Granular ferric hydroxide adsorbent for phosphate removal: demonstration preparation and field study

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ABSTRACT

Ferric hydroxide (FHO), which has high phosphate adsorption capacity, was prepared by precipitation at industrial scale and then fabricated via the drum granulation method with cross-linked poly(vinyl alcohol) as the binder. The optimum binder/FHO powder ratio was 0.6 for producing a granular adsorbent with a high phosphate adsorption capacity and stability. The Langmuir maximum adsorption capacities of powder and granular FHOs were 74.07 mg g^{-1} and 56.18 mg g^{-1} at $\text{pH } 7.0 \pm 0.2$, respectively, which were higher than those of other reported phosphate adsorbents under neutral or acidic conditions. Phosphate-loaded granular FHO could be regenerated by NaOH solution. Columns containing the granular FHO were used for phosphate removal from ozonated secondary effluents of a municipal wastewater treatment plant at space velocity (SV) of 2 and 5 h^{-1} . During more than 2 months' operation, the average removal percentage of PO_4^{3-} was more than 90% and the turbidity and concentration of COD_{Mn} in the effluents were lower than in the influents. In addition, energy dispersive X-ray results suggested that active sites inside the granular FHO were available for phosphate removal. The results demonstrated that granular FHO can be applied as an assist technology for phosphate removal from secondary effluents.

Key words | adsorption, field test, granulation, phosphate removal, secondary effluents

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INTRODUCTION

Excess discharge of phosphorus into surface waters often causes eutrophication, which affects the water quality through consumption of dissolved oxygen and destroys aquatic life (Correll 1998). Biological processes and chemical precipitation have been mainly used for phosphate removal from municipal wastewater (Morse *et al.* 1998; Clauson-Kaas *et al.* 2004). However, these techniques are both associated with disadvantages such as operational difficulties, sludge production, phosphate recycling and, especially, incomplete removal (Morse *et al.* 1998; Blaney *et al.* 2007). Additionally, the presence of low concentrations of phosphate (even less than 1 mg l^{-1}) in the treated municipal wastewater may cause eutrophication if the streams discharge into lakes or reservoirs (Zhao & Sengupta 1998; Peleka & Deliyanni 2009). Therefore, adsorption has been considered as an assist technology with efficient and cost-benefit performance for steady phosphate removal from water (Wei *et al.* 2008), particularly for low phosphate concentrations (Tian *et al.* 2009). Many types of phosphate adsorbents have

been investigated, including raw or modified low-cost materials (Tian *et al.* 2009; Boyer *et al.* 2011) and metal oxides (Zeng *et al.* 2004; Pan *et al.* 2009). Among these, ferric based oxides/hydroxides have proved to exhibit excellent selective adsorption of phosphate (Chitrakar *et al.* 2006). Therefore, for convenience of operation in fixed-bed units and reuse, it is important to fabricate powdered ferric-based oxides/hydroxides into granular adsorbents.

The easily realized methods for the preparation of granular adsorbents are coating and loading, which involve coating or impregnating active components onto a carrier (Mezenner & Bensmaili 2009; Tian *et al.* 2009; Aryal & Liakopoulou-Kyriakides 2011). However, these adsorbents suffer from low adsorption capacity due to limited amounts of active components, and lack the mechanical strength and durability for prolonged operation in fixed-bed units (Chen *et al.* 2011). Among several granulation technologies reported (Salman *et al.* 2007; Dou *et al.* 2013), the drum granulation method is considered to be the simplest continuous mechanism and is

widely used in the granulation of fertilizers. It can fabricate higher porosity granules with larger powder loadings from powdered materials without a carrier core. Recently, the drum granulation method has been reported to be successfully applied in the preparation of granular schwertmannite for arsenate adsorption (Dou *et al.* 2013). To fabricate a durable adsorbent for operation in fixed-bed units by drum granulation, the binder is very important in order to make individual particles coalesce and to provide cohesive forces at particle contact points, so that the granules are able to tolerate stress (Walker 2007). According to previous research, poly (vinyl alcohol) (PVA) had been successfully used as a binder for granulation of a iron–aluminum–cerium (Fe–Al–Ce) trimetal hydroxide adsorbent for fluoride (F) removal (Zhao *et al.* 2012). Therefore, it is worthwhile to investigate the fabrication of granular ferric based adsorbents for phosphate removal using the above method. Meanwhile, to promote the application of a granular adsorbent, it is also important to realize demonstration of the preparation at industrial scale and conduct field tests for treatment of secondary effluents.

In the present study, a ferric hydroxide (FHO) powder was prepared at industrial-scale in a factory and then fabricated by drum granulation using cross-linked PVA as the binder to obtain a granular FHO adsorbent. The binder/FHO powder ratio was optimized to prepare a suitable granular FHO for phosphate removal. The adsorption capacity of the granular FHO was investigated through batch tests and compared with other phosphate adsorbents. The adsorption performance of the granular FHO for secondary effluents from a municipal wastewater treatment plant was evaluated by field column testing for more than 2 months, showing an attractive application potential.

MATERIALS AND METHODS

Materials

The technical grade ferric sulfate and NaOH were supplied by the Xinbang Chemical Company (Shandong, China). The KH_2PO_4 (guaranteed reagent, GR) and other analytical reagent (AR) grade chemicals were all obtained from the China National Medicines Company (Beijing, China).

Adsorbent preparation and its granulation

The FHO powder was prepared by precipitation as described in a previous publication (Schwertmann & Cornell 2000),

with modifications, in a factory at Dongying City, Shandong Province China. Specifically, 3 m^3 of a ferric sulfate solution with 0.10 mol l^{-1} Fe and 0.73 m^3 6 mol l^{-1} of a NaOH solution were mixed under continuous stirring at 100 rpm. The NaOH solution was added gradually, and the relationship between the volume of NaOH solution and the pH of the reaction system during the preparation process are shown in Figure S1 (see Supplementary Information, available in the online version of this paper). After aging at room temperature for 12 h, the precipitate was washed with tap water until the electrical conductivity of the supernatant was below 4.0 mS cm^{-2} , and then sprayed at 271°C to a fine powder. The preparation steps and illustrative photographs are shown in Figure S2 (available in the online version of this paper).

The powder was fabricated with the same binder used in our previous study (Zhao *et al.* 2012) via the drum granulation method on an oscillating granulator. After drying at 65°C , the granules were sieved to give a particle size range of 1.4–1.7 mm. A schematic diagram of the preparation process is illustrated in Figure 1(a).

Characterization

The specific surface areas and pore size distribution of the powder and granular FHO adsorbents were determined using a Specific Surface Area Analyzer (TriStar II 3020; Micromeritics Instrument Corporation, USA). The X-ray diffraction pattern of the FHO powder was recorded on an X-ray Diffractometer (X'Pert Pro Mp, Panalytical, The Netherlands). The selective dissolution of amorphous iron oxides from FHO was conducted using a previously reported method (Chao & Zhou 1983). The surface morphology of the powder and granular FHOs and distributions of phosphorus on the transverse sections of the granular FHO granules after field column testing were revealed by an Energy Dispersive X-ray (EDX) Analytical Spectrometer (EDAX Inc., USA) connected to a Scanning Electron Microscope (SEM, S-3000N; HITACHI, Japan). The stability of granular FHO in water was evaluated by a previously reported method (Zhao *et al.* 2012).

Phosphate adsorption experiments

For adsorption isotherm experiments, a stock solution containing 500 mg l^{-1} phosphate ion (PO_4^{3-}) was prepared by dissolving 0.7165 g of KH_2PO_4 in 1 l deionized water. Working solutions (initial PO_4^{3-} concentrations, $5\text{--}200 \text{ mg l}^{-1}$) were prepared by diluting the stock solution with deionized water. The 0.20 g samples of granular adsorbent and 100 ml

Figure 1 | Schematic of the preparation process steps and images of powder and granular FHOs (at binder/powder ratio 0.6) ((a) preparation process steps of the granular FHO; (b) image of the FHO powder; (c) image of the granular FHO; (d) SEM image of the FHO powder; (e) SEM image of the granular FHOs).

working solutions were added to 250 mL conical flasks and shaken at 130 rpm, 25 °C for 24 h.

The test solution pH was adjusted to pH 7.0 ± 0.2 with 0.1 mol l⁻¹ HCl or 0.1 mol l⁻¹ NaOH. The samples were then filtered using 0.45 μm membrane filters. The residual PO₄³⁻ concentrations were determined at 700 nm with an Ultra-violet/visible Spectrophotometer (U-3010, Hitachi, Japan) by the molybdenum-blue ascorbic acid method of a blue soluble complex formed between phosphate, ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and antimony potassium tartrate (K(SbO)C₄H₄O₆·1/2H₂O) in the presence of ascorbic acid as reducing agent. The adsorption experiments were carried out in triplicate and average values were reported.

The amount of adsorbed PO₄³⁻ (Q_e , mg g⁻¹) was determined as follows:

$$Q_e = (C_0 - C_e) \times V / m \quad (1)$$

where C_0 and C_e are the initial and final PO₄³⁻ concentrations (mg l⁻¹), respectively, V is the volume of test solution (l), and m is the mass of the granular adsorbent (g).

Regeneration experiments

Three gram samples of granular FHO were loaded in 2,000 ml conical flasks containing 1,500 ml solutions with 20 mg l⁻¹ PO₄³⁻, and shaken at 130 rpm, 25 °C for 48 h. The granular FHO was collected and washed using

deionized water and dried at 65 °C. The recovered granular FHOs at 5 g l⁻¹ were soaked in 20 ml NaOH solutions of different concentration for 4 h. The PO₄³⁻ concentrations in the adsorption and desorption solutions were determined by the same method as described above. After desorption, the granular FHO was activated using 20 ml dilute sulfuric acid at pH 4.0 for 1 h followed by washing with deionized water. After regeneration, the adsorption capacity of the granular FHOs was tested at the same initial PO₄³⁻ concentration and granule dosage as for the adsorption step. The regeneration experiments were carried out in triplicate and average values were reported.

The desorption efficiency and regeneration efficiency were determined as follows:

$$\text{Desorption efficiency} = \frac{\text{the amount of PO}_4^{3-} \text{ desorbed}}{\text{the amount of PO}_4^{3-} \text{ adsorbed (fresh)}} \times 100\% \quad (2)$$

$$\text{Regeneration efficiency} = \frac{\text{the amount of PO}_4^{3-} \text{ adsorbed (reuse)}}{\text{the amount of PO}_4^{3-} \text{ adsorbed (fresh)}} \times 100\% \quad (3)$$

Field column test

Perspex columns with an inner diameter of 5 cm and height of 60 cm were used to evaluate the adsorption performance of granular FHO in treating secondary effluents

which discharge into lakes or other natural water bodies. The ozonated secondary effluents from a municipal wastewater treatment plant were subjected to further treatment by ozonation and biological activated carbon in a pilot-scale system, and then fed into the columns. The water quality of the influents and effluents of the columns were sampled at regular time intervals for water quality analysis during the more than 2 months' operation. For the influents, the pH was 7.46–8.42 (average: 8.03), the turbidity was 0.20–5.42 (average: 0.70), the concentration

of dissolved organic carbon (DOC) was 5.52–12.01 (average: 8.23 mg l⁻¹), the concentration of permanganate index (COD_{Mn}) was 4.37–8.46 mg l⁻¹ (average: 5.37 mg l⁻¹), and PO₄³⁻ concentration was 0.21–1.40 mg l⁻¹ (average: 0.63 mg l⁻¹), respectively. The adsorbent volume was 600 ml, and the space velocities (SV, the volume of treatment water per hour/the volume of granular FHO in the perspex column) were 2 and 5 h⁻¹. A picture of the columns used in the field test is shown in Figure 2(b).

Figure 2 | Field column test ((a) PO₄³⁻ removal performance by the granular FHO; (b) the columns used in the field column test; (c) SEM pattern of a granular FHO after used in the field column test; (d) mapping mode image of phosphorus element distribution along the cross-section of the granular FHO (dot-P)).

RESULTS AND DISCUSSION

Characterization of FHO powder

The FHO powder prepared by precipitation and spray drying in a factory was composed of loose and spherical particles, as shown in Figure 1(b) and (d). The Brunauer–Emmett–Teller (BET) specific surface area of the FHO powder was $220.6 \text{ m}^2 \text{ g}^{-1}$ and the pore volume was $0.33 \text{ cm}^3 \text{ g}^{-1}$. The X-ray diffraction (XRD) pattern (Figure S3, available in the online version of this paper) illustrated that the FHO powder had an amorphous structure with a small amount of schwertmannite (according to PDF 47–1775). The results of selective dissolution confirmed that the FHO powder was composed of more than 90.7% amorphous ferric hydroxide. In summary, the FHO was a powder with large specific surface area, abundant pores and amorphous structure, which are beneficial for achieving high adsorption capacity (Zhang *et al.* 2005).

Granulation of FHO powder

Because the FHO was a loose powder, a binder was essential to make individual particles coalesce and fabricate a durable granular adsorbent (Walker 2007). The binder, which was the same as that used in a previous study, (Zhao *et al.* 2012) was introduced, and the effects of the binder/powder ratio on the granulation process were evaluated. The properties and phosphate adsorption capacity of granular FHOs with different ratios are shown in Table S1 (available in the online version of this paper). When the binder/powder ratio was 0.3 or less, the mixture was still loose and could not be made into granules via drum granulation. When the binder/powder ratio rose to 0.6, the wet mass was mixed well and could be fabricated into granules (Figure S4(c)) (Figure S4 is available in the online version of this paper). After drying, these granules showed good stability (91.0%) owing to the micro-particles of the FHO being combined together by the binder (Figure S4(e)). When the binder/powder ratio continued to rise up to 1.0, the stability of granular FHO increased slightly to 97.2%, while the BET specific surface areas and adsorption capacity were basically the same. However, the wet mass of the binder/powder ratio 1.0 was too sticky to pass easily through the machine, which decreased the production yield of the granular FHO significantly, and the cleaning of the machine was difficult. Therefore, the binder/powder ratio of 0.6 was selected as the optimum ratio for subsequent experiments.

Phosphate removal performance of optimized granular FHO

The equilibrium PO_4^{3-} adsorption isotherms and Langmuir maximum adsorption capacities for powder and granular FHO are shown in Figure S4 and Table 1. As shown in Table 1, the adsorption capacity of FHO powder was 74.07 mg g^{-1} , which was higher than that of some commercial powder adsorbents (hydrotalcite, 60 mg g^{-1} ; aluminium oxide S, 34.57 mg g^{-1}) (Peleka & Deliyanni 2009). After granulation, the adsorption capacity and BET surface area of granular FHO were 56.18 mg g^{-1} and $177.0 \text{ m}^2 \text{ g}^{-1}$, which were 75.8% and 80.2% those of powder FHO, respectively.

Table 1 also lists the adsorption capacities of six granular metal oxide adsorbents prepared by impregnation, loading or extrusion in other studies. The adsorption capacities of three ferric oxide/hydroxide adsorbents prepared by impregnation or loading were 7.04, 10.60 and 50 mg g^{-1} at neutral pH (Blaney *et al.* 2007; Mezenner & Bensmaili 2009; Yue *et al.* 2010). The adsorption capacities of the other three adsorbents tested under acidic conditions were also below 50 mg g^{-1} (Tian *et al.* 2009; Yue *et al.* 2010; Aryal & Liakopoulou-Kyriakides 2011). Among all of the above adsorbents, the granular FHO showed the highest adsorption capacity at neutral pH. This may be attributed to its large powder loading (more than 99% per dry adsorbent) and high specific surface area ($177.0 \text{ m}^2 \text{ g}^{-1}$). Therefore, the relatively high phosphate adsorption capacity of granular FHO at neutral pH is a major advantage.

Regeneration and reuse

Regeneration and reuse ability is as important as high adsorption capability for an advanced adsorbent, and can significantly reduce running cost. Regeneration agents such as NaOH have been used for phosphate-loaded adsorbents composed of metals or metal oxides such as lanthanum/aluminum pillared montmorillonite (Tian *et al.* 2009), polymer-based nanosized hydrated ferric oxides (Pan *et al.* 2009), and Fe(III)-treated *Staphylococcus xylosus* biomass (Aryal & Liakopoulou-Kyriakides 2011). According to the adsorption mechanism, HPO_4^{2-} exchanges with surface OH groups, forming an inner sphere complex (Chitrakar *et al.* 2006). So, in the present study, the phosphate-loaded granular FHOs were regenerated by NaOH solutions of different concentrations. As shown in Figure S5 (available in the online version of this paper), the desorption efficiency increased from 75.2% to 85.7% with the increase of NaOH

Table 1 | Comparison of adsorption capacity of the powder and granular FHO with two commercial powder adsorbents and six granular metal oxide adsorbents for phosphate

Adsorbents	Powder/ Granule	Average size (mm)	BET surface area (m ² g ⁻¹)	Granulation method	Adsorption capacity, Q_m (mg g ⁻¹)	References
FHO	Powder	–	220.6	–	74.07 (pH 6.8–7.2) ^a	This study
Commercial hydrotalcite	Powder	0.015	44.0	–	60 (pH 6.5) ^a	Peleka & Deliyanni (2009)
Aluminium oxide S	Powder	0.05–0.20	200.0	–	34.57 (pH 6.5) ^a	Peleka & Deliyanni (2009)
Granular FHO	Granule	1.4–1.7	177.0	Drum granulation	56.18 (pH 6.8–7.2) ^a 5.24 (SV 2, pH 7.5–8.4) ^c	This study
Hybrid anion exchanger with hydrated ferric oxide	Granule	–	–	Impregnation	7.04 (pH 7–7.5) ^b	Blaney <i>et al.</i> (2007)
Iron hydroxide-eggshell waste	Granule	0.05–0.32	–	Loading	10.60 (pH 7.0) ^a	Mezenner & Bensmaili (2009)
Polymer-based nanosized hydrated ferric oxides	Granule	0.6–1.0	27.5	Loading	50 (pH 6.4–6.7) ^b	Pan <i>et al.</i> (2009)
Lanthanum/aluminum pillared montmorillonite	Granule	0.15	–	Loading	39.91 (La) ^a 31.28 (Al) ^a (pH 5.0)	Tian <i>et al.</i> (2009)
Fe(III)-treated <i>Staphylococcus xyloso</i> biomass	Granule	–	–	Loading	47.39 (pH 3.0) ^a	Aryal & Liakopoulou-Kyriakides (2011)
Red mud granular adsorbent	Granule	1.5	6.5	Extrusion	7.4 (pH 3.0) ^b	Yue <i>et al.</i> (2010)

^aCalculated from the adsorption isotherms by Langmuir equation, mg (PO₄³⁻)/g (Adsorbent).^bExperimental data of adsorption isotherms, mg (PO₄³⁻)/g (Adsorbent).^cCalculated from field column tests, mg (PO₄³⁻)/g (Adsorbent).

concentration from 0.5 to 2 mol l⁻¹. Further increase in NaOH concentration (up to 5 mol l⁻¹) did not significantly enhance the desorption efficiency of phosphate. Based on the desorption efficiency and the dosage of NaOH, the granular FHO regenerated by 2 mol l⁻¹ NaOH solution was selected, and 94.8% regeneration efficiency was achieved compared with the fresh sample. On the other hand, the PO₄³⁻ concentration in the used 2 mol l⁻¹ NaOH solution was 44.80 mg l⁻¹ (in the form of inorganic phosphate). And it may be possible to employ the regeneration solution in PO₄³⁻ recovery as hydroxyapatite (HAP) by calcite-seeded crystallization (Plant & House 2002). This suggested that the phosphate loaded on the granular FHO can be easily desorbed using a 2 mol l⁻¹ NaOH solution, and the material has good potential for use as an adsorbent for phosphate removal.

Field column test

Although the granular FHO showed efficiency for phosphate adsorption from synthetic water in batch tests, it is also necessary to evaluate its application potential for treatment of secondary effluents in field column tests. Therefore, the adsorption performance of granular FHO for treating actual ozonated secondary effluents from a municipal wastewater treatment plant was evaluated. The secondary effluents were subjected to treatment by ozonation and biologically activated carbon in a pilot-scale system, and then fed into columns at SV 2 h⁻¹ and 5 h⁻¹, respectively. During more than 2 months' operation, the column system kept running steadily without blocking, which exhibited high mechanical strength and durability of the granular FHO used in fixed-bed units. The removal performance of PO₄³⁻ by granular FHO from the secondary effluents are shown in Figure 2(a) and Table S2 (available in the online version of this paper). After 3,280 bed volumes (BV) and 8,200 BV water treatment, the accumulated adsorption capacities were 5.24 mg g⁻¹ and 12.82 mg g⁻¹ for SV 2 and SV 5, while the average removal percentages of PO₄³⁻ were 93.2% and 91.0%, respectively. Due to the low influent PO₄³⁻ concentration (0.21–1.40 mg l⁻¹) and limited operation time of the field column tests, the PO₄³⁻ adsorption capacity in the field column tests was lower than the Langmuir maximum adsorption capacities in batch tests. However, the results indicated that the high concentration of competing ions in secondary effluents had no influence on selective adsorption of granular FHO for low concentrations of phosphate. At the end of more than 2 months' operation, the concentrations of PO₄³⁻ in the effluents were still below 0.06 mg l⁻¹ for both operation velocities, which suggested that the adsorption capacity of

granular FHOs was not exhausted and the adsorbent could continue to be used. Besides the effective removal of phosphate, the turbidity and concentration of DOC and COD_{Mn} in the effluents were also 46, 21 and 16% lower than in the influents, indicating that the adsorbent not only had durability for operation in columns, but also could remove other contaminants. Thus, the granular FHO has excellent selective capacity and application potential for phosphate removal from secondary effluents.

The SEM image of a FHO granule taken from the column after more than 2 months' operation is shown in Figure 2(c). It is clearly shown that the granule had high porosity and an abundant pore structure with small anomalous particles. To determine whether the phosphate ions could diffuse into the granule and if the inner surface was available for the adsorption of phosphate in the field column test, the phosphorus element distribution inside the granular FHOs was investigated. SEM-EDX in mapping mode can confirm the distribution of the analyzed element on an adsorbent surface and has been employed successfully for the direct detection of distribution maps of As, F or Cu in granular adsorbents (Lai *et al.* 2000; Zhang *et al.* 2010; Zhao *et al.* 2012). Figure 2(d) illustrates the phosphorus distribution along the cross-section of the granular FHO after operation in the field column test. The phosphorus is represented as bright points, and can be seen to be spread over the cross-section of the granular FHO, suggesting that nearly all active sites on the inner surface of the granular FHO were available for the adsorption of phosphate.

CONCLUSIONS

An FHO powder was prepared at industrial-scale and successfully fabricated into granules by drum granulation using cross-linked PVA as the binder. The optimum granular FHO granules were fabricated at the binder/FHO powder ratio 0.6 and exhibited a higher adsorption capacity compared to other phosphate adsorbents under neutral or acidic conditions. The phosphate-loaded granular FHO could be regenerated by 2 mol l⁻¹ NaOH solution to achieve 94.8% regeneration efficiency. In a field column test for treatment of secondary effluents, the average removal percentage of PO₄³⁻ after more than 2 months was more than 90%, and almost all of the active sites inside the granular FHO were available for phosphate adsorption. The granular FHO shows excellent potential for use as an assist technology for advanced treatment of secondary effluents.

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