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Facile upscaled synthesis of layered iron oxide nanosheets and their application in phosphate removal†

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Layered iron oxide nanosheet material is a new efficient adsorbent which is here developed and investigated for removing the eutrophicant phosphate from water. The layered Fe^{II}/Fe^{III} hydroxide chloride (green rust; GR) with dodecanoate, followed by solid state oxidation and exfoliation, by which the yield of the product can be easily scaled up. The obtained product exhibits a distinct platy structure with a minimal Fe^{III} oxide sheet thickness of 1 nm and lateral size of 100 to 200 nm as observed by means of high resolution transmission electronic microscopy, selected area electronic diffraction and atomic force microscopy. The Fe^{III} nanosheets can be well dispersed and stable in aqueous solution, showing a low tendency of aggregation. The performance of the obtained nanosheets to remove phosphate has been evaluated in kinetic and batch experiments under different environmental conditions (*i.e.* interfering anions and pH). The kinetic study shows that phosphate removal by the iron oxide quickly reaches a plateau with the rate constant k_2 ranging from 5.2×10^{-4} to 1.4×10^{-3} g ($\mu\text{mol}^{-1} \text{min}^{-1}$) for the initial phosphate concentrations of 40 and 80 $\mu\text{mol L}^{-1}$ (1.2 to 2.4 mg P per L) at pH 7. The maximum phosphate adsorption capacity of the layered Fe^{III} nanosheets is 2540 $\mu\text{mol g}^{-1}$ (about 77 mg g^{-1} ; 4006 $\mu\text{mol P per g Fe}$) at pH 5, showing excellent potential for phosphate removal from wastewater. Our results also indicate that the performance of the layered Fe^{III} nanosheets for phosphate removal is selective. X-ray photoelectron spectroscopic analyses of O 1s, Fe 2p and P 2p spectra provide evidence for phosphate removal by forming inner-sphere Fe–O–P surface complexes. The cost-effective, environmentally friendly and highly efficient layered Fe^{III} nanosheet material is a promising material for the removal of phosphate or other oxyanions in future water treatment technologies.

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1. Introduction

Phosphorus is an essential nutrient for all living organisms, and as such phosphorus is present in all parts of ecosystems, not only food production systems. Phosphorus is mainly discharged in the form of phosphate into aquatic environments from soils, sediments, industries and *via* household waste.¹ Excessive levels of phosphorus will cause severe adverse effects on the ecosystem, such as eutrophication of lakes, lagoons and rivers. Concurrently, phosphorus is also a limited resource that needs

to be captured and reused. Thus, phosphorus recovery from the aquatic environment does not only prevent the loss of nutrient resources, but also eliminate serious environmental problems. Various physicochemical approaches have been developed to recover phosphate from wastewater, such as precipitation, crystallization, anion exchange, and sorption.^{1–6} Typically, in virtue of advanced nanotechnology, a number of nanomaterials with unique structures have been developed exhibiting excellent efficiency for removing phosphate.^{4–6}

As a class of anionic clays, layered double hydroxides (LDHs) comprise positively charged trioctahedral metal hydroxide layers and interlayer anions with the general formula of $[\text{M}^{\text{II}}_{(1-x)}\text{M}^{\text{III}}_x(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} and M^{III} denote di- and tri-valent metal ions, A^{n-} is the counter anion and m is the number of water molecules located in the interlayers between the metal hydroxide layers.^{7–9} The positively charged metal hydroxide layers can be considered to be formed by partial substitution of divalent cations (M^{II}) in a brucite-like (*i.e.* $\text{Mg}(\text{OH})_2$) structure by trivalent cations (M^{III}).¹⁰ The features of the positively charged brucite-like sheets and relatively weak bonding of interlayer anions result in LDHs with strong anion

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exchange and adsorption capacities, showing high prospects for removing various oxyanion pollutants in water treatment.¹¹ LDHs are considered as efficient adsorbents to remove phosphate with adsorption capacities ranging from 16 to 47 mg P per g.^{3,11–13} Studies show that the adsorption capacity of LDHs is notably determined by the composition and properties of the metal hydroxide layers.^{11,14} For example, the increase of trivalent Al ions or the addition of tetravalent Zr into the metal hydroxide layers can significantly enhance phosphate removal,^{1,15} whereas, this can increase the release of toxic elements such as Al into the aquatic environment.¹¹ Meanwhile, the performance of LDHs is also affected by the properties of interlayer anions due to their different affinities with brucite-like layers. For example, a previous study showed that NO_3^- type Zn/Al LDH exhibits much stronger adsorption for phosphate than CO_3^{2-} and Cl^- intercalated LDHs.¹⁶ Though calcination of LDHs prior to their application in water cleanup can cope with this problem, the release of metal cations to solution during rehydration of calcined forms may be severe.^{10,11}

Iron oxides are well known for their strong phosphate binding affinity and capacity, hence, an interesting approach is to use iron-rich LDHs as a source of iron oxide.¹⁷ Green rusts (GRs) are a class of monometallic iron bearing LDHs ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ LDHs), which are intermediate products forming during iron oxidization/corrosion. This type of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ LDH is very active and unstable in air, and readily transforms to other iron (hydro)oxides such as goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), amorphous ferrihydrite and magnetite depending on the type of anions in the interlayers (e.g. Cl^- , SO_4^{2-}). These transformations lead to poorer oxyanion adsorption compared with GRs.^{18,19} Genin and Legrand reported that CO_3^{2-} type GR could be converted to layered “ferrie” oxhydroxylcarbonate GR ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH) *via* rapid oxidation in H_2O_2 , whereas, the observed evidence of structural transformation based on X-ray and electronic diffractions could not fully support this hypothesis.^{20,21} Recently, we successfully synthesized organic GR interleaved with dodecanoate anions whose structure remained intact and highly crystalline after complete solid state oxidation of Fe^{II} to Fe^{III} in air.^{22,23} This $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH can be an ideal choice for production of Fe^{III} oxides for phosphate recovery due to a high potential specific surface area and good dispersion in water solution. However, no such study has been carried out yet. Besides, the yield of this product using existing one-pot synthesis methods (Table S1†) severely constrains its further application.²²

In this study, we developed a new facile approach of upscaled synthesis of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH *via* simple precipitation and oxidation of Fe^{II} , followed by exfoliation of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH to the layered Fe^{III} nanosheets by removing hydrophobic dodecanoate anions. The as-synthesized $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH and its exfoliated product were then subjected to systematic characterization. Finally, the as-synthesized $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH and its layered Fe^{III} nanosheets were examined for removing phosphate which is the main phosphorus form found in eutrophied wastewaters.

2. Experimental

2.1 Materials

Iron(II) chloride salt ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; purity > 98%) and dodecanoic acid ($\text{C}_{12}\text{H}_{24}\text{O}_2$; purity > 99%) were purchased from Alfa Aesar. All chemicals were of analytical grade, and used without further purification. Milli-Q water (18.2 M Ω cm) and ultrapure argon (purity > 99.9995%) were used throughout the experiments.

2.2 Synthesis of dodecanoate intercalated $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH

Dodecanoate intercalated $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH(C12)) was synthesized by solid-state-oxidation of dodecanoate intercalated GR (GR(C12); $\text{Fe}^{\text{II}} : \text{Fe}^{\text{III}} = 3 : 1$) derived from anion exchange of chloride containing green rust (GR(Cl)) with dodecanoate anions (Scheme 1).

GR(Cl) was prepared by partial oxidation of freshly precipitated ferrous hydroxide ($\text{Fe}(\text{OH})_2$) at room temperature.²¹ Briefly, FeCl_2 and NaOH solutions were mixed with a $[\text{Fe}^{2+}]/[\text{OH}^-]$ ratio of 0.7, to obtain a final concentration of 0.36 M for iron. This mixed solution (200 mL) was vigorously stirred using a magnetic bar under the protection of an Ar gas stream at $25 \pm 1^\circ\text{C}$. A rate of 1.5 mL min⁻¹ O_2 was pumped into the solution during continuous stirring, meanwhile, the pH of the solution was simultaneously monitored throughout the whole reaction. After approximately 1.5 h reaction where about 1/4 of the total Fe^{II} ions was oxidized to Fe^{III} , the pump was turned off and the greenish-blue suspension was further aged for 24 h without exposing to oxygen at room temperature.

The aged GR(Cl) slurry was separated by centrifugation at a speed of 2500g for 5 min, and dispersed immediately in 500 mL of 0.2 M Ar-bubbled sodium dodecanoate solution (30% ethanol). The glass container was capped with a rubber septum and equipped with in- and outlets, which allowed flushing with Ar gas to remove trace oxygen in headspace. The solution was stirred mildly for 3 days to exchange chloride interlayer anions with dodecanoate anions. The resulting GR(C12) was further washed with an Ar-bubbled mixture of ethanol and water prior to freeze-drying. Finally, $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH was obtained by exposing the completely dried GR(C12) particles as a thin layer of powder with thickness less than 1 mm in a glass container to air for 24 h.

2.3 Exfoliation of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH to layered nanosheets

The synthesized $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH (1.0 g) was mixed with 1.0 L of MilliQ water in a glass flask using magnetic stirring. The pH

Scheme 1 Schematic illustration of the synthesis of layered Fe^{III} nanosheets. From left to right: Chloride GR (GR(Cl)) is exchanged with dodecanoate to form GR(C12), which is subsequently oxidized to $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH and finally exfoliated to produce Fe^{III} nanosheets.

was adjusted to 12.7 *via* charge reversal of the Fe^{III} nanosheets. The suspension was magnetically stirred for 24 h to achieve complete exfoliation, consequently, the resulting suspension was repeatedly centrifuged and re-dispersed in ethanol to remove dodecanoate anions. The dispersion of Fe^{III} layer nanosheets in MilliQ water was facilitated using a sonicator equipped with a microtip at 200 W (Ultrasonic processor, Shanghai) for 1 h in an ice bath. To remove large aggregated or unexfoliated particles, the resulting orange colloidal suspension was then centrifuged at 1000g for 10 min.

2.4 Characterization of the layered Fe^{III} nanosheets and their precursors

The chemical composition of the products was analyzed by dissolving appropriate amounts of the solids in 0.1 M HCl. The Fe^{II} contents within GR(Cl) and GR(C12) were determined by using a modified phenanthroline method,²⁴ while the content of total Fe was analyzed by using an Optima 8300 inductive coupled plasma optical emission spectrometer (ICP-OES; PerkinElmer, USA). The contents of chloride and dodecanoate ions within the solids were measured by using a Dionex ICS-2100 ion chromatograph (IC), and an Agilent 6890 series gas chromatograph equipped with a flame-ionization detector (GC-FID, USA), respectively (details are given in ESI S1†).

Powder X-ray diffractograms for the as-synthesized products from GR(Cl) to exfoliated Fe^{III} layered nanosheets were tracked using an X'Pert PRO MRD diffractometer (PANalytical, Netherlands) applying monochromatic Cu K α radiation ($\lambda = 0.15405$ nm) with a scanning rate of 5° min⁻¹. The morphology and size of Fe^{III}/Fe^{III} LDH and its exfoliated nanosheets were examined with a Hitachi S-3000N scanning electronic microscope coupled with a DEAX Energy Dispersive Spectrometer (SEM/EDS), and a JEOL 2100F transmission electronic microscope (TEM) operating at 200 kV. A Veeco nanoscope IIIa atomic force microscopy system (AFM) was used to analyze the topography of the Fe^{III} layered nanosheets in contact mode using a Si-tip cantilever with a force constant of 2 N m⁻¹. Fourier transformation infrared spectroscopy (FT-IR) spectra of the samples were obtained by using a Nicolet 8700 spectrometer (Thermo Scientific, USA). The specific Brunauer-Emmett-Teller (BET) surface area was determined by the nitrogen adsorption method using a Micromeritics ASAP2000 Surface Area Analyzer (Micromeritics instrument corporation, USA). 20 mg of powder samples were degassed at room temperature using a vacuum pump for two hours before the measurement. Thermogravimetric analyses (TGA) of the Fe^{III}/Fe^{III} LDH and its exfoliated nanosheets were performed using a Pyris1 TGA (PerkinElmer Instruments, USA) with the temperature set up to 800 °C, and collected at a heating rate of 5 °C min⁻¹. The zeta potential of the layered Fe^{III} nanosheets as a function of pH from 3 to 10 was monitored by using a Zetasizer Nano ZS (Malvern, England).

2.5 Removal of phosphate by using Fe^{III} layered nanosheets

Both sorption isotherms and kinetic experiments were used to study the removal efficiency of phosphate by the Fe^{III}

nanosheets at different pHs. Besides, the influence of various co-existing anions (*i.e.* Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻) on phosphate removal was also addressed. The Fe^{III} nanosheet suspension (0.1–0.2 g L⁻¹ as Fe) was obtained *via* the exfoliation process as described above, and used for the following sorption experiments.

The sorption kinetics study was performed by spiking appropriate amounts of P stock solution into each 7 mL Fe^{III} nanosheet suspension to achieve an initial P concentration of 40 and 80 μ M, respectively. The solution was maintained at pH 7.0 throughout the whole contact period, and the ionic strength was controlled with 0.1 M NaNO₃. At each described reaction time (0 to 24 h), the supernatant was sampled.

The phosphate sorption isotherm experiments were conducted at 25 $\pm$ 1 °C with an ionic strength of 0.1 M NaNO₃. The Fe^{III} nanosheet suspensions were brought into contact with phosphate with varying initial concentrations of 0 to 1500 μ M for 24 h at pH 5, 7.5 and 9, respectively. Besides, the competitive sorption of background anions (*i.e.* Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻) onto the Fe^{III} nanosheets was further investigated using different ionic strengths from 0 to 0.5 M at pH 7. The supernatants were collected by centrifugation of the Fe^{III} nanosheet suspensions after 24 h equilibration. The phosphate concentrations in supernatants were analyzed by using a molybdate colorimetric (Murphy-Riley) procedure with absorbance measured using a U-2900 UV-vis spectrophotometer (Hitachi, Japan) at a wavelength of 720 nm.²⁵

3. Results and discussion

3.1 Synthesis of GR(Cl) and anion exchange to GR(C12)

The chloride form of GR (GR(Cl)) was initially synthesized. The chemical composition analysis shows that the ratio of Fe^{II}/Fe^{III} is about 3.2 (Table S2†), in line with the ideal ratio of 3 and as seen in a previous study.²⁶ As shown in Fig. 1a, the XRD pattern of the as-synthesized GR(Cl) exhibits intense basal reflections with a *d*-spacing of 0.78 nm, in line with previous findings.^{26,27}

Fig. 1 XRD diffractograms of (a) GR(Cl), (b) GR(C12), (c) Fe^{III}/Fe^{III} LDH intercalated with dodecanoate, and (d) the exfoliated Fe^{III} nanosheet product.

After further anion exchange with dodecanoate anions, basal reflections in the XRD pattern systematically shifts to a lower angular range (Fig. 1b). This is due to the swelling of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ iron hydroxide sheets to a d -spacing of 3.5 nm, as a result of successful intercalation of dodecanoate anions into layers. The low content of Cl within the obtained GR(C12) demonstrates the high purity of the GR(C12), and consequently, resulting in the high purity of the obtained $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH in the following process of oxidation (Table S2; ESI S2†). A similar XRD pattern for GR(C12) was also reported by using a direct one-pot synthesis method.²³ Additionally, the FT-IR spectrum further confirms the intercalation of dodecanoate anions into the interlayers, which shows strong C-H vibrations ($2950\text{--}2850\text{ cm}^{-1}$) and COO^- vibrations ($1567\text{--}1451\text{ cm}^{-1}$) for GR(C12) (Fig. 2b).

3.2 $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH and exfoliation to layered Fe^{III} nanosheets

During the solid state oxidation process, the greenish blue GR(C12) particles gradually turn to orange-yellow color, indicating full oxidation of Fe^{II} to Fe^{III} within GR(C12). Meanwhile, according to Fig. 1c, the XRD of the fully oxidized product shows a similar pattern to that of GR(C12), consequently, demonstrating the preservation of the layered structure of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH. This is in accordance with our previous studies by using one-pot synthesis.²² The FT-IR analysis of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH shows C-H and COO^- vibrations consistent with those for GR(C12) (Fig. 2). This demonstrates that the electrostatic interaction between interlayered dodecanoate anions and iron (ox) hydroxide sheets is still intact after full oxidation of GR(C12).²² The SEM and TEM images (Fig. 3a and c) of the oxidized

Fig. 2 The FTIR spectra of (a) dodecanoic acid (C12), (b) $\text{Fe}^{\text{III}}\text{-C12}$, (c) $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH (precipitate of Fe^{3+} and dodecanoate), and (d) the Fe^{III} nanosheet material.

Fig. 3 (a) SEM images of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH, and (b) the layered Fe^{III} nanosheets after exfoliation; (c) the TEM images of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH, and (d) the exfoliated layered Fe^{III} nanosheets; (e) the AFM image and the corresponding height profile for the marked line in the image for the synthesized Fe^{III} nanosheets mapped in tapping mode.

$\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH particles depict a nice hexagonal platy shape in analogy with other LDHs.⁸ The EDS analysis shows the elemental composition within $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH consisting of mainly C, O and Fe (Fig. S1†). As shown in Fig. 3, the selected area electron diffraction (SAED) of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH exhibits typical hexagonal spots with a calculated lattice constant $a = 0.25\text{ nm}$, which indicates a highly ordered structure within the layers (ab plane). The double spots at each location can be ascribed to diffractions from overlapping layers with different orientations. This evidence shows that the in-plane brucite-type structure is kept intact during oxidation when the interlayer is stabilized by dodecanoate as also seen in our previous investigation.²² This is new in comparison with a previous study showing that the layered structure of $\text{GR}(\text{CO}_3)$ was damaged after rapid oxidation by hydrogen peroxide.²⁸

The $\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$ LDH was further exfoliated to the Fe^{III} nanosheets by treatment with base and washing with ethanol to remove dodecanoate anions, which is confirmed by chemical analysis and EDS analysis as given in Fig. S1 and Table S2.† The XRD pattern clearly shows that all basal reflections disappeared due to loss of regular orientation and stacking of layers (Fig. 1d; Table S2†). After exfoliation no crystalline iron oxide impurity was observed as seen from the XRD pattern (Fig. 1). The FT-IR

Fig. 4 TGA analysis of the Fe^{III}/Fe^{III} LDH and its exfoliated layered Fe^{III} nanosheets.

spectrum of the Fe^{III} nanosheets also reveals the removal of dodecanoate anions. The result suggests that deprotonation of hydroxyl groups on the iron(III) (oxy)hydroxide layers resulting in a negative surface charge leads to repulsion and elimination of dodecanoate interlayer anions, finally achieving exfoliation of Fe^{III}/Fe^{III} LDH.²² The TEM image (Fig. 3d) displays that the exfoliated Fe^{III} nanosheets are present as layered structure (Fig. 3d). The SAED shows a similar electron diffraction pattern to its precursor Fe^{III}/Fe^{III} LDH, which suggests its in-plane crystalline structure with a highly ordered structure in *ab* planes in line with evidence from other exfoliated LDHs.^{7,29} This further demonstrates that the as-prepared Fe^{III} nanosheets *via* the anion exchange approach show a similar crystalline structure with that synthesized *via* the one-pot method. Moreover, the AFM image (Fig. 3e) shows that the obtained layered Fe^{III} nanosheets have an average height of about 1 nm which is about 2 times the theoretical thickness of 0.48 nm for a single layered metal hydroxide layer in LDH. The increased thickness measured by AFM has also been observed in our previous study.²² This can be due to the strong hydration of the layered Fe^{III} nanosheets, subsequently causing the presence of adsorbed water molecules on both the surfaces of the Fe^{III} nanosheets. The TGA analysis shows that the weight of the layered Fe^{III} nanosheets remains stable at over 250 °C, indicating the loss of surface water associated with the solid, while the weight loss of the Fe^{III}/Fe^{III} LDH continues at over 600 °C probably due to the additional removal of dodecanoate groups within the interlayers of the Fe^{III}/Fe^{III} LDH (Fig. 4). The maximum yield of the layered Fe^{III} nanosheet product in our trials is about 0.2 kg, and can be still further scaled up to a larger quantity level. This is the advantage of using this new upscaled method other than one-pot synthesis with a maximum yield of 0.4 g (details have been specified in ESI S2†).

3.3 Phosphate removal by Fe^{III} nanosheets

Fig. 5 shows that phosphate adsorption onto Fe^{III} nanosheets is time dependent, and the adsorption kinetics can be well described by the pseudo-second order model (eqn (1)).

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

Fig. 5 Pseudo-second order model fitted adsorption kinetics of phosphate towards the Fe^{III} nanosheets in 0.1 M NaNO₃ medium at pH 7.0 with initial concentrations of 40 μmol L⁻¹ (▲ and △) and 80 μmol L⁻¹ (● and ○). The solid content of the Fe^{III} nanosheets is 0.1 g L⁻¹. The dashed and solid curves were obtained by fitting adsorption data with the pseudo-second-order equation (eqn (1)).

where q_t is the amount of adsorbed phosphate on the Fe^{III} nanosheets at any time t (μmol g⁻¹), k_2 and q_e denote the rate constant of phosphate adsorption (g (μmol⁻¹ min⁻¹)), and the amount of adsorbed phosphate on the adsorbent at equilibrium time (μmol g⁻¹), respectively. The phosphate adsorption is very fast and efficient with the rate constant k_2 ranging from 5.2×10^{-4} to 1.4×10^{-3} g (μmol⁻¹ min⁻¹) for the initial concentrations of 40 and 80 μmol L⁻¹ (1.24 to 2.4 mg P per L) at pH 7.0, and maximum adsorption of 396 and 775 μmol g⁻¹ can be reached within 1 hour. Our results show that only a dosage of 0.1 g L⁻¹ is sufficient to remove excess phosphate of 80 μmol L⁻¹ (2.4 mg P per L) from water.

The isotherms of phosphate adsorption on a synthesized Fe^{III} nanosheets can be successfully fitted by the Langmuir model with R^2 ranging from 0.945 to 0.988 (eqn (2))

$$C_s = \frac{K_L C_{\max} C_w}{1 + K_L C_w} \quad (2)$$

where C_s (μmol g⁻¹) and C_w (μmol L⁻¹) represent the adsorbed phosphate on Fe^{III} nanosheets and free phosphate concentration in the aqueous phase; K_L and $C_{\max}$ are Langmuir adsorption affinity and phosphate adsorption capacity of Fe^{III} nanosheets.

Phosphate adsorption on the Fe^{III} nanosheet materials was performed at pH 5.0, 7.0 and 9.0, respectively. The results reveal that the maximum adsorption capacity of phosphate on the Fe^{III} nanosheet materials can reach up to 2540 μmol g⁻¹ depending on pH (Table 1; Fig. 6a), which shows much higher phosphate adsorption than poorly crystalline goethite (270 μmol g⁻¹),

Table 1 Langmuir isotherm parameters for phosphate adsorption onto the Fe^{III} nanosheets at three different pHs

pH	NaNO ₃ (mol L ⁻¹)	K_L (L μmol ⁻¹)	$C_{\max}$ (μmol g ⁻¹)	R^2
5.0	0.1	0.02 ± 0.01	2540 ± 92	0.983
	0	0.03 ± 0.01	2497 ± 104	0.953
7.0	0.1	0.02 ± 0.01	1502 ± 81	0.946
9.0	0.1	0.06 ± 0.02	868 ± 41	0.988

Fig. 6 (a) Adsorption isotherms for phosphate bonding to the Fe^{III} nanosheet material at pH 5.0 (●), 7.0 (■) and 9.0 (▲). Each adsorption isotherm was fitted using all raw data obtained in triplicate ($n = 21$). Data points refer to averages of triplicates, vertical bars represent the standard deviation ($n = 3$); (b) pH adsorption edge for phosphate bonding to the layered Fe^{III} nanosheets (left y-axis), along with a zeta potential of the layered Fe^{III} nanosheets (right y-axis) in a pH range of 3 to 10. The dosage of adsorbent is 0.1 g L⁻¹, while the initial concentration of phosphate is 150 μmol L⁻¹.

lepidocrocite (270 μmol g⁻¹), akaganeite (450 μmol g⁻¹) and iron bearing LDH (1450 μmol g⁻¹) particles (Table 2) from previous studies,^{1,2,30} and slightly higher than 2490 μmol g⁻¹ for amorphous ferrihydrite which is generally considered as the most efficient iron oxide adsorbent for phosphate.³¹ This may be attributed to the relatively higher specific surface area (185 m² g⁻¹) of the Fe^{III} nanosheet material and in particular to

the high aspect ratios of the particles. The phosphate adsorption capacity of the exfoliated Fe^{III} nanosheets remarkably increases in comparison to its precursor Fe^{III}/Fe^{III} LDH with intercalated dodecanoate ions, which shows an adsorption capacity of 605 μmol g⁻¹ at pH 5.0 (Table 2; figure not shown), and the analogous layered Mg/Fe LDH (Table 2). The notable increase of phosphate adsorption in the nanosheet material is probably due to the exposure of adsorption sites in the inter-layer which was inaccessible in the intact LDH.³² By normalizing the phosphate adsorption to iron content, the ratio of adsorbed phosphate to Fe (P/Fe) of 4006 μmol (per g Fe) for the layered Fe^{III} nanosheets is significantly higher than 3761 μmol (per g Fe) due to the slightly high iron content of ferrihydrite (Table 2). However, the notably high P/Fe of 6444 μmol (per g Fe) for Mg/Fe LDH cannot be used for comparison, since both Mg and Fe are responsible for the removal of phosphate.¹

As depicted in Fig. 6a and b, the phosphate adsorption by the Fe^{III} nanosheet materials decreases with the increase of pH from 3 to 10. It is well known that phosphate ions can present in different states according to their $pK_{a,1}$ of 2.15, $pK_{a,2}$ of 7.20 and $pK_{a,3}$ of 12.33.¹⁶ Hence, the predominating species is H₂PO₄⁻ (approximately 100%) at pH 5, while HPO₄²⁻ ions show almost 100% dominance at pH 9. Nevertheless, the surface of the Fe^{III} nanosheets appears to have less positive charge, and finally becoming negatively charged at higher pH according to zeta potential data (Fig. 6b), consequently, causing greater electrostatic repulsion to the more negatively charged HPO₄²⁻ as pH increases. This is in agreement with previous findings by Chitrakar and co-workers.³⁴

Anions such as NO₃⁻, Cl⁻, SO₄²⁻ and CO₃²⁻ are ubiquitous anions and ligands in natural waters, which may affect the efficiency of the phosphate removal. As illustrated in Fig. 7, the adsorption of phosphate by the Fe^{III} nanosheets slightly increases in the presence of the monovalent anions NO₃⁻ or Cl⁻ with concentrations up to 0.5 M at pH 7 (PO₄²⁻/Xⁿ⁻ up to 2000, X represents coexisting anions), which may imply the phosphate adsorbed *via* inner-sphere association in line with previous findings of phosphate sorption onto other iron oxyhydroxides.^{35,36} At pH 5 where almost 100% of phosphate ions exist as monocharged H₂PO₄⁻, phosphate

Table 2 Comparison of the adsorption capacities of different adsorbents for removing phosphate

Adsorbent	pH	Fe ^a (%)	BET surface area (m ² g ⁻¹)	Max. P (μmol g ⁻¹)	P/Fe (μmol g ⁻¹)	Ref.
Fe ^{III} nanosheets	5	63.4	185	2540	4006	This study
Fe ^{III} nanosheets	7	63.4		1522	2401	This study
Fe ^{III} /Fe ^{III} LDH	5	37.2	32	605	1626	This study
Goethite	5	62.9	63	270	429	2
Akaganeite	5	55.8	94	450	806	2
Lepidocrocite	5	62.9	85	270	429	2
Granulated ferric hydroxide	5.5	55.8	280	770	1380	30
Ferrihydrite	6	66.2	187	2490	3761	31
Mg/Fe-LDH	6	22.5	NA ^b	1450	6444	1

^a The iron contents of the Fe^{III}/Fe^{III} LDH and Fe^{III} nanosheets were retrieved from Table S2; the iron contents of goethite, akaganeite, lepidocrocite, granulated ferric hydroxide (100% akaganeite) and ferrihydrite were obtained from the Mineralogy database,³³ while the iron content for Mg/Fe-LDH was calculated based on the formula of Mg₂Fe(OH)₅CO₃. ^b NA: not available.

Fig. 7 Influence of different anions on the adsorption of phosphate to the layered Fe^{III} nanosheets in comparison with that without addition of background electrolyte at pH 7.0. The error bar represents standard deviation ($n = 3$). The insert is the adsorption isotherms of phosphate onto Fe^{III} nanosheets in the presence (●) and absence (×) of 0.1 M NaNO_3 at pH 5.0. Asterisks indicate that the phosphate adsorption is significantly different from that without addition of electrolyte ($p < 0.05$).

adsorption is high and hardly affected by the presence of nitrate (Fig. 7). The addition of the bivalent anions SO_4^{2-} or CO_3^{2-} (present as HCO_3^-) up to 0.05 M leads to a slight decrease of the phosphate removal, but not statistically significant ($p > 0.05$; $\text{PO}_4^{2-}/\text{X}^{n-} \leq 200$), whereas, there is a significant decrease of phosphate adsorption at higher concentrations (0.1 to 0.5 M), indicating the strong competition of SO_4^{2-} or CO_3^{2-} (present as HCO_3^-) ions with phosphate binding with the Fe^{III} nanosheet material but only at higher concentrations. A similar observation was reported for phosphate adsorption by amorphous granulated ferric hydroxide,³⁰ indicating that the iron bearing materials such as the Fe^{III} nanosheets have strong selectivity to adsorb phosphate, as a consequence, they can be considered as ideal adsorbents for removing phosphate ions from natural waters.

3.4 XPS surface analysis

The high resolution spectra of O 1s, Fe 2p and P 2p for the Fe^{III} nanosheet material before and after reaction with phosphate are given in Fig. 8. The XPS analysis shows notable changes of the O 1s spectra before and after phosphate adsorption at pH 5 (Fig. 8a). Peak fitting of the O 1s spectra results in three different components at ~ 529.8 eV, ~ 531.0 eV and ~ 532.8 eV corresponding to O–Fe bonding, OH/O–P bonding, and adsorbed water, respectively,³⁵ the O 1s spectra clearly show a significant increase of the binding energy at ~ 531.0 eV compared to that at 529.8 eV as a result of phosphate bonding. Even though it is difficult to discern differences between the binding energies of O–H and O–P in Fe^{III} nanosheets,³⁵ the enhanced relative intensity at ~ 531 eV compared to that at 529.8 eV can be due to binding of phosphate to O–Fe, subsequently leading to the formation of Fe–O–P bonding. This is similar to our previous findings on the O 1s spectra for the SO_4^{2-} containing $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$

Fig. 8 (a) O 1s and (b) Fe 2p spectra of the Fe^{III} nanosheets before and after reaction with $250 \mu\text{mol L}^{-1}$ phosphate at pH 5, respectively; (c) P 2p spectra of the Fe^{III} nanosheets before and after reaction with $250 \mu\text{mol L}^{-1}$ phosphate at pH 5 and pH 7, respectively.

LDH,²² and phosphate adsorption to ferrihydrite.³⁵ The appearance of P 2p spectra at a binding energy of ~ 133.4 eV after phosphate adsorption indicates the successful phosphate loading on the Fe^{III} nanosheets (Fig. 8c). Interestingly, the binding energy of ~ 133.4 eV observed for phosphate on the Fe^{III} nanosheets is very similar to 133.6 eV for reference FePO_4 and phosphate adsorbed ferrihydrite,³⁵ which can further confirm the assumption of the formation of Fe–O–P bonding obtained in O 1s spectra. The significant increase of the XPS intensity of the P 2p signal with pH decreasing from 7.0 to 5.0 is in agreement with the increased adsorption of phosphate by the Fe^{III} nanosheets with decreasing pH (Fig. 6; Table 1). The XPS analyses of the O 1s, Fe 2p and P 2p spectra provide spectroscopic evidence for phosphate adsorption to the Fe^{III} nanosheets by forming an inner-sphere complex of the Fe–O–P type. However, the overlapping of the binding energies of O–H with O–P peaks (Fig. 8b) hinders

further distinguishing between monodentate and bidentate surface complexation of phosphate on the Fe^{III} oxide nanosheets, which needs to be investigated in future work.

4. Conclusions

In this work, an upscaled facile method was successfully developed for the synthesis of the layered Fe^{III} nanosheet material by means of anion exchange, solid-state oxidation and exfoliation. Its structure was well characterized by means of XRD, FT-IR, AFM, TGA, XPS, and electronic microscopies. Our results confirm that the as-synthesized Fe^{III} nanosheet material consists of tabular particles which comprise sheets with regular in-plane ordering of atoms, and which has a high BET surface area (185 m² g⁻¹). Our study further demonstrates that the synthesized layered Fe^{III} nanosheet material can strongly and rapidly adsorb phosphate ions which are considered to be the main pollutant causing eutrophication in lake and seawater. The maximum adsorption of phosphate by the Fe^{III} nanosheet material is up to 2540 µmol P per g (4006 µmol P per g Fe) depending on pH, which is considerably higher than those by other crystalline iron oxides such as goethite and lepidocrocite. In addition, the data suggest that the layered Fe^{III} nanosheets show adsorption selectivity towards phosphate even in the presence of high concentrations of background ions such as SO₄²⁻, NO₃⁻ and CO₃²⁻ up to 0.05 M. XPS surface analysis clearly shows the binding of phosphate with the layered Fe^{III} nanosheet material and the formation of inner-sphere Fe–O–P complexes. Overall, the successfully synthesized layered Fe^{III} nanosheet material is considered as a cost-effective, environmentally friendly and highly efficient adsorbent for removing the phosphate pollutant from eutrophic water. The Fe^{III} nanosheet material also has perspectives as coating material for filter bed substrates in water treatment technologies.

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