

Selective and efficient extraction of iron from water systems with a recyclable phytate-polyaniline hydrogel

Chaoyun Tang^{a, b, c}, Maricely Ramírez-Hernández^c, Belvin Thomas^b, Tewodros Asefa^{b, c, *}

^a Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, 7098 Liuxian Boulevard, Shenzhen, 518060, China

^b Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ, 08854, USA

^c Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, 98 Brett Road, Piscataway, NJ, 08854, USA

ARTICLE INFO

Handling Editor: Zhen Leng

Keywords:

Hydrogel
Phytate-polyaniline
Iron extraction
Water treatment
Adsorption

ABSTRACT

Iron is an essential element for various physiological processes in our body. However consuming excess iron can affect our health. Thus, any excess iron that may be present in domestic water sources needs to be removed to make such water useable in the community. In this work, phytate-polyaniline hydrogel is synthesized with a simple method and then shown to selectively and efficiently adsorb and extract Fe ions (both in 2+ and 3+ forms) from aqueous solutions. The hydrogel can adsorb 99.94% of Fe from an aqueous solution containing 29.08 mg/L of Fe³⁺ ions at pH = 7, and its maximum adsorption capacity for Fe is 0.841 mmol/g. Moreover, the hydrogel can do so even in the presence of many other common metal ions in water and in a wide pH range. In addition, the Fe adsorbed in the hydrogel can easily be removed via a simple procedure, and the hydrogel can be recycled and reused multiple times to remove Fe from aqueous solutions with nearly similar performances as the original material.

1. Introduction

Iron is the fourth most abundant element on earth. Iron also accounts for over 90% of global metal production and is the most widely used metal for industrial, commercial, and household purposes (Khadse et al., 2015; Mao et al., 2021). As a result, a lot of iron makes it into many water systems worldwide by leaching from iron-bearing rocks, soil, minerals, and iron-based waste materials (Ma et al., 2018). Furthermore, due to its non-degradability and environmental persistence, iron can remain or accumulate in water systems beyond acceptable limits for an extended length of time. According to the World Health Organization (WHO) standard, the permissible limit of iron in drinking water is 0.3 mg/L; however, elevated concentrations of iron in fresh groundwater in the range of 0.5–50 mg/L in some parts of the world (Ramakrishnaiah et al., 2009; Maneechakr and Karnjanakom, 2017; Wang et al., 2021a; Prakash and Somashekar, 2006; Wołowiec et al., 2019) and up to 80 mg/L in many developing countries (Chaturvedi and Dave, 2012; Chakraborti et al., 2011) are commonly found.

Although the human body needs some iron for various metabolic processes, including oxygen transport, deoxyribonucleic acid (DNA) synthesis, and electron transport (Abbaspour et al., 2014), the continu-

ous consumption of excessive iron, if present in drinking water sources, can cause various health issues, including eye disorder, cancer, skin cell damage, heart diseases, diabetes, central nervous system disorder, infertility, and hematopoiesis (Lynch et al., 2018). Other problems associated with excessive iron in domestic indoor and outdoor water supplies are metallic taste, odor, discoloration, and turbidity. Hence, the treatment of water possessing excess iron is essential to produce a safe and clean supply of water for household consumption (Das et al., 2007; Abinandan et al., 2020).

Various methods involving oxidation-precipitation-filtration processes, adsorption using calcium carbonate-based minerals, separation through filtration systems, and electrocoagulation have been developed to remove excess iron present in various water systems (Zhang et al., 2018; Khatri et al., 2017; Tian et al., 2022). However, many of these existing methods have limited capabilities in removing small concentrations of iron from aqueous solutions. Some of them also exhibit a low efficiency to remove iron, an insufficient durability, inadaptability to different pH's, and toxicity (Alimohammadi et al., 2017). Thus, new methods, especially involving nanomembranes (Le and Nunes, 2016; Peng et al., 2015; Lu et al., 2021a, 2021b; Zhang et al., 2021), nanoparticles (Qu et al., 2008), nanotubes (Alimohammadi et al., 2017), and

* Corresponding author. Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ, 08854, USA.

E-mail address: tasefa@chem.rutgers.edu (T. Asefa).

<https://doi.org/10.1016/j.jclepro.2022.135006>

Received 22 June 2022; Received in revised form 17 October 2022; Accepted 28 October 2022
0959-6526/© 20XX

nanocomposites (Nandeshwar et al., 2016; Li et al., 2021), are currently being explored to remove iron more effectively from water systems to acceptable levels. Methods such as dielectric barrier discharge plasma and ozone oxidation were also recently reported to remove metal ions, such as iron, from tap water (Khanom and Hayashi, 2021; Nasrollahzadeh et al., 2021). In other reports, nanoporous membranes made from graphene and carbon nanomaterials were shown to remove various pollutants from water and other systems via various adsorbate-adsorbate interactions (Han et al., 2013; Yap et al., 2021; Muthusaravanan et al., 2018; Yin et al., 2020; Zhu et al., 2020). The practical application of such nanomaterials for water treatment is, however, limited by their inherent susceptibility to aggregate and thereby lose their adsorption properties (Saleem and Zaidi, 2020). Moreover, nanomaterials are inherently difficult to remove or recover from aqueous systems after their use (Alonso et al., 2013). Besides, the possible toxicity associated with some of the nanomaterials themselves cannot be ignored. These issues thus beg for environmentally friendly materials that are easier to use as adsorbents to separate iron from water systems (Luo et al., 2021).

Phytate, which is a major form of inorganic phosphate ester in plant seeds, has an excellent binding affinity to iron (Bretti et al., 2012; Marolt et al., 2020; Yu et al., 2012). Thus, by coupling phytate with polymers, such as polyaniline (PANI), it is possible to make polymers possessing the metal-binding properties of phytate (Kim et al., 2017). Besides, phytate can tailor the structural and surface properties of the polymer; for example, it can help the polymer behave as a hydrogel and make it suitable as an adsorbent in aqueous media (Pan et al., 2012; Hu et al., 2019). However, the potential application of such polymer hydrogels for adsorption and extraction of Fe, especially for water treatment, has not been demonstrated before.

We show here, for the first time, that phytate-bound polyaniline hydrogel synthesized by a simple synthetic route can effectively remove iron ions (in form of both Fe^{2+} and Fe^{3+}) from aqueous solutions in a wide pH range. The hydrogel's unique, strong affinity to iron ions further enables it to selectively remove iron ions even in the presence of other metal ions that are common in water systems. In other words, the hydrogel has a much better affinity to iron ions than to other metal ions, and thus adsorbs the former much more than other ions even when they co-exist in solutions. Furthermore, the iron ions adsorbed by the hydrogel can easily be removed via a simple treatment, and the hydrogel can be fully recycled and reused as an adsorbent multiple times without losing its adsorption performance to remove iron.

2. Experimental

2.1. Chemicals

All chemicals and reagents used for the experiments in this work were purchased from Sigma-Aldrich. They were all used as received and without further purification.

2.2. Synthesis of hydrogel

Phytate-polyaniline-based hydrogel (also named Hgel) was synthesized via a one-step template-free synthetic method as described elsewhere (Pan et al., 2012), with a minor modification. In a typical synthesis, aniline (0.5 mL) and phytic acid solution (1 mL, 50% wt./wt. in water) were dissolved in deionized (DI) water (2 mL). This ratio was chosen because it was optimal to produce the hydrogel (Pan et al., 2012). After ultrasonication for 30 min, a homogenous solution was obtained. Ammonium persulfate (0.286 g) was dissolved in DI water (1 mL) in a separate flask to obtain a second solution. The second solution was poured into the first solution, and the mixture was cooled quickly to ~ 4 °C in a fridge. The solution was then kept there for 24 h to let the polymerization and cross-linking reactions involving aniline and phy-

tate occur. The resulting phytate-polyaniline hydrogel was washed with DI water five times under vacuum filtration to remove any residual acid or reaction by-products and then dried in an oven at 80 °C. Finally, a black-green colored powder product (phytate-polyaniline) was obtained. Note that the resulting dried material(s) are called hydrogel as they can take up a lot of water, besides the Fe ions, and become a gel again. Such a definition has also been previously used for cross-linked polymers in dried powder form as long as they can adsorb lots of water and swell when kept in aqueous solutions.

2.3. Adsorption of iron and other common metal ions by phytate-polyaniline hydrogel

First, the adsorption properties of phytate-polyaniline toward several common metal ions in water systems were studied. For this, solutions containing different types of metal nitrates (0.4 mmol in each case), namely, iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc(II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper(II) nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese(II) nitrate hexahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), or magnesium(II) nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), were prepared by dissolving each salt in DI water (6 mL). Into each of these aqueous solutions, as-synthesized phytate-polyaniline (100 mg) was dropped, and the mixtures were shaken for a brief period. The mixtures were then kept under static condition at room temperature for 6 h, and then filtered. The solid materials were washed with DI water three times and then ethanol three times under vacuum filtration to remove any residual ions. The residues were then dried in an oven at 80 °C overnight. The products were denoted as Hgel + M_x , where M represents Fe, Co, Ni, Zn, Cu, Mn, and Mg, and x stands for the amount of metal ions in millimole used in each solution for the adsorption studies.

2.4. Detailed investigation of the adsorption properties of the hydrogel toward iron ions

To investigate the adsorption properties of phytate-polyaniline hydrogel toward Fe in its 2+ oxidation state, a solution of iron(II) nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (0.4 mmol in 6 mL DI water) was prepared and mixed with the hydrogel with the same procedure as what was applied for the other metal ions, including $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, above.

The adsorption properties of phytate-polyaniline hydrogel toward different concentrations of Fe^{3+} ions in aqueous solutions were investigated by preparing solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ containing 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, 3.0, or 4.0 mmol in 6 mL DI water. These solutions correspond to initial concentrations of 4.2, 8.3, 16.7, 33.3, 66.7, 133.3, 200, 266.7, 333.3, 500, and 666.7 $\mu\text{mol/mL}$ (or 233, 465, 931, 1862, 3723, 7446, 11169, 14892, 18615, 27922, and 37230 mg/L), respectively. Each solution was mixed with the hydrogel using the same procedure as above. The final concentrations of Fe^{3+} ions in the solutions after the adsorption process (6 h) were determined based on their intensities at the absorption maximum at 510 nm corresponding to Fe^{3+} ions in the filtrate, which were measured with a UV-Vis spectrophotometer (Lambda 850 UV/Vis, PerkinElmer).

To investigate the effect of pH of the solution on the absorption properties of the hydrogel toward Fe ions, aqueous solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.025 mmol in 6 mL DI water or ca. 4.17 mmol/L) at different pH's (namely, 1, 2, 3, 4, 5, 6, 7, and 8) were prepared and used for the experiments with otherwise the same procedure.

2.5. Investigation of the recyclability of the hydrogel for extraction of Fe ions from solutions

2.5.1. Removal of iron from hydrogel

Dried phytate-polyaniline (100 mg) was dropped into an aqueous solution containing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.4 mmol) in DI water (6 mL), and the mixture was shaken briefly. After keeping it under static condition at room temperature for 6 h, the mixture was filtered. The solid product on the filter paper was washed with DI water three times, followed by ethanol three times, to remove any residual Fe^{3+} ions. This was followed by washing the material over the filter paper under vacuum filtration with an aqueous NaOH solution (1 M, 10 mL), then with DI water (10 mL), and finally with an aqueous HCl solution (1 M, 10 mL), three times in each case. Finally, the solid material was washed with DI water and dried in an oven at 80 °C overnight. This gave a hydrogel denoted as Hgel + $\text{Fe}_{0.4}$ -Re, where "Re" represents the removal of iron from the hydrogel.

2.5.2. Recovery of hydrogel

First, Hgel + $\text{Fe}_{0.4}$ -Re (100 mg) was taken and dropped into DI water (6 mL). Then, phytic acid solution (10 μL , 50% wt./wt. in water) was added into the solution. After shaking it well, the mixture was kept under static condition at room temperature for one day/6 h. It was then filtered, and the solid product was rinsed under vacuum filtration with DI water three times, followed by ethanol three times, to remove any residual phytic acid on it. Finally, the material was dried in an oven at 80 °C overnight, and the product was denoted as Hgel + $\text{Fe}_{0.4}$ -RC, where "RC" means recycled (Re-Cycled).

2.5.3. Adsorption of iron with the recovered hydrogel

Hgel + $\text{Fe}_{0.4}$ -RC (100 mg) was dropped into an aqueous solution prepared from $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.4 mmol) and DI water (6 mL). The mixture was shaken well and kept under static condition at room temperature for one day. It was then filtered, and the solid product was washed with DI water three times, followed by ethanol three times, to remove any residual ions on it. The solid material was dried in an oven at 80 °C overnight. The resulting material was named Hgel + $\text{Fe}_{0.4}$ -RC + $\text{Fe}_{0.4}$.

To evaluate the recyclability of the hydrogel, the above steps (i.e., the removal of the adsorbed Fe^{3+} ions, the recovery of the hydrogel, and the reloading of Fe^{3+} ions on the recovered hydrogel) were repeated three times using the same procedure. The Fe-reloaded hydrogels successively were named as "-RL1st", "-RL2nd", and "-RL3rd".

3. Results and discussions

3.1. Synthesis and characterization of phytate-polyaniline hydrogel

Phytate-polyaniline hydrogel, which has a strong ability to efficiently adsorb Fe^{2+} and Fe^{3+} ions, is synthesized by following a procedure schematically illustrated in Scheme 1. Aniline is polymerized in an aqueous solution containing phytic acid using sodium persulfate as a polymerization initiating agent. In the synthesis, the phytate ions formed from the deprotonation of phytic acid cross-links polyaniline chains via both electrostatic and hydrogen-bonding interactions. The process finally produces phytate-polyaniline hydrogel (which is also called Hgel). As illustrated in Scheme 1, besides serving as a cross-linker for polyaniline (polymer) chains, phytate has a second important function: It serve as a chelating agent or ligand for the Fe ions helping the hydrogel to adsorb these metal ions effectively from solutions, due to its strong binding affinity for Fe ions than to other metal ions.

The hydrogel is then characterized by various methods, and its adsorption properties toward various metal ions, mainly Fe, in solution are studied. Its powder X-ray diffraction (XRD) pattern shows an amorphous structure (Fig. 1a). The thermogravimetric analysis (TGA) curve

of the hydrogel (Fig. 1b) shows that the polymer decomposes in air almost completely by around 650 °C. N_2 adsorption/desorption measurements show that the hydrogel has largely microporous and microporous structures a Brunauer-Emmett-Teller (BET) surface area of 38 m^2/g . Field emission scanning electron microscope (FESEM) images (Fig. 1d and e) reveal that the polymer has coral-like dendritic/branched nanofibers with visible macropores and micropores in its structures. Contact angle measurements using water as a probe liquid on the hydrogel (Fig. 1f) show that the drops of water placed on it get quickly sucked in, indicating its strong hydrophilicity. The presence of phytate groups in the polymer is evidenced with elemental mapping of phosphorus atoms with energy-dispersive X-ray spectroscopy (EDS) in a transmission electron microscope (TEM) (Fig. 1g).

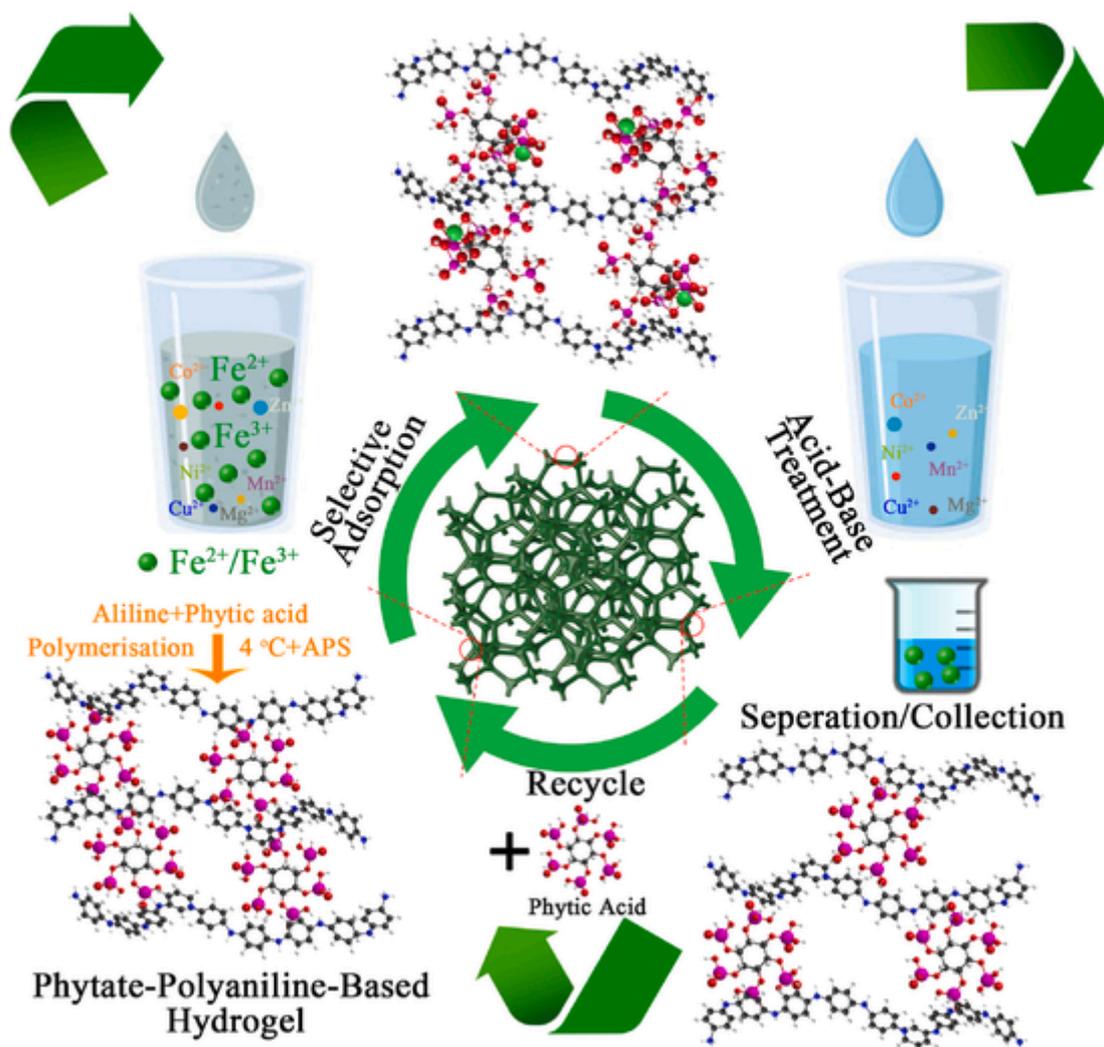
3.2. Adsorption of Fe and other ions by phytate-polyaniline hydrogel

The ability of the phytate-polyaniline hydrogel to adsorb various metal ions in aqueous solutions under oxidic condition (which means, in the presence of dissolved oxygen) is then tested. The oxidic condition is applied in the adsorption experiments as it mimics real conditions. Metals such as Fe^{2+} ions can undergo oxidation in many real conditions where there is (dissolved) oxygen. This may in turn affect the adsorption properties of the hydrogel toward the metal ions. It turns out that the Fe^{2+} ions tested for the hydrogel's adsorption remains unchanged even under oxidic (real) conditions, as confirmed with Fe^{2+} -specific test we performed using the FerroZine® assay. As shown in Fig. S1, first, the hydrogel is immersed in a series of solutions containing several common metal ions in water systems, namely, Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Mn^{2+} , and Mg^{2+} ions in deionized (DI) water, containing the same concentration of metal ion and ionic strength. After 6 h, thoroughly washing the materials with DI water and then ethanol under vacuum filtration, dried in an oven at 80 °C overnight before being analyzed. The resulting phytate-polyaniline materials containing metals, (i.e., Hgel + M_x , where M represents Fe, Co, Ni, Zn, Cu, Mn, or Mg, and x is the amount of metal ions in millimole used in the solutions) are characterized.

The powder X-ray diffraction (XRD) patterns of all dried metal-loaded hydrogels are like that of pristine hydrogel (see Fig. S2). Notably, they all show no crystalline peaks. These results suggest that the hydrogel largely maintains its overall structures after adsorbing metals and that the metal ions adsorbed in it do not form crystallites. This is true even for those Hgel + M_x hydrogels obtained by stirring Hgel with a high concentrations of metal ions or those containing the largest amount of Fe^{3+} ions. However, as the species forming from the metals such as Fe can also form poorly crystalline metal oxides, hydroxides, or other phases, the absence of XRD peaks does not necessarily rule out the presence of such materials.

Thermogravimetric analysis (TGA) of the metal-loaded materials is performed in an air atmosphere, and the results are displayed in Fig. 2a. The TGA curve of Hgel + $\text{Fe}_{0.4}$ shows that the weight of the residue of this metal-doped hydrogel at 800 °C is 20.63%. However, the TGA curves of pristine hydrogel (Hgel-Pristine) and the hydrogels containing other metal ions (Hgel + M_x) show that they all have residues with weight percent of ca. 0.002%. Note that this weight percent corresponds to the mass of non-decomposable, non-gaseous material (i.e., Fe species and/or carbon). The results thus show that the amount for Hgel + $\text{Fe}_{0.4}$ is much larger than those of Hgel-Pristine Hgel + M_x . These results indicate that Hgel hydrogel has a much greater preference to adsorb Fe ions to many other metal ions.

For further comparison, two more hydrogels are prepared, one by mixing Hgel with all metal ions together in the same solution and another by mixing Hgel with all metal ions except Fe ions. The two hydrogels are analyzed by TGA (Fig. S3). While the residue of the former at 800 °C has a weight of 26.05%, that of the latter has a weight of only 1.39%. This substantial difference in the weights of residue of these two



Scheme 1. A schematic of the synthetic procedure leading to phytate-polyaniline hydrogel (Hgel) and its selective and efficient adsorption of Fe^{2+} and Fe^{3+} ions from aqueous solutions are shown. The recyclability and reuse of the hydrogel as an adsorbent in multiple cycles for the treatment of water containing excessive iron ions is also illustrated.

materials is obviously caused by Fe, which is also confirmed by ICP-OES analysis (see below). So, this result clearly corroborates the remarkable ability of the Hgel hydrogel to adsorb and extract Fe from aqueous solutions even in the presence of many other common metal ions.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used to determine the exact amounts of each metal adsorbed by the hydrogels. The results, along with the final weights of the residues of the hydrogels in the TGA curves at 800 °C, are provided in Fig. 2. The values obtained by ICP-OES are expectedly much lower than the weights of the residues of each material at 800 °C because the residues of the materials in the TGA involve the transformation of metals to metal oxides as well as the formation of carbon black via the carbonization of the polymer, especially in the presence of metals (Zhang et al., 2014; Wang et al., 2016; Yan et al., 2002). The Fourier transform infrared (FTIR) spectra of all metal-loaded hydrogels (Fig. S4) largely show similar bands to that of pristine hydrogel, except for the peak at ca. 1384 cm^{-1} in the former. The peak at ca. 1384 cm^{-1} relates to O=P–O–M metal-polymer conjugate bonds, implying the phytate is the main site through which the metal ions bind or get adsorbed (Tang et al., 2022; Wang et al., 2021b).

The TGA curves of hydrogels loaded with Fe^{2+} or Fe^{3+} ions (Fig. S5) look similar, indicating that phytate-polyaniline hydrogel appears to possess similar adsorption properties toward both types of Fe ions. In other words, this hydrogel is very effective to adsorb and remove iron

in both of its oxidation forms from aqueous solutions. For convenience, all discussions hereafter thus focus only on Fe^{3+} ions, unless mentioned otherwise. It is worth adding that even if the Fe^{2+} ions tested in the experiments are performed in oxidic condition, they remain not oxidized, as confirmed with Fe^{2+} -specific test we performed using the FerroZine® assay.

To investigate the adsorption capacity of the hydrogels for Fe ions in a wide concentration range, solutions of Fe^{3+} ions with concentrations in the range of 3.125 μmol –4 mmol of Fe^{3+} in 6 mL are prepared and used for the test in two different ranges. The first range tested is between 0.025 and 4.0 mmol in 6 mL, and the TGA curves of the hydrogels (Fig. 3) show that the ones mixed with solutions with larger amounts of Fe ions give higher amounts of residues at 800 °C. However, after reaching a maximum weight of 24.85%, which is for the hydrogel stirred with a solution of 1.6 mmol Fe^{3+} in 6 mL DI water, the final weights of the residues start to decrease even if the amount of Fe in the solution is increased.

Meanwhile, the ICP-OES results show that the amount of Fe in the hydrogels increases until it reaches a maximum value of 4.26 wt%, which corresponds to the hydrogel mixed with a solution of 0.8 mmol Fe^{3+} in 6 mL DI water. Fig. S6 also shows that the amount of Fe^{3+} ions adsorbed in the hydrogel increases at first, due to the increased concentration gradient (Gongming et al., 2014). It then reaches a maximum value (0.841 mmol/g) when the concentration of Fe^{3+} ions is increased

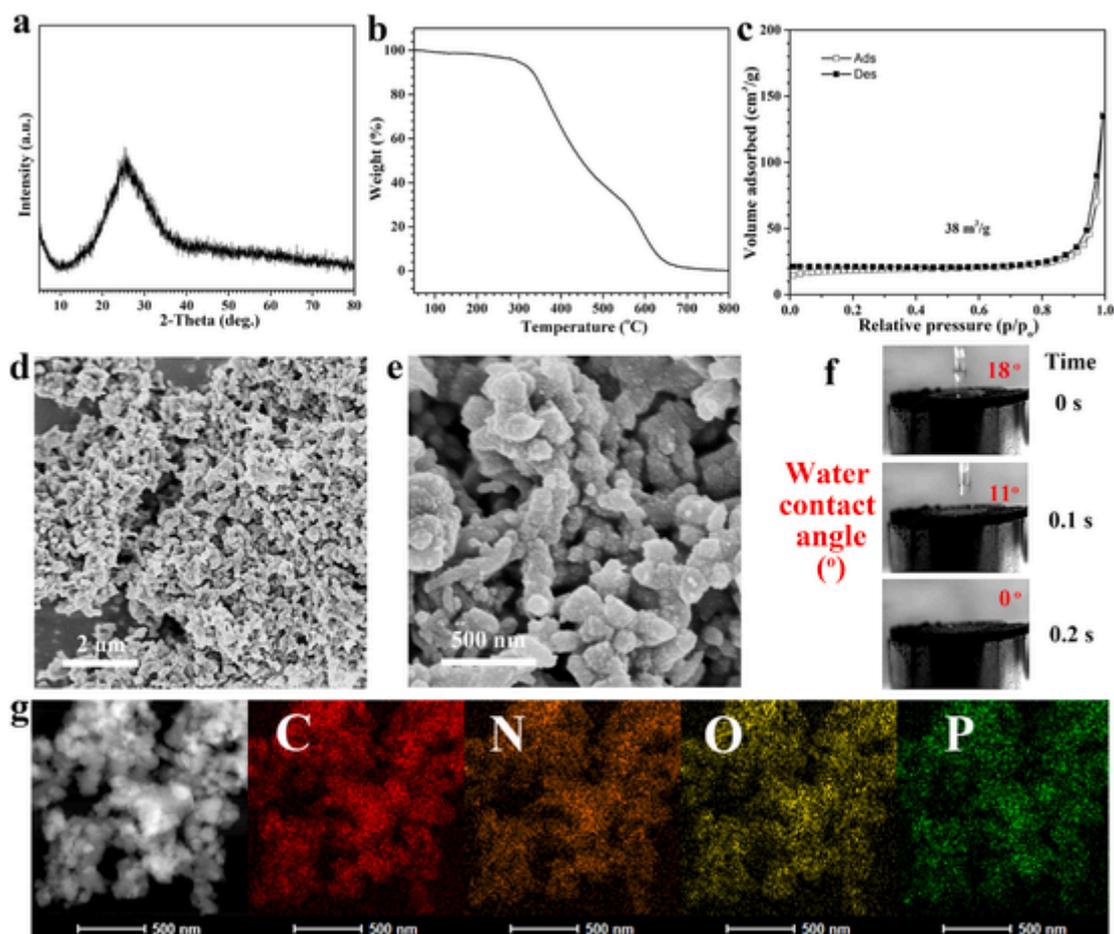


Fig. 1. (a) Powder X-ray diffraction (XRD) pattern, (b) thermogravimetric analysis (TGA) curve, (c) N_2 gas adsorption-desorption isotherm, (d,e) field emission scanning electron microscopy (FESEM) images, (f) contact-angle measurement using water drops, and (g) TEM and elemental mapping images obtained with energy-dispersive X-ray spectroscopy in TEM of phytate-polyaniline hydrogel (Hgel).

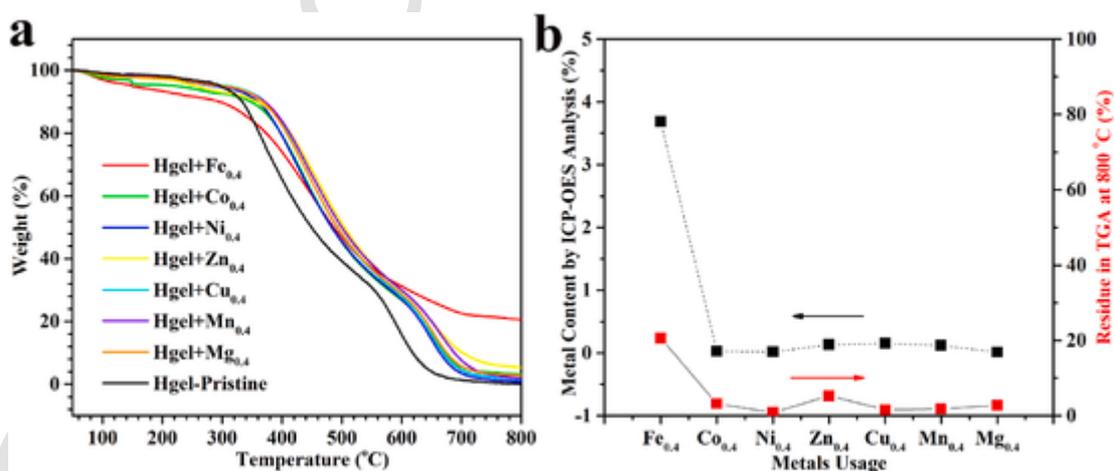


Fig. 2. (a) TGA curves of hydrogels prepared by mixing phytate-polyaniline with solutions of different metal ions (0.4 mmol in 6 mL DI water in each case), and then separating and drying them, are shown. (b) The final weights of the residues of the materials at 800 °C on TGA curves and the amounts of metals in them, as determined by ICP-OES, are displayed.

to 0.8 mmol in 6 mL DI water. Thereafter though, the adsorption of Fe^{3+} ions in the hydrogel decreases, indicating that excess amount of Fe^{3+} ions in solution makes the hydrogel's ability to adsorb the metal ions decrease. Nevertheless, this drop in the adsorption capacity of the hydrogel for Fe, when the amount of Fe ions increases from 3.0 to 4.0 mmol in 6 mL DI water, is very small, i.e., from 0.697 to

0.691 mmol/g. And this is only because the hydrogel gets saturated by Fe species more when the amount of Fe^{3+} in the solution is increased.

The second range of concentrations of Fe^{3+} ions used for the studies is 29 to 3723 mg/L (which correspond to 3.125 μ mol to 0.4 mmol of Fe^{3+} ions in 6 mL). This entails an important range especially given that the concentrations of Fe ions in water systems that are subjected to treatment are usually < 1000 mg/L (Khatri et al., 2017). The digital im-

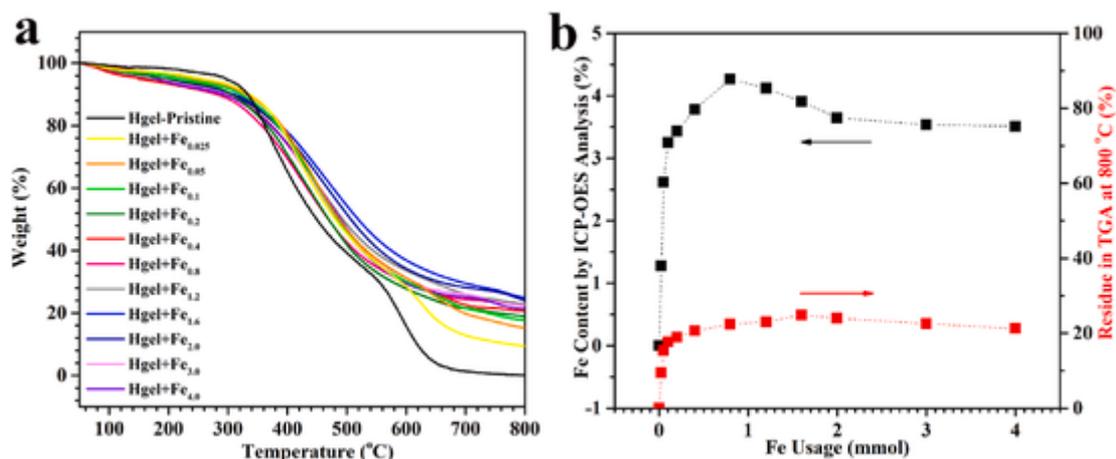


Fig. 3. (a) TGA curves of hydrogels prepared by mixing phytate-polyaniline with different concentrations of Fe^{3+} ions for 6 h, and then separating, washing, and drying them. (b) The final weights of residues of the different Fe-loaded hydrogels at 800 °C, and the amounts of Fe in them, as determined by ICP-OES, are depicted.

ages of solutions containing different concentrations of Fe^{3+} ions before and after being mixed with the hydrogel are provided in Fig. 4a. And the efficiency of the hydrogel to remove Fe from the solutions is provided in Fig. 4b. Notably, the hydrogel's efficiency to remove Fe from a solution with an initial concentration of Fe^{3+} ions of 29.08 mg/L is found to be 99.94%. It is evident that the percentage of Fe that the hydrogel removes expectedly decreases as the initial concentration of Fe in the solution is increased, because the polymer gets saturated more quickly.

As pH is one of the most critical parameters that can affect the adsorption of metal ions from solutions, the effects of the initial pH of the solution in the range of 1–8 on the phytate-polyaniline-based hydrogel's ability to remove Fe^{3+} ions from aqueous solutions are then studied (Fig. S7). The initial concentration of Fe^{3+} ions is kept as 232.69 mg/L, which is chosen based on a previous report (Khatri et al., 2017). The pH is adjusted with 0.1 M HNO_3 , 0.1 M NaOH, and 0.1 M NH_4OH solutions, and without using a buffer. And the adjustment is done after addition of Fe^{3+} ions into the solution, and higher pH's, such as pH 11, are not used to avoid the formation of precipitates. Graphs of final concentrations of Fe in the solutions in mg/L or the efficiency of the hydrogel to remove Fe ions versus the initial pH of the solutions are shown in Fig. S7. When the initial pH of the solution is between 5 and 8, the efficiency

of the hydrogel to remove Fe is >99%. When the initial pH of the solution is set at 3, the hydrogel's adsorption capacity is dropped slightly (to 98–99%), which suggests that lower pH slightly reduces the hydrogel's ability to remove Fe ions. Nevertheless, phytate-polyaniline hydrogel still has a very high adsorption capacity for Fe (>98%) in a wide pH range, making it a unique adsorbent for Fe in solutions compared with many adsorbents previously reported for Fe ions (see Table S1).

3.3. Recyclability of phytate-polyaniline hydrogel as an adsorbent

Finally, we have developed a straightforward method to recycle the hydrogel and reuse it as an adsorbent to extract Fe in water systems many times. The method involves washing the Fe-loaded hydrogel with an alkaline solution, followed by an acidic solution, while the sample is on a filter paper. The XRD pattern of the Fe-loaded hydrogel washed with NaOH solution (1 M) under vacuum filtration (Fig. 5a) shows peaks that are typical of $\text{Fe}(\text{OH})_3$ (JCPDS card No. 22–0346) (Huo et al., 2019; Mizukoshi et al., 2009). This indicates that the Fe ions in the hydrogel transform to $\text{Fe}(\text{OH})_3$ after being treated with an alkaline solution. After the hydrogel is subsequently washed with an aqueous HCl solution (1 M) and dried, though, its XRD pattern no longer shows the XRD peaks associated with $\text{Fe}(\text{OH})_3$. The TGA curve of the base- and

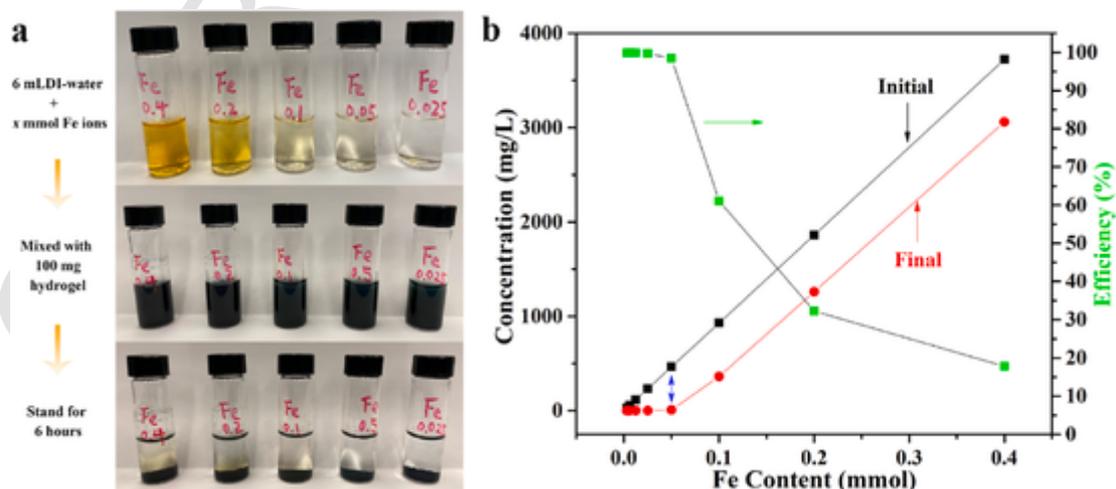


Fig. 4. (a) Digital images of different concentrations of Fe^{3+} ions in aqueous solutions and their mixtures with phytate-polyaniline hydrogel (100 mg), right after mixing and after keeping the mixtures under static condition for 6 h, are shown. In the latter case, the solutions are visibly clearer indicating the removal of the Fe^{3+} ions from the solutions by the hydrogel. (b) The corresponding initial and final concentrations of Fe^{3+} ions in the solutions (in mg/L) before and after being mixed with the hydrogel. The efficiency of the hydrogel to remove Fe^{3+} ions from the solutions with different initial concentrations, which is also given in mmol in 6 mL solution as shown in (a), are also displayed.

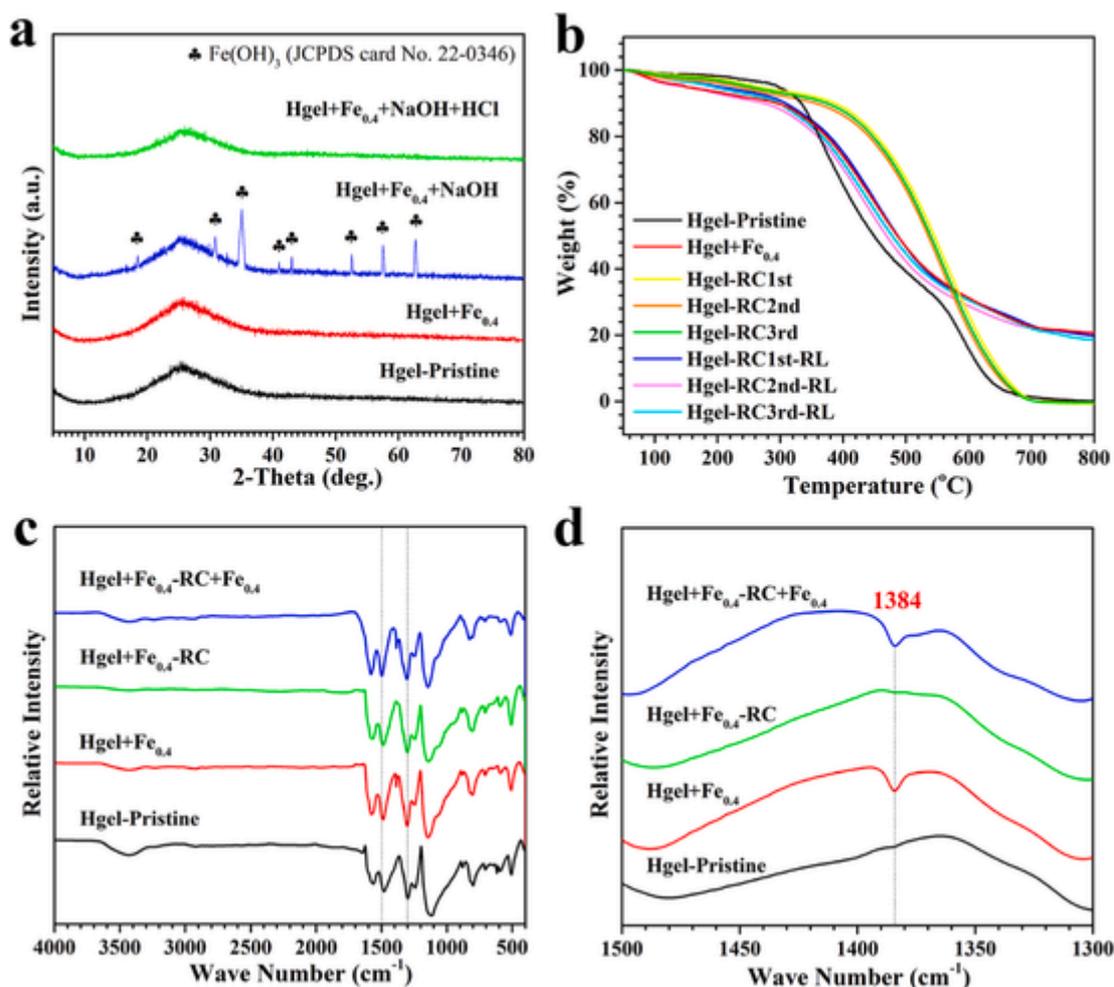


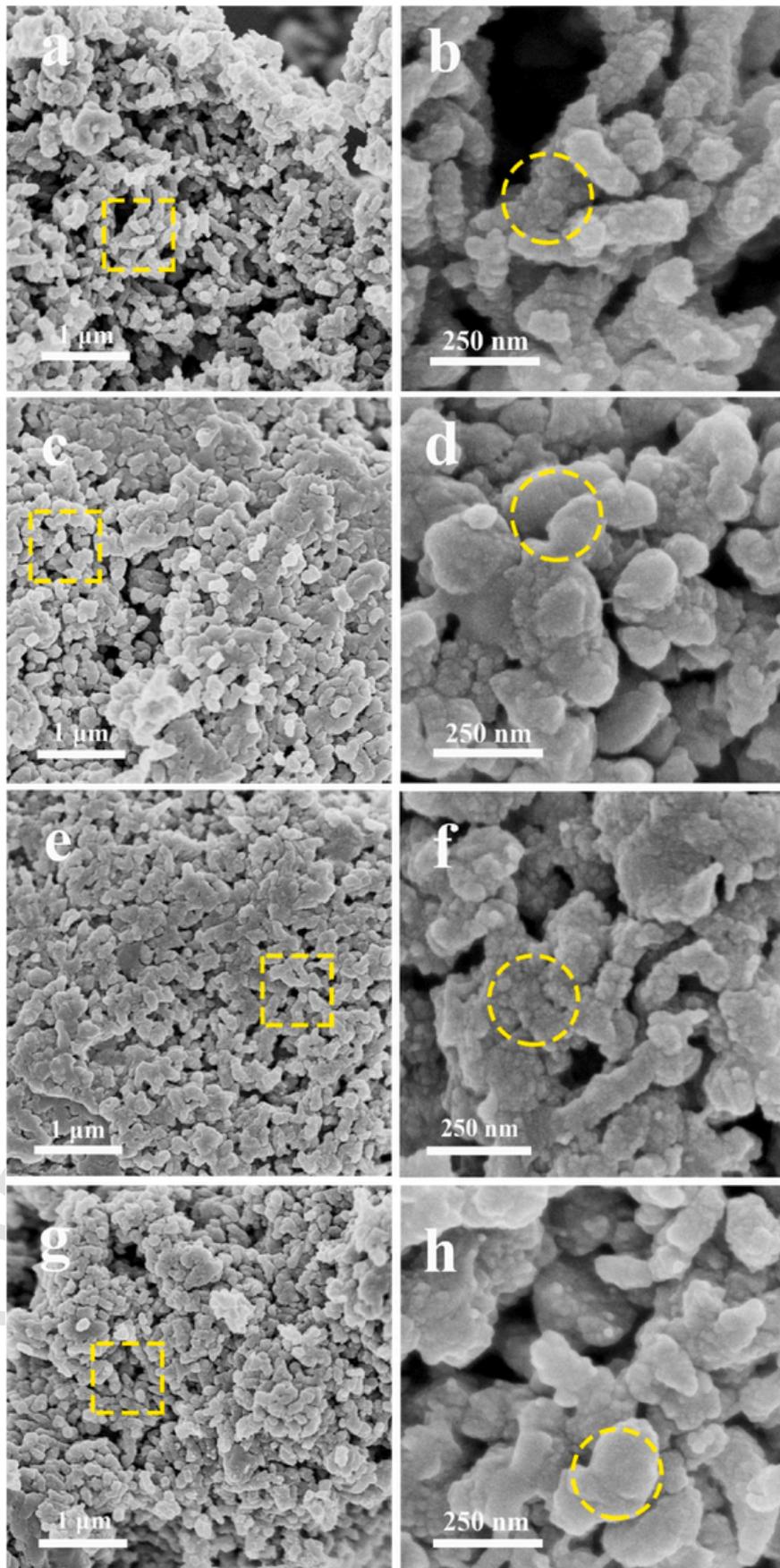
Fig. 5. (a) XRD patterns of phytate-polyaniline hydrogel mixed with 0.4 mmol Fe³⁺ ions in 6 mL DI water, before and after successive treatments with NaOH and HCl solutions. (b) TGA curves of phytate-polyaniline hydrogel after three cycles of adsorption of Fe³⁺ ions and then washing. Note that, in the names of the hydrogels, “RC” represents the recycled hydrogel, and RL represents the Fe-“reloaded” hydrogel in the names of the materials. (c) FTIR spectra of phytate-polyaniline hydrogel after recycling and re-adsorbing Fe³⁺ ions. (d) FTIR spectrum showing only the region between 1300 and 1500 cm⁻¹.

then acid-treated hydrogel in air atmosphere (Fig. 5b) shows a final residue at 800 °C of only 0.01 wt%. These results indicate that the Fe adsorbed in the hydrogel can be removed by converting it to Fe(OH)₃ with an alkaline solution, and then dissolving and washing off the Fe(OH)₃ with an acidic solution via the following reactions: Fe³⁺ (aq) + OH⁻ → Fe(OH)₃(s) and Fe(OH)₃(s) + 3H⁺(aq) → Fe³⁺ (aq) + 3H₂O(l). This is corroborated by the disappearance of the peak at ca. 1384 cm⁻¹ in FTIR spectra of the acid-washed hydrogel, the peak corresponding to Fe–O bonds that is seen in the FTIR spectrum of the original Fe-loaded hydrogel (Fig. 5c and d) (Hernández-Alvarado et al., 2016). ICP-OES analysis of the recycled hydrogel recovered using a filter paper also shows only 0.049 wt% Fe, which is small, further confirming the near-complete removal of Fe from the hydrogel with such a simple washing procedure involving an alkaline solution, followed by an acidic solution.

The recycled hydrogel is mixed with Fe³⁺ ions by stirring it with a fresh solution containing 0.4 mmol Fe³⁺ ions in 6 mL DI water. The TGA curve of the resulting material gives a residue at 800 °C with weight of 20.95 wt%. The FTIR spectrum of the material shows, once again, the peak at ca. 1384 cm⁻¹ corresponding to Fe-polymer conjugate. ICP-OES analysis indicates that Fe adsorbed by the recycled hydrogel is 4.24 wt%, which is similar to the amount adsorbed by the same hydrogel in the first cycle. Even after recycling it three times with the same procedure, the hydrogel shows a similar TGA curve to the other ones (Fig. 5b). Similarly, ICP-OES analysis of the hydrogel that is

recycled and reloaded with Fe three times shows that it possesses 4.19 wt% Fe. These results collectively indicate that the recycled hydrogel has similar structural and compositional features and adsorption properties as the original one. The results also demonstrate the recovery and recyclability of the hydrogel, along with its unique adsorption properties for Fe.

The hydrogels recovered after a few cycles are characterized further by FESEM to investigate the possible changes in their structures and morphologies during the recycling process (Fig. 6). While the pristine hydrogel shows coral-like micro-structures with some nanoparticles on its surfaces, the one treated with a solution of 0.4 mmol Fe³⁺ ions in 6 mL DI water shows expanded structures and surfaces with less visible nanoparticles. After subsequent recycling, the structures shrink and more nanoparticles are visible on the surfaces of the hydrogel. After re-adsorption with Fe³⁺ ions in the second cycle, the hydrogel shows similar structures as the first case. Overall, phytate-polyaniline hydrogel largely maintains its structural features during the recycling process, after it adsorbs and extracts Fe³⁺ ions from aqueous solutions and then recovered and recycled using via filtration over a filter paper. Even after three cycles, the hydrogel still retains the typical microstructures of the pristine one (Fig. S8), further proving its excellent recyclability.



◀ **Fig. 6.** FESEM images of phytate-polyaniline hydrogel before and after being subjected to multiple recycling steps as an adsorbent: (a,b) Hgel-pristine, (c,d) Hgel + Fe_{0.4}, (e,f) Hgel-RC, and (g,h) Hgel-RC + Fe_{0.4}. The yellow circled areas in b and f show some nanoparticles.

4. Conclusions

In conclusion, phytate-polyaniline-based hydrogel is synthesized by a simple method and demonstrated to efficiently adsorb and extract both Fe²⁺ and Fe³⁺ ions from aqueous solutions. Furthermore, the hydrogel could do so selectively to iron ions even if various other common metal ions were co-present in the solutions. The hydrogel could adsorb as high as >99.94% Fe(III) ions from solutions, and the adsorption capacity of the hydrogel for Fe was found to be at least 0.841 mmol/g. A simple method has also been developed to recycle the hydrogel and reuse it many times as an adsorbent for Fe ions in solutions. Even after three cycles, the recovered hydrogel could adsorb Fe ions as effectively and selectively as the original one. The high adsorption capacity, recyclability, and selectivity to iron ions would all make this phytate-polyaniline hydrogel a promising cost-effective adsorbent for treating water sources containing excess Fe ions.

CRedit authorship contribution statement

Chaoyun Tang: co-conceived the idea, did most of the experiments, and wrote the draft manuscript and revised the final manuscript. **Maricely Ramírez-Hernández:** contributed to some of the experimental works, and, helped with analysis of some of the sam-

Supplementary Material

Detailed descriptions of instrumental used for characterization of the materials and data analysis (digital images, XRD patterns, TGA curves, FTIR spectra, and SEM images), and a table containing a summary or comparison of the catalytic performances of different adsorbents for iron ions from the literature are included in the Supporting Information.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2022.135006>.

References

- Abbaspour, N., Hurrell, R., Kelishadi, R., 2014. Review on iron and its importance for human health. *J. Res. Med. Sci.* 19 (2), 164–174.
- Abinandan, S., Praveen, K., Subashchandrabose, S.R., Venkateswarlu, K., Megharaj, M., 2020. Life cycle assessment for the environmental sustainability of the immobilized acid-adapted microalgal technology in iron removal from acid mine drainage. *ACS Sustain. Chem. Eng.* 8 (41), 15670–15677. <https://doi.org/10.1021/acssuschemeng.0c05341>.
- Alimohammadi, V., Sedighi, M., Jabbari, E., 2017. Experimental study on efficient removal of total iron from wastewater using magnetic-modified multi-walled carbon nanotubes. *Ecol. Eng.* 102, 90–97. <https://doi.org/10.1016/j.ecoleng.2017.01.044>.
- Alonso, A., Muñoz-Berbel, X., Vigués, N., Rodríguez-Rodríguez, R., Macanás, J., Muñoz, M., Mas, J., Muraviev, D.N., 2013. Superparamagnetic ag@co-nanocomposites on granulated cation exchange polymeric matrices with enhanced antibacterial activity for the environmentally safe purification of water. *Adv. Funct. Mater.* 23 (19), 2450–2458. <https://doi.org/10.1002/adfm.201202663>.
- Bretti, C., Cigala, R.M., Lando, G., Milea, D., Sammartano, S., 2012. Sequestering ability of phytate toward biologically and environmentally relevant trivalent metal cations. *J. Agric. Food Chem.* 60 (33), 8075–8082. <https://doi.org/10.1021/jf302007v>.
- Chakraborti, D., Das, B., Murrill, M.T., 2011. Examining India's groundwater quality management. *Environ. Sci. Technol.* 45 (1), 27–33. <https://doi.org/10.1021/es101695d>.
- Chaturvedi, S., Dave, P.N., 2012. Removal of iron for safe drinking water. *Desalination* 303, 1–11. <https://doi.org/10.1016/j.desal.2012.07.003>.
- Das, B., Hazarika, P., Saikia, G., Kalita, H., Goswami, D.C., Das, H.B., Dube, S.N., Dutta, R.K., 2007. Removal of iron from groundwater by ash: a systematic study of a traditional method. *J. Hazard Mater.* 141 (3), 834–841. <https://doi.org/10.1016/j.jhazmat.2006.07.052>.
- Gongming, Q., Li, M., Wang, F., Liu, X., 2014. Removal of fe³⁺ from aqueous solution by natural apatite. *J. Surf. Eng. Mater. Adv. Technol.* 4, 14–20. <https://doi.org/10.4236/jsemat.2014.4.1003>.

ples using electron microscopy techniques. **Belvin Thomas:** contributed to some of the experimental works, and, helped with analysis of some of the samples using X-ray photoemission spectroscopy. **Tewodros Asefa:** co-conceived the idea, reviewed, wrote, and, revised the manuscript, and, submitted the final versions of the manuscript, ensured that the descriptions in the manuscript are accurate and agreed by all authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

CT acknowledges the financial support from the Post-doctoral Later-stage Foundation Project of Shenzhen Polytechnic (6019211006 K).

- Han, Y., Xu, Z., Gao, C., 2013. Ultrathin graphene nanofiltration membrane for water purification. *Adv. Funct. Mater.* 23 (29), 3693–3700. <https://doi.org/10.1002/adfm.201202601>.
- Hernández-Alvarado, L.A., Hernández, L.S., Lomelí, M.A., Miranda, J.M., Narváez, L., Diaz, I., Escudero, M.L., 2016. Phytic acid coating on mg-based materials for biodegradable temporary endoprosthetic applications. *J. Alloys Compd.* 664, 609–618. <https://doi.org/10.1016/j.jallcom.2016.01.011>.
- Hu, Q., Li, G., Liu, X., Zhu, B., Chai, X., Zhang, Q., Liu, J., He, C., 2019. Superhydrophilic phytic-acid-doped conductive hydrogels as metal-free and binder-free electrocatalysts for efficient water oxidation. *Angew. Chem. Int. Ed.* 58 (13), 4318–4322. <https://doi.org/10.1002/anie.201900109>.
- Huo, W., Li, L., Zhang, Y., Li, J., Xu, Q., Zhang, B., Zhang, L., Li, X., 2019. Monodispersed hierarchical γ -aloooh/fe(oh)₃ micro/nanoflowers for efficient oxygen evolution reaction. *Front. Mater.* 6. <https://doi.org/10.3389/fmats.2019.00154>.
- Khadse, G.K., Patni, P.M., Labhasetwar, P.K., 2015. Removal of iron and manganese from drinking water supply. *Sustain. Water Resour. Manag.* 1 (2), 157–165. <https://doi.org/10.1007/s40899-015-0017-4>.
- Khanom, S., Hayashi, N., 2021. Removal of metal ions from water using oxygen plasma. *Sci. Rep.* 11 (1), 9175. <https://doi.org/10.1038/s41598-021-88466-3>.
- Khatir, N., Tyagi, S., Rawtani, D., 2017. Recent strategies for the removal of iron from water: a review. *J. Water Proc. Eng.* 19, 291–304. <https://doi.org/10.1016/j.jwpe.2017.08.015>.
- Kim, H.J., Im, S., Kim, J.C., Hong, W.G., Shin, K., Jeong, H.Y., Hong, Y.J., 2017. Phytic acid doped polyaniline nanofibers for enhanced aqueous copper(ii) adsorption capability. *ACS Sustain. Chem. Eng.* 5 (8), 6654–6664. <https://doi.org/10.1021/acssuschemeng.7b00898>.
- Le, N.L., Nunes, S.P., 2016. Materials and membrane technologies for water and energy sustainability. *SMT Trends* 7, 1–28. <https://doi.org/10.1016/j.susmat.2016.02.001>.
- Li, F., Li, N., Wang, S., Qiao, L., Yu, L., Murto, P., Xu, X., 2021. Self-repairing and damage-tolerant hydrogels for efficient solar-powered water purification and desalination. *Adv. Funct. Mater.* 31 (40), 2104464. <https://doi.org/10.1002/adfm.202104464>.
- Lu, H., Shi, W., Zhao, F., Zhang, W., Zhang, P., Zhao, C., Yu, G., 2021a. Solar water purification: high-yield and low-cost solar water purification via hydrogel-based

- membrane distillation (adv. Funct. Mater. 19/2021). Adv. Funct. Mater. 31 (19), 2170135. <https://doi.org/10.1002/adfm.202170135>.
- Lu, H., Shi, W., Zhao, F., Zhang, W., Zhang, P., Zhao, C., Yu, G., 2021b. High-yield and low-cost solar water purification via hydrogel-based membrane distillation. Adv. Funct. Mater. 31 (19), 2101036. <https://doi.org/10.1002/adfm.202101036>.
- Luo, J., Yu, D., Hristovski, K.D., Fu, K., Shen, Y., Westerhoff, P., Crittenden, J.C., 2021. Critical review of advances in engineering nanomaterial adsorbents for metal removal and recovery from water: mechanism identification and engineering design. Environ. Sci. Technol. 55 (8), 4287–4304. <https://doi.org/10.1021/acs.est.0c07936>.
- Lynch, S., Pfeiffer, C.M., Georgieff, M.K., Brittenham, G., Fairweather-Tait, S., Hurrell, R.F., McArdle, H.J., Raiten, D.J., 2018. Biomarkers of nutrition for development (bond)—iron review. J. Nutr. 148 (Suppl. 1_1), 1001S–1001S1067S. <https://doi.org/10.1093/jn/nxx036>.
- Ma, J., Ma, Y., Yu, F., 2018. A novel one-pot route for large-scale synthesis of novel magnetic cnts/fe@c hybrids and their applications for binary dye removal. ACS Sustain. Chem. Eng. 6 (7), 8178–8191. <https://doi.org/10.1021/acssuschemeng.7b04668>. Manechchakr, P., Karnjanakom, S., 2017. Adsorption behaviour of Fe(II) and Cr(VI) on activated carbon: surface chemistry, isotherm, kinetic and thermodynamic studies. J. Chem. Thermodyn. 106, 104–112. <https://doi.org/10.1016/j.jct.2016.11.021>.
- Mao, M., Yan, T., Shen, J., Zhang, J., Zhang, D., 2021. Selective capacitive removal of heavy metal ions from wastewater over Lewis base sites of S-doped Fe–N– cathodes via an electro-adsorption process. Environ. Sci. Technol. 55 (11), 7665–7673. <https://doi.org/10.1021/acs.est.1c01483>.
- Marolt, G., Gričar, E., Pihlar, B., Kolar, M., 2020. Complex formation of phytic acid with selected monovalent and divalent metals. Front. Chem. 8. <https://doi.org/10.3389/fchem.2020.582746>.
- Mizukoshi, Y., Shuto, T., Masahashi, N., Tanabe, S., 2009. Preparation of superparamagnetic magnetite nanoparticles by reverse precipitation method: Contribution of sonochemically generated oxidants. Ultrason. Sonochem. 16 (4), 525–531. <https://doi.org/10.1016/j.ultrsonch.2008.12.017>. Muthusaravanan, S., Sivarajasekar, N., Vivek, J.S., Paramasivan, T., Naushad, M., Prakashmaran, J., et al., 2018. Phytoremediation of heavy metals: mechanisms, methods and enhancements. Environ. Chem. Lett. 16 (4), 1339–1359. <https://doi.org/10.1007/s10311-018-0762-3>.
- Nandeshwar, S.N., Mahakalakar, A.S., Gupta, R.R., Kyzas, G.Z., 2016. Green activated carbons from different waste materials for the removal of iron from real wastewater samples of nag river, India. J. Mol. Liq. 216, 688–692. <https://doi.org/10.1016/j.molliq.2015.12.065>.
- Nasrollahzadeh, M., Sajjadi, M., Irvani, S., Varma, R.S., 2021. Carbon-based sustainable nanomaterials for water treatment: state-of-art and future perspectives. Chemosphere 263, 128005. <https://doi.org/10.1016/j.chemosphere.2020.128005>.
- Pan, L., Yu, G., Zhai, D., Lee, H.R., Zhao, W., Liu, N., Wang, H., Tee, B.C.-K., Shi, Y., Cui, Y., Bao, Z., 2012. Hierarchical nanostructured conducting polymer hydrogel with high electrochemical activity. Proc. Natl. Acad. Sci. USA 109 (24), 9287–9292. <https://doi.org/10.1073/pnas.12026slkw36109>.
- Peng, L., Chen, X., Zhang, Y., Du, Y., Huang, M., Wang, J., 2015. Remediation of metal contamination by electrokinetics coupled with electrospun polyacrylonitrile nanofiber membrane. Process Saf. Environ. Protect. 98, 1–10. <https://doi.org/10.1016/j.psep.2015.06.003>. Prakash, K.L., Somashekar, R., 2006. Groundwater quality—assessment on anekal taluk, Bangalore Urban District, India. J. Environ. Biol. 27 4, 633–637.
- Qu, S., Huang, F., Yu, S., Chen, G., Kong, J., 2008. Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with fe₂o₃ particles. J. Hazard Mater. 160 (2), 643–647. <https://doi.org/10.1016/j.jhazmat.2008.03.037>.
- Ramakrishnaiah, C.R., Sadashivaiah, C., Ranganna, G., 2009. Assessment of water quality index for the groundwater in Tumkur Taluk, Karnataka State, India. E-J CHEM 6, 757424. <https://doi.org/10.1155/2009/757424>.
- Saleem, H., Zaidi, S.J., 2020. Developments in the application of nanomaterials for water treatment and their impact on the environment. Nanomaterials 10 (9), 1764.
- Tang, C., Thomas, B., Ramírez-Hernández, M., Mikmeková, E.M., Asefa, T., 2022. Metal-functionalized hydrogels as efficient oxygen evolution electrocatalysts. ACS Appl. Mater. Interfaces 14 (18), 20919–20929. <https://doi.org/10.1021/acsmi.2c01667>.
- Tian, T., Zhou, K., Li, Y.-S., Liu, D.-F., Yu, H.-Q., 2022. Recovery of iron-dependent autotrophic denitrification activity from cell-iron mineral aggregation-induced reversible inhibition by low-intensity ultrasonication. Environ. Sci. Technol. 56 (1), 595–604. <https://doi.org/10.1021/acs.est.1c05553>.
- Wang, H., Lin, J., Shen, Z.X., 2016. Polyaniline (PANI) based electrode materials for energy storage and conversion. J SCI-ADV MATER DEV 1 (3), 225–255. <https://doi.org/10.1016/j.jsamd.2016.08.001>. 5 June 2021 Wang, Z., Li, T.-T., Peng, H.-K., Ren, H.-T., Lou, C.-W., Lin, J.-H., 2021a. Low-cost hydrogel adsorbent enhanced by trihydroxy melamine and β-cyclodextrin for the removal of Pb(II) and Ni(II) in water. J. Hazard Mater. 411, 125029. <https://doi.org/10.1016/j.jhazmat.2020.125029>.
- Wang, Z., Li, T.-T., Peng, H.-K., Ren, H.-T., Lou, C.-W., Lin, J.-H., 2021b. Low-cost hydrogel adsorbent enhanced by trihydroxy melamine and β-cyclodextrin for the removal of pb(ii) and ni(ii) in water. J. Hazard Mater. 411, 125029. <https://doi.org/10.1016/j.jhazmat.2020.125029>. Wołowicz, M., Pruss, A., Komorowska-Kaufman, M., Lasocka-Gomula, I., Rzepa, G., Bajda, T., 2019. The properties of sludge formed as a result of coagulation of backwash water from filters removing iron and manganese from groundwater. SN Appl. Sci. 1, 639. <https://doi.org/10.1007/s42452-019-0653-7>.
- Yan, H., Kajita, M., Toshima, N., 2002. Polymerization of aniline using iron(III) catalyst and ozone, and kinetics of oxidation reactions in the catalytic system. Macromol. Mater. Eng. 287 (8), 503–508. [https://doi.org/10.1002/1439-2054\(20020801\)287:8<503::AID-MAME503>3.0.CO;2-N](https://doi.org/10.1002/1439-2054(20020801)287:8<503::AID-MAME503>3.0.CO;2-N).
- Yap, P.L., Nine, M.J., Hassan, K., Tung, T.T., Tran, D.N.H., Losic, D., 2021. Graphene-based sorbents for multipollutants removal in water: a review of recent progress. Adv. Funct. Mater. 31 (9), 2007356. <https://doi.org/10.1002/adfm.202007356>. Yin, Z., Cui, C., Chen, H., Duoni, Yu, X., Qian, W., 2020. The application of carbon nanotube/graphene-based nanomaterials in wastewater treatment. Small 16 (15), 1902301. <https://doi.org/10.1002/sml.201902301>.
- Yu, S., Cowieson, A., Gilbert, C., Plumstead, P., Dalsgaard, S., 2012. Interactions of phytate and myo-inositol phosphate esters (ip1-5) including ip5 isomers with dietary protein and iron and inhibition of pepsin. J. Anim. Sci. 90 (6), 1824–1832. <https://doi.org/10.2527/jas.2011-3866>.
- Zhang, Y., Dou, C., Li, L., Wang, Y., 2014. A practical way to prepare thin polyaniline nanofibers with ferric nitrate as an oxidant. POLYM SCI SER A + 56 (2), 146–151. <https://doi.org/10.1134/S0965545X14020138>.
- Zhang, Y., Yan, K., Ji, F., Zhang, L., 2018. Enhanced removal of toxic heavy metals using swarming biohybrid adsorbents. Adv. Funct. Mater. 28 (52), 1806340. <https://doi.org/10.1002/adfm.201806340>.
- Zhang, S., Hedtke, T., Zhu, Q., Sun, M., Weon, S., Zhao, Y., Stavitski, E., Elimelech, M., Kim, J.-H., 2021. Membrane-confined iron oxychloride nanocatalysts for highly efficient heterogeneous fenton water treatment. Environ. Sci. Technol. 55 (13), 9266–9275. <https://doi.org/10.1021/acs.est.1c01391>. Zhu, L., Shen, D., Luo, K.H., 2020. A critical review on VOCs adsorption by different porous materials: species, mechanisms and modification methods. J. Hazard Mater. 389, 122102.