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# Heavy metals removal using hydrogel-supported nanosized hydrous ferric oxide: Synthesis, characterization, and mechanism

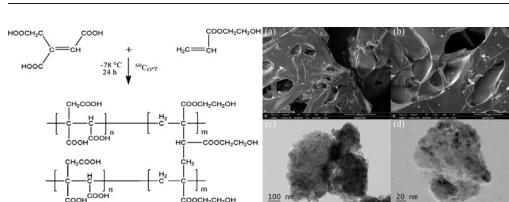
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## HIGHLIGHTS

- Poly(*trans*-Aconitic acid/2-hydroxyethyl acrylate) hydrogel was synthesized.
- Nanosized hydrous ferric oxide was supported onto the hydrogel successfully.
- The hybrid hydrogel showed high adsorption capacity towards target metals.
- Inner sphere complexation predominated the adsorption process.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new polymer-supported hybrid adsorbent (HFO-P(TAA/HEA)) for highly efficient removal of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  from wastewater was developed by supporting hydrous ferric oxide (HFO) nanoparticles onto a porous poly(*trans*-Aconitic acid/2-hydroxyethyl acrylate) hydrogel (P(TAA/HEA)) with *in situ* precipitation method. Swelling kinetics, scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), Fourier transform infrared spectra (FTIR) and X-ray photoelectron spectroscopy (XPS) were used for characterization of the prepared HFO-P(TAA/HEA). The characterization data demonstrated that the hybrid hydrogel HFO-P(TAA/HEA) was successfully fabricated, and swelling ability as well as thermal stability was promoted after loading. The results of batch equilibrium experiments indicated that pH and temperature significantly influenced the adsorption process and adsorption of heavy metals was better fitted to Langmuir and pseudo-second-order models. Selectivity of HFO-P(TAA/HEA) towards heavy metals was greatly improved under the calcium ions competition at higher concentration compared to P(TAA/HEA). Competitive adsorption evidenced the priority order in multifold metal species system was  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ . What's more, FTIR and XPS analyses manifested that heavy metals might mainly be adsorbed via inner sphere complexation. These findings revealed that hydrogel HFO-P(TAA/HEA) is a potential adsorption material to remove the heavy metals from polluted water.

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## 1. Introduction

With the development of economy, wastewaters containing heavy metals are produced in metal finishing, alloy manufacturing, welding, electroplating, and mining industries, which have posed a grave menace

to environment and public health (Alsohaimi et al., 2015; Hua et al., 2012; Repo et al., 2013). Heavy metals are usually physically or chemically removed from the contaminated water through membrane filtration (Thong et al., 2014), electrochemical method (Basha et al., 2011), chemical precipitation (Gupta et al., 2012), ion exchange (Kozlov et al., 2015) and adsorption (Jiang et al., 2014). Adsorption is most promising and attractive and has been widely used due to its characteristics of cost effectiveness, simple operation, fewer secondary pollution and high efficiency among these methods (Shen et al., 2015; Liu et al., 2010).

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Special attention has been paid to the application of three-dimensional cross-linked hydrogels as adsorbents for highly effective removal of heavy metals. In general, hydrogel has advantages such as backbones with different functional groups, high internal specific surface area, excellent water uptake, and porous structure (Peng et al., 2012). Many monomers containing one or more functional groups such as amide, acylamino, sulfonic acid groups, hydroxyl and carboxyl have been selected for synthesis of copolymer hydrogels (Ionita et al., 2013; Vasudevan et al., 2014; Wang and Li, 2015; Wu and Li, 2013; Dragan, 2014). Zhao et al. (Zhao and Mitomo, 2008) investigated removal of copper ions by CM-cellulose/chitosan physical hydrogel and found that the bond between copper ion and  $-\text{COOH}$  played an important role for adsorption of  $\text{Cu(II)}$ . Katarina M. Antić et al. (Antić et al., 2015) synthesized P(HEA/IA) copolymers using itaconic acid (IA) and 2-hydroxyethyl acrylate (HEA) to remove  $\text{Cd}^{2+}$ . Their results suggested that adsorption might function through chelation and ion exchange between heavy metals and functional groups. 2-Hydroxyethyl acrylate (HEA) is a hydrophilic monomer with several functional groups such as  $-\text{COO}$  and  $-\text{OH}$  and it has been researched extensively as the skeleton of copolymers (Zhu and Li, 2015). *trans*-Aconitic acid (TAA) is a monomer containing several carboxyl ( $-\text{COOH}$ ) groups. Despite of quantities of studies on copolymer hydrogel, hydrogel polymerized by gamma radiation using HEA and TAA as monomers has not been reported and applied to separate and recover the heavy metals from wastewater to date.

Hydrous ferric oxide (HFO) nanoparticles have been proved as one of the most valuable adsorbents for dealing with heavy metals due to the fact that they have specific affinity for adsorbing metal ions and large specific surface area, besides, they are also cost effective, chemically stable, and environmentally benign (Fan et al., 2005; Qiu et al., 2012). Despite high heavy metal removal capacity, such fine submicron particles and their aggregates cannot be directly put into use because of their inherent disadvantages such as excessive pressure drop, poor mechanical rigidity and low hydraulic conductivity (Qiu et al., 2013). To overcome these drawbacks, HFO nanoparticles were immobilized within porous carriers such as activated carbon, diatomite and polymeric sorbents (Ilesan et al., 2008). Synthetic polymeric adsorbents containing sound skeleton strengths, nanoporous structures, tunable surface chemistry and crosslinking matrices have turned into the most suitable adsorbents for decontamination of heavy metals from water (Lofrano et al., 2016). Pan et al. (2010) synthesized a hybrid adsorbent (HFO-001) to remove heavy metals by loading HFO nanoparticles onto a resin D-001 and explored its radical adsorption property. Despite lots of studies on HFO nanoparticles and synthetic polymeric adsorbents have been conducted, the *in situ* combination of HFO with a copolymer hydrogel has not yet been reported. Therefore, immobilizing HFO nanoparticles within hydrogel to fabricate a hybrid adsorbent which has good adsorption property towards heavy metals in wastewater would be necessary and significant.

A novel hydrogel P(TAA/HEA) (poly(*trans*-Aconitic acid/2-hydroxyethyl acrylate)) was synthesized via  $^{60}\text{Co}$ - $\gamma$ -induced polymerization and then followed by the *in situ* loading of HFO nanoparticles in this study. Swelling kinetics, SEM, TEM, XRD, TGA, FTIR and XPS were utilized to characterize the synthesized HFO-P(TAA/HEA) hydrogel. Adsorption isotherms and kinetics were analyzed and effects of pH, temperature and competing calcium ions were investigated, as well as the competitive adsorption study. Moreover, the possible adsorption mechanism was inferred based on the results of FTIR and XPS spectra.

## 2. Materials and methods

### 2.1. Materials

*trans*-Aconitic acid (TAA) and 2-hydroxyethyl acrylate (HEA) were bought from Sigma-Aldrich, USA. The main reagents ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), Sodium hydroxide (NaOH), lead nitrate

( $\text{Pb}(\text{NO}_3)_2$ ), copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), cadmium nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), and nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), which were all of analytical purity, were bought from SINOPHARM, China.

### 2.2. Synthesis of P(TAA/HEA) hydrogel

Reaction of monomers during radiation was illustrated in Fig. 1 and the procedures could be described by the following steps: (1) TAA and HEA were mixed at monomers ratio 1:9 (mol/mol) in deionized water (v./v. = 2:3). The hydrogel with this monomers ratio and proportion of water had the best adsorption capacity and swelling ability in the previous work. The mixture was then purified by nitrogen gas for 20 min to remove dissolved oxygen. (2) The mixture was then irradiated with a  $^{60}\text{Co}$ - $\gamma$  source for 24 h to total dose of 20 kGy in dry ice-alcohol bath at  $-78^\circ\text{C}$ . The  $^{60}\text{Co}$ - $\gamma$  source is installed at Nanjing University of Aeronautics and Astronautics Radiation Center. (3) The copolymer hydrogels were then sliced into  $5 \times 5 \times 5$  mm dimension of cubes and then washed drastically by deionized water. Then the clean copolymer hydrogels were put into a vacuum oven at  $50^\circ\text{C}$  to eliminate any water in the hydrogel matrix.

### 2.3. Synthesis of HFO-P(TAA/HEA) hydrogel

The hybrid HFO-P(TAA/HEA) hydrogel was fabricated according to Pan et al. (2010). Firstly, 5 g of dried hydrogels were transferred into 500 mL aqueous solution containing 36.86 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and the mixture was stirred in a thermostatic oscillator at  $25^\circ\text{C}$  for 24 h (150 rpm). Secondly, the Fe(III)-type hydrogels were then filtered and vacuum desiccated. After that, the hydrogels were put into a NaOH-NaCl solution (2% w/v concentration each) and then stirred for 3 h in thermostatic oscillator (150 rpm). Thirdly, the obtained hydrogels were washed thoroughly with deionized water and then washed with ethanol-water solution (50:50 (v/v)). Finally, the hydrogels were put into a vacuum oven at  $50^\circ\text{C}$  for 24 h to get rid of water and stored in a vacuum desiccator for further study.

### 2.4. Characterization methods

Conventional gravimetric process was utilized to investigate the swelling property (Cheng et al., 2015). Dried hydrogels were immersed in deionized water and then the swollen hydrogels were weighed at

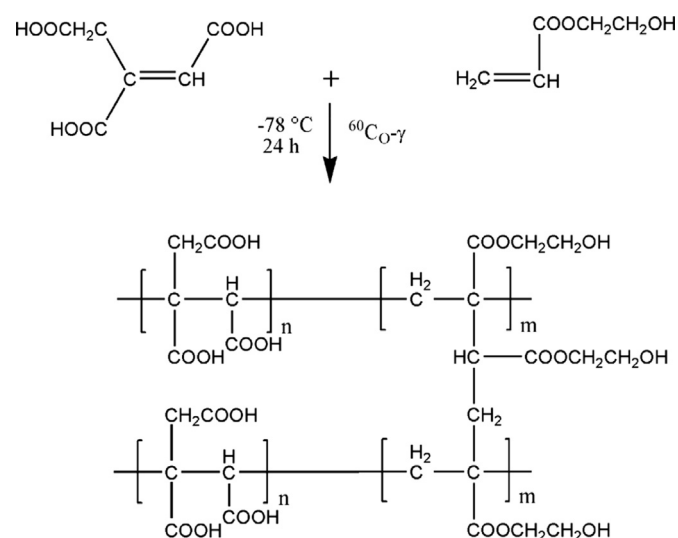


Fig. 1. Diagram for synthesis of P(TAA/HEA) hydrogel.

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