



## Removal of Cr(VI) using iron nanoparticles supported on porous cation-exchange resin



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### ABSTRACT

In this study, the iron nanoparticles were synthesized by ferrous sulfate method using  $\text{LiBH}_4$  as a reducing agent. The reduction of Cr(VI) to Cr(III) by iron nanoparticles supported on a porous cation-exchange resin and the retention of Cr(III) and Fe(III) as products on the resin were achieved in a single step. The size and surface area of iron nanoparticles were determined by transmission electron microscopy and BET surface area analysis. The loading of the iron nanoparticles on porous cationic resin support was confirmed by field emission scanning electron microscopy and energy dispersive X-ray spectroscopy as well as chemical analysis. Porous cationic support material composed of sulphonated styrene–divinylbenzene copolymer of three different diameter sizes i.e., 1.2–45, 45–150 and 150–270  $\mu\text{m}$  was synthesized by suspension polymerization. The cationic support was characterized by FTIR spectroscopy, mercury porosimetry, particle size analysis, and sulphonic acid content estimations. The iron nanoparticles were dispersed into porous cationic support material and then the composite was applied for reduction of Cr(VI). The reduction capacity of Cr(VI) was higher in smaller size diameter of support material (1.2 to 45  $\mu\text{m}$ ) as compared to the larger diameter. Fe(III) and Cr(III) produced from the reaction of  $\text{Fe}^0$  and Cr(VI) were adsorbed onto the porous cationic support material. The reduction capacity of Cr(VI) and adsorption capacities of Fe(III) and Cr(III) were evaluated at different temperatures, concentrations of iron nanoparticles loaded on porous cationic exchange resin and pH.

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### 1. Introduction

Chromium and its derivatives are extensively used in electroplating, dyes, textiles and leather industries. Chromium is present either as hexavalent Cr(VI) or trivalent Cr(III) in the effluents of these industries (Çengelöglu et al., 2003). Solubility, mobility and bioavailability of Cr(VI)-compounds are higher as compared to sparingly soluble Cr(III) species. Cr(VI) species are known to be detrimental to human health due to their toxicity and carcinogenic nature, whereas Cr(III) species are not toxic and are essential to a mammalian system except at elevated concentrations in our ecosystem. The maximum permissible limit in waste-water is reported at 5 ppm for Cr(III) and 0.05 ppm for Cr(VI) (Pehlivan and Cetin, 2009). So, the removal of Cr from contaminated water is an active area of research and development. Among other methods used for removal of Cr(VI) from water, the methods based on anion exchange resin for the removal of metal ions from aqueous media are generally advantageous over the other techniques because of better selectivity of resins for metals, production of less sludge volume, and compliance with strict discharge specifications (Shi et al.,

2009). Several researches on anion exchange resins have been reported in literature (Gurgel et al., 2009; Pehlivan and Cetin, 2009; Shi et al., 2009). The main disadvantage of anion exchange resin is the involvement of highly toxic chemicals in the production of anion exchange resin, which endangers our environment as well as raises the cost of the resin.

In environment remediation, iron nanoparticles have a wide range of applications, e.g., removal of Cu(II) and Co(II) ions (Üzüm et al., 2009), treatment of uranium-contaminated waste effluent (Dickson and Scott, 2010), inactivation of microbes (Diao and Yao, 2009), degradation of toxic organic molecules like metolachlor (Satapanajuru et al., 2003), and reduction of Cr(VI) to Cr(III) (Shao-Feng et al., 2005). Reduction of Cr(VI) to Cr(III) by zerovalent iron nanoparticles is favorable based on thermodynamics of the process and has a potential application in the remediation of Cr(VI) pollution. Zerovalent iron nanoparticles undergo rapid oxidation, hydrolysis and immediate agglomeration into micrometer particles that have low reactivity. Long time storage of iron nanoparticle is difficult as they tend to aggregate (Li et al., 2010). The immobilization of iron nanoparticles on a support material provides protection from oxidation and hydrolysis in water (Ponder et al., 2001). In some early research, a non-porous PolyFlo resin has been reported as a polymer support to disperse iron nanoparticles (Ponder et al., 1999, 2001). Recently, sepiolite (Esfahani et al., 2014),

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bentonite (Shi et al., 2011a,b; Xi et al., 2011), kaolinite (Zhang et al., 2011), starch (Alidokht et al., 2011), polysaccharides (Chang et al., 2011), cellulose acetate (Wu et al., 2005) and organo-montmorillonite (Li et al., 2010) have been reported as polymer support materials for the dispersion of iron nanoparticles.

The polymer support material may be porous or non-porous. The use of porous polymer support enhances rate of removal of iron and other metals (Ponder et al., 2001). The nature of dispersant may improve the mobility of iron nanoparticles as it allows the material to penetrate deep into soil networks for environmental remediation (Naubactep et al., 2012). The dispersant may be ionic surface change, e.g., polyacrylic acid, carboxymethyl cellulose (Raychoudhury et al., 2010), or non-ionic surface change, e.g., starch (Alidokht et al., 2011). One of the distinct applications of support material with metal nanoparticles is the combined effect of degradation of target metal ions and sorption of the resultant byproducts. For such types of applications, cationic resins are most suitable materials, e.g., copper nanoparticles were used for the degradation of aqueous carbon tetrachloride and the resultant copper cations were adsorbed by the cationic support in a single step (Lin et al., 2005). In another study, silica fume was reported as a support material, which strongly binds Fe (III) and Cr (III) by-product of Cr (VI) reduction by iron nanoparticles (Li et al., 2011). The use of mesoporous cationic support has been reported for the sorption of Fe(III) and Cr(III) byproducts, which was produced as a result of reduction of Cr(VI) by iron nanoparticles on the polymer surface (Fu et al., 2013).

In the present study, iron nanoparticles have been synthesized and dispersed in porous functional support, which prevent agglomeration of nanoparticles as well as enrich the Fe(III) and Cr(III) ions produced as a result of reductive reaction between Cr (VI) and Fe<sup>0</sup> in a single step. The effect of particle size of polymer support, temperature and pH in the reduction of Cr(VI) by iron nanoparticles supported on cation-exchange resin was studied.

## 2. Materials and methods

### 2.1. Synthesis of iron nanoparticles

Zerovalent iron nanoparticles were synthesized by a method as described earlier by Ponder et al. (2001) except that LiBH<sub>4</sub> was used as a reducing agent in place of NaBH<sub>4</sub>. FeSO<sub>4</sub> · 7H<sub>2</sub>O (6.15 g) was dissolved in 50-mL distilled de-mineralized water (EC 1.5 μS/cm) and pH was adjusted to 7.0 with 3.8 M NaOH solution. The solution was transferred to a 1000-mL three neck round bottom flask and nitrogen gas was purged to create an inert atmosphere in the reaction flask. The solution of flask was kept under fast and constant stirring. LiBH<sub>4</sub> (1.72 g) was added carefully and slowly into the solution. The chemical reaction proceeded very fast with large foaming and effervescence. The color of the reaction solution was finally changed to black and stirring was continued for another 30–40 min. The black iron-precipitates were filtered, washed with de-mineralized water and acetone. The final residual product as iron nanoparticles was stored in acetone for characterization.

### 2.2. Synthesis of polymer support

Styrene-co-Divinylbenzene was synthesized in the form of spherical resin beads by suspension polymerization (Malik, 2009; Malik et al., 2010). The polymerization mixture comprised of styrene, divinylbenzene and petroleum ether in a 1:1:2 ratios by volume and benzoyl peroxide (1% by weight to the polymerization mixture). Aqueous phase was prepared by dissolving gum-Arabic and gelatin by 1 % wt./vol each in distilled water. One part by volume of the polymerization mixture was suspended in five parts of the aqueous phase under stirring for ½ h at room temperature. The temperature was then raised to 80 °C in steps and maintained for 20 h. The copolymer beads were filtered out through a Buchner funnel, washed with hot water and

segregated into desired sizes. The un-reacted monomers/homo-polymers were extracted from the copolymer beads with acetone. The beads were dried at 110 °C until constant dry weight (W<sub>d</sub>) and the density (d) was calculated from the weight and volume of dried beads. The recovered yield of copolymers was more than 80% with 60% purity of copolymerization of styrene–divinyl benzene in all the experiments. So, the cross-linking was calculated by correcting the purity of divinylbenzene as follows:

$$\text{Cross-linkage(\%)} = \% \text{purity of DVB} \times V_{\text{DVB}} / (V_{\text{DVB}} + V_{\text{sty}})$$

The percentage of porogen or diluents in the reaction mixture was calculated by the volumes of diluents (V<sub>diluents</sub>), monomer and cross-linker (V<sub>monomer</sub> + V<sub>cross-linker</sub>) by using the following relationship:

$$\text{Dilution(\%)} = 100V_{\text{diluents}} / (V_{\text{monomer}} + V_{\text{cross-linker}} + V_{\text{diluents}})$$

where “V<sub>diluents</sub>” is the volume of diluents and “V<sub>monomer</sub>” is the volume of monomers used.

### 2.3. Sulphonation of copolymer

A slurry of oven dried copolymer beads and sulfuric acid (98% pure) 1:5 ratios (wt/vol) was transferred to a reaction vessel and kept at 98 °C for 2 h. Then, the slurry was poured slowly into a beaker containing ice-cold demineralized water (20-times volume) at stirring condition. The resin beads were filtered and washed with demineralized water till the effluent was free of acid.

### 2.4. Dispersion of iron nanoparticles on polymer support

The dispersion of iron nanoparticles on polymer support was made following by the method as described by Wu et al. (2005). The freshly synthesized iron nanoparticles were dispersed into ethanol/acetone (1:4 vol/vol) solvent mixture. The ratio of iron nanoparticles to organic solvent mixture was kept at 1:10 wt/vol. Then, the dispersed mixture was substituted with the known weight of cationic resin at desired ratios. The slurry of composite was sonicated for 10 min followed by continuous stirring for about 2 h. Then, the composite was centrifuged to remove excess organic solvent, dried in vacuum oven at 50 °C and stored in desiccator for further studies.

### 2.5. Quantitative determination of iron supported on polymer support

Freshly synthesized iron nanoparticles (1.0 g) supported on resin were immersed in 30-mL of 0.1 M HCl solution and kept at constant agitation for 8 h. Then, composite was washed thoroughly with distilled water followed by the method as previously described by Tong et al. (2011). The iron contents in washed solution were analyzed by atomic absorption spectroscopy (Hitachi Z 8000 Atomic Absorption Spectrometer).

### 2.6. Characterization of iron nanoparticles

Morphology and particle size of iron nanoparticles were determined by transmission electron microscope (JEOL JEM 1010). Field emission scanning electron microscopy (MIRA 3 LM, TESCAN Inc., USA) was used to characterize the polymer resin support with and without loaded iron nanoparticles. For electron microscopic studies, the samples were sonicated for 5 min in methanol prior to analysis. The samples were mounted on a stub of metal with adhesive and coated with gold using JFC-1500 ion sputtering device. Surface area (BET area) of the synthesized iron nanoparticles was measured (5 point isotherm) by using nitrogen adsorption method with Surface Area Analyzer (Micrometrics Instrument Co., USA). The sample was dried and degassed automatically overnight under the flow of nitrogen prior to analysis.

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