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# Pretreatment by recyclable Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH magnetic nano-adsorbent to dephosphorize for the determination of trace F<sup>−</sup> and Cl<sup>−</sup> in phosphorus-rich solutions

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The magnetic nano-adsorbent Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH (Mg/Al-type layered double hydroxide) with a CO<sub>3</sub><sup>2−</sup> interlayer anion has been synthesized successfully on Fe<sub>3</sub>O<sub>4</sub> nanoparticles via a urea hydrothermal method. It is confirmed that the nano-adsorbent can adsorb PO<sub>4</sub><sup>3−</sup> rapidly and efficiently in multi-ion solutions; meanwhile, it did not adsorb any F<sup>−</sup> and Cl<sup>−</sup>, even with a high amount of the nano-adsorbent or a longer adsorption time. This behaviour is beneficial for applications to remove PO<sub>4</sub><sup>3−</sup> in phosphorus-rich solutions, and especially can be utilized to determine trace F<sup>−</sup> and Cl<sup>−</sup> anions in phosphorus-rich solutions by physical and chemical analysis methods including ion chromatography without serious interference from PO<sub>4</sub><sup>3−</sup> for trace determinations. Herein, the hydrothermally synthesized Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH was characterized via SEM, TEM, SAED, XRD, FTIR, magnetic hysteresis loop analysis and adsorption–desorption isotherm analysis. The structure and stability, adsorption mechanism, magnetic saturation value, specific surface area, total pore volume, phosphate adsorption capacity and recyclability are discussed. Using the optimized pretreatment conditions, Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH was utilized successfully to adsorb PO<sub>4</sub><sup>3−</sup> in real samples and determine trace F<sup>−</sup> and Cl<sup>−</sup> accurately by ion chromatography; this would be very beneficial for continuous analysis and on-line tests by physical and chemical analysis methods without interference from PO<sub>4</sub><sup>3−</sup> in phosphorus-rich samples, leaving F<sup>−</sup> and Cl<sup>−</sup> even if in a trace content.

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## 1 Introduction

Currently, phosphate materials or its hybrid materials, presented as crystal, glass or ceramics, are widely applied<sup>1</sup> in numerous fields such as optics and electronics, as well as medical biomaterials for applications<sup>2</sup> in bone grafting and regeneration, drug delivery, *etc.* However, in the determination of target ions in solutions containing these materials, the matrix phosphate anion PO<sub>4</sub><sup>3−</sup> seriously interferes in determinations by methods such as spectrophotometry,<sup>3</sup> neutron activation,<sup>4</sup> molecular absorption spectrometry,<sup>5</sup> graphite furnace,<sup>6</sup> electrothermal atomic absorption spectrometry,<sup>7</sup> and inductively coupled plasma mass spectrometry.<sup>8</sup> To determine anion impurities, the commonly used chromatography method will be affected seriously by interference from the phosphate anion. The signal from a high

concentration PO<sub>4</sub><sup>3−</sup> will cover the peak or deform the peak shape of the target anion.<sup>9–11</sup> Furthermore, it will make the analytical column overloaded, which will shorten the service life of the column. Once the analytical column is overloaded, a ghost peak will appear, or the next injection may not even be allowed.<sup>11</sup> Although solutions with a high concentration of PO<sub>4</sub><sup>3−</sup> can be diluted greatly, this also reduces the content of the target anion, leading to a content much lower than the detection limit.<sup>10</sup> After fully rinsing the loops<sup>11</sup> of the chromatograph for several runs using deionized water, a certain amount of PO<sub>4</sub><sup>3−</sup> as carryover resulting from the previous injection may still be observed even if a blank sample is used. Therefore, an appropriate sample pretreatment to dephosphorize solutions with a high PO<sub>4</sub><sup>3−</sup> content is particularly important.<sup>10,11</sup>

A further issue is specifically related to the determination of trace F<sup>−</sup> and Cl<sup>−</sup> anions in phosphorus-rich solutions. If F<sup>−</sup> anions from the raw materials and products of the phosphate industry such as from phosphate ore, phosphate fertilizer, phosphogypsum enter the biological chain continuously during manufacturing processes, storage and utilization, the bio-accumulated F<sup>−</sup> will pose a serious threat to human life. Thus, it is necessary to monitor trace F<sup>−</sup> and Cl<sup>−</sup> anions in phosphorus-

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rich raw materials and final products.<sup>12</sup> Moreover, hydroxyapatite is a particularly promising bone-grafting material for dental and orthopaedic applications. The addition of trace  $F^-$  can construct a microenvironment favouring bone healing and bone regeneration,<sup>13</sup> but its trace amount must be strictly controlled to avoid cell death or necrosis.<sup>14</sup> Thus, all the above-mentioned factors make the accurate determination of trace  $F^-$  and  $Cl^-$  in phosphorus-rich solutions necessary, with the aim to fully keep  $F^-$  and  $Cl^-$  and adsorb  $PO_4^{3-}$  as much as possible during the pretreatment, which should be developed.

Layered double hydroxides (LDHs) are two-dimensional nanostructured anionic clays, with the general formula of  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}^{n-}yH_2O]^{x-}$ , where M is a metal cation and A is the interlayer anion with  $n$ -valence.<sup>15,16</sup> Strong chemical bonds exist within the layer of  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ , but the bonds between the interlayer anion of  $[A_{x/n}^{n-}yH_2O]^{x-}$  and the layer of  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$  are relatively weak. This makes LDHs promising ion-exchangers<sup>17</sup> for applications to adsorb the  $PO_4^{3-}$  anion.<sup>17–30</sup>

To efficiently adsorb  $PO_4^{3-}$ , the interlayer anion choice will play a key role. Based on LDHs, there are some good options to use the  $Cl^-$  anion,<sup>17,20,22–24,31</sup> or  $NO_3^-$  anion,<sup>19,21,32</sup> or  $Cl^-$  and  $SO_4^{2-}$  anions<sup>25</sup> as the interlayer anion. They can be used to adsorb  $PO_4^{3-}$  effectively, but their adsorption efficiencies are inevitably affected by carbon dioxide ( $CO_2$ ) or carbonate ( $CO_3^{2-}$ ) from the preparation process of the LDH, the solution environment and even the atmosphere.<sup>17,19,25</sup>

Employing  $CO_3^{2-}$  as the interlayer anion, Zn–Al–LDH,<sup>18</sup> Zr-modified MgFe–LDH( $CO_3$ ),<sup>27</sup>  $Fe_3O_4@Mg$ –Al–LDH,<sup>26</sup> Mg–Fe LDH<sup>28</sup> and  $Fe_3O_4@gelatin$ -encapsulated hydrotalcite<sup>33</sup> were prepared to adsorb  $PO_4^{3-}$  successfully by a co-precipitation method. By comparison, the hydrothermal method is a better way to prepare LDH with the  $CO_3^{2-}$  interlayer anion using urea, which can well control the size and crystallinity of the prepared nanoparticle.<sup>15</sup> In the investigations for the preparation of LDH with  $CO_3^{2-}$  *via* the urea hydrolysis method,<sup>29,30,34–54</sup> only two LDHs have been used as a phosphate adsorbent.<sup>29,30</sup> Cu–Al LDH (CuAl/biomass carbon fibre-layered double hydroxide)<sup>29</sup> was synthesized at 110 °C for 12 h, and Zn–Al LDHs<sup>30</sup> were synthesized at 150 °C for 36 h.

Herein, an Mg–Al LDH was hydrothermally synthesized with  $Mg(NO_3)_2$ ,  $Al(NO_3)_3$ , and urea, using  $CO_3^{2-}$  as the interlayer anion. To utilize magnetic solid phase extraction (MSPE), which can achieve the purpose of phosphate adsorption and its rapid separation,  $Fe_3O_4$  magnetic nanoparticles were introduced into the Mg–Al LDH nano-adsorbent during the hydrothermal synthetic process. Using the prepared  $Fe_3O_4@Mg/Al-CO_3$ -LDH magnetic nano-adsorbent, adsorption–determination and recycle procedures were conducted, as described in Section 2.3. As described in Section 3.1, its structural properties were characterized *via* SEM, TEM, FTIR, and XRD, and its magnetic property, specific surface area, and porosity were also analysed. After optimizing the pretreatment conditions, as discussed in Section 3.2, the stability and recyclability after 15 cycles with high adsorption capacity is shown in Section 3.3. More importantly, it was found that the hydrothermally synthesized  $Fe_3O_4@Mg/Al-CO_3$ -LDH magnetic nano-adsorbent only adsorbed  $PO_4^{3-}$ , not  $F^-$  and  $Cl^-$  in solution.

This is undoubtedly beneficial to accurately determine the content of  $F^-$  and  $Cl^-$  in phosphate solutions by chromatography, and the practical applications are introduced in Section 4.

## 2 Experimental

### 2.1 Hydrothermally synthesized $Fe_3O_4@Mg/Al-CO_3$ -LDH

The magnetic layered double hydroxide nano-adsorbent  $Fe_3O_4@Mg/Al-CO_3$ -LDH was synthesized *via* a urea hydrothermal method. After several trials, 0.6 g of  $Fe_3O_4$  nanoparticles (ultrafine powder purchased from Macklin) was used and added to 15 mL solution of 0.1 mol L<sup>−1</sup> NaOH (AR grade). After the mixture was dispersed by ultrasonication for 10 min, it was separated using a magnet for further use. Then 2.044 g  $Mg(NO_3)_2 \cdot 6H_2O$  (AR grade), 1.500 g  $Al(NO_3)_3 \cdot 9H_2O$  (AR grade), and 1.68 g urea ( $CH_4N_2O$ , AR grade) were added to 70 mL deionized water (Millipore Milli-Q Direct 8). The mixed salt solution was further mixed using a vortex mixer (NP-30S) for 15 min. The activated  $Fe_3O_4$  and mixed salt solution were transferred to an autoclave and mixed for 2 h using the vortex mixer. Then the autoclave was heated at 120 °C for 12 h. Next, the autoclave was cooled to room temperature. The obtained product was separated by a magnet and washed with deionized water and ethanol (AR grade) three times, followed by drying in an oven at 60 °C for 12 h. Finally, the  $Fe_3O_4@Mg/Al-CO_3$ -LDH magnetic nano-adsorbent was obtained.

### 2.2 Instruments

SEM analysis was performed using an Inspect F50 field-emission scanning electron microscope (FEI) with a resolution of 2.0 nm. An acceleration voltage of 10 kV was applied during secondary electron imaging.

TEM analysis was performed using a JEM-2100F high-resolution field-emission transmission electron microscope (JEOL) with a point resolution of 0.24 nm and line resolution of 0.10 nm. To observe the morphology of the nanoparticles, the bright-field mode was utilized. To observe the electron diffraction from different regions on the nanoparticle, the selected area mode was utilized. An acceleration voltage of 200 kV was applied for both modes. The nanoparticles were dispersed by ethanol to form a suspending liquid before observation.

FTIR spectra were measured using a Nicolet Nexus Fourier transform infrared spectrometer (Thermo Fisher), in the range of 4000 to 400 cm<sup>−1</sup> with a resolution of 4 cm<sup>−1</sup>. The nanoparticles were mixed with KBr (SP grade) in the mass ratio of 1 : 100. After grinding in an agate mortar, the mixture was pressed into a thin disc sample.

XRD patterns were collected using a SmartLab9 X-ray diffractometer (Rigaku) with Cu-K $\alpha$  radiation of  $\lambda = 0.15418$  nm in the  $2\theta$  range of 0.08–78° with the scanning step of 0.02° and the step time of 2 s.

Magnetic hysteresis loop analysis was performed using a SQUID vibrating sample magnetometer (Quantum Design) in the magnetic field range of  $\pm 30\,000$  Oe.

Specific surface area and porosity were fitted from the  $N_2$  adsorption–desorption isotherms, which were determined at 77



K using an ASAP 2460 Accelerated Surface Area and Porosimeter System (Micromeritics).

The contents of  $F^-$ ,  $Cl^-$ , and  $PO_4^{3-}$  were determined using an ICS 5000+ ion chromatograph (Thermo Fisher) with a 25  $\mu$ L sample loop and a conductivity detector. An IonPac® AS18 (250 mm  $\times$  4.0 mm i.d.) was applied as the anion exchange analytical column, which was protected by the guard column of IonPac® AG18 (50 mm  $\times$  4.0 mm i.d.). The temperature of the column compartment was set to 30  $^{\circ}$ C. For the eluent of NaOH solution, the flow rate through the anion exchange analytical column was 1.00 mL min $^{-1}$ , and its concentration was automatically adjusted by an electrolytic eluent generator. When the test time was set to 35 min, the eluent concentration would be 25 mmol (0–13 min), 40 mmol (13–30 min), and 25 mmol (30–35 min). Manual injection was done in the operation.

### 2.3 Adsorption–determination and recycle procedures

The two main procedures are exhibited in Fig. 1 to adsorb  $PO_4^{3-}$  in a solution of  $Fe_3O_4@Mg/Al$ -CO $_3$ -LDH for the determination of  $F^-$  and  $Cl^-$ , and to recycle and reuse  $Fe_3O_4@Mg/Al$ -CO $_3$ -LDH.

Specifically, 50 mg of the synthesized magnetic nano-adsorbent was added to 80 mL of sample solution. They were mixed in a beaker by a vortex mixer for 5 min. After the adsorbent was isolated from the suspension with a magnet, the residual solution was filtered using a 0.22  $\mu$ m membrane. It was bubbled with  $N_2$  for 30 s to remove  $CO_3^{2-}$ , and then passed through an OnGuard II H column to remove the metal cations. At this time, the residual solution after adsorption on the  $Fe_3O_4@Mg/Al$ -CO $_3$ -LDH nanoparticles could be introduced into the ion chromatograph to determine  $F^-$  and  $Cl^-$ .

For the recycle procedure, the used  $Fe_3O_4@Mg/Al$ -CO $_3$ -LDH was collected and placed in 15 mL desorption solution, 5 wt% NaOH and 10 wt%  $Na_2CO_3$  (AR grade), and further mixed using a vortex mixer for 30 min. With the aid of a magnet, the  $Fe_3O_4@Mg/Al$ -CO $_3$ -LDH nanoparticles were washed with deionized water and ethanol three times. This was followed by drying in an oven at 60  $^{\circ}$ C for 12 h, and then  $Fe_3O_4@Mg/Al$ -CO $_3$ -LDH was regenerated for use for a new cycle adsorption. It should be noted that NaOH in the desorption solution will not affect the stability of  $Mg/Al$ -CO $_3$ -LDH since it was synthesized in an environment of NaOH, as indicated in Section 2.1.

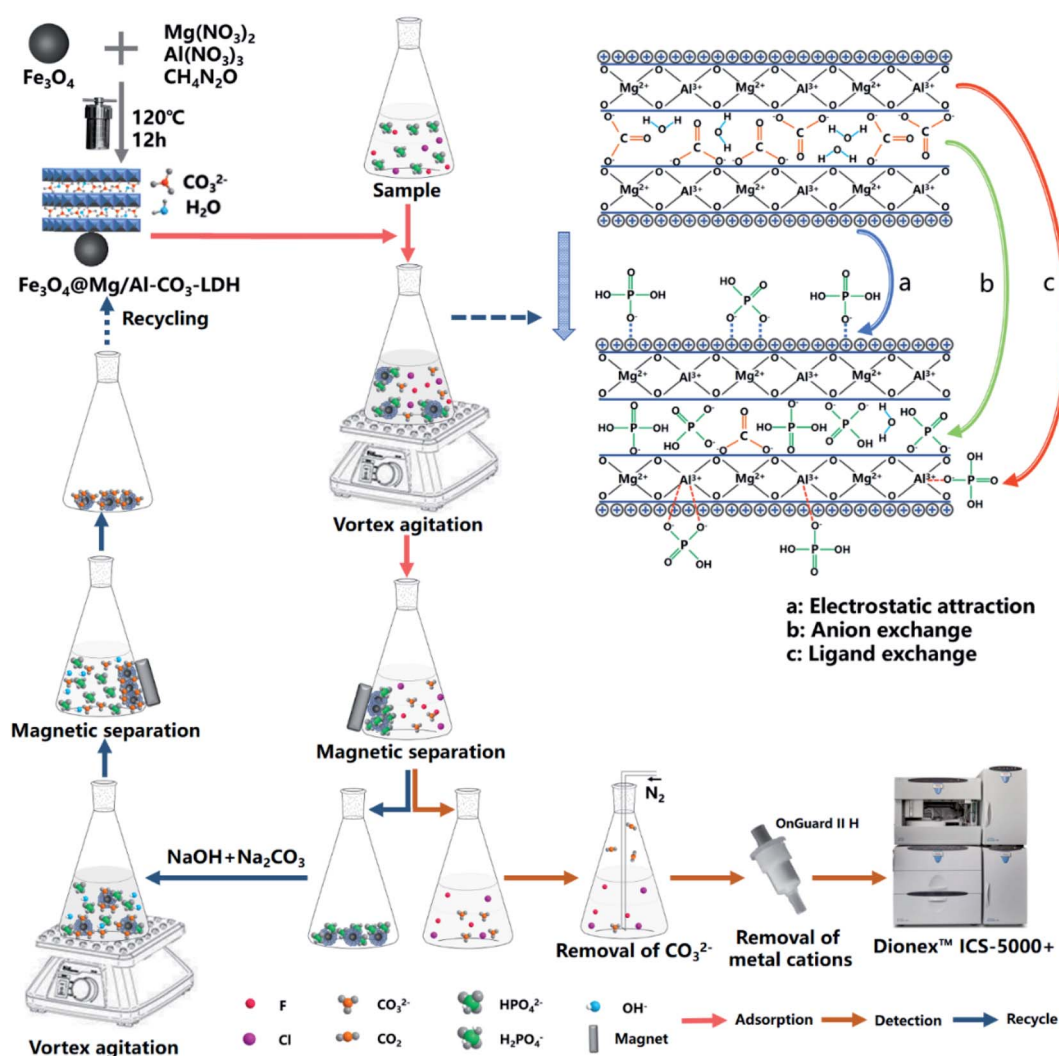


Fig. 1 Schematic illustration of the synthesis, adsorption, determination and recycle processes.





To evaluate the recyclability of the magnetic adsorbent, the phosphate adsorption capacity per unit mass of  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  was measured for each cycle. Briefly, 50 mg of the magnetic adsorbent was added to 80 mL mixed solution with  $1.00 \text{ mg L}^{-1} \text{ F}^-$ ,  $1.00 \text{ mg L}^{-1} \text{ Cl}^-$  and  $C_0 = 100 \text{ mg P per L PO}_4^{3-}$  (based on P). Then, it was processed by 60 min mixing/adsorption, magnetic solid phase extraction-separation, filtering, bubbling, cation removal and chromatographic determination, as stated above. After determining the remaining phosphate concentration,  $C_e$ , which is also the equilibrium  $\text{PO}_4^{3-}$  concentration in the solution, the adsorption capacity,  $Q_e$ , of  $\text{PO}_4^{3-}$  was calculated by  $Q_e = (C_0 - C_e)V/m$ , where  $V$  is the solution volume in L and  $m$  is the dry weight of the nano-adsorbent in g.

## 3 Results and discussion

### 3.1 Characterization of $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$

Fig. 2 shows the electron microscopy analysis of  $\text{Fe}_3\text{O}_4$  and the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nanoparticles. Both the SEM and bright-field TEM images show that  $\text{Fe}_3\text{O}_4$  is an octahedral nanoparticle with clear edges and smooth surface, and its size is about 120 nm, as shown in Fig. 2(a) and (b). On the surface of  $\text{Fe}_3\text{O}_4$ ,  $\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  was synthesized *via* the urea hydrothermal method. The shape of these irregular  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  nanoparticles is not like the octahedron of  $\text{Fe}_3\text{O}_4$ , and on their surface, some protuberances exist, as shown in Fig. 2(c). According to the bright-field TEM image shown in Fig. 2(d), these protuberances also can be observed at the outer boundary of the bright gray region, and the bright gray region surrounding the dark region of  $\text{Fe}_3\text{O}_4$  is characterized by a flake-like matrix. This is similar to the morphology of  $\text{Fe}_3\text{O}_4@\text{CuMgAl-LDH}$  nanoparticles.<sup>55</sup> Due to the stacking of many small flakes, the hydrothermally synthesized  $\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$

on  $\text{Fe}_3\text{O}_4$  nanoparticles appears to consist of an agglomeration of plate-like structures.<sup>56</sup>

Fig. 3(a) shows the high-resolution TEM image of the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ , where the bottom-left dark region and the bottom-right bright region were chosen for SAED, as shown in Fig. 3(b) and (c), respectively. The selected area electron diffraction (SAED) for the dark region clearly shows 4.910 Å, 3.193 Å, 2.469 Å and 1.698 Å diffractions, corresponding to the (111), (220), (222) and (422) planes of  $\text{Fe}_3\text{O}_4$  (PDF card: #19-0629). Also, the SAED for the bright region shows 1.541 Å and 1.476 Å diffractions, corresponding to the (110) and (113) planes of  $\text{Mg}/\text{Al-LDH}$  (PDF card: #89-0460). Although the diffraction spots for the bright region are somewhat blurred, as shown in Fig. 3(c), the hexagonal diffraction pattern can still be observed, which is the typical diffraction pattern of LDH crystals.<sup>55</sup>

Thus, the above electron microscopic analysis indicates that during the hydrothermal process,  $\text{Fe}_3\text{O}_4$  retains its original crystalline state, and  $\text{Mg}/\text{Al-LDH}$  is grown as small crystal plates. Their crystallization is also indicated by the XRD pattern shown in Fig. 4(a) for as-synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ . The diffraction peaks at the  $2\theta$  values of  $18.24^\circ$  (111),  $30.08^\circ$  (220),  $35.46^\circ$  (311),  $37.04^\circ$  (222),  $43.12^\circ$  (400),  $53.50^\circ$  (422),  $57.04^\circ$  (511), and  $62.56^\circ$  (400) correspond to the octahedral  $\text{Fe}_3\text{O}_4$  crystal,<sup>26</sup> and the peaks at the  $2\theta$  values of  $11.54^\circ$  (003),  $23.44^\circ$  (006),  $35.46^\circ$  (012),  $61.02^\circ$  (110), and  $62.56^\circ$  (113) correspond to the  $\text{Mg-Al-LDH}$  crystal.<sup>26,57</sup> More importantly, after 15 cycles of  $\text{PO}_4^{3-}$ -adsorption and regeneration of  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ , as stated in Section 2.3, both the XRD peak positions and intensities remained almost unchanged, as shown in Fig. 4(a) and (b). This indicates that even after 15 cycles, the

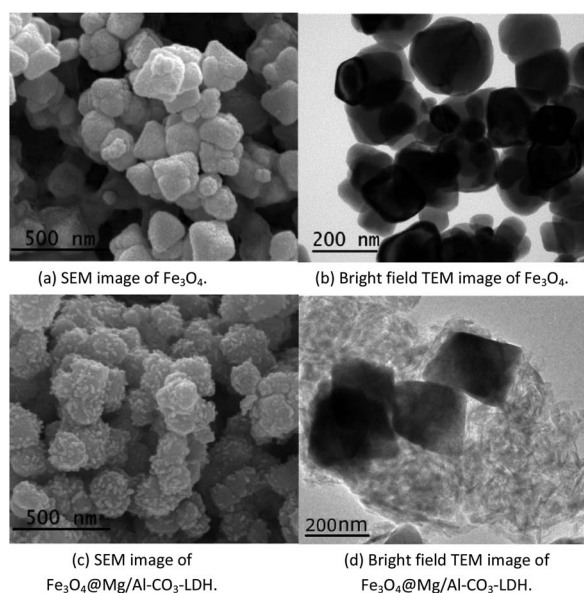


Fig. 2 Electron microscopy analysis of  $\text{Fe}_3\text{O}_4$  nanoparticles and prepared  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent.

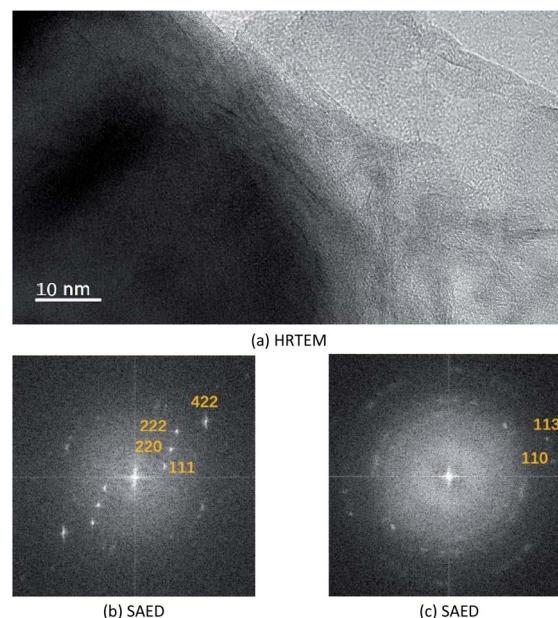


Fig. 3 High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) for prepared  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ , where (b) corresponds to the area at the bottom-left of (a), and (c) corresponds to the area at the bottom-right of (a).



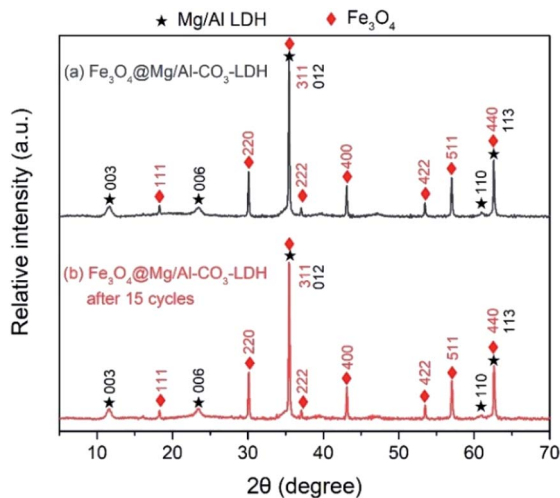


Fig. 4 XRD patterns of Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH magnetic nano-adsorbent before and after 15 cycles of PO<sub>4</sub><sup>3-</sup> adsorption and regeneration.

Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH magnetic nano-adsorbent can still maintain its structural stability, and thus has important potential for recycling.<sup>58</sup>

To explore the adsorption and desorption of PO<sub>4</sub><sup>3-</sup>, the FTIR spectra of Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH were measured for the as-synthesized, PO<sub>4</sub><sup>3-</sup>-adsorbed, and regenerated after 15 cycles of PO<sub>4</sub><sup>3-</sup> adsorption samples, as shown in Fig. 5(a)–(c), respectively. The Fe–O vibration peak<sup>59</sup> appeared at 586 cm<sup>−1</sup> before and after adsorption and desorption, showing the stable assembly between Fe<sub>3</sub>O<sub>4</sub> and Mg/Al-CO<sub>3</sub>-LDH.

As shown in Fig. 5(a), the spectrum of the as-synthesized sample exhibits peaks at 448 cm<sup>−1</sup>, 681 cm<sup>−1</sup>, and 788 cm<sup>−1</sup>, which are attributed to the vibration of Mg–OH,<sup>60</sup> Mg–O–Al,<sup>61</sup> and Al–OH,<sup>60</sup> respectively. The two peaks located at 3445 cm<sup>−1</sup> and 1637 cm<sup>−1</sup> are related to the stretching and bending modes

of the water molecule existing in the interlayer structure, respectively.<sup>62</sup> These peaks indicate the successful synthesis of the layered structure Mg/Al-LDH. As the interlayer anion, the vibration of CO<sub>3</sub><sup>2-</sup> appears<sup>35</sup> at 1362 cm<sup>−1</sup> and 1502 cm<sup>−1</sup>. During the hydrothermal process, urea decomposes at high temperature and produces the CO<sub>3</sub><sup>2-</sup> anion,<sup>63</sup> which then enters Mg/Al-LDH to form the interlayer anion. Moreover, there is a small peak located at 1385 cm<sup>−1</sup>, corresponding to the NO<sub>3</sub><sup>−</sup> vibration, but it is rather weak. This is due to the use of nitrate during the synthetic process, where a small amount of NO<sub>3</sub><sup>−</sup> existing in Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH was not replaced by CO<sub>3</sub><sup>2-</sup>.

As shown in Fig. 5(b), in the spectrum of the PO<sub>4</sub><sup>3-</sup>-adsorbed sample, the Fe–O vibration and the stretching and bending modes of the water molecule remained, but the vibrations resulting from Mg–OH, Mg–O–Al, and Al–OH almost disappear. Especially, there is no CO<sub>3</sub><sup>2-</sup> vibration at 1502 cm<sup>−1</sup>, and only a very weak CO<sub>3</sub><sup>2-</sup> peak at 1362 cm<sup>−1</sup>. On the other hand, new peaks at 2484 cm<sup>−1</sup>, 2401 cm<sup>−1</sup>, 1088 cm<sup>−1</sup>, and 901 cm<sup>−1</sup> appear, which are due to the vibrations of PO<sub>4</sub><sup>3-</sup>.<sup>25,64,65</sup> These results clearly indicate that the anion exchange<sup>26</sup> really occurred for Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH after adsorbing PO<sub>4</sub><sup>3-</sup>, which is the process to use PO<sub>4</sub><sup>3-</sup> to replace CO<sub>3</sub><sup>2-</sup>. It is most probably the first mechanism for the synthesized Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH to adsorb PO<sub>4</sub><sup>3-</sup> in solution. Due to the disappearance of the vibrations of Mg–OH and Al–OH, it means that they can be protonated and become positively charged, and thus they can adsorb the negatively charged PO<sub>4</sub><sup>3-</sup> due to electrostatic adsorption on the surface of LDH.<sup>29</sup> This may be the second mechanism to adsorb PO<sub>4</sub><sup>3-</sup> in solution. The disappearance of the vibration of Mg–O–Al may be possibly explained by the fact that, as a ligand anion,<sup>29</sup> PO<sub>4</sub><sup>3-</sup> can be complexed with the Al<sup>3+</sup> cation on the surface of Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH. This ligand exchange may be the third mechanism to adsorb PO<sub>4</sub><sup>3-</sup> in solution. The ability to perform these three mechanisms for the synthesized Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH is consistent with the reported PO<sub>4</sub><sup>3-</sup>-adsorbed LDHs.<sup>26,29,33</sup>

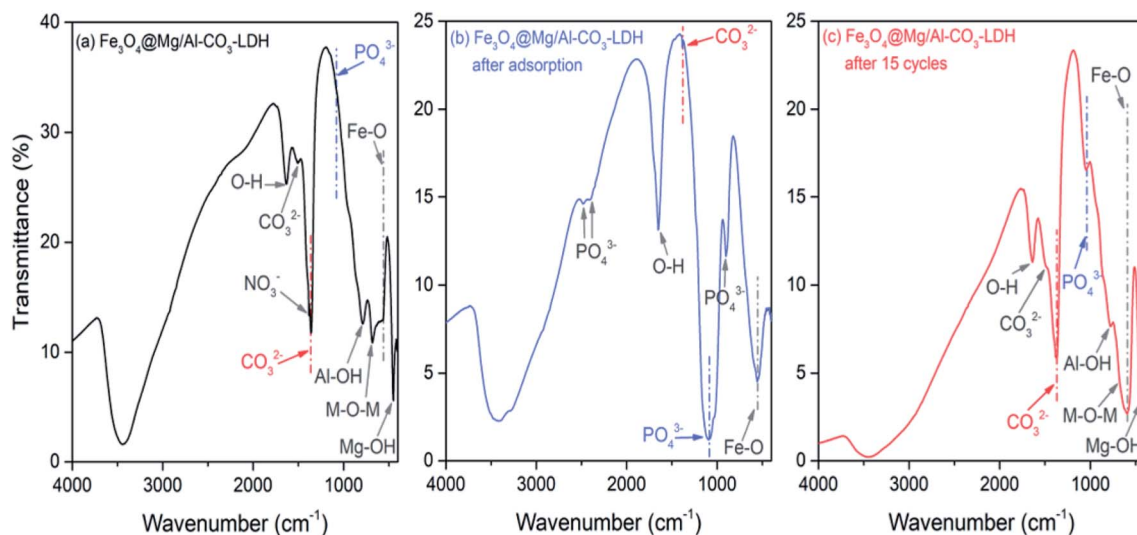


Fig. 5 FTIR spectra of Fe<sub>3</sub>O<sub>4</sub>@Mg/Al-CO<sub>3</sub>-LDH magnetic nano-adsorbents. (a) As-prepared, (b) PO<sub>4</sub><sup>3-</sup>-adsorbed, and (c) regenerated after 15 cycles of PO<sub>4</sub><sup>3-</sup> adsorption.



As shown in Fig. 5(c), in the spectrum of the regenerated sample after 15 cycles of  $\text{PO}_4^{3-}$ -adsorption, the positions and intensities of the FTIR peaks are almost the same as that in Fig. 4(a) of the as-synthesized sample. This means that the desorption was successful, and the regenerated  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  returned to its original state with a strong ability to be recycled. It should be noted that there is still a weaker peak at  $1088\text{ cm}^{-1}$  due to  $\text{PO}_4^{3-}$ , which indicates a small amount of was  $\text{PO}_4^{3-}$  left in  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  after 15 cycles. However, it had no great effect on the phosphate adsorption capacity, as stated in Section 3.3, since most of the interlayer anions were exchanged by  $\text{CO}_3^{2-}$  during the desorption process.

It was reported<sup>52</sup> that for  $\text{MgAl-LDO}$  calcined at  $500\text{ }^\circ\text{C}$  for 4 h after its synthesis, the FTIR band of  $-\text{OH}$  was shifted to a higher frequency from  $1644\text{ cm}^{-1}$  to  $1664\text{ cm}^{-1}$  after  $\text{F}^-$  adsorption, which may be due to the adsorption of  $\text{F}^-$ . However, as can be seen in Fig. 5(a)–(c), the band due to  $\text{OH}$  appears at  $1637\text{ cm}^{-1}$ ,  $1640\text{ cm}^{-1}$ , and  $1638\text{ cm}^{-1}$  for the as-synthesized,  $\text{PO}_4^{3-}$ -adsorbed, and regenerated  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  samples, respectively. Thus, the absence of a shift in the  $\text{OH}$  band means that the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  did not adsorb  $\text{F}^-$ . This is in good agreement with the determination results by ion chromatography, indicating there was no change for the trace concentrations of  $\text{F}^-$  and  $\text{Cl}^-$  before and after adsorption (see Fig. 8 and 9 in Section 3.2, respectively). According to the literature, phosphate adsorption by some non-LDH adsorbents<sup>66–70</sup> and some LDH adsorbents<sup>23–26,31,33</sup> is greatly affected by  $\text{F}^-$  or  $\text{Cl}^-$  due to their adsorption. For LDHs, considering the bonding strength between the layers and interlayer anions in aqueous solution,<sup>17</sup> the strength of phosphates is generally higher than that of  $\text{F}^-$  and  $\text{Cl}^-$ . Since there is a large amount of phosphate in aqueous solution, the adsorption possibility of phosphate is higher than that of  $\text{F}^-$  or  $\text{Cl}^-$ . However, it is still inevitable that a small amount of  $\text{F}^-$  and  $\text{Cl}^-$  will be adsorbed,<sup>23–26,31,33</sup> although this possibility is small. Thus, to further decrease this possibility, for the synthesized nano-adsorbent of  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ ,  $\text{CO}_3^{2-}$  was employed as the interlayer anion. The bonding strength of  $\text{CO}_3^{2-}$  is the highest,<sup>17</sup> much greater than that of  $\text{F}^-$  and  $\text{Cl}^-$ . During the phosphate adsorption process, a lot of  $\text{CO}_3^{2-}$  anions will be exchanged in the solution, which will further inhibit the adsorption of trace  $\text{F}^-$  and  $\text{Cl}^-$  anions. Moreover, if some  $\text{OH}^-$  anions exist in solution, the adsorption efficiencies<sup>19</sup> will further decline due to the combined effects of increasing competition from the  $\text{OH}^-$  anion and the Coulomb repulsion between the negative-charged surface of the LDH adsorbent and  $\text{F}^-$  or  $\text{Cl}^-$ . If there is insufficient positive charge such as  $\text{H}^+$  on the surface of the LDH adsorbent, and there are enough anions such as  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ , which have a much higher bonding strength than  $\text{F}^-$  and  $\text{Cl}^-$ , to strongly compete with  $\text{F}^-$  and  $\text{Cl}^-$  anions, the synthesized magnetic nano-adsorbent  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  should not adsorb  $\text{F}^-$  and  $\text{Cl}^-$  anions.

Fig. 6 shows the magnetic hysteresis loops of  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  before and after 15 cycles of  $\text{PO}_4^{3-}$ -adsorption. Compared with the magnetic saturation value of  $102\text{ emu g}^{-1}$  for the pure  $\text{Fe}_3\text{O}_4$  nanoparticles, that for the as-synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  drops to  $36.75\text{ emu g}^{-1}$

since the non-magnetic  $\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  shields the magnetic  $\text{Fe}_3\text{O}_4$ . Even if after 15 cycles, it was still  $36.47\text{ emu g}^{-1}$ . This value is sufficient to achieve repeated rapid magnetic extraction and separation. More importantly, it should be noted that the two loop curves before and after  $\text{PO}_4^{3-}$ -adsorption come close to coinciding in shape. This truthfully reflects that the thickness of the  $\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  coating layer did not change, which indicates almost no etching and degradation occurred even after 15 cycles of adsorption, separation and desorption. Based on this, the structural stability indicated by the above Fig. 4(b), which is also the result after 15 cycles of  $\text{PO}_4^{3-}$ -adsorption, means that the two-dimensional crystalline nanostructure of  $\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  and the interlayer anion  $\text{CO}_3^{2-}$  in the layered double hydroxide were both maintained rather stably. Actually, it can be seen in Fig. 5(c) that after 15 cycles of adsorption, separation and desorption, the FTIR peak intensity of  $\text{CO}_3^{2-}$  is as strong as that of the as-synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ , as seen in Fig. 5(a). This means that the content of  $\text{CO}_3^{2-}$  was almost fully recovered even after 15 cycles of  $\text{PO}_4^{3-}$ -desorption, which can provide an excellent performance for stable dephosphorization.

Fig. 7(a) and (b) show the  $\text{N}_2$  adsorption-desorption isotherms and BJH (Barrett-Joyner-Halenda) pore diameter distribution curves of  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ , respectively. In Fig. 7(a), there is a clear hysteresis loop at a high relative pressure of  $P/P_0 > 0.6$ , which is a typical type IV adsorption isotherm<sup>28</sup> according to the IUPAC classification. When  $P/P_0 > 0.9$ , there is no saturated adsorption platform, and rapid adsorption and desorption occur in this high pressure region. This indicates that the loop can be further classified as type H3,<sup>28</sup> which means the pores in  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  are mainly mesoporous. This was verified by Fig. 7(b), where the pore size distribution is mainly in the range of 5–50 nm, with an average size of  $15.1\text{ nm}$  and total pore volume of  $0.59\text{ cm}^3\text{ g}^{-1}$ . The formation of these mesoporous pores in  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  is related to the slit-shaped pores or voids created within the aggregates of platy particles.<sup>28,71</sup> Generally, the

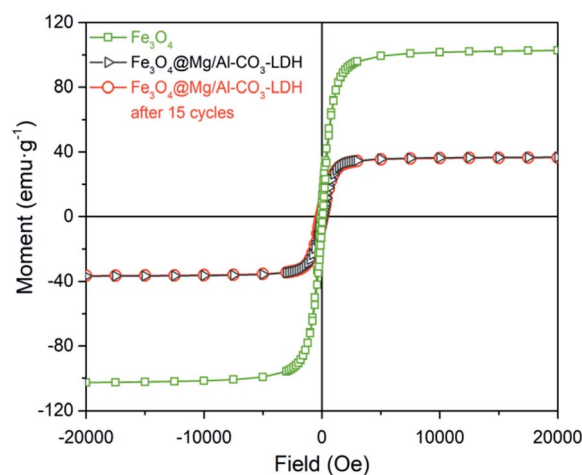


Fig. 6 Magnetic hysteresis loop analysis for  $\text{Fe}_3\text{O}_4$  nanoparticle, and prepared  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent before and after 15 cycles of  $\text{PO}_4^{3-}$ -adsorption and regeneration.





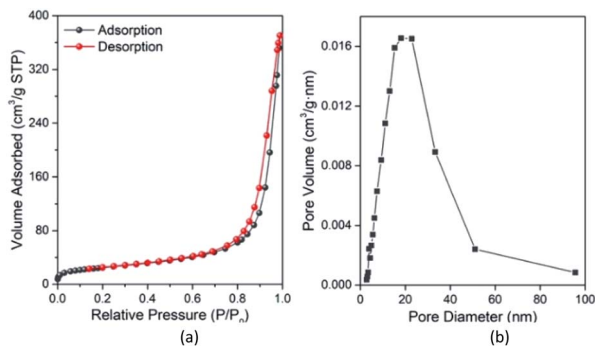


Fig. 7  $N_2$  adsorption-desorption isotherms (a) and Barrett-Joyner-Halenda (BJH) pore diameter distribution curve (b) of the prepared  $Fe_3O_4@Mg/Al-CO_3-LDH$  magnetic nano-adsorbent.

specific surface area and total pore volume will affect the chance of contact between the adsorbent and the adsorbate, thereby affecting the adsorption effect of the adsorbent.<sup>28,72</sup> According to the BET (Brunauer-Emmett-Teller) method,<sup>73</sup> the specific surface area of  $Fe_3O_4@Mg/Al-CO_3-LDH$  was calculated to be  $88.4 \text{ m}^2 \text{ g}^{-1}$ . Thus, the hydrothermally synthesized  $Fe_3O_4@Mg/Al-CO_3-LDH$  can adsorb  $PO_4^{3-}$  in solution rapidly and efficiently.

### 3.2 Optimized pretreatment by $Fe_3O_4@Mg/Al-CO_3-LDH$

For 80 mL solution containing  $1.00 \text{ mg L}^{-1} F^-$ ,  $1.00 \text{ mg L}^{-1} Cl^-$  and  $100 \text{ mg P per L } PO_4^{3-}$  are the optimized adsorbent amount and adsorption time for  $Fe_3O_4@Mg/Al-CO_3-LDH$ , respectively. These optimized pretreatment conditions were utilized for the analysis of real samples, as stated in Section 4.

By using different amounts of  $Fe_3O_4@Mg/Al-CO_3-LDH$  magnetic nano-adsorbent to adsorb  $PO_4^{3-}$  for the same adsorption time of 60 min, Fig. 8 shows the chromatograms, in which three chromatographic peaks at about 3 min, 7 min, 22 min correspond to  $F^-$ ,  $Cl^-$ , and  $PO_4^{3-}$ , respectively. Their concentrations were calculated based on their peak area, and plotted at the top of Fig. 8. With the addition of  $Fe_3O_4@Mg/Al-CO_3-LDH$  in the solution, the concentration of both  $F^-$  and  $Cl^-$  was always maintained at around  $1.00 \text{ mg L}^{-1}$  with the fluctuation of  $\pm 2\%$ , as shown in the top-left and top-middle of Fig. 8. This indicates that  $Fe_3O_4@Mg/Al-CO_3-LDH$  will not adsorb any  $F^-$  and  $Cl^-$  anions in the solution regardless of the adsorbent amount used, which is the most important factor to determine trace  $F^-$  and  $Cl^-$  in solution. On the other hand, only a small amount of the nano-adsorbent, such as 20 and 50 mg, could make the residual  $PO_4^{3-}$  concentration decrease greatly from  $100 \text{ mg P per L}$  to  $64.5$  and  $49.5 \text{ mg P per L}$ , respectively, as shown in the top-right of Fig. 8. However, when the adsorbent amount was further increased to  $80 \text{ mg}$ , the residual  $PO_4^{3-}$  concentration did not further decrease since equilibrium between  $PO_4^{3-}$  and  $CO_3^{2-}$  was reached. Thus, the optimized adsorbent amount of  $50 \text{ mg } Fe_3O_4@Mg/Al-CO_3-LDH$  is enough for  $80 \text{ mL}$  solution with  $100 \text{ mg P per L } PO_4^{3-}$ .

By using  $50 \text{ mg } Fe_3O_4@Mg/Al-CO_3-LDH$  to adsorb  $PO_4^{3-}$  in  $80 \text{ mL}$  solution for different times, the residual concentration of

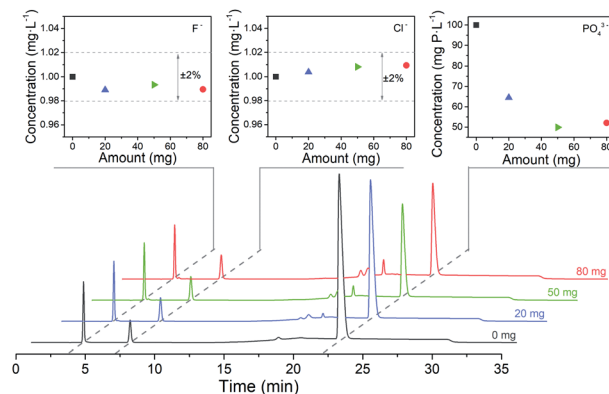


Fig. 8 Chromatograms for the solution with  $1.00 \text{ mg L}^{-1} F^-$ ,  $1.00 \text{ mg L}^{-1} Cl^-$  and  $100 \text{ mg P per L } PO_4^{3-}$  using  $0, 20, 50$ , and  $80 \text{ mg } Fe_3O_4@Mg/Al-CO_3-LDH$  magnetic nano-adsorbent, respectively. The same adsorption time of  $60 \text{ min}$  was applied.

$PO_4^{3-}$  and  $F^-$  and  $Cl^-$  anions in the solution was determined by chromatography, as plotted in Fig. 9. According to Fig. 9(a), the concentration of both  $F^-$  and  $Cl^-$  was maintained at around  $1.00 \text{ mg L}^{-1}$  with the fluctuation of  $\pm 2\%$ , regardless of the adsorbent time used. Similarly, as indicated in the plots at the top of Fig. 8,  $Fe_3O_4@Mg/Al-CO_3-LDH$  did not adsorb any  $F^-$  and  $Cl^-$  anions in the solution, no matter how long the interaction time. However, for  $PO_4^{3-}$ , even with fast magnetic separation immediately after the addition of  $Fe_3O_4@Mg/Al-CO_3-LDH$  in the solution, the residual  $PO_4^{3-}$  concentration directly declined to  $72.9 \text{ mg P per L}$ . Also, after  $2$  and  $5 \text{ min}$  adsorption, it decreased to  $60.3$  and  $52.2 \text{ mg P per L}$ , respectively. With a further increase in the adsorption time, the adsorption of  $PO_4^{3-}$  slows down to the equilibrium stage, until the residual  $PO_4^{3-}$  concentration finally reached  $48.1 \text{ mg P per L}$  after  $120 \text{ min}$  adsorption. According to the formula for phosphate adsorption capacity,<sup>74</sup> as stated in Section 2.3, the capacity of  $Fe_3O_4@Mg/Al-CO_3-LDH$  is  $83.04 \text{ mg P per g}$  for  $120 \text{ min}$  adsorption. Even for  $5 \text{ min}$  adsorption, it is still as high as  $76.48 \text{ mg P per g}$ . Thus, the optimized adsorption time was chosen to be  $5\text{--}60 \text{ min}$  for the solution using  $50 \text{ mg } Fe_3O_4@Mg/Al-CO_3-LDH$ .

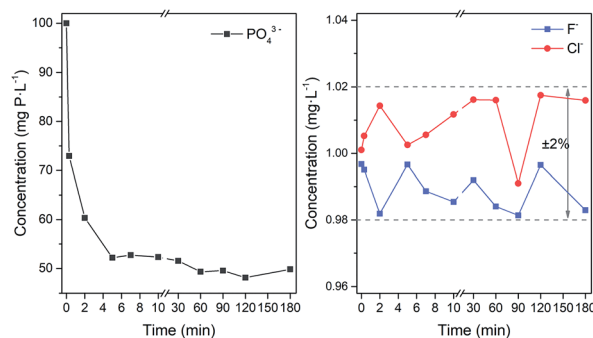
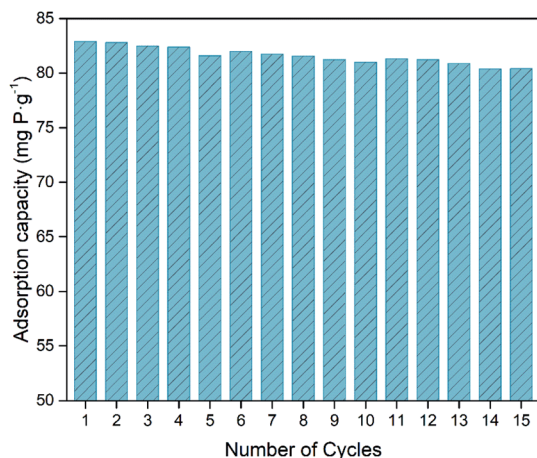


Fig. 9 Determined concentrations by chromatography for  $80 \text{ mL}$  solution with  $1.00 \text{ mg L}^{-1} F^-$ ,  $1.00 \text{ mg L}^{-1} Cl^-$  and  $100 \text{ mg P per L}$  with the adsorption time. In the adsorption experiment, the used  $Fe_3O_4@Mg/Al-CO_3-LDH$  magnetic nano-adsorbent is  $50 \text{ mg}$ .



**Fig. 10** Phosphate adsorption capacities of  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent for 15 cycles of  $\text{PO}_4^{3-}$ -adsorption-desorption, respectively. For each cycle, 80 mL solution with  $1.00 \text{ mg L}^{-1} \text{ F}^-$ ,  $1.00 \text{ mg L}^{-1} \text{ Cl}^-$  and  $100 \text{ mg P per L}$  is adsorbed by  $50 \text{ mg Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent for 60 min. The desorption solution is  $15 \text{ mL}$  mixture of  $5 \text{ wt\% NaOH}$  and  $10 \text{ wt\% Na}_2\text{CO}_3$  and the desorption time is 30 min.

### 3.3 Recyclability of $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$

The recyclability of an adsorbent is vital for its practical application,<sup>31,58</sup> and the premise for recycling is the stability of its structure. The crystalline structure stability, the adsorption stability, and the coating layer stability of  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  after 15 cycles of  $\text{PO}_4^{3-}$ -adsorption and regeneration were

confirmed by XRD, as shown in Fig. 4(b), FTIR, as shown in Fig. 5(c), and magnetic hysteresis loop analysis, as shown in Fig. 6, respectively.

To evaluate the recyclability of the  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent, the phosphate adsorption capacities were determined for each cycle and shown in Fig. 10, where the 60 min adsorption, 30 min desorption and regeneration processes are stated in Section 2.3. The initial capacity of  $83.04 \text{ mg P per g}$  calculated from Fig. 9 was used for the as-synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ . For the subsequent cycles, the phosphate adsorption capacity decreased but very slowly. Even after 15 desorption-adsorption cycles, the capacity was still as high as  $80.41 \text{ mg P per g}$ , which is only  $3.2\%$  lower than the initial  $83.04 \text{ mg P per g}$ . Among the 15 cycles, the maximum decrease occurred in the 5th cycle, but not more than  $1\%$ , and the average decrease was as low as  $\sim 0.2\%$ . This clearly indicates that the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  has excellent recyclability and stability, maintaining high phosphate adsorption capacities even after manifold cycles.

Table 1 presents the phosphate adsorption capacity, adsorption time, and recycle number of various magnetic adsorbents. These adsorbents, LDH adsorbents with interlayer anion and non-LDH adsorbents, can all be used to efficiently adsorb  $\text{PO}_4^{3-}$  in solution. Compared with most of the adsorbents, the phosphate capacity per unit mass of the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  is as high as  $76.48 \text{ mg P per g}$ , higher than  $1.8675\text{--}36.9 \text{ mg P per g}$ , but somewhat lower<sup>25,31,69,74</sup> than  $128\text{--}252.88 \text{ mg P per g}$  of these four adsorbents. However, they used about  $360\text{--}4320 \text{ min}$  to adsorb phosphates in solution. It

**Table 1** Comparison of the adsorption time, adsorption capacity and the number of reuse cycles by various magnetic adsorbents for the adsorption of the  $\text{PO}_4^{3-}$  phosphate group

Adsorbent	Interlayer anion for LDH <sup>g</sup>	Adsorption time (min)	Adsorption capacity <sup>a</sup> (mg P per g)	Cycle no.	Ref.
ZnFeZr adsorbent@ $\text{Fe}_3\text{O}_4/\text{SiO}_2$	$\text{Cl}^-$	60		20	23
Magnetic Fe/Mn oxide composites (TS-N)	$\text{Cl}^-$	90	26.0		24
$\text{Fe}_3\text{O}_4/\text{Zn}-\text{Al}-\text{Fe}-\text{La-LDH}$	$\text{Cl}^-$ and $\text{SO}_4^{2-}$	1440	169.5	4 <sup>b</sup>	25
$\text{Fe}_3\text{O}_4@\text{Zn}-\text{Al-LDH}$	$\text{CO}_3^{2-}$	60	36.9		26
$\text{Fe}_3\text{O}_4@\text{Mg}-\text{Al-LDH}$			31.7		
$\text{Fe}_3\text{O}_4@\text{Ni}-\text{Al-LDH}$			26.5		
$\text{Fe}/\text{CaCO}_3\text{-PVA}$	Non-LDH		16.7		75
$\text{Fe}/\text{MgCO}_3\text{-PVA}$			16.3		
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CeO}_2$	Non-LDH	1440	10.8	2 <sup>c</sup>	76
$\text{Ce-Ti}@\text{Fe}_3\text{O}_4$	Non-LDH	1440	11.10		66
Carboxylated chitosan- $\text{Fe}_3\text{O}_4$	Non-LDH	60	1.8675		67
La-chitosan magnetic spheres	Non-LDH	300	27.78		68
$\text{ZrO}_2/\text{Fe}_3\text{O}_4$	Non-LDH	1440	29.5		77
Magnetic <i>Caragana korshinskii</i> biochar/Mg-Al-LDH	$\text{Cl}^-$	720	252.88	5 <sup>d</sup>	31
$\text{Fe}_3\text{O}_4@\text{alkali-treated calcium-silicate}$	Non-LDH	4320	128	2 <sup>e</sup>	69
$\text{Fe}_3\text{O}_4@\text{gelatin encapsulated hydrotalcite}$	$\text{CO}_3^{2-}$	40	32.73	4 <sup>f</sup>	33
$\text{NrGO}/\text{Fe}_3\text{O}_4$	Non-LDH	360	135.3	5	74
Humic acid coated magnetite nanoparticles	Non-LDH	180	28.9		70
$\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$	$\text{CO}_3^{2-}$	5	76.48	15	This work

<sup>a</sup> Adsorption capacity of phosphate,  $Q_e = (C_0 - C_e)V/m$ , where  $C_0$  and  $C_e$  are the initial and equilibrium phosphate concentration in  $\text{mg L}^{-1}$ ,  $V$  is the volume of phosphate solution in L, and  $m$  is the dry weight of the adsorbent in g. <sup>b</sup> The adsorption capacity decreased to  $31 \text{ mg g}^{-1}$  after 4 cycles.

<sup>c</sup> The adsorption capacity decreased to  $25.71 \text{ mg g}^{-1}$  after 5 cycles. <sup>d</sup> The adsorption efficiency was reduced to  $70.01\%$  after 4 cycles. <sup>e</sup> The adsorption capacity decreased to  $4.8 \text{ mg g}^{-1}$  after 2 cycles. <sup>f</sup> The adsorption capacity decreased to  $20.2 \text{ mg g}^{-1}$  after 2 cycles. <sup>g</sup> The information is summarized from the description of preparation processes, or FTIR, XPS and other characterization in refs.





should be noted that the capacity is related to the adsorption time used. Even if the adsorption time used is as fast as 5 min, which is 1/8–1/288 of the reported times listed in Table 1, the adsorption capacity of 76.48 mg P per g for  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  is high enough to adsorb  $\text{PO}_4^{3-}$  rapidly and efficiently so as to determine  $\text{F}^-$  and  $\text{Cl}^-$  without serious interference due to  $\text{PO}_4^{3-}$ . In the case of the recycle number, which is one of the vital properties for the recyclability of an adsorbent, it is 15 cycles for  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$ , more than the reported 2–5 cycles,<sup>23</sup> but there was no information about the phosphate adsorption capacity. According to Table 1, if only considering magnetic LDHs with a  $\text{CO}_3^{2-}$  interlayer anion,  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  behaves very well to adsorb  $\text{PO}_4^{3-}$  in solution, with four times greater cycle number and two times greater phosphate adsorption capacity.

## 4 Analysis of real samples

Phosphate and fluorophosphate laser glasses contain high  $\text{PO}_4^{3-}$  and a certain amount of various monovalent, divalent, trivalent metal cations. The leaching solutions from these glasses were determined before and after adsorption pretreatment using the  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent, and the chromatograms are shown in Fig. 11. As seen in Fig. 11(a) for the phosphate ( $\text{P}_2\text{O}_5$  molar ratio of both N31 and N41 glasses is close to 60%) with high  $\text{PO}_4^{3-}$  but low  $\text{F}^-$  and  $\text{Cl}^-$ , the strong peak at 22.36 min due to  $\text{PO}_4^{3-}$  is too overloaded, and thus it seems to be a leading peak with 100  $\mu\text{S}$  conductivity. After the adsorption pretreatment, the 22.36 min peak shape became normal and its intensity decreased greatly

to 10  $\mu\text{S}$ . This indicates that  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  could efficiently adsorb  $\text{PO}_4^{3-}$  in the multi-ion leaching solution in a short time of only 5 min. On the other hand,  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  did not adsorb any  $\text{F}^-$  or  $\text{Cl}^-$ . The peaks at 3.79 and 7.34 min are due to  $\text{F}^-$  and  $\text{Cl}^-$ , respectively, and their intensities did not change after the adsorption pretreatment. As seen in Fig. 11(b) for the fluorophosphate with a high  $\text{F}^-$  and  $\text{PO}_4^{3-}$  content but low  $\text{Cl}^-$ , the 22.36 min  $\text{PO}_4^{3-}$  peak almost disappeared after the adsorption pretreatment by  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  for 5 min. The strong  $\text{F}^-$  peak at 3.79 min and the weak  $\text{Cl}^-$  peak at 7.34 min did not change after the pretreatment. Regardless of a high or low  $\text{PO}_4^{3-}$  content in a multi-ion solution, the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent can adsorb and extract  $\text{PO}_4^{3-}$  rapidly. Also, regardless of a high or low  $\text{F}^-$  or  $\text{Cl}^-$  content in a multi-ion solution, the addition and extraction of the nano-adsorbent did not result in any change in the contents of  $\text{F}^-$  or  $\text{Cl}^-$ . These two facts determine the usefulness of the nano-adsorbent for specific applications, *i.e.* the removal of  $\text{PO}_4^{3-}$ , and especially the determination of  $\text{F}^-/\text{Cl}^-$  after removing  $\text{PO}_4^{3-}$  in a multi-ion solution. By using the  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  adsorption pretreatment, the pretreated solution can be utilized for other determination techniques or methods since there will be no serious interference from  $\text{PO}_4^{3-}$  in the solution. Considering chromatography, the determination time for the accurate determination of  $\text{F}^-$  and  $\text{Cl}^-$  can be greatly shortened after removing  $\text{PO}_4^{3-}$ . More importantly, without being affected by  $\text{PO}_4^{3-}$  and fully retaining trace  $\text{F}^-$  and  $\text{Cl}^-$ , a continuous analysis or on-line test can be done during processes in the laboratory and industry in fields such as pharmaceuticals and biomaterials. If  $\text{PO}_4^{3-}$  is not removed from a  $\text{PO}_4^{3-}$ -rich solution, the next injection must not be allowed.<sup>11</sup>

By chromatography, Table 2 lists the determined results of  $\text{F}^-$  and  $\text{Cl}^-$  for various real samples, such as a certified reference ore material (GBW07108 containing F, Cl and P, as well as 66 other elements), silicate glass, fluorophosphate glass, phosphate laser glasses, and environmental water samples. Specifically, 80 mL sample solution was pretreated using  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  under the optimized conditions. For the certified ore sample, the determined values of 0.395 and 0.0071  $\text{mg L}^{-1}$  are very close to the certified values of 0.406 and 0.0078  $\text{mg L}^{-1}$  for  $\text{F}^-$  and  $\text{Cl}^-$ , respectively. After determining  $\text{F}^-$  and  $\text{Cl}^-$  for the other samples, a certain amount of  $\text{F}^-$  and  $\text{Cl}^-$  standard solutions was added, *i.e.* the added content was 1.00  $\text{mg L}^{-1}$ . Subsequently, the contents of  $\text{F}^-$  and  $\text{Cl}^-$  in the solution re-pretreated by  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  were measured again. Accordingly, the spiked recoveries were calculated. As seen in Table 2, these spiked recoveries were all within an acceptable range of 95.7–104.9%. Thus, the above determinations prove the accuracy to determine  $\text{F}^-$  and  $\text{Cl}^-$  in multi-ion solutions pretreated by the synthesized  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent.

It should be noted that the pH values of real sample solutions may vary from sample to sample, especially when dissolving solid samples by acid or alkali. The pH value of the solution will affect the existing form of phosphate anions,<sup>17,26,29</sup> such as  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ . Thus, two phosphate

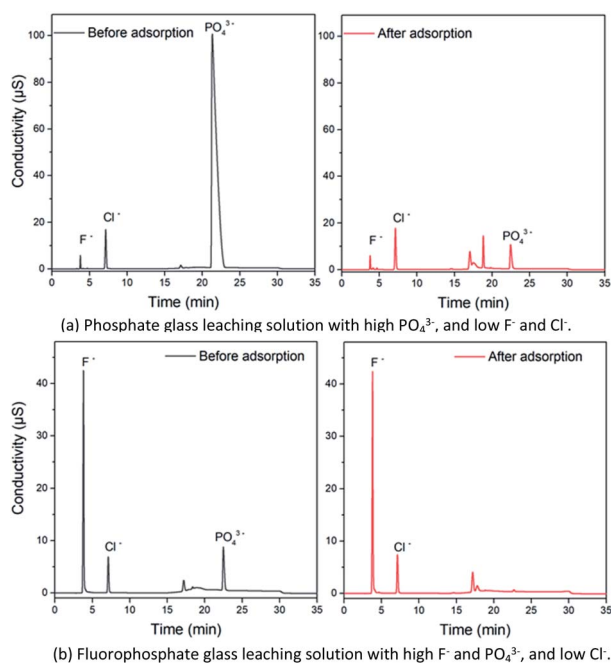


Fig. 11 Chromatograms for the leaching solutions of phosphate glass (a) and fluorophosphate glass (b) before and after 5 min adsorption by 50 mg  $\text{Fe}_3\text{O}_4@\text{Mg}/\text{Al}-\text{CO}_3\text{-LDH}$  magnetic nano-adsorbent.

**Table 2** Determination of  $F^-$  and  $Cl^-$  anions in a certified reference ore sample, silicate glasses, fluorophosphate glasses, phosphate glasses and river water samples by ion chromatography after adsorption pretreatment by  $Fe_3O_4@Mg/Al-CO_3-LDH$ 

Sample	$F^-$			$Cl^-$		
	Added ( $mg\ L^{-1}$ )	Found ( $mg\ L^{-1}$ )	Recovery (%)	Added ( $mg\ L^{-1}$ )	Found ( $mg\ L^{-1}$ )	Recovery (%)
GBW07108 <sup>a</sup>	0.406 <sup>b</sup>	0.395	97.3	0.078 <sup>b</sup>	0.071	91.0
	1.00	1.444	104.9	1.00	1.092	102.1
Silicate glass	0	9.970	—	0	0.083	—
	1.00	10.927	95.7	1.00	1.069	98.6
Fluorophosphate glass	0	21.972	—	0	0.066	—
	1.00	23.012	104.0	1.00	1.060	99.4
N31 phosphate glass, pot melting	0	0.744	—	0	0.251	—
	1.00	1.738	99.4	1.00	1.245	99.4
N41 phosphate glass, pot melting	0	0.814	—	0	0.585	—
	1.00	1.800	98.6	1.00	1.558	97.3
N41 phosphate glass, continuous melting	0	1.267	—	0	0.459	—
	1.00	2.277	101.0	1.00	1.501	104.2
River water	0	0.153	—	0	7.351	—
	1.00	1.150	99.7	1.00	8.338	98.7

<sup>a</sup> The certified reference ore samples were approved by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, which were mainly composed of silicate, carbonate and oxide of Al, Fe, Mg and Ca. <sup>b</sup> The certified content of  $F^-$  and  $Cl^-$  in the certified reference material GBW07108.

solutions were obtained by dissolving high purity  $Na_3PO_4$  or  $NaH_2PO_4$  in deionized water without adding any acid and alkali, and treated with the magnetic nano-adsorbent of  $Fe_3O_4@Mg/Al-CO_3-LDH$ , and their ion chromatogram peaks due to phosphate greatly decreased. The large decrease indicates the effective adsorption of both  $Na_3PO_4$  and  $NaH_2PO_4$  solutions. This implies that no matter the existing form of phosphate anions, such as  $PO_4^{3-}$  and  $H_2PO_4^-$ , the synthesized  $Fe_3O_4@Mg/Al-CO_3-LDH$  can adsorb them efficiently. On the other hand, the pH value of real sample solutions as in the above applications is not adjusted by acid and alkali to avoid any further disturbance in the trace determination of  $F^-$  and  $Cl^-$  by ion chromatography.

## 5 Conclusion

Using the urea hydrothermal method, the layered double hydroxide  $Mg/Al-CO_3-LDH$  was synthesized and aggregated as small crystal plates on  $Fe_3O_4$  nanoparticles, which retained its original crystalline state with high magnetism. The magnetic saturation value of  $36.47\ emu\ g^{-1}$  was sufficient to achieve rapid magnetic extraction-separation during  $PO_4^{3-}$ -adsorption by  $Fe_3O_4@Mg/Al-CO_3-LDH$ . As a recyclable magnetic nano-adsorbent, its structural stability was confirmed after 15 regeneration cycles for  $PO_4^{3-}$ -adsorption and desorption. The vibrations of the  $CO_3^{2-}$  and  $PO_4^{3-}$  groups, and the  $Mg-OH$ ,  $Al-OH$ , and  $Mg-O-Al$  bonds indicated that the mechanism for the adsorption of  $PO_4^{3-}$  by  $Fe_3O_4@Mg/Al-CO_3-LDH$  is related to the anion exchange between the interlayer anion  $CO_3^{2-}$  and  $PO_4^{3-}$  in solution, the LDH surface electrostatic adsorption for  $PO_4^{3-}$  in solution, and the ligand exchange between LDH and  $PO_4^{3-}$  in solution. Since mesoporous pores are created within the aggregates of small crystal plates during the synthesis of  $Fe_3O_4@Mg/Al-CO_3-LDH$ , its large specific surface area and total pore volume are  $88.4\ m^2\ g^{-1}$  and  $0.59\ cm^3\ g^{-1}$ , respectively.

These endow the magnetic nano-adsorbent with a high phosphate adsorption capacity of  $83.04\ mg\ P$  per  $g$  for 120 min adsorption, or still up to  $76.48\ mg\ P$  per  $g$  for rapid 5 min adsorption. Even after 15 desorption-adsorption cycles, the capacity was still as high as  $80.41\ mg\ P$  per  $g$  with only a decline by 3.2%. Compared with other magnetic LDHs with  $CO_3^{2-}$ , the synthesized  $Fe_3O_4@Mg/Al-CO_3-LDH$  exhibited very good ability to adsorb  $PO_4^{3-}$ , with four times greater cycle number, two times greater phosphate adsorption capacity, and eight-twelve times less adsorption time. More importantly, regardless of a high or low  $F^-$  or  $Cl^-$  content, and regardless of the used amount and adsorption time of  $Fe_3O_4@Mg/Al-CO_3-LDH$ , the addition and extraction of the nano-adsorbent did not result in any change in the contents of  $F^-$  and  $Cl^-$  in a multi-ion solution. Thus, the usefulness of the synthesized  $Fe_3O_4@Mg/Al-CO_3-LDH$  is concentrated on two specific applications, the removal of  $PO_4^{3-}$ , and especially the accurate determination of  $F^-$  and  $Cl^-$  after the removal of  $PO_4^{3-}$ . By optimizing the nano-adsorbent amount and adsorption time,  $Fe_3O_4@Mg/Al-CO_3-LDH$  was successfully utilized to adsorb  $PO_4^{3-}$  rapidly and determine  $F^-/Cl^-$  accurately by ion chromatography for real samples such as certified reference ore materials, phosphate laser glass, fluorophosphate glass, silicate glass and environmental water samples. Currently, these applications are greatly beneficial for product quality monitoring for extremely hazardous  $F^-$  and  $Cl^-$  to protect the ecological environment. On the other hand, excess P will lead to widespread eutrophication in aquatic environments, in which algal blooms are also harmful towards human health due to cyanotoxins.<sup>78</sup> With the further development and progress on the adsorption capacity, adsorption recovery velocity, and adsorption kinetics,<sup>78,79</sup> studies will be devoted to online applications and widening the scope of these significant methods using LDH adsorbents, which will contribute immensely to environmental protection.



## Conflicts of interest

There are no conflicts to declare.

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