Pretreatment by recyclable Fe3O4@Mg/Al-CO3-LDH magnetic nano-adsorbent to dephosphorize for the determination of trace F– and Cl– in phosphorus-rich solutions

Si Chen, Yongchun Xu, Yu Tang, Wei Chen, Shubin Chen, Lili Hu, Georges Boulon

To cite this version:
Si Chen, Yongchun Xu, Yu Tang, Wei Chen, Shubin Chen, et al.. Pretreatment by recyclable Fe3O4@Mg/Al-CO3-LDH magnetic nano-adsorbent to dephosphorize for the determination of trace F– and Cl– in phosphorus-rich solutions. RSC Advances, 2020, 10 (72), pp.44361-44372. 10.1039/D0RA07761E . hal-03093623

HAL Id: hal-03093623
https://hal.science/hal-03093623
Submitted on 4 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Pretreatment by recyclable Fe$_3$O$_4$@Mg/Al-CO$_3$-LDH magnetic nano-adsorbent to dephosphorize for the determination of trace F$^-$ and Cl$^-$ in phosphorus-rich solutions

Si Chen,$^{ab}$ Yongchun Xu,$^{ab}$ Yu Tang,$^{ab}$ Wei Chen,$^{ab}$ Shubin Chen,$^{ab}$ Lili Hu$^{ab}$ and Georges Boulon$^{bc}$

The magnetic nano-adsorbent Fe$_3$O$_4$@Mg/Al-CO$_3$-LDH (Mg/Al-type layered double hydroxide) with a CO$_3^{2-}$ interlayer anion has been synthesized successfully on Fe$_3$O$_4$ nanoparticles via a urea hydrothermal method. It is confirmed that the nano-adsorbent can adsorb PO$_4^{3-}$ rapidly and efficiently in multi-ion solutions; meanwhile, it did not adsorb any F$^-$ and Cl$^-$, even with a high amount of the nano-adsorbent or a longer adsorption time. This behaviour is beneficial for applications to remove PO$_4^{3-}$ in phosphorus-rich solutions, and especially can be utilized to determine trace F$^-$ and Cl$^-$ anions in phosphorus-rich solutions by physical and chemical analysis methods including ion chromatography without serious interference from PO$_4^{3-}$ for trace determinations. Herein, the hydrothermally synthesized Fe$_3$O$_4$@Mg/Al-CO$_3$-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$_3$O$_4$@Mg/Al-CO$_3$-LDH was utilized successfully to adsorb PO$_4^{3-}$ in real samples and determine trace F$^-$ and Cl$^-$ 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$_4^{3-}$ in phosphorus-rich samples, leaving F$^-$ and Cl$^-$ even if in a trace content.

1 Introduction

Currently, phosphate materials or its hybrid materials, presented as crystal, glass or ceramics, are widely applied in numerous fields such as optics and electronics, as well as medical biomaterials for applications 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$_4^{3-}$ seriously interferes in determinations by methods such as spectrophotometry, neutron activation, molecular absorption spectrometry, graphite furnace, electrothermal atomic absorption spectrometry, and inductively coupled plasma mass spectrometry. 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$_4^{3-}$ will cover the peak or deform the peak shape of the target anion. 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. Although solutions with a high concentration of PO$_4^{3-}$ can be diluted greatly, this also reduces the content of the target anion, leading to a content much lower than the detection limit. After fully rinsing the loops of the chromatograph for several runs using deionized water, a certain amount of PO$_4^{3-}$ 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$_4^{3-}$ content is particularly important.

A further issue is specifically related to the determination of trace F$^-$ and Cl$^-$ anions in phosphorus-rich solutions. If F$^-$ 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$^-$ will pose a serious threat to human life. Thus, it is necessary to monitor trace F$^-$ and Cl$^-$ anions in phosphorus-rich solutions. 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$_4^{3-}$ will cover the peak or deform the peak shape of the target anion. 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. Although solutions with a high concentration of PO$_4^{3-}$ can be diluted greatly, this also reduces the content of the target anion, leading to a content much lower than the detection limit. After fully rinsing the loops of the chromatograph for several runs using deionized water, a certain amount of PO$_4^{3-}$ 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$_4^{3-}$ content is particularly important.

A further issue is specifically related to the determination of trace F$^-$ and Cl$^-$ anions in phosphorus-rich solutions. If F$^-$ 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$^-$ will pose a serious threat to human life. Thus, it is necessary to monitor trace F$^-$ and Cl$^-$ anions in phosphorus-rich solutions.
rich raw materials and final products. 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, but its trace amount must be strictly controlled to avoid cell death or necrosis. Thus, all the abovementioned factors make the accurate determination of trace F− and Cl− in phosphate-rich solutions necessary, with the aim to fully keep F− and Cl− and adsorb PO4 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 [M1−x−2y+x3z−(OH)2]z[Ax+y−n−nH2O]−n, where M is a metal cation and A is the interlayer anion with n-valence. Strong chemical bonds exist within the layer of [M1−x−2y+x3z−(OH)2]z, but the bonds between the interlayer anion of [Ax+y−n−nH2O]−n and the layer of [M1−x−2y+x3z−(OH)2]z are relatively weak. This makes LDHs promising ion-exchangers for applications to adsorb the PO4 3− anion.

To efficiently adsorb PO4 3−, the interlayer anion choice will play a key role. Based on LDHs, there are some good options to use the Cl− anion,17,18,20–24,31 or NO3− anion,19,21,12 or Cl− and SO4 2− anions25 as the interlayer anion. They can be used to adsorb PO4 3− effectively, but their adsorption efficiencies are inevitably affected by carbon dioxide (CO2) or carbonate (CO3 2−) from the preparation process of the LDH, the solution environment and even the atmosphere.17,19,25

Employing CO3 2− as the interlayer anion, Zn–Al-LDH,99 Zr-modified MgFe-LDH(CO3)2,77 Fe3O4@Mg–Al-LDH,26 Mg–Fe LDH28 and Fe3O4@gelatin-encapsulated hydroxalite39 were prepared to adsorb PO4 3− successfully by a co-precipitation method. By comparison, the hydrothermal method is a better way to prepare LDH with the CO3 2− interlayer anion using urea, which can well control the size and crystallinity of the prepared nanoparticle.13 In the investigations for the preparation of LDH with CO3 2− via the urea hydrolysis method, only two LDHs have been used as a phosphate adsorbent.30,38 Cu–Al LDH (CuAl/biomass carbon fibre-layered double hydroxide)29 was synthesized at 110 °C for 12 h, and Zn–Al LDHs28 were synthesized at 150 °C for 36 h.

Herein, an Mg–Al LDH was hydrothermally synthesized with Mg(NO3)2, Al(NO3)3, and urea, using CO3 2− as the interlayer anion. To utilize magnetic solid phase extraction (MSPE), which can achieve the purpose of phosphate adsorption and its rapid separation, Fe3O4 magnetic nanoparticles were introduced into the Mg–Al LDH nano-adsorbent during the hydrothermal synthetic process. Using the prepared Fe3O4@Mg/Al-CO3-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 Fe3O4@Mg/Al-CO3-LDH magnetic nano-adsorbent only adsorbs PO4 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 Fe3O4@Mg/Al-CO3-LDH

The magnetic layered double hydroxide nano-adsorbent Fe3O4@Mg/Al-CO3-LDH was synthesized via a urea hydrothermal method. After several trials, 0.6 g of Fe3O4 nanoparticles (ultrafine powder purchased from Macklin) was used and added to 15 mL solution of 0.1 mol L−1 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(NO3)2·6H2O (AR grade), 1.500 g Al(NO3)3·9H2O (AR grade), and 1.68 g urea (CH3N2O, 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-305) for 15 min. The activated Fe3O4 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 Fe3O4@Mg/Al-CO3-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−1 with a resolution of 4 cm−1. 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-Kα radiation of λ = 0.15418 nm in the 2θ 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 ±30 000 Oe.

Specific surface area and porosity were fitted from the N2 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 μL sample loop and a conductivity detector. An IonPac® AS18 (250 mm × 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 × 4.0 mm i.d.). The temperature of the column compartment was set to 30 °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$_3$O$_4$@Mg/Al-CO$_3$-LDH for the determination of $F^-$ and $Cl^-$, and to recycle and reuse Fe$_3$O$_4$@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 μm 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$_3$O$_4$@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$_3$O$_4$@Mg/Al-CO$_3$-LDH was collected and placed in 15 mL desorption solution, 5 wt% NaOH and 10 wt% Na$_2$CO$_3$ (AR grade), and further mixed using a vortex mixer for 30 min. With the aid of a magnet, the Fe$_3$O$_4$@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 °C for 12 h, and then Fe$_3$O$_4$@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 Fe₃O₄@Mg/Al-CO₃-LDH was measured for each cycle. Briefly, 50 mg of the magnetic adsorbent was added to 80 mL mixed solution with 1.00 mg L⁻¹ F⁻, 1.00 mg L⁻¹ Cl⁻ and C₀ = 100 mg P per L PO₄³⁻ (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, Cₑ, which is also the equilibrium PO₄³⁻ concentration in the solution, the adsorption capacity, Qₑ, of PO₄³⁻ was calculated by Qₑ = (C₀ − Cₑ)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 Fe₃O₄@Mg/Al-CO₃-LDH

Fig. 2 shows the electron microscopy analysis of Fe₃O₄ and the synthesized Fe₃O₄@Mg/Al-CO₃-LDH magnetic nanoparticles. Both the SEM and bright-field TEM images show that Fe₃O₄ 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 Fe₃O₄, Mg/Al-CO₃-LDH was synthesized via the urea hydrothermal method. The shape of these irregular Fe₃O₄@Mg/Al-CO₃-LDH nanoparticles is not like the octahedral Fe₃O₄ crystal, 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 Fe₃O₄ is characterized by a flake-like matrix. This is similar to the morphology of Fe₃O₄@CuMg-Al-LDH nanoparticles. Due to the stacking of many small flakes, the hydrothermally synthesized Mg/Al-CO₃-LDH on Fe₃O₄ nanoparticles appears to consist of an agglomeration of plate-like structures.

Fig. 3(a) shows the high-resolution TEM image of the synthesized Fe₃O₄@Mg/Al-CO₃-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 Fe₃O₄ (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 Mg/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.

Thus, the above electron microscopic analysis indicates that during the hydrothermal process, Fe₃O₄ retains its original crystalline state, and Mg/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 Fe₃O₄@Mg/Al-CO₃-LDH. The diffraction peaks at the 2θ values of 18.24° (111), 30.08° (220), 35.46° (311), 37.04° (222), 43.12° (400), 53.50° (422), 57.04° (511), and 62.56° (400) correspond to the octahedral Fe₃O₄ crystal, and the peaks at the 2θ values of 11.54° (003), 23.44° (006), 35.46° (012), 61.02° (110), and 62.56° (113) correspond to the Mg-Al-LDH crystal. More importantly, after 15 cycles of PO₄³⁻-adsorption and regeneration of Fe₃O₄@Mg/Al-CO₃-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...
Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbent can still maintain its structural stability, and thus has important potential for recycling.²⁸

To explore the adsorption and desorption of PO₄³⁻, the FTIR spectra of Fe₃O₄@Mg/Al-CO₃-LDH were measured for the as-synthesized, PO₄³⁻-adsorbed, and regenerated after 15 cycles of PO₄³⁻-adsorption samples, as shown in Fig. 5(a)-(c), respectively. The Fe–O vibration peak²⁹ appeared at 586 cm⁻¹ before and after adsorption and desorption, showing the stable assembly between Fe₃O₄ and Mg/Al-CO₃-LDH.

As shown in Fig. 5(a), the spectrum of the as-synthesized sample exhibits peaks at 448 cm⁻¹, 681 cm⁻¹, and 788 cm⁻¹, which are attributed to the vibration of Mg–OH,³⁰ Mg–O–Al,³¹ and Al–OH,³² respectively. The two peaks located at 3445 cm⁻¹ and 1637 cm⁻¹ are related to the stretching and bending modes of the water molecule existing in the interlayer structure, respectively.³² These peaks indicate the successful synthesis of the layered structure Mg/Al-LDH. As the interlayer anion, the vibration of CO₃²⁻ appears at 1362 cm⁻¹ and 1502 cm⁻¹. During the hydrothermal process, urea decomposes at high temperature and produces the CO₃²⁻ anion,³³ which then enters Mg/Al-LDH to form the interlayer anion. Moreover, there is a small peak located at 1385 cm⁻¹, corresponding to the NO₃⁻ vibration, but it is rather weak. This is due to the use of nitrate during the synthetic process, where a small amount of NO₃⁻ existing in Fe₃O₄@Mg/Al-CO₃-LDH was not replaced by CO₃²⁻.

As shown in Fig. 5(b), in the spectrum of the PO₄³⁻-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 CO₃²⁻ vibration at 1502 cm⁻¹, and only a very weak CO₃²⁻ peak at 1362 cm⁻¹. On the other hand, new peaks at 2484 cm⁻¹, 2401 cm⁻¹, 1088 cm⁻¹, and 901 cm⁻¹ appear, which are due to the vibrations of PO₄³⁻.³⁵⁻³⁶ These results clearly indicate that the anion exchange³⁶ really occurred for Fe₃O₄@Mg/Al-CO₃-LDH after adsorbing PO₄³⁻, which is the process to use PO₄³⁻ to replace CO₃²⁻. It is most probably the first mechanism for the synthesized Fe₃O₄@Mg/Al-CO₃-LDH to adsorb PO₄³⁻ 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 PO₄³⁻ due to electrostatic adsorption on the surface of LDH.³⁷ This may be the second mechanism to adsorb PO₄³⁻ in solution. The disappearance of the vibration of Mg–O–Al may be possibly explained by the fact that, as a ligand anion,³⁸ PO₄³⁻ can be complexed with the Al³⁺ cation on the surface of Fe₃O₄@Mg/Al-CO₃-LDH. This ligand exchange may be the third mechanism to adsorb PO₄³⁻ in solution. The ability to perform these three mechanisms for the synthesized Fe₃O₄@Mg/Al-CO₃-LDH is consistent with the reported PO₄³⁻-adsorbed LDHs.²⁶,²⁹,³¹

Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbent before and after 15 cycles of PO₄³⁻-adsorption and regeneration.

Fig. 4 XRD patterns of Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbent before and after 15 cycles of PO₄³⁻-adsorption and regeneration.

Fig. 5 FTIR spectra of Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbents. (a) As-prepared, (b) PO₄³⁻-adsorbed, and (c) regenerated after 15 cycles of PO₄³⁻-adsorption.
As shown in Fig. 5(c), in the spectrum of the regenerated sample after 15 cycles of PO₄³⁻-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 Fe₃O₄@Mg/Al-CO₃-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 cm⁻¹ due to PO₄³⁻, which indicates a small amount of was PO₄³⁻ left in Fe₃O₄@Mg/Al-CO₃-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 CO₃²⁻ during the desorption process.

It was reported that for MgAl-LDO calcined at 500 °C for 4 h after its synthesis, the FTIR band of –OH was shifted to a higher frequency from 1644 cm⁻¹ to 1664 cm⁻¹ after F⁻ adsorption, which may be due to the adsorption of F⁻. However, as can be seen in Fig. 5(a)–(c), the band due to OH appears at 1637 cm⁻¹, 1640 cm⁻¹, and 1638 cm⁻¹ for the as-synthesized PO₄³⁻-adsorbed, and regenerated Fe₃O₄@Mg/Al-CO₃-LDH samples, respectively. Thus, the absence of a shift in the OH band means that the synthesized Fe₃O₄@Mg/Al-CO₃-LDH did not adsorb F⁻. This is in good agreement with the determination results by ion chromatography, indicating there was no change for the trace concentrations of F⁻ and 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 is greatly affected by F⁻ or Cl⁻ due to their adsorption. For LDHs, considering the bonding strength between the layers and interlayer anions in aqueous solution, the strength of phosphates is generally higher than that of F⁻ and Cl⁻. Since there is a large amount of phosphate in aqueous solution, the adsorption possibility of phosphate is higher than that of F⁻ or Cl⁻. However, it is still inevitable that a small amount of F⁻ and Cl⁻ will be adsorbed, although this possibility is small. Thus, to further decrease this possibility, for the synthesized nano-adsorbent of Fe₃O₄@Mg/Al-CO₃-LDH, CO₃²⁻ was employed as the interlayer anion. The bonding strength of CO₃²⁻ is the highest, much greater than that of F⁻ and Cl⁻. During the phosphate adsorption process, a lot of CO₃²⁻ anions will be exchanged in the solution, which will further inhibit the adsorption of trace F⁻ and Cl⁻ anions. Moreover, if some OH⁻ anions exist in solution, the adsorption efficiencies will further decline due to the combined effects of increasing competition from the OH⁻ anion and the Coulomb repulsion between the negatively charged surface of the LDH adsorbent and F⁻ or Cl⁻. If there is insufficient positive charge such as H⁺ on the surface of the LDH adsorbent, and there are enough anions such as CO₃²⁻ and PO₄³⁻, which have a much higher bonding strength than F⁻ and Cl⁻, to strongly compete with F⁻ and Cl⁻ anions, the synthesized magnetic nano-adsorbent Fe₃O₄@Mg/Al-CO₃-LDH should not adsorb F⁻ and Cl⁻ anions.

Fig. 6 shows the magnetic hysteresis loops of Fe₃O₄ and Fe₃O₄@Mg/Al-CO₃-LDH before and after 15 cycles of PO₄³⁻-adsorption. Compared with the magnetic saturation value of 102 emu g⁻¹ for the pure Fe₃O₄ nanoparticles, that for the as-synthesized Fe₃O₄@Mg/Al-CO₃-LDH drops to 36.75 emu g⁻¹ since the non-magnetic Mg/Al-CO₃-LDH shields the magnetic Fe₃O₄. Even if after 15 cycles, it was still 36.47 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 PO₄³⁻-adsorption come close to coinciding in shape. This truthfully reflects that the thickness of the Mg/Al-CO₃-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 PO₄³⁻-adsorption, means that the two-dimensional crystalline nanostructure of Mg/Al-CO₃-LDH and the interlayer anion CO₃²⁻ 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 CO₃²⁻ is as strong as that of the as-synthesized Fe₃O₄@Mg/Al-CO₃-LDH, as seen in Fig. 5(a). This means that the content of CO₃²⁻ was almost fully recovered even after 15 cycles of PO₄³⁻-desorption, which can provide an excellent performance for stable dephosphorization.

Fig. 7(a) and (b) show the N₂ adsorption–desorption isotherms and BJH (Barrett–Joyner–Halenda) pore diameter distribution curves of Fe₃O₄@Mg/Al-CO₃-LDH, respectively. In Fig. 7(a), there is a clear hysteresis loop at a high relative pressure of P/P₀ > 0.6, which is a typical type IV adsorption isotherm according to the IUPAC classification. When P/P₀ > 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, which means the pores in Fe₃O₄@Mg/Al-CO₃-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 nm and total pore volume of 0.59 cm³ g⁻¹. The formation of these mesoporous pores in Fe₃O₄@Mg/Al-CO₃-LDH is related to the slit-shaped pores or voids created within the aggregates of platy particles. Generally, the
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.26,72 According to the BET (Brunauer–Emmett–Teller) method,73 the specific surface area of Fe3O4@Mg/Al-CO3-LDH was calculated to be 88.4 m² g⁻¹. Thus, the hydrothermally synthesized Fe3O4@Mg/Al-CO3-LDH can adsorb PO4³⁻ in solution rapidly and efficiently.

3.2 Optimized pretreatment by Fe3O4@Mg/Al-CO3-LDH

For 80 mL solution containing 1.00 mg L⁻¹ F⁻, 1.00 mg L⁻¹ Cl⁻ and 100 mg P per L PO4³⁻ are the optimized adsorbent amount and adsorption time for Fe3O4@Mg/Al-CO3-LDH, respectively. These optimized pretreatment conditions were utilized for the analysis of real samples, as stated in Section 4.

By using different amounts of Fe3O4@Mg/Al-CO3-LDH magnetic nano-adsorbent to adsorb PO4³⁻ 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 PO4³⁻, respectively. Their concentrations were calculated based on their peak area, and plotted at the top of Fig. 8. With the addition of Fe3O4@Mg/Al-CO3-LDH in the solution, the concentration of both F⁻ and Cl⁻ was always maintained at around 1.00 mg L⁻¹ with the fluctuation of ±2%, as shown in the top-left and top-middle of Fig. 8. This indicates that Fe3O4@Mg/Al-CO3-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 PO4³⁻ concentration decrease greatly from 100 mg P per L to 64.5 and 49.5 mg P per L, respectively, as shown in the top-right of Fig. 8. However, when the absorbent amount was further increased to 80 mg, the residual PO4³⁻ concentration did not further decrease since equilibrium between PO4³⁻ and CO3²⁻ was reached. Thus, the optimized adsorbent amount of 50 mg Fe3O4@Mg/Al-CO3-LDH is enough for 80 mL solution with 100 mg P per L PO4³⁻.

By using 50 mg Fe3O4@Mg/Al-CO3-LDH to adsorb PO4³⁻ in 80 mL solution for different times, the residual concentration of PO4³⁻ 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 mg L⁻¹ with the fluctuation of ±2%, regardless of the adsorbent time used. Similarly, as indicated in the plots at the top of Fig. 8, Fe3O4@Mg/Al-CO3-LDH did not adsorb any F⁻ and Cl⁻ anions in the solution, no matter how long the interaction time. However, for PO4³⁻, even with fast magnetic separation immediately after the addition of Fe3O4@Mg/Al-CO3-LDH in the solution, the residual PO4³⁻ concentration directly declined to 72.9 mg P per L. Also, after 2 and 5 min adsorption, it decreased to 60.3 and 52.2 mg P per L, respectively. With a further increase in the adsorption time, the adsorption of PO4³⁻ slows down to the equilibrium stage, until the residual PO4³⁻ concentration finally reached 48.1 mg P per L after 120 min adsorption. According to the formula for phosphate adsorption capacity,74 as stated in Section 2.3, the capacity of Fe3O4@Mg/Al-CO3-LDH is 83.04 mg P per g for 120 min adsorption. Even for 5 min adsorption, it is still as high as 76.48 mg P per g. Thus, the optimized adsorption time was chosen to be 5–60 min for the solution using 50 mg Fe3O4@Mg/Al-CO3-LDH.
3.3 Recyclability of Fe₃O₄@Mg/Al-CO₃-LDH

The recyclability of an adsorbent is vital for its practical application, and the premise for recycling is the stability of its structure. The crystalline structure stability, the adsorption stability, and the coating layer stability of Fe₃O₄@Mg/Al-CO₃-LDH after 15 cycles of PO₄³⁻-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 Fe₃O₄@Mg/Al-CO₃-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 mg P per g calculated from Fig. 9 was used for the as-synthesized Fe₃O₄@Mg/Al-CO₃-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 mg P per g, which is only 3.2% lower than the initial 83.04 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 ~0.2%. This clearly indicates that the synthesized Fe₃O₄@Mg/Al-CO₃-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 PO₄³⁻ in solution. Compared with most of the adsorbents, the phosphate capacity per unit mass of the synthesized Fe₃O₄@Mg/Al-CO₃-LDH is as high as 76.48 mg P per g, higher than 1.8675–36.9 mg P per g, but somewhat lower than 128–252.88 mg P per g of these four adsorbents. However, they used about 360–4320 min to adsorb phosphates in solution. It

| Adsorbent                                | Interlayer anion for LDH | Adsorption time (min) | Adsorption capacity (mg P per g) | Cycle no. | Ref. |
|------------------------------------------|--------------------------|-----------------------|----------------------------------|-----------|-----|
| ZnFeZr adsorbent@Fe₃O₄/SiO₂             | Cl⁻                      | 60                    | 20                               | 23        |     |
| Magnetic Fe/Mn oxide composites (TS-N)  | Cl⁻                      | 90                    | 26.0                             | 24        |     |
| Fe₃O₄/Zn-Al-Fe-La-LDH                   | Cl⁻ and SO₄²⁻            | 1440                  | 169.5                            | 25        |     |
| Fe₃O₄@Zn-Al-LDH                         | CO₃²⁻                    | 60                    | 36.9                             | 26        |     |
| Fe₃O₄@Mg-Al-LDH                         |                         |                       | 31.7                             | 26        |     |
| Fe₃O₄@Ni-Al-LDH                         |                         |                       | 26.5                             | 26        |     |
| Fe/CaCO₃_PVA                             | Non-LDH                  |                       | 16.7                             | 75        |     |
| Fe/MgCO₃_PVA                             | Non-LDH                  |                       | 16.3                             | 75        |     |
| Fe₃O₄@SiO₂–CeO₂                          | Non-LDH                  | 1440                  | 10.8                             | 2³        | 76  |
| Ce-Ti@ Fe₃O₄                             | Non-LDH                  | 1440                  | 11.10                            | 66        |     |
| Carboxylated chitosan–Fe₃O₄              | Non-LDH                  | 60                   | 1.8675                           | 67        |     |
| La-chitosan magnetic spheres             | Non-LDH                  | 300                   | 27.78                            | 68        |     |
| ZrO₂/Fe₃O₄                               | Non-LDH                  | 1440                  | 29.5                             | 77        |     |
| Magnetic Caragana korshinskii biochar/Mg–Al-LDH | Cl⁻                      | 720                   | 252.88                           | 5⁴        | 31  |
| Fe₃O₄@alkali-treated calcium-silicate    | Non-LDH                  | 4320                  | 128                              | 2⁵        | 69  |
| Fe₃O₄@gelatin encapsulated hydroxalite   | CO₃²⁻                    | 40                    | 32.73                            | 4²        | 33  |
| NiO/Fe₃O₄                                | Non-LDH                  | 360                   | 135.3                            | 5         | 74  |
| Humic acid coated magnetite nanoparticles| Non-LDH                  | 180                   | 28.9                             | 70        |     |
| Fe₃O₄@Mg/Al-CO₃-LDH                      | CO₃²⁻                    | 5                     | 76.48                            | 15        | This work |

* Adsorption capacity of phosphate, $Q_e = (C_0 - C_e)W/m$, where $C_0$ and $C_e$ are the initial and equilibrium phosphate concentration in mg L⁻¹, $W$ is the volume of phosphate solution in L, and $m$ is the dry weight of the adsorbent in g. The adsorption capacity decreased to 31 mg g⁻¹ after 4 cycles. The adsorption capacity decreased to 25.71 mg g⁻¹ after 5 cycles. The adsorption efficiency was reduced to 70.01% after 4 cycles. The adsorption capacity decreased to 4.8 mg g⁻¹ after 2 cycles. The adsorption capacity decreased to 20.2 mg g⁻¹ after 2 cycles. 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 Fe₃O₄@Mg/Al-CO₃-LDH is high enough to adsorb PO₄³⁻ rapidly and efficiently so as to determine F⁻ and Cl⁻ without serious interference due to PO₄³⁻. 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 Fe₃O₄@Mg/Al-CO₃-LDH, more than the reported 2–5 cycles. The reported recycle number could reach up to 20 cycles,²¹ but there was no information about the phosphate adsorption capacity. According to Table 1, if only considering magnetic LDHs with a CO₃²⁻ interlayer anion, Fe₃O₄@Mg/Al-CO₃-LDH behaves very well to adsorb PO₄³⁻ 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 PO₄³⁻ 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 Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbent, and the chromatograms are shown in Fig. 11. As seen in Fig. 11(a) for the phosphate (P₂O₅ molar ratio of both N31 and N41 glasses is close to 60%) with high PO₄³⁻ but low F⁻ and Cl⁻, the strong peak at 22.36 min due to PO₄³⁻ is too overloaded, and thus it seems to be a leading peak with 100 μS conductivity. After the adsorption pretreatment, the 22.36 min peak shape became normal and its intensity decreased greatly to 10 μS. This indicates that Fe₃O₄@Mg/Al-CO₃-LDH could efficiently adsorb PO₄³⁻ in the multi-ion leaching solution in a short time of only 5 min. On the other hand, Fe₃O₄@Mg/Al-CO₃-LDH did not adsorb any F⁻ or Cl⁻. The peaks at 3.79 and 7.34 min are due to F⁻ and Cl⁻, respectively, and their intensities did not change after the adsorption pretreatment. As seen in Fig. 11(b) for the fluorophosphate with a high F⁻ and PO₄³⁻ content but low Cl⁻, the 22.36 min PO₄³⁻ peak almost disappeared after the adsorption pretreatment by Fe₃O₄@Mg/Al-CO₃-LDH for 5 min. The strong F⁻ peak at 3.79 min and the weak Cl⁻ peak at 7.34 min did not change after the pretreatment. Regardless of a high or low PO₄³⁻ content in a multi-ion solution, the synthesized Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbent can adsorb and extract PO₄³⁻ rapidly. Also, regardless of a high or low F⁻ or 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 F⁻ or Cl⁻. These two facts determine the usefulness of the nano-adsorbent for specific applications, i.e. the removal of PO₄³⁻, and especially the determination of F⁻/Cl⁻ after removing PO₄³⁻ in a multi-ion solution. By using the Fe₃O₄@Mg/Al-CO₃-LDH adsorption pretreatment, the pretreated solution can be utilized for other determination techniques or methods since there will be no serious interference from PO₄³⁻ in the solution. Considering chromatography, the determination time for the accurate determination of F⁻ and Cl⁻ can be greatly shortened after removing PO₄³⁻. More importantly, without being affected by PO₄³⁻ and fully retaining trace F⁻ and 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 PO₄³⁻ is not removed from a PO₄³⁻-rich solution, the next injection must not be allowed.¹¹

By chromatography, Table 2 lists the determined results of F⁻ and 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 Fe₃O₄@Mg/Al-CO₃-LDH under the optimized conditions. For the certified ore sample, the determined values of 0.395 and 0.0071 mg L⁻¹ are very close to the certified values of 0.406 and 0.0078 mg L⁻¹ for F⁻ and Cl⁻, respectively. After determining F⁻ and Cl⁻ for the other samples, a certain amount of F⁻ and Cl⁻ standard solutions was added, i.e. the added content was 1.00 mg L⁻¹. Subsequently, the contents of F⁻ and Cl⁻ in the solution re-pretreated by Fe₃O₄@Mg/Al-CO₃-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 F⁻ and Cl⁻ in multi-ion solutions pretreated by the synthesized Fe₃O₄@Mg/Al-CO₃-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,¹⁷,²⁶,²⁹ such as PO₄³⁻, HPO₄²⁻ and H₂PO₄⁻. 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 Fe₃O₄@Mg/Al-CO₃-LDH magnetic nano-adsorbent.
solutions were obtained by dissolving high purity Na₃PO₄ or NaH₂PO₄ in deionized water without adding any acid and alkali, and treated with the magnetic nano-adsorbent of Fe₃O₄@Mg/Al-CO₃-LDH, and their ion chromatogram peaks due to phosphate anions, such as PO₄³⁻ and H₂PO₄⁻, the synthesized Fe₃O₄@Mg/Al-CO₃-LDH can adsorb them effectively. 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-CO₃-LDH was synthesized and aggregated as small crystal plates on Fe₃O₄ 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 PO₄³⁻-adsorption by Fe₃O₄@Mg/Al-CO₃-LDH. As a recyclable magnetic nano-adsorbent, its structural stability was confirmed after 15 regeneration cycles for PO₄³⁻-adsorption and desorption. The vibrations of the CO₃²⁻ and PO₄³⁻ groups, and the Mg–OH, Al–OH, and Mg–O–Al bonds indicated that the mechanism for the adsorption of PO₄³⁻ by Fe₃O₄@Mg/Al-CO₃-LDH is related to the anion exchange between the interlayer anion CO₃²⁻ and PO₄³⁻ in solution, the LDH surface electrostatic adsorption for PO₄³⁻ in solution, and the ligand exchange between LDH and PO₄³⁻ in solution. Since mesoporous pores are created within the aggregates of small crystal plates during the synthesis of Fe₃O₄@Mg/Al-CO₃-LDH, its large specific surface area and total pore volume are 88.4 m² g⁻¹ and 0.59 cm³ 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 CO₃²⁻, the synthesized Fe₃O₄@Mg/Al-CO₃-LDH exhibited very good ability to adsorb PO₄³⁻, 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 Fe₃O₄@Mg/Al-CO₃-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 Fe₃O₄@Mg/Al-CO₃-LDH is concentrated on two specific applications, the removal of PO₄³⁻, and especially the accurate determination of F⁻ and Cl⁻ after the removal of PO₄³⁻. By optimizing the nano-adsorbent amount and adsorption time, Fe₃O₄@Mg/Al-CO₃-LDH was successfully utilized to adsorb PO₄³⁻ 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. With the further development and progress on the adsorption capacity, adsorption recovery velocity, and adsorption kinetics, 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.

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 Fe₃O₄@Mg/Al-CO₃-LDH

| Sample                  | F⁻ Added (mg L⁻¹) | F⁻ Found (mg L⁻¹) | F⁻ Recovery (%) | Cl⁻ Added (mg L⁻¹) | Cl⁻ Found (mg L⁻¹) | Cl⁻ Recovery (%) |
|------------------------|------------------|------------------|-----------------|------------------|------------------|-----------------|
| GBW07108              | 0.406 b          | 0.395            | 97.3            | 0.078 b          | 0.071            | 91.0            |
| Silicate glass        | 1.00             | 1.444            | 104.9           | 1.00             | 1.092            | 102.1           |
|                        | 0.00             | 0.251            | 0               | 0.00             | 0.083            | 0               |
| Fluorophosphate glass | 1.00             | 9.970            | 0               | 1.00             | 1.069            | 98.6            |
|                        | 1.00             | 10.297           | 95.7            | 1.00             | 1.060            | 99.1            |
| N31 phosphate glass, pot melting | 0.00 | 0.744 | 0 | 1.00 | 0.251 | 0 |
|                        | 1.00             | 1.738            | 99.4            | 1.00             | 1.245            | 99.4            |
| N41 phosphate glass, pot melting | 0.00 | 0.814 | 0 | 1.00 | 0.585 | 0 |
|                        | 1.00             | 1.800            | 98.6            | 1.00             | 1.558            | 97.3            |
| N41 phosphate glass, continuous melting | 0.00 | 1.267 | 0 | 1.00 | 0.459 | 0 |
| River water            | 0.00             | 0.153            | 0               | 1.00             | 7.351            | 104.2           |
|                        | 1.00             | 1.150            | 99.7            | 1.00             | 8.338            | 98.7            |

a 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. b The certified content of F⁻ and Cl⁻ in the certified reference material GBW07108.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The research work was financially supported by Nd-doped phosphate laser glass projects from National Major Science and Technology Project of China, National High Technology Research and Development Program for Inertial Confinement Fusion of China.

References

1. F. Vasconcelos, S. Cristol, J. Paul, L. Montagne, F. Mauri and L. Delevoye, Magn. Reson. Chem., 2010, 48, S142–S150.
2. A. Salama, Int. J. Biol. Macromol., 2019, 127, 606–617.
3. H. Parham and N. Rahbar, Talanta, 2009, 80, 664–669.
4. V. P. Kolotov and E. A. Araf, J. Radioanal. Nucl. Chem., 1993, 172, 357–362.
5. P. Venkateswarlu, Anal. Chim. Acta, 1992, 262, 33–40.
6. Z. Ni, Z. Rao and M. Li, Anal. Chim. Acta, 1996, 334, 177–182.
7. P. Bermejo-Barrera, A. Moreda-Piñeiro and A. Bermejo-Barrera, Spectrochim. Acta, Part B, 2002, 57, 327–337.
8. U. Nygren, H. Ramebæk, D. C. Baxter and C. Nilsson, J. Anal. At. Spectrom., 2005, 20, 529.
9. F. S. Stover, J. Chromatogr. A, 2002, 956, 121–128.
10. L. E. Vanatta, D. E. Coleman and A. Woodruff, J. Chromatogr. A, 2003, 997, 269–278.
11. E. Kaiser, J. S. Rohrer and K. Watanabe, J. Chromatogr. A, 1999, 850, 167–176.
12. L. Al Attar, M. Al-Oudat, K. Shamali, B. A. Ghany and S. Kanakri, Environ. Technol., 2012, 33, 143–152.
13. W. Qiao, R. Liu, Z. Li, X. Luo, B. Huang, Q. Liu, Z. Chen, J. Tsoi, Y. X. Su, K. Cheung, J. P. Matinlinna, K. Yeung and Z. Chen, Biomater. Sci., 2018, 6, 2951–2964.
14. D. Štepec and M. Ponikvar-Svet, Acta Chim. Slov., 2019, 66, 255–275.
15. F. L. Theiss, G. A. Ayoko and R. L. Frost, Appl. Surf. Sci., 2016, 383, 200–213.
16. V. Rives and M. Angeles Ulibarri, Coord. Chem. Rev., 1999, 181, 61–120.
17. Q. Zhang, F. Ji, T. Zhao, Q. Shen, D. Fang, L. Kuang, L. Jiang and S. Ding, Appl. Clay Sci., 2019, 174, 159–169.
18. M. P. Bernardo and C. Ribeiro, Mater. Res., 2018, 21, e20171001.
19. F. Li, J. Jin, Z. Shen, H. Ji, M. Yang and Y. Yin, J. Hazard. Mater., 2020, 388, 121734.
20. C. V. Luengo, M. A. Volpe and M. J. Avena, J. Environ. Chem. Eng., 2017, 5, 4656–4662.
21. H. Hatami, A. Fotovat and A. Halajnia, Appl. Clay Sci., 2018, 152, 333–341.
22. S. M. Ashekuzzaman and J. Jiang, Process Saf. Environ. Prot., 2017, 107, 454–462.
23. A. Drenkova-Tuhtan, M. Schneider, M. Franzreb, C. Meyer, C. Gellermann, G. Sextl, K. Mandel and H. Steinmetz, Water Res., 2017, 109, 77–87.
24. C. Chon, D. Cho, I. Nam, J. Kim and H. Song, J. Soils Sediments, 2018, 18, 946–956.
25. W. Qiao, H. Bai, T. Tang, J. Miao and Q. Yang, Colloids Surf., A, 2019, 577, 118–128.
26. L. Yan, K. Yang, R. Shan, T. Yan, J. Wei, S. Yu, H. Yu and B. Du, J. Colloid Interface Sci., 2015, 448, 508–516.
27. R. Chitrakar, S. Tetzuka, J. Hosokawa, Y. Makita, A. Sonoda, K. Ooi and T. Hirotsu, J. Colloid Interface Sci., 2010, 349, 314–320.
28. K. S. Triantafyllidis, E. N. Peleka, V. G. Konvokis and P. P. Mavros, J. Colloid Interface Sci., 2010, 342, 427–436.
29. F. Hu, M. Wang, X. Peng, F. Qiu, T. Zhang, H. Dai, Z. Liu and Z. Cao, Colloids Surf., A, 2018, 555, 314–323.
30. J. Zhou, S. Yang, J. Yu and Z. Shu, J. Hazard. Mater., 2011, 192, 1114–1121.
31. Q. Cui, G. Jiao, J. Zheng, T. Wang, G. Wu and G. Li, RSC Adv., 2019, 9, 18641–18651.
32. B. Bekele, L. Lundehoj, N. D. Jensen, U. G. Nielsen and C. Forano, Appl. Clay Sci., 2019, 176, 49–57.
33. I. A. Kumar and N. Viswanathan, J. Environ. Chem. Eng., 2018, 6, 208–217.
34. M. Ogawa and H. Kaiho, Langmuir, 2002, 18, 4240–4242.
35. F. Yang, S. Sun, X. Chen, Y. Chang, F. Zha and Z. Lei, Appl. Clay Sci., 2016, 123, 134–140.
36. M. M. Rao, B. R. Reddy, M. Jayalakshmi, V. S. Jaya and B. Sridhar, Mater. Res. Bull., 2005, 40, 347–359.
37. S. Ma, C. Fan, G. Huang, Y. Li, X. Yang and K. Ooi, Eur. J. Inorg. Chem., 2010, 2010, 2079–2083.
38. S. Li, Y. Shen, D. Liu, L. Fan, X. Zheng and J. Yang, Compos. Interfaces, 2012, 19, 489–498.
39. J. Wang, D. Li, X. Yu, M. Zhang and X. Jing, Colloid Polym. Sci., 2010, 288, 1411–1418.
40. T. Hibino and H. Ohya, Appl. Clay Sci., 2009, 45, 123–132.
41. B. Li, J. He and D. G. Evans, Chem. Eng. J., 2008, 144, 124–137.
42. P. Zhang, T. Yamaguchi, B. N. Nair, K. Miyajima and G. M. Anilkumar, RSC Adv., 2014, 4, 41051–41058.
43. M. Yang, J. Liu, Z. Chang, G. R. Williams, D. O’Hare, X. Zheng, X. Sun and X. Duan, J. Mater. Chem., 2011, 21, 14741–14746.
44. S. Radha and A. Navrotsky, J. Phys. Chem. C, 2014, 118, 29836–29844.
45. B. Li and J. He, J. Phys. Chem. C, 2008, 112, 10909–10917.
46. G. K. Sarma and M. H. Rashid, J. Chem. Eng. Data, 2018, 63, 2957–2965.
47. X. Lei, W. Lu, Q. Peng, H. Li, T. Chen, S. Xu and F. Zhang, Appl. Catal., A, 2011, 399, 87–92.
48. X. Yuan, Y. Wang, J. Wang, C. Zhou, Q. Tang and X. Rao, Chem. Eng. J., 2013, 221, 204–213.
49. B. Zhu, L. Chen, T. Yan, J. Xu, Y. Wang, M. Chen and H. Jiang, Water Sci. Technol., 2018, 78, 1179–1188.
50. P. Zhang, T. He, P. Li, X. Zeng and Y. Huang, Langmuir, 2019, 35, 13562–13569.
51. Y. Zhang, L. Wang, L. Zou and D. Xue, J. Cryst. Growth, 2010, 312, 3367–3372.
52. L. Bo, Q. Li, Y. Wang, L. Gao, X. Hu and J. Yang, Environ. Prog. Sustainable Energy, 2016, 35, 1420–1429.
53 M. N. Sepehr, K. Yetilmezsoy, S. Marofi, M. Zarrabi, H. R. Ghaffari, M. Fingas and M. Foroughi, *J. Taiwan Inst. Chem. Eng.*, 2014, 45, 2786–2800.

54 M. R. Berber, I. H. Hafez, K. Minagawa, M. Katoh, T. Mori and M. Tanaka, *J. Mol. Struct.*, 2013, 1033, 104–112.

55 H. Zhang, G. Zhang, X. Bi and X. Chen, *J. Mater. Chem. A*, 2013, 1, 5934–5942.

56 U. Costantino, F. Marmottini, M. Nocchetti and R. Vivani, *Eur. J. Inorg. Chem.*, 1998, 1439–1446.

57 M. Shao, F. Ning, J. Zhao, M. Wei, D. G. Evans and X. Duan, *J. Am. Chem. Soc.*, 2011, 134, 1071–1077.

58 K. Mandel, A. Drenkova-Tuhtan, F. Hutter, C. Gellermann, H. Steinmetz and G. Sextl, *J. Mater. Chem. A*, 2013, 1, 1840–1848.

59 N. Ammavasi and R. Mariappan, *J. Environ. Chem. Eng.*, 2018, 6, 5645–5654.

60 R. Zeng, Z. Liu, F. Zhang, S. Li, Q. He, H. Cui and E. Han, *Trans. Nonferrous Met. Soc. China*, 2015, 25, 1917–1925.

61 J. Shou, C. Jiang, F. Wang, M. Qiu and Q. Xu, *J. Mol. Liq.*, 2015, 207, 216–223.

62 S. Arghavani-Beydokhti, M. Rajabi and A. Asghari, *Anal. Methods*, 2018, 10, 1305–1314.

63 W. H. R. Shaw and J. J. Bordeaux, *J. Am. Chem. Soc.*, 1955, 77, 4729–4733.

64 V. Siva Kumar, A. H. Padmasri, C. V. V. Satyanarayana, I. Ajit Kumar Reddy, B. David Raju and K. S. Rama Rao, *Catal. Commun.*, 2006, 7, 745–751.

65 F. Loretta, S. Perumal and S. Ramalingom, *Asian J. Chem.*, 2013, 25, 1921–1926.

66 A. A. Markeb, L. A. Ordosgoitia, A. Alonso, A. Sánchez and X. Font, *RSC Adv.*, 2016, 6, 56913–56917.

67 E. Mohammadi, H. Daraei, R. Ghanbari, S. Dehestani Athar, Y. Zandsalimi, A. Ziae, A. Maleki and K. Yetilmezsoy, *J. Mol. Liq.*, 2019, 273, 116–124.

68 R. Cheng, L. Shen, Y. Zhang, D. Dai, X. Zheng, L. Liao, L. Wang and L. Shi, *Water*, 2018, 10, 1659.

69 D. Jiang, Y. Amano and M. Machida, *J. Environ. Chem. Eng.*, 2017, 5, 4229–4238.

70 M. Rashid, N. T. Price, M. Á. Gracia Pinilla and K. E. O’Shea, *Water Res.*, 2017, 123, 353–360.

71 O. Mrózek, P. Ecorchard, P. Vorník, J. Ederer, D. Smržová, M. Š. Slušná, A. Machálková, M. Nevořalová and H. Beneš, *Appl. Clay Sci.*, 2019, 169, 1–9.

72 M. Gilanizadeh and B. Zeynizadeh, *New J. Chem.*, 2018, 42, 8553–8566.

73 N. Passe-Coutrin, S. Altenor, D. Cossette, C. Jean-Marius and S. Gaspard, *Microporous Mesoporous Mater.*, 2008, 111, 517–522.

74 M. Y. Akram, S. Ahmed, L. Li, N. Akhtar, S. Ali, G. Muhuydin, X. Zhu and J. Nie, *J. Environ. Chem. Eng.*, 2019, 7, 103137.

75 C. Han, J. Lalney, N. Iyanna and M. N. Nadagouda, *Mater. Chem. Phys.*, 2017, 198, 115–124.

76 J. Liu, J. Cao, Y. Hu, Y. Han and J. Zhou, *Water Sci. Technol.*, 2017, 76, 2867–2875.

77 J. Wang, X. Shao, J. Liu, Q. Zhang, J. Ma and G. Tian, *Mater. Chem. Phys.*, 2020, 249, 123024.

78 F. Yang, S. Zhang, Y. Sun, D. C. W. Tsang, K. Cheng and Y. S. Ok, *J. Hazard. Mater.*, 2019, 365, 665–673.

79 D. Fang, X. Zhuang, L. Huang, Q. Zhang, Q. Shen, L. Jiang, X. Xu and F. Ji, *Sci. Total Environ.*, 2020, 725, 138490.