Stability of hydrous ferric oxide nanoparticles encapsulated inside porous matrices: Effect of solution and matrix phase

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HIGHLIGHTS

- The stability and reactivity of HFOs encapsulated inside different matrix phases was investigated.
- Positive charge and narrower pore structure of matrices facilitated HFOs retaining.
- The encapsulated HFO nanoparticles have stronger binding energy than the bare HFOs.
- Coexisting phosphate anions suppressed the dissolution/transformation of HFOs.

GRAPHICAL ABSTRACT
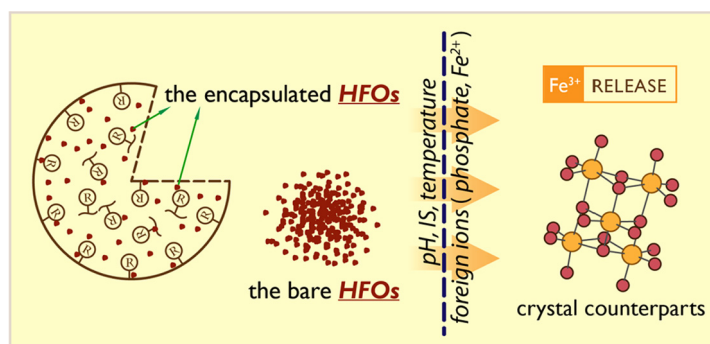
ABSTRACT

Nanocomposite adsorbents synthesized by in-situ nucleation of hydrous ferric oxide nanoparticles (HFOs) within porous matrices have been extensively studied and applied in polluted water remediation. In this study a series of nanocomposites were developed by loading HFOs inside different porous materials, including anion exchanger (Resin$^+$), cation exchanger (Resin$^-$), neutral-chloromethyl resin (Resin^0) and granular activated carbon (GAC), and the stability of the encapsulated HFOs was investigated as a function of pH, ionic strength, temperature and coexisting foreign ions (Fe^{2+}/PO$_4^{3-}$). Protonation-induced Fe^{3+} release was observed for all the tested nanocomposites, and increasing ionic strength of solution facilitated Fe^{3+} release. HFOs encapsulated in Resin$^+$ phase retarded Fe^{3+} release as compared to those in Resin$^-$/Resin^0 phases. Meanwhile, the HFOs retention capacity increased drastically (e.g., from 20.7% to 75.8% at pH 1.35) with decrease in the average pore diameter of Resin^0 from 32.5 nm to 9.5 nm. Coexisting phosphate not only efficiently suppressed the dissolution of HFOs inside the porous matrices, but hindered their transformation into other crystalline counterparts. Catalytic structural transformation of amorphous HFO phases into thermodynamically more stable phases by Fe(II), commonly observed in bare HFOs systems, was not observed for the encapsulated HFOs. Additionally, EXAFS analyses indicated that the HFOs in Resin$^-$ phase have stronger binding energy with Cu(II) ions than the bare HFOs. These results are expected to provide necessary information for the optimization of such nanocomposite adsorbents and their practical applications.

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1. Introduction

Innovative adsorbent materials with enhanced selectivity, efficiency, reactivity and reliability are the essential modules of enabling water treatment technologies required to mitigate the growing gap between clean water demand and supply [1]. Nanocomposite adsorbents developed by embedding metal (oxyhydr)oxide nanoparticles, such as hydrous ferric/manganese/aluminum oxides, inside pore structures of millimeter-scale porous matrices have been emerging as promising candidates to remove priority pollutants that are present at low concentrations in aqueous solution [2–4].

In the past decades, hydrous ferric oxide nanoparticles (HFOs) have proven to be highly efficient and economical scavengers for wastewater polluted by heavy metal ions [5,6], phosphate [7,8], arsenate/arsenite [9,10], and natural organic matter (NOM) [11,12]. These ferric nano-oxyhydroxides of disordered structures provide a high surface area/bulk ratio, high reactivity and amphoteric surface functional groups [5,6,13]. Despite their great potential in water purification, these nano-sized particles have inevitable limitations toward their direct practical applications [4,14,15]: a) tendency to self-aggregate and consequently lose activity in water; b) lack of robust and strong mechanical structure; c) causing excessive pressure when applied in flow-through systems as fine or ultrafine particles; and d) concerns of potential adverse effects on human health with the possibility to release nanoparticles into the environment.

To address the above issues, nanocomposite adsorbents were developed by in situ nucleating HFOs within porous matrices of large sizes, such as activated carbon [16,17], diatomite [18], chitosan [19], and polymeric adsorbents [4,14,20], and the resultant hybrid adsorbents maintain the unique adsorption properties of HFOs and can overcome the associated hurdles. Some of these nanocomposite adsorbents have been successfully applied in field-scale water treatment, and demonstrated desirable performance in efficient removal of heavy metal ions, phosphate and arsenate from circumneutral wastewater composed of simple ions [20–22]. However, the stability of the encapsulated HFOs in such nanocomposite adsorbents has not been systematically investigated, especially when applied in relatively complicated conditions. Specifically, the decomposition and phase transformation of the HFOs dwelling inside the heterogeneous porous matrices are still poorly understood with respect to pH, ionic strength, temperature and coexisting interfering ions, despite the various investigations have been carried out on bare HFOs.

Bare HFOs (i.e., amorphous two-line ferrihydrite) are thermodynamically metastable and prone to spontaneous/stimulated recrystallization into more stable crystalline counterparts (such as goethite, lepidocrocite or hematite) under certain conditions [23,24]. Extensive studies revealed that, at acidic pH but relatively low temperature when Fe(III) solubility is higher, goethite is the dominant end product formed via a dissolution/reprecipitation mechanism, whereas hematite is the main final end product at high temperature no matter what pH value it is [23,25,26]. Additionally, the stability of HFOs could be interfered with by foreign ions bound to their surface groups [27–29]. Juraj Majzlan [28] investigated the effect of phosphate on thermodynamic stabilization of hydrous ferric oxide by experimentally determining enthalpies of formation, and found that the phosphate-enriched HFOs were less soluble than the anion-free HFOs under mildly acidic conditions. Galvez et al. [29] also found that, by a structural incorporation mechanism, phosphate ion can affect the final product formation and even their morphologies from HFOs transformation at different pH and temperature. Additionally, Fe(II)-induced phase transformation of HFOs has been widely recognized as a common process in anoxic environments primarily through redox transition between aqueous Fe(II) and solid Fe(III) phases. Here introduction of Fe(II) could induce reductive dissolution of HFOs and subsequently recrystallize HFOs into crystalline phases varying in their retention and reducing capacity [30–32].

Polymeric adsorbents themselves are appropriate sequestrators for many of ubiquitous pollutants due to their vast surface area, excellent mechanical strength, and tunable surface chemistry and pore structure [4,33]. In the past decade, they have been emerging as a promising type of matrix materials for loading HFOs [14,20,34]. Various HFO nanocomposite adsorbents have been developed by confining HFO nanoparticles within the special cross-linked structure of polymeric adsorbents. The resultant hybrid adsorbents exhibited significantly enhanced performance in removing strictly regulated pollutants like anionic As(III/V) or P(V) species from wastewater [20,34]. Due to the feasibility in tailoring the pore structure and surface chemistry of polymeric adsorbents, we can accordingly adjust the size/morphology of the loaded HFOs and consequently their reactivities. For example, Wang et al. [35] found that the particle size of HFOs decreased with decreasing pore size of its host material, and higher capacities and faster kinetics toward arsenite adsorption were achieved. Furthermore, the charged functional groups covalently bonded on the skeletal structure of polymeric adsorbents could greatly favor the dispersion of targeted pollutant ions inside the porous matrix structure, and thus enhance the adsorption performance on the basis of the Donnan principle [22,34].

In the present study, a series of HFO nanocomposite adsorbents were synthesized by an in-situ synthesis method, that is, using Fe(III) (Fe^{3+} or $FeCl_4^-$) ions as HFOs precursor followed by an alkaline post-treatment. Various polymeric adsorbents (including $Resin^0$/$Resin^+$/$Resin^-$, which possess neutral chloromethyl/positive quaternary ammonium/negative sulfate functional groups, respectively) and granular activated carbon (GAC) were selected as the matrix materials. The dissolution of HFO nanoparticles inside the heterogeneous porous matrices was then investigated with respect to pH (acidic pH range, which can be encountered in situations such as a regeneration process), ionic strength, and coexisting phosphate. The effect of the matrix pore structure on the decomposition of the encapsulated HFOs was also studied, where various homologous $Resin^0$ matrices with different pore structures were developed by post-crosslinking the same batch of initial $Resin^0$ to varying degrees. We also investigated phase transformation of the encapsulated HFOs with coexisting aqueous phosphate/Fe(II) ions as a function of time and temperature (25, 50, 75 °C). Additionally, comparison of binding energy toward pollutant ions (Cu[II] as a case study) between bare HFOs and the encapsulated HFO was conducted to inspect the effect of matrix structure on the intrinsic properties of the encapsulated HFOs.

2. Materials and methods

2.1 Materials

The starting material to develop various polymeric adsorbents with different surface chemistry and pore structure, i.e., a commercially available polymer (polystyrene-divinylbenzene, St-DVB) with the crosslinking density of about 8%, was provided by Zhenguang Industrial Co. (Hangzhou, China). Prior to use, the St-DVB was sieved with the sizes of spherical beads ranging from 0.4 to 0.6 mm in diameter, and subjected to respective washing with NaOH and HCl dilute solution, and then subsequent extraction with ethanol in a soxhlet apparatus to remove possible residue impurities. The granular activated carbon (GAC) was obtained from Jinbei Fine Chemical Co. (Tianjin, China), and similar cleaning procedure was carried out. All other chemicals are purchased from Shanghai Reagent Station (Shanghai, China) in A.R. grade and used without further purification.

2.2. Synthesis of $Resin^0$, $Resin^+$ and $Resin^-$ from St-DVB

The three types of St-DVB derivatives were synthesized as following (see details in SI Text S1): $\boldsymbol{Resin^0}$, the chloromethylated type of St-DVB, was synthesized by chloromethylating St-DVB with chloromethyl