanlian@hnu.edu.cn (D Huang)

10 Abstract

Magnetic chlorapatite nanoparticles (MNCLAP) was synthesized and used as 11 adsorbent to remove Zn^{2+} , Cd^{2+} and Pb^{2+} from aqueous solutions. The synthesized 12 MNCLAP was characterized by scanning electron microscopy (SEM), energy 13 dispersive analysis system of X-ray (EDAX), transmission electron microscopy (TEM) 14 X-ray powder diffraction (XRD) and magnetization curves. Influence of different 15 sorption parameters, such as equilibration time, initial heavy metal concentration, the 16 amount of MNCLAP, pH values and competition adsorption were investigated in this 17 study. Moreover, the desorption experiment was also carried out to explore the 18 adsorption property of MNCLAP. The adsorption kinetic data has a very high 19 correlation coefficient ($R^2 = 0.9999$) with the pseudo-second-order kinetic model, and 20 the Langmuir model was used in describing adsorption isotherms. The maximum 21 adsorption capacities of MNCLAP adsorbent towards Zn^{2+} , Cd^{2+} and Pb^{2+} were 22 1.1769, 1.1022 and 1.1546 mmol g⁻¹, respectively. EDTA solution was the best 23 efficient eluant for heavy metal desorption with 25.94%, 22.95% and 32.84% released 24 rate of Zn^{2+} , Cd^{2+} and Pb^{2+} , respectively. Experimental results revealed that the 25 prepared MNCLAP combined both the properties of chlorapatite and magnetic 26 material and it showed remarkable advantages in heavy metal removal from aqueous 27 solutions. 28

29 Keywords

Magnetic chlorapatite nanopaticles; Adsorption; Desorption; Zinc (II); Lead (II);
Cadmium (II)

32 **1. Introduction**

Heavy metals like zinc (Zn), cadmium (Cd) and lead (Pb) in environments are 33 34 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 35 36 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 37 attracted wide attentions [8-10]. Many techniques were used to remove toxic heavy 38 metals from polluted water, such as adsorption, chemical precipitation, filtration, 39 complexing, and electrochemical treatment [11,12]. Adsorption technologies have 40 gained the most attention owing to its simple operation, economy and merits of 41 efficiency [13,14]. The commonly used prevalent adsorbents includes hydroxyapatite, 42 zeolites, clays, activated carbons, polymeric materials and biomass [15,16]. At present, 43 many papers have investigated the functions of environmental mineral material for the 44 treatment of heavy metal in wastewater. It has been reported that zeolites [17,18], 45 montmorillonite [19,20], rectorite [21,22], graphene [23-26], diatomite [27,28] and 46 other minerals were effective to remove heavy metals from wastewater [29,30] with 47 low cost. However, these adsorbents have low separation inconvenience and low 48 absorption capacity; therefore, efforts are still needed to find new promising 49 adsorbents. 50

Phosphate (P) amendments have been widely recognized as a low-cost, effective and non-disruptive material for the treatment of heavy metals. Apatite materials $[Ca_{10}(PO_4)_6X_2, X=F, Cl, Br, OH]$ with special crystal chemistry characteristics are

54	becoming the most promising P-based materials for the heavy metal removal from
55	wastewater [31,32]. As a kind of apatite, chlorapatite $[Ca_{10}(PO_4)_6Cl_2 (CLAP)]$ is an
56	ideal material for heavy metal removal since the complexes of CLAP and heavy metal
57	were highly stable under oxidizing and reducing conditions, and CLAP has a high
58	adsorption capacity for heavy metals [33-36]. On the other hand, CLAP can be easily
59	synthesized and even has no toxicity to organism, thus it is possible to regulate the
60	concentrations of Pb, Cd, Zn, and other heavy metals in environment [37-38].
61	Additionally, it has also been confirmed that CLAP could transfer the metals from
62	unstable fraction to stable fraction and reduce the toxicity by precipitation, ion
63	exchange and adsorption effect [39-42]. In our previous study, we found that the
64	modified CLAP could immobilize heavy metals in polluted sediment with a high
65	efficiency through precipitation and adsorption effect [43]. However, the modified
66	CLAP could not be applied in aquatic environment since it is difficult to remove the
67	loaded-nanoparticles from polluted water with the only use of CLAP. In consideration
68	of the potential eutrophication risk induced by the application of P-materials, CLAP is
69	almost banned in wastewater treatment. As a fast, efficient and economical way to
70	separate materials from aquatic environment, magnetic separation technology has
71	been widely used in wastewater treatment and gained extensively attention [44,45].
72	Therefore, the combination of CLAP and magnetic separation technology may be a
73	promising way to make the possible use of CLAP in removal of Zn^{2+} , Cd^{2+} and Pb^{2+}
74	from water solution without posing secondary pollution to the environment [46].

75 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 76 remove Zn^{2+} , Cd^{2+} and Pb^{2+} from water solution. The MNCLAP was expected to 77 78 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 79 magnetic material plays as an assistant for the separation of loaded-nanoparticles from 80 polluted water. In addition, using MNCLAP as an adsorbent to remove heavy metals 81 from water solution has never been reported in the literature before. The 82 characterization and the adsorption experiments of the MNCLAP adsorbents were 83 also investigated in details below. 84

2. Experimental materials and methods

86 2.1. Materials

Cadmium chloride hemidihydrate (CdCl₂·2H₂O), zinc chloride (ZnCl₂), lead nitrate (Pb(NO₃)₂), iron (II) chloride tetrahydrate (FeCl₂·4H₂O), iron (III) chloride hexahydrate (FeCl₃·6H₂O), ammonia (25%), trisodium phosphate dodecahydrate (Na₃PO₄·12H₂O) and calcium chloride dehydrate (CaCl₂·2H₂O). All solutions were prepared from their nitrate salts (AR) with ultra-pure water.

92 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 $FeCl_3 \cdot 6H_2O$ (3.7 mmol) and $FeCl_2 \cdot 4H_2O$ (1.85 mmol) were dissolved in 30 mL deoxygenated water under a nitrogen atmosphere and then solicited for 10 minutes. After that, 10 mL of 25 % ammonia solution was added

to the above solution under mechanical stirring with the formation of black precipitate. 98 After 15 minute, an amount of 50 mL of CaCl₂·2H₂O (6.08 g L⁻¹, pH=11) and an 99 amount of 50 mL of Na₃PO₄·12H₂O (3.9369 g L⁻¹, pH=11) solutions were added to 100 the resulted precipitate solution drop wisely under mechanical stirring. After 30 101 minutes, the solution was heated at 90°C for 2 hour and then cooled without stirring 102 for 12 to 24 hour at room temperature. Then used magnet to separate precipitate and 103 washed the precipitate repeatedly with deionized water till neutrality. The products 104 were dried in the oven at 90°C for 4 hours then grinded them into powder. Finally, the 105

- 106 products were the prepared MNCLAP.
- 107 2.3. Adsorbent characterization

The morphology of synthesized MNCLAP was characterized using a scanning 108 electron microscope (SEM) (Quanta TM-250, USA). Transmission electron 109 microscopy (TEM, FEI Titan 300-kV FEG) attached with energy dispersive analysis 110 system of X-ray (EDAX) system was employed to investigate the nanoparticle 111 structure. Images of the materials were obtained at an accelerating voltage of 20 kV. 112 X-ray diffraction (XRD) patterns of MNCLAP samples were studied using AXS D8 113 Advance, LynxEye array detector equipped with Cu-Ka radioactive source (λ =0.154 114 nm). The angle of diffraction was varied from 10° to 80° at the speed of $2^{\circ}/\text{min}$. The 115 magnetic properties were characterized by magnetization curves using a HH-50 116 vibrating sample magnetometer under the condition of sensitivity 20 mV. 117

118 2.4. Adsorption experiments

At room temperature ($25 \pm 1^{\circ}$ C), the experimental adsorption of Zn²⁺, Cd²⁺ and

Pb²⁺ were carried out according to the batch method. The initial concentration of three heavy metals in conical flasks was 2×10^{-3} mol L⁻¹ (20 mL, pH=5 ± 0.1) and the dosage of MNCLAP adsorbent was 0.1 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).

127 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 2×10^{-3} mol L⁻¹ (20 mL, pH=5 ± 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.

133 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} 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.

139 2.4.3. Effect of MNCLAP amount

140 The conical flasks containing different amount (0.05, 0.07, 0.1, 0.2, 0.3 and 0.5 g 141 L^{-1}) of MNCLAP adsorbent and 2 × 10⁻³ mol L^{-1} of metal solution were shaken on a 142 constant temperature water bath oscillator for 24 h. After the completely reaction, the
143 samples were taken out and the MNCLAP adsorbent was separated by a magnet while
144 the final heavy metal concentrations were measured by AAS.

145 *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 HNO₃ or 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.

152 *1.4.5. Competitive adsorption*

In the competitive adsorption experiment, one heavy metal ion concentration was fixed to 2×10^{-3} mol L⁻¹ with other heavy metal ions concentration varying from 10^{-4} to 10^{-2} 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} mol L⁻¹ were selected, which was in consistent with isotherm experiment. Other conditions were the same with the process we mentioned above.

160 *2.5. Desorption experiments*

In this part, in order to assess the reversibility of Zn^{2+} , Cd^{2+} and 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

 $\times 10^{-2}$ mol L⁻¹ of Zn²⁺, Cd²⁺ and Pb²⁺ to reach the equilibration. After that, the mixture 164 was separated by a magnet and the residual heavy metal concentrations were 165 measured by AAS. Then the heavy metal-loaded MNCLAP adsorbent separated from 166 the mixture was extensively washed by ultra-pure water with several times and dried 167 at 90°C in an oven. Secondly, 0.10 g of dried MNCLAP adsorbent was added into 168 four kinds of eluants (20 mL) separately, which includes Ca(NO₃)₂, EDTA, HCl and 169 NaOH. The samples were placed in a constant temperature water bath oscillator and 170 shaken for 24 h. At last, the samples were taken out and the MNCLAP adsorbent was 171 separated by a magnet while the final heavy metal concentrations were measured by 172 AAS. 173

- 174 **3. Results and discussion**
- 175 *3.1. Characterization of MNCLAP*

Fig. 1 was the SEM micrograph of MNCLAP. As can be seen from in Fig. 1, the 176 synthesized MNCLAP was in spherical shape with a rough surface. Fig. 2 was the 177 TEM image of synthesized MNCLAP. From the TEM image, we can see that the 178 average diameter of these particles was estimated at approximately 20 nm. Fig. 3 179 showed the EDAX spectra of MNCLAP adsorbents unloaded and loaded with Zn²⁺, 180 Cd²⁺ and Pb²⁺, respectively. Fig. 3 showed the MNCLAP adsorbents were consisted 181 of calcium, phosphorus, iron and oxygen and the composition of each element were 182 shown in Table 1. From Table 1 we can see that iron and oxygen were successfully 183 presented in MNCLAP adsorbents with a remarkable content. Comparing the spectras 184 of loaded MNCLAP (Fig. 3b, Fig. 3c and Fig. 3d) with unloaded MNCLAP (Fig. 3a), 185

the zinc peak, cadmium peak and lead peak could be observed in Fig. 3b, Fig. 3c and Fig. 3d, respectively, which suggested that Zn^{2+} , Cd^{2+} and Pb^{2+} had been adsorbed on the surface of MNCLAP successfully.

Fig. 4 showed the XRD pattern of prepared MNCLAP adsorbent. It can be seen in 189 Fig.4 that the main components of MNCLAP were apatite (chlorapatite), magnetite 190 (Fe_3O_4) and maghemite (Fe_2O_3) . It suggested that the MNCLAP was successfully 191 synthesized and magnetite (Fe₃O₄) and maghemite (Fe₂O₃) acted as magnetic material 192 in it. The magnetization curve of the MNCLAP was measured under room conditions 193 and results were shown in Fig. 5. It can be seen from the Fig. 5 that the saturation 194 magnetization was 40.68 emu g^{-1} , suggesting that there was a strong magnetic 195 response to a magnetic field. It has been known that the saturation magnetization, 196 which indicated the maximum magnetic strength, is a most important parameter 197 magnetic separation. Previous study has reported that 16.3 emu g^{-1} of saturation 198 magnetization was enough for magnetic separations with a conventional magnet [48]. 199 Therefore, in our study, the synthesized MNCLAP has the enough ability to be 200 separated from solutions. Fig. S1 showed the separation process of the MNCLAP 201 adsorbent from the mixture solution, which we can see that the MNCLAP absorbent 202 can be successfully separated from the solutions by an external magnetic field. Thus, 203 sufficient evidences confirmed that the MNCLAP adsorbent synthesized in this 204 experiment can be used as magnetic adsorbents to remove Zn^{2+} , Cd^{2+} and Pb^{2+} from 205 the solution. 206

207 *3.2. Adsorption experiment*

208 3.2.1. Sorption kinetics

209 The sorption kinetics experiments were conducted in this study and results were presented in Fig. 6. Fig. 6 showed that the adsorption of Zn^{2+} , Cd^{2+} and Pb^{2+} by 210 211 MNCLAP was separated into two distinct stages: the adsorption of metal was increased quickly in the first two hours and then slowed down until reached to the 212 adsorption equilibrium. The time for adsorption equilibrium was estimated to 24 h 213 since there was only a slight increase of adsorption quantity after 24 h and it could 214 almost be neglected in consideration of the sorption system. Therefore, the contact 215 time we chosen in this study was 24 h. 216

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:

220 $\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$ (1)

Where q_t (mmol g⁻¹) represented the amount of heavy metal ions adsorbed on MNCLAP at *t* time (hour) and q_e (mmol g⁻¹) indicated the amounts of heavy metal ions adsorbed on MNCLAP at equilibrium time, *k* (g mmol⁻¹ h⁻¹) 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 Zn²⁺, Cd²⁺, and Pb²⁺, respectively, which indicated

that the sorption process of the present experiment was in consistent with the pseudo 229 second-order kinetic model. According to previous studies [49], 230 the pseudo-second-order kinetic model was found to be suitable to describe the kinetics of 231 metal sorption by different apatite materials: Chojnacka et al. studied the equilibrium 232 and kinetic modeling of chromium (III) sorption by animal bones using the 233 pseudo-second-order kinetic model [50]; Cheung et al. used the pseudo-second-order 234 kinetic model to investigate the sorption kinetic for the removal of cadmium ions from 235 effluents using bone char [51]; Chaturvedi et al. also studied sorption kinetics and 236 leach ability of heavy metal from the contaminated soil amended with immobilizing 237 agent (humus soil and hydroxyapatite) using the pseudo-second-order kinetic model 238 [52] and the pseudo-second-order kinetic model was also used in Saxena et al. study 239 to analyze the sorption of uranium by low-cost rock phosphate [53]. 240

241 *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^{-4} to 10^{-2} mol L⁻¹. 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:

249
$$\frac{C_{\rm e}}{q_e} = \frac{1}{q_m^b} + \frac{C_e}{q_m}$$
 (2)

250

Where q_e (mmol g⁻¹) was the amount of metal ions adsorbed on MNCLAP at

equilibrium time, q_m (mmol g⁻¹) was the maximum adsorption capacity of MNCLAP, 251 $c_e \pmod{L^{-1}}$ was the amount of metal ions in the liquid at equilibrium time, b (L mol⁻¹) 252 was the Langmuir constant and it was related to the energy of adsorption. By plotting 253 c_e/q_e versus c_e of the plot the constants b and q_m can be obtained from the intercept 254 and slope of the linear plot, respectively. The results from Fig. 7 showed that the 255 correlation coefficients for the adsorption of Zn^{2+} , Cd^{2+} and Pb^{2+} on MNCLAP were 256 0.9998, 0.9997 and 0.9996, respectively, indicating that the Langmuir adsorption 257 isotherm was appropriate for describing the experimental data. The Langmuir 258 constants for Zn²⁺, Cd²⁺ and Pb²⁺ were 0.3047×10^3 , 0.3215×10^3 and 0.4098×10^3 L 259 mol⁻¹, respectively, demonstrating that the MNCLAP had better adsorption affinity for 260 Pb^{2+} than Zn^{2+} and Cd^{2+} since the Langmuir constant has a positive relationship with 261 the binding energy. The maximum adsorption capacities of MNCLAP for Zn^{2+} , Cd^{2+} 262 and Pb²⁺ were 1.1769, 1.1022 and 1.1546 mmoL g⁻¹, respectively. In previous studies, 263 researchers have demonstrated the maximum adsorption capacities of hydroxyapatite 264 for Zn^{2+} and Cd^{2+} were 0.592 and 0.568 mmoL g⁻¹, respectively [54]. Reddad et al. 265 investigated the adsorption behaviors of Zn^{2+} , Cd^{2+} and Pb^{2+} by using the sugar beet 266 pulp as adsorbent and found that the maximum adsorption capacities of sugar beet 267 pulp for Zn^{2+} , Cd^{2+} and Pb^{2+} were 0.2706, 0.2161 and 0.3556 mmoL g⁻¹, respectively. 268 Some literatures about the heavy metal adsorption by other adsorbents were 269 summarized in Table 3. From Table 3 we can see that prepared MNCLAP has an 270 absolute advantage in the adsorption of Zn^{2+} , Cd^{2+} and Pb^{2+} with much higher 271 adsorption capacity than other adsorbents. That may attribute to the special crystal 272

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:

276
$$\operatorname{Ca}_{10}(\operatorname{PO}_4)_6\operatorname{Cl}_2 + x\operatorname{M}^{2+} \xrightarrow{}_{direct \ adsorption} (\operatorname{M}_x, \operatorname{Ca}_{10-x})(\operatorname{PO}_4)_6\operatorname{Cl}_2 + x\operatorname{Ca}^{2+}$$
(3)

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

278 3.2.3. Effect of MNCLAP amount

In order to determine relationship between MNCLAP amount and the heavy 279 metals adsorption quantities, sorption experiment was conducted with the MNCLAP 280 amount ranging from 0.05 to 0.5 g L^{-1} and results were shown in Fig. 8. Results 281 demonstrated that the adsorbed heavy metals, including Zn^{2+} , Cd^{2+} and Pb^{2+} , were 282 increased with the increasing of MNCLAP amount at the beginning. Then the 283 adsorption amount reached to the maximum at the MNCLAP dosage of 0.1 g L^{-1} . 284 After that, the adsorption amount was experienced a sharply decrease with the 285 increasing of MNCLAP amount. The possible explanation was that at the initial stage 286 with a quantitative amount of heavy metals, the adsorption process was accelerated by 287 providing more adsorption sites through increasing the dosage of MNCLAP before 288 reached to the maximum (saturation). However, when the adsorption reached to the 289 equilibrium, the heavy metal retained in solutions can not adsorb on the available 290 adsorption sites of added MNCLAP since the same cations were distributed on greater 291 amount of surface. Thus the optimum adsorption amount of MNCLAP for three metal 292 ions removal was 0.1 g L^{-1} , which was used in the following experiment. 293

294 *3.2.4. Effect of pH*

To investigate the influence of initial pH on heavy metal adsorption, the initial 295 pH ranging from 4-10 were selected for the pH experiment. The relationship between 296 the adsorbed amount of heavy metals by MNCLAP and pH values was shown in Fig. 297 9. As can be seen from the Fig. 9, with the increase of pH value, the amount of 298 adsorbed metal ions (including Zn²⁺, Cd²⁺ and Pb²⁺) was gradually increased. A 299 remarkable increase can be noticed when pH exceeded 8, after which the adsorption 300 amount increased dramatically. The possible explanation for this phenomenon may be 301 that the heavy metal ions started to precipitate under extremely alkaline conditions, 302 leading to the reduction of metal ions in solution. In the early study of Chen et al., 303 they also found that the initial solution pH could greatly affect the metal sorption 304 mechanism by apatite, along with the changes of metal-apatite reaction products [62]. 305 Pyromorphite-type minerals such as ZnO, CdCO₃ or Cd(OH)₂, and Pb₃(CO₃)₂(OH)₂ 306 were confirmed to be apatite-induced adsorption products of Zn^{2+} , Cd^{2+} and Pb^{2+} 307 under alkaline condition, respectively [62]. Additionally, Smičiklas et al. also reported 308 that the sorption of Zn^{2+} , Cd^{2+} and Pb^{2+} by hydroxyapatite was increased with an 309 increase of pH, they demonstrated that the ion exchange, specific cation sorption, 310 dissolution-precipitation were the mechanisms involved [56]. Related equations were 311 shown in below: 312

313
$$\operatorname{Ca}_{10}(\operatorname{PO}_4)_6\operatorname{Cl}_2 + x\operatorname{M}^{2+} \xrightarrow{}_{\text{ion-exchange}} (\operatorname{M}_{10-x}\operatorname{Pb}_x)(\operatorname{PO}_4)_6\operatorname{Cl}_2 + x\operatorname{Ca}^{2+}$$
(4)

314
$$\operatorname{Ca}_{10}(\operatorname{PO}_4)_6\operatorname{Cl}_2 + 12\operatorname{H}^+ \to \operatorname{dissolution} 10\operatorname{Ca}^{2+} + 6\operatorname{H}_2\operatorname{PO}_4^- + 2\operatorname{Cl}^-$$
 (5)

315
$$10M^{2+} + 6H_2PO_4^- + 2Cl^- \xrightarrow{}_{precipitation} M_{10}(PO_4)_6Cl_2 + 12H^+$$
 (6)

316 where M^{2+} represented the heavy metal ions.

The relationship between the adsorption capacity of MNCLAP and the initial 318 concentration of Zn^{2+} , Cd^{2+} and Pb^{2+} with the total metal concentration unchanged 319 was shown in Fig. 10. It can be seen from Fig. 10 that the adsorption capacity of Zn^{2+} , 320 Cd^{2+} and Pb^{2+} experienced some reductions with the coexistence of other heavy metal 321 ions. An interesting phenomenon was found in the competition adsorption behaviors 322 among the estimated metal ions: the adsorption capacity of MNCLAP on Zn²⁺ was 323 reduced from 0.9556 to 0.1326 mmol g^{-1} and from 0.9168 to 0.0976 mmol g^{-1} with the 324 initial concentration of Cd^{2+} and Pb^{2+} varying from 10^{-4} moL L^{-1} to 10^{-2} moL L^{-1} (Fig. 325 10a), respectively; the adsorption amount of Cd^{2+} on MNCLAP was reduced from 326 0.9386 to 0.1535 mmol g^{-1} and from 0.9071 to 0.1053 mmol g^{-1} with the initial 327 concentration of Zn^{2+} and Pb^{2+} varying from 10^{-4} moL L⁻¹ to 10^{-2} moL L⁻¹ (Fig. 10b), 328 respectively; the adsorption capacity of MNCLAP on Pb²⁺ was reduced from 0.9725 329 to 0.2219 mmol g^{-1} , and from 0.9872 to 0.2168 mmol g^{-1} with the initial concentration 330 of Zn^{2+} and Cd^{2+} varying from 10^{-4} moL L⁻¹ to 10^{-2} moL L⁻¹ (Fig. 10c), respectively, 331 that was to say, the coexistence of other heavy metal ions may greatly reduce the one 332 type metal adsorption by MNCLAP since the maximum adsorption capacities of 333 MNCLAP adsorbent towards single Zn^{2+} , Cd^{2+} or Pb^{2+} are 1.1769, 1.1022 and 1.1546 334 mmol g^{-1} , respectively. This fact indicated that Zn^{2+} , Cd^{2+} and Pb^{2+} were adsorbed in 335 the same sites and they would compete for the adsorption sites on MNCLAP 336 absorbent in the binary system. Results also indicated that the adsorption capacity of 337 Zn^{2+} and Cd^{2+} were reduced more apparently with the presence of Pb^{2+} in the binary 338

339 system. That may attribute to the higher Langmuir constant of Pb²⁺ than Zn²⁺ and 340 Cd²⁺ during the adsorption, which was in consistent with the study of Corami et al. 341 [63]. Consequently, owing to the higher Langmuir constant, effects of the coexistence 342 of Zn²⁺ and Cd²⁺ on Pb²⁺ adsorption were more slightly and the reduction of Pb²⁺ 343 adsorption capacity induced by Cd²⁺ was more apparent than Zn²⁺. It confirmed that 344 the adsorption affinity of MNCLAP was in the order of: Pb²⁺ > Cd²⁺ > Zn²⁺.

345 *3.3. Desorption experiment*

The results of desorption experiment were shown in Table 4. Results showed that 346 the EDTA solution may induce the biggest heavy metal ions desorption amount from 347 the metal-loaded MNCLAP absorbent. This phenomenon may attribute to the 348 complex formed by EDTA and metal ions which possesses lower sorption affinity for 349 MNCLAP adsorbents [64]. It can be found that whether under the extreme acid or 350 alkaline conditions, only trace amounts of metal ions can be desorbed, and the 351 desorbed Zn^{2+} and Cd^{2+} were almost negligible under the alkaline condition. 352 Additionally, the desorption rates of Zn^{2+} , Cd^{2+} and Pb^{2+} in $Ca(NO_3)_2$ solutions were 353 15.96%, 14.15%, and 15.13%, respectively. This may due to the reversible process of 354 ion-exchange [shown in equation (4)] between the MNCLAP adsorbents and the 355 solution: Ca²⁺ may concentrate on the surface of MNCLAP adsorbents while the 356 concentration of Ca^{2+} in solutions was higher than that of MNCLAP adsorbents, 357 leading to the desorption of heavy metals. 358

359 **4. Conclusions**

360

In this study, a new class of magnetic chlorapatite nanoparticles was synthesized

and its possibility to remove Zn^{2+} , Cd^{2+} and Pb^{2+} from water solution was investigated. 361 The product MNCLAP was characterized by SEM, EDAX, TEM, XRD and 362 magnetization curves, and these results demonstrated that the MNCLAP was in 363 spherical shape within about 20 nm. Laboratory tests showed that prepared MNCLAP 364 could not only remove the heavy metal ions from water solutions but also can be 365 easily separated from the solutions by using an external magnetic field. The maximum 366 adsorption capacities of MNCLAP adsorbent towards Zn^{2+} , Cd^{2+} and Pb^{2+} were 367 1.1769, 1.1022 and 1.1546 mmol g^{-1} , respectively, which showed a much higher 368 adsorption capacity than other adsorbents reported before. It also can be obtained that 369 the optimum dosage of MNCLAP adsorbent for Zn^{2+} , Cd^{2+} and Pb^{2+} was 0.1 g L⁻¹ and 370 the adsorption amount was increased with the pH ranging from 4 to 8. In the binary 371 component system, MNCLAP adsorbent showed a better adsorption affinity for Pb²⁺ 372 than for Zn^{2+} and Cd^{2+} . The EDTA solution was confirmed to be the most efficient 373 eluant for desorption of metals from MNCLAP. These experimental results showed 374 that in MNCLAP adsorbent the chlorapatite may act as an adsorption agent with a 375 high adsorption capacity and the magnetic material played as an assistant for the 376 separation of loaded-nanoparticles from polluted water. It was the first time to 377 combine both the properties of chlorapatite and magnetic material and the MNCLAP 378 showed remarkable advantages in heavy metal removal from aqueous solutions. The 379 prominent advantage of prepared MNCLAP adsorbents with paramagnetism and high 380 adsorption capacity was particularly important for its possible practical application 381 and the mechanisms involved in the adsorption should be studied in future. 382

383 Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (51521006, 51378190, 51278176,51579098 and 51108178), the National Program for Support of Top-Notch Young Professionals of China (2014), the Program for New Century Excellent Talents in University (NCET-13-0186), Hunan Provincial and Technology plan Project (No.2016Rs3026), Scientific Research Fund of Hunan Provincial Education Department (521293050) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT-13R17).

392 **References**

- [1] P. Trivedi, L. Axe, Modeling Cd and Zn sorption to hydrous metal oxides,
 Environ. Sci. Technol. 34 (2000) 2215-2223.
- [2] G.M. Zeng, M. Chen, Z. Zeng, Risks of neonicotinoid pesticides, Science 340
 (2003) 1403-1403.
- [3] G.M. Zeng, M. Chen, Z. Zeng, Shale gas: Surface water also at risk, Nature 499
 (2013) 239-245.
- 399 [4] L. Hu, C. Zhang, G. Zeng, G. Chen, J. Wan, Z. Guo, H. Wu, Z. Yu, Y. Zhou, J. Liu,
- Metal-based quantum dots: synthesis, surface modification, transport and fate in
 aquatic environments and toxicity to microorganisms, RSC Adv. 6 (2016)
 78595-78610.
- 403 [5] L. Hu, G. Zeng, G. Chen, H. Dong, Y. Liu, J. Wan, A. Chen, Z. Guo, M. Yan, H.
- 404 Wu, Treatment of landfill leachate using immobilized Phanerochaete chrysosporium
- loaded with nitrogen-doped TiO₂ nanoparticles, J. Hazard. Mater. 301 (2016) 106-118.
- 406 [6] L. Tang, G.M. Zeng, G.L. Shen, Y.P. Li, Y. Zhang, D.L. Huang, Rapid detection
- 407 of picloram in agricultural field samples using a disposable immunomembrane-based
- 408 electrochemical sensor, Environ. Sci. Technol. 42 (2008) 1207-1212.
- 409 [7] Z. Yang, Z. Fang, L. Zheng, W. Cheng, P. E. Tsang, J. Fang, D. Zhao, Remediation
- 410 of lead contaminated soil by biochar-supported nano-hydroxyapatite, Ecotox. Environ.
- 411 Saf. 132 (2016) 224-230.
- 412 [8] W. Yantasee, C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J.
- 413 Wiacek, G.E. Fryxell, C. Timchalk, M.G. Warner, Removal of heavy metals from

- 414 aqueous systems with thiol functionalized superparamagnetic nanoparticles, Environ.
- 415 Sci. Technol. 41 (2007) 5114-5119.
- 416 [9] T. Fan, Y. Liu, B. Feng, G.M. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X.
- Wang, Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: Isotherms, kinetics and thermodynamics, J. Hazard. Mater. 160 (2008)
 655-661.
- 420 [10] R. Liu, D. Zhao, Synthesis and characterization of a new class of stabilized
- 421 apatite nanoparticles and applying the particles to in situ Pb immobilization in a
- 422 fire-range soil, Chemosphere 91 (2013) 594-601.
- 423 [11] H.P. Wu, C. Lai, G.M. Zeng, J. Liang, J. Chen, J.J. Xu, J. Dai, X.D. Li, J.F. Liu,
- 424 M. Chen, L.H. Lu, L. Hu, J. Wan, The interactions of composting and biochar and
- 425 their implications for soil amendment and pollution remediation: a review, Crit. Rev.
- 426 Biotechnol. (2016) 1-11.
- 427 [12] D.L. Huang, W.J. Xue, G.M. Zeng, J. Wan, G. Chen, C. Huang, C. Zhang, M.
- 428 Cheng, P. Xu, Immobilization of Cd in river sediments by sodium alginate modified
- 429 nanoscale zero-valent iron: Impact on enzyme activities and microbial community
- 430 diversity, Water. Res. 106 (2016) 15-25.
- 431 [13] G. Crini, Recent developments in polysaccharide-based materials used as
 432 adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (2005) 38-70.
- 433 [14] D.L. Huang, C. Wang, P. Xu, G.M. Zeng, B.A. Lu, N.J. Li, C. Huang, C. Lai,
- 434 M.H. Zhao, J.J. Xu, A coupled photocatalytic-biological process for phenol

- degradation in the *Phanerochaete chrysosporium*-oxalate-Fe₃O₄ system, Int. Biodeter. 435
- Biodeg. 97 (2015) 115-123. 436
- 437 [15] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review,
- Bioresource Technol. 97 (2006) 1061-1085. 438
- [16] J.L. Gong, B. Wang, G.M. Zeng, C.P. Yang, C.G. Niu, Q.Y. Niu, W.J. Zhou, Y. 439
- Liang, Removal of cationic dyes from aqueous solution using magnetic multi-wall 440
- carbon nanotube nanocomposite as adsorbent, J. Hazard. Mater. 164 (2009) 441
- 1517-1522. 442

- [17] R. Apiratikul, P. Pavasant, Sorption of Cu²⁺, Cd²⁺, and Pb²⁺ using modified 443 zeolite from coal fly ash, Chem. Eng. J. 144 (2008) 245-258. 444
- [18] S.K. Pitcher, R.C. Slade, N.I. Ward, Heavy metal removal from motorway 445 stormwater using zeolites, Sci. Total. Environ. 334–335 (2004) 161-166. 446
- [19] P. Wu, W. Wu, S. Li, N. Xing, N. Zhu, P. Li, J. Wu, C. Yang, Z. Dang, Removal 447
- of Cd²⁺ from aqueous solution by adsorption using Fe-montmorillonite, J. Hazard. 448 Mater. 169 (2009) 824-830. 449
- [20] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural 450 and modified kaolinite and montmorillonite: a review, Adv. Colloid. Interface. 140 451 (2008) 114-131.
- [21] Y. Huang, X. Ma, G. Liang, H. Yan, Adsorption of phenol with modified 453 rectorite from aqueous solution, Chem. Eng. J. 141 (2008) 1-8. 454
- [22] Y. Huang, X. Ma, G. Liang, Y. Yan, S. Wang, Adsorption behavior of Cr(VI) on 455
- organic-modified rectorite, Chem. Eng. J. 138 (2008) 187-193. 456

- 457 [23] H. Wang, X.Z. Yuan, Y. Wu, H.J. Huang, G.M. Zeng, Y. Liu, X.L. Wang, N.B.
- Lin, Y. Qi, Adsorption characteristics and behaviors of graphene oxide for Zn(II)
 removal from aqueous solution, Appl. Surf. Sci. 279 (2013) 432-440.
- 460 [24] H. Wang, X.Z. Yuan, Y. Wu, X.H. Chen, L.J. Leng, G.M. Zeng, Photodeposition
- 461 of metal sulfides on titanium metal-organic frameworks for excellent
 462 visible-light-driven photocatalytic Cr(VI) reduction, Rsc Adv. 5 (2015) 32531-32535.
- 463 [25] Y. Wu, H. Luo, H. Wang, C. Wang, J. Zhang, Z. Zhang, Adsorption of hexavalent
- 464 chromium from aqueous solutions by graphene modified with
- 465 cetyltrimethylammonium bromide, J. Colloid. Interf. Sci. 394 (2013) 183-191.
- 466 [26] Y. Wu, H. Luo, H. Wang, L. Zhang, P. Liu, L. Feng, Fast adsorption of nickel
- 467 ions by porous graphene oxide/sawdust composite and reuse for phenol degradation
 468 from aqueous solutions, J. Colloid. Interf. Sci. 436 (2014) 90-98.
- 469 [27] A. Mohammad, Al-Ghouti, A.M. Majeda, Khraisheh, M. Tutuji, Flow injection
- potentiometric stripping analysis for study of adsorption of heavy metal ions ontomodified diatomite, Chem. Eng. J. 104 (2004) 83-91.
- 472 [28] M. Šljivić, I. Smičiklas, S. Pejanović, I. Plećaš, Comparative study of Cu^{2+}
- adsorption on a zeolite, a clay and a diatomite from Serbia, Appl. Clay. Sci. 43 (2009)
- 474 33-40.
- 475 [29] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C.
- 476 Huang, G.X. Xie, Use of iron oxide nanomaterials in wastewater treatment: A review,
- 477 Sci. Total. Environ. 424 (2012) 1-10.

- 478 [30] Y. Zhang, G.M. Zeng, L. Tang, D.L. Huang, X.Y. Jiang, Y.N. Chen, A
 479 hydroquinone biosensor using modified core-shell magnetic nanoparticles supported
 480 on carbon paste electrode, Biosens. Bioelectron. 22 (2007) 2121-2126.
- 481 [31] C.S. Sundaram, N. Viswanathan, S. Meenakshi, Defluoridation chemistry of
- 482 synthetic hydroxyapatite at nano scale: equilibrium and kinetic studies, J. Hazard.
- 483 Mater. 155 (2008) 206-215.
- 484 [32] D.L. Huang, R.Z. Wang, Y.G. Liu, G.M. Zeng, C. Lai, P. Xu, B.A. Lu, J.J. Xu, C.
- 485 Wang, C. Huang, Application of molecularly imprinted polymers in wastewater
- 486 treatment: a review, Environ. Sci. Pollut. R. 22 (2015) 963-977.
- 487 [33] S. Mignardi, A. Corami, V. Ferrini, Evaluation of the effectiveness of
- 488 phosphatetreatment for the remediation of mine waste soils contaminated with Cd,
- 489 Cu,Pb, and Zn, Chemosphere 86 (2012) 354–360.
- 490 [34] A.S Knox, D.I. Kaplan, M.H. Paller, Phosphate sources and their suitability
- 491 forremediation of contaminated soils, Sci. Total. Environ. 357 (2006) 271–279.
- 492 [35] P. Miretzky, A. Fernandez-Cirelli, Phosphates for Pb immobilization in soils:
- 493 areview, Environ. Chem. Lett. 6 (2008) 121–133.
- J.C. Zwonitzer, G.M. Pierzynski, G.M. Hettiarachchi, of 494 [36] Effects phosphorusadditions lead, cadmium, bioavailabilities 495 on and zinc in ametal-contaminated soil, Water. Air. Soil. Poll. 143 (2003) 193-209. 496
- 497 [37] W.N. Wang, Y. Kaihatsu, F. Iskandar, K. Okuyama, highly luminous hollow
- 498 chloroapatite phosphors formed by a template-free aerosol route for solid-state
- 499 lighting, Chem. Mater. 21 (2009) 4685-4691.

- 500 [38] A. Fahami, B. Nasiri-Tabrizin, R. Ebrahimi-Kahrizsangi, Mechanosynthesis and
- characterization of chlorapatite nanopowders, Mater. Lett. 110 (2013) 117–121.
- 502 [39] B. Nasiri-Tabrizi, A. Fahami, Synthesis and characterization of chlorapatite-ZnO
- 503 compositenanopowders, Ceram. Int. 40 (2014) 2697–2706.
- 504 [40] T.T. Eighmy, A.E. Kinner, E.L. Shaw, J.D.E. Jr, C.A. Francis, Chlorapatite
- 505 (Ca₅(PO₄)₃Cl) Characterization by XPS: An Environmentally Important Secondary
- 506 Mineral, Surf. Sci. Spectra 6 (1999) 210-218.
- 507 [41] M. Srinivasan, C. Ferraris, T. White, Cadmium and Lead Ion Capture with Three
- 508 Dimensionally Ordered Macroporous Hydroxyapatite, Environ. Sci. Technol. 40 509 (2006) 7054-7059.
- 510 [42] R. Liu, D. Zhao, Reducing leachability and bioaccessibility of lead in soils using
- a new class of stabilized iron phosphate nanoparticles, Water Res. 41 (2007)
 2491-2502.
- [43] J. Wan, C. Zhang, G.M. Zeng, D.L. Huang, L. Hu, C. Huang, H. Wu, L. Wang,
 Synthesis and evaluation of a new class of stabilized nano-chlorapatite for Pb
 immobilization in sediment, J. Hazard. Mater. 320 (2016) 278-288.
- 516 [44] V. Rocher, J.M. Siaugue, V. Cabuil, A. Bee, Removal of organic dyes by
- magnetic alginate beads, Water Res. 42 (2008) 1290-1298.
- 518 [45] X.J. Hu, J.S. Wang, Y.G. Liu, X. Li, G.M. Zeng, Z.L. Bao, X.X. Zeng, A.W.
- 519 Chen, F. Long, Adsorption of chromium (VI) by ethylenediamine-modified
- 520 cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics, J.
- 521 Hazard. Mater. 185 (2011) 306-314.

- 522 [46] D.L. Huang, G.M. Zeng, C.L. Feng, S. Hu, X.Y. Jiang, L. Tang, F.F. Su, Y.
- 523 Zhang, W. Zeng, H.L. Liu, Degradation of lead-contaminated lignocellulosic waste by
- 524 Phanerochaete chrysosporium and the reduction of lead toxicity, Environ. Sci.
- 525 Technol. 42 (2008) 4946-4951.
- 526 [47] K. Mori, S. Kanai, T. Hara, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda,
- 527 Development of ruthenium-hydroxyapatite-encapsulated superparamagnetic γ -Fe₂O₃
- 528 nanocrystallites as an efficient oxidation catalyst by molecular oxygen, Chem. Mater.
- 529 19 (2007) 1249–1256.
- 530 [48] Z. Ma, Y. Guan, H. Liu, Synthesis and characterization of micron-sized
- 531 monodisperse superparamagnetic polymer particles with amino groups, J. Polym. Sci.
- 532 Pol. Chem. 43 (2005) 3433-3439.
- 533 [49] P. Xu, G.M. Zeng, D.L. Huang, C. Lai, M.H. Zhao, Z. Wei, N.J. Li, C. Huang,
- G.X. Xie, Adsorption of Pb (II) by iron oxide nanoparticles immobilized
 Phanerochaete chrysosporium: equilibrium, kinetic, thermodynamic and mechanisms
 analysis, Chem. Eng. J. 203 (2012) 423-431.
- 537 [50] K. Chojnacka, Equilibrium and kinetic modelling of chromium(III) sorption by
- animal bones, Chemosphere 59 (2005) 315-320.
- [51] C.W. Cheung, J.F. Porter, G. Mckay, Sorption kinetic analysis for the removal of
- cadmium ions from effluents using bone char, Water Res. 35 (2001) 605-612.
- 541 [52] P.K. Chaturvedi, C.S. Seth, V. Misra, Sorption kinetics and leachability of heavy
- 542 metal from the contaminated soil amended with immobilizing agent (humus soil and
- 543 hydroxyapatite), Chemosphere 64 (2006) 1109-1114.

- [53] S. Saxena, S.F. D'Souza, Heavy metal pollution abatement using rock phosphate 544
- mineral, Environ. Int. 32 (2006) 199-202. 545
- [54] Y. Xu, F.W. Schwartz, S.J. Traina, Sorption of Zn^{2+} and Cd^{2+} on hydroxyapatite 546
- surfaces, Environ. Sci. Technol. 28 (1994) 1472-1480. 547
- [55] H. M. Selim, Phosphate in Soils: Interaction with Micronutrients, Radionuclides 548
- and Heavy Metals, CRC Press, 2015. 549
- [56] I. Smiciklas, A. Onjia, S. Raicević, D. Janaćković, M. Mitrić, Factors influencing 550
- the removal of divalent cations by hydroxyapatite, J. Hazard. Mater. 152 (2008) 876. 551
- [57] Z. Reddad, C. Gerente, Y. Andres, C.P. Le, Adsorption of several metal ions onto 552
- a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol. 36 553 (2002) 2067-2073. 554
- [58] L. Bai, H. Hu, W. Fu, J. Wan, X. Cheng, L. Zhuge, L. Xiong, Q. Chen, Synthesis 555
- of a novel silica-supported dithiocarbamate adsorbent and its properties for the 556
- removal of heavy metal ions, J. Hazard. Mater. 195 (2011) 261-275. 557
- [59] M. Iqbal, R.G.J. Edyvean, Biosorption of lead, copper and zinc ions on loofa 558
- sponge immobilized biomass of *Phanerochaete chrysosporium*, Miner. Eng. 17 (2004) 559 217-223.
- [60] F. An, B. Gao, X. Dai, M. Wang, X.H. Wang, Efficient removal of heavy metal 561
- ions from aqueous solution using salicylic acid type chelate adsorbent, J. Hazard. 562
- Mater. 192 (2011) 956-962. 563

- [61] F. Ge, M.M. Li, H. Ye, B.X. Zhao, Effective removal of heavy metal ions Cd²⁺,
- 565 Zn^{2+} , Pb^{2+} , Cu^{2+} , from aqueous solution by polymer-modified magnetic nanoparticles,
- 566 J. Hazard. Mater. 366 (2012) 211-212.
- 567 [62] X. Chen, J. V. Wright, J. L. Conca, L. M. Peurrung, Effects of pH on heavy
- metal sorption on mineral apatite, Environ. Sci. Technol. 31 (1997) 624-631
- 569 [63] A. Corami, S. Mignardi, V. Ferrini, Cadmium removal from single- and
- 570 multimetal (Cd+Pb+Zn+Cu) solutions by sorption on hydroxyapatite, J. Colloid
- 571 Interface Sci. 317 (2008) 402–408.

572 [64] Y.J. Wang, J.H. Chen, Y.X. Cui, S.Q. Wang, D.M. Zhou, Effects of 573 low-molecularweight organic acids on Cu (II) adsorption onto hydroxyapatite 574 nanoparticles, J. Hazard. Mater. 162 (2009) 1135–1140.

575

- 576 **Figure captions:**
- **Figure 1.** SEM micrograph of the synthesized MNCLAP adsorbents.
- 578 **Figure 2.** TEM micrograph of the synthesized MNCLAP adsorbents.
- 579 Figure 3. EDAX spectrum of the magnetic adsorbents: (a) MNCLAP; (b) MNCLAP
- loaded with Zn^{2+} ; (c) MNCLAP loaded with Cd^{2+} ; (d) MNCLAP loaded with Pb^{2+} .
- 581 **Figure 4.** XRD pattern of the MNCLAP.
- **Figure 5.** The magnetic hysteresis loop diagram of the MNCLAP.
- **Figure 6.** Adsorption kinetic curves of heavy metals by MNCLAP adsorbents.
- **Figure 7.** Adsorption isotherms curves of heavy metals by MNCLAP adsorbents.
- 585 **Figure 8.** The effect of MNCLAP amount.
- **Figure 9.** The effect of initial pH values on the amount of the heavy metals adsorbed
- 587 on MNCLAP adsorbents.

Figure 10. The competitive of adsorption behavior of Zn^{2+} , Cd^{2+} and Pb^{2+} : (a) the relationship between the adsorption capacity of Zn^{2+} and the equilibrium concentrations of $Zn^{2+}-Cd^{2+}$ and $Zn^{2+}-Pb^{2+}$; (b) the relationship between the adsorption capacity of Cd^{2+} and the equilibrium concentrations of $Cd^{2+}-Zn^{2+}$ and $Cd^{2+}-Pb^{2+}$; (c) the relationship between the adsorption capacity of Pb^{2+} and the equilibrium concentrations of $Pb^{2+}-Zn^{2+}$ and $Pb^{2+}-Cd^{2+}$.

595 Tables:

596 **Table 1**

597 The chemical composition of before and after loaded Zn^{2+} , Cd^{2+} and Pb^{2+}

Substance (At %)	Ca	Р	0	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

Table 2

Substance	q_e	k	R^2
Zn^{2+}	0.9881	0.1200	0.9999
Cd^{2+}	1.0045	0.1782	0.9999
Pb ²⁺	0.9304	0.1264	0.9999

600 MNCLAP of Zn^{2+} , Cd^{2+} and Pb^{2+} of adsorption kinetic parameters



Table 3

603 C	Comparison	of adsorption	a capacities	of various	adsorbents	towards Zn ²⁺	$, Cd^{2+}$	and Pb^{2+} .
-------	------------	---------------	--------------	------------	------------	--------------------------	-------------	-----------------

Type of adsorbent	Adsorption capacities (mmol g ⁻¹)			References
	Zn ²⁺	Cd^{2+}	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

Table 4

Eluants	Initial pH	Finial pH			Desorbed (%)		
		Zn^{2+}	Cd^{2+}	Pb ²⁺	Zn^{2+}	Cd^{2+}	Pb ²⁺
EDTA $(0.003 \text{ mol } \text{L}^{-1})$	2.64	5.25	5.64	5.77	25.94	22.95	32.84
HCl $(0.01 \text{ mol } L^{-1})$	2.22	4.92	4.08	3.82	5.98	5.99	8.42
NaOH (0.01 mol L^{-1})	11.94	9.17	9.59	9.43	0.99	0.76	4.38
$Ca(NO_3)_2 (0.01 \text{ mol } L^{-1})$	5.71	6.31	6.74	6.63	15.96	14.15	15.13

607 Desorption of Zn^{2+} , Cd^{2+} and Pb^{2+} from loaded MNCLAP adsorbents.