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Enhanced reactivity of nZVI embedded into supermacroporous cryogels for highly efficient Cr(VI) and total Cr removal from aqueous solution

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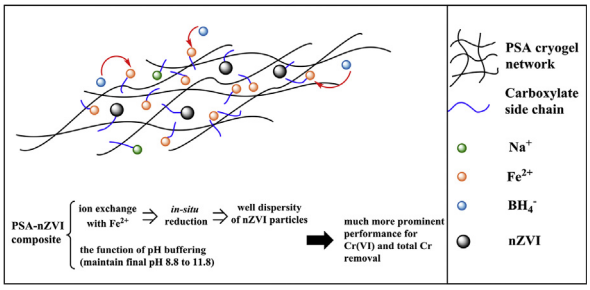
HIGHLIGHTS

- PSA-nZVI composites were synthesized with nZVI uniformly distributed.
- PSA-nZVI composites showed much more remarkable performance for Cr (VI) and total Cr removal than free nZVI particles.
- PSA cryogel functioned as an excellent carrier and a pH buffering agent.
- Reduction, adsorption and precipitation might be all involved in removal mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel supermacroporous PSA-nZVI composites with nanoscale zero-valent iron particles (nZVI) embedded into poly (sodium acrylate) (PSA) cryogels were synthesized through ion exchange followed by *in-situ* reduction. The magnetic composites were evaluated for material characterizations and their efficiency for Cr(VI) and total Cr removal from aqueous medium in batch experiments. PSA-nZVI composites with high nZVI loading capacity up to 128.70 mg Fe/g PSA were obtained, and the interconnected macroporous structure of PSA cryogel remained unaltered with nZVI uniformly distributed on PSA cryogel as determined by TGA, SEM, TEM, XRD and XPS analyses. PSA-nZVI composites showed faster reaction rate than free nZVI both for Cr(VI) and total Cr removal, suggesting no mass transfer resistance and the enhanced reactivity of nZVI in PSA carrier. PSA-nZVI composites exhibited much more remarkable performance for Cr(VI) and total Cr removal than free nZVI particles in high removal capacity and broad pH application range (pH 4–10). The reaction mechanisms were also elucidated with XPS analyses before and after Cr(VI) reduction reactions. These results demonstrate that PSA cryogel acts as an excellent carrier and shows multiple functions in nZVI particle dispersion, pH buffering and oxidation resistance in addition to immobilizing nZVI particles from release.

1. Introduction

Water contamination is a long-standing and severe environmental problem, and attracts increasing attention due to the

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shortage of clean water. Water polluted by heavy metals is becoming more focused owing to the toxicity and threat to human health. Aqueous chromium is a kind of major pollutants generally resulting from improper discharge of wastewater contaminated by chromium (Li et al., 2016). Chromium usually exists at two oxidation states (chromite [Cr(III)] and chromate [Cr(VI)]) that are characterized by different chemical behavior and bio-toxicity. Cr(VI) with high oxidative property is known for its high toxicity to plants, animals, human beings and its high solubility at any pH, as well as weak adsorption on mineral/soil surfaces in natural aqueous medium (Ai et al., 2008; Montesinos et al., 2014; Gueye et al., 2015). The form of Cr(VI) in aqueous solution is mostly $HCrO_4^-$ between pH 1.0 to 6.0 and CrO_4^{2-} when pH > 6.0. While Cr(III) is less soluble and toxic than Cr(VI) and can be readily precipitated as chromium hydroxide ($Cr(OH)_3$) at weak basic condition (Mohan and Pittman, 2006). Hence, it is regarded as a satisfactory solution that high mobile and toxic Cr(VI) is reduced to less soluble and toxic Cr(III), followed by removal of Cr(III) with the synergistic effect of adsorption and co-precipitation (Dong et al., 2016). WHO sets maximum acceptable concentration of 0.05 mg L^{-1} for total chromium in drinking water (Montesinos et al., 2014). However, total Cr concentration in natural water and wastewater contaminated by chromium is far more than the allowable guideline. Therefore, it is quite urgent to explore novel and effective ways for Cr(VI) and total Cr removal.

The removal of Cr species in any form from aquatic environments is an extremely important issue and a very difficult task (Ozay et al., 2011). Accordingly, many studies on the removal of Cr from aqueous medium necessitate the use of different techniques, such as chemical reduction, precipitation, and adsorption (Sahiner et al., 2016). However, the most frequently used technique is adsorption using inorganic clay, zeolite, alumina oxide and carbon or activated carbon as adsorbents. Unfortunately, the materials mentioned above are costly with low adsorption capacity and reaction rate, as well as difficult separation and recycle from aqueous media (Ozay et al., 2011; Sahiner et al., 2016; ur Rehman et al., 2017). Additionally, these adsorption materials often display no reduction ability toward the detoxification of Cr(VI)-contaminated media by transformation of Cr(VI) to Cr(III) (Li et al., 2016). Therefore, materials with highly efficient reduction ability and magnetic properties have gained a lot of attention due to the reductive properties and readily removal ability with the applied magnetic field (Ozay et al., 2009; Andrabi et al., 2016).

In recent years, nZVI particle has drawn much attention for its good potential in Cr treatment and remediation, as well strong magnetic properties (Ling and Zhang, 2014). The physic-chemical properties and reductive capacity can facilitate its rapid removal of Cr(VI). Unfortunately, there are still technical challenges associated with its application. nZVI particles tend to agglomerate because of strong magnetic property and larger surface area, and this leads to micrometer scale particles, low mobility and chemical reactivity, which, in turn, may bring about a negative effect on the reduction capacity (Fu et al., 2014; Calderon and Fullana, 2015; Wu et al., 2015). To address these issues, technologies have been attempted to develop supporting materials to enhance the dispersibility and reactivity of nZVI particles, such as clay materials (bentonite/montmorillonite, zeolite and kaolinite) (Shi et al., 2011; Zhang et al., 2011, 2013; Arancibia-Miranda et al., 2016), inorganic oxide materials (Fe_2O_3 and Fe_3O_4) (Ai et al., 2008; Wu et al., 2009), organic materials (chitosan and starch) (He and Zhao, 2005; Geng et al., 2009) and multifunctional material (biochar and graphene) (Li et al., 2016; Su et al., 2016). However, most of these composite materials are powders or tiny spheres, which are inconvenient to remove or formed great quantities of sludge in water treatment engineering. In addition, direct application of free nZVI in water treatment system may result in the loss of nZVI particles into environment and lead to secondary pollution, which imposes limitations on the practical industrial implication (Zhu et al., 2009). Therefore, it is of great necessity to seek a novel supporting material for nZVI particles, which could immobilize nZVI particles and be convenient to be separated from reaction medium as well as retain their reactivity.

Cryogel, a special form of hydrogels, is prepared by copolymerization at subzero temperatures with pore size up to a hundred micrometer and interconnected polymeric networks (Sahiner and Yildiz, 2014; Sahiner et al., 2016) and much attention has been paid to cryogel duo to its remarkable properties such as biocompatibility, nontoxicity, and supermacroporous interconnected pore structure (Păduraru et al., 2012; Zheng et al., 2013; ur Rehman et al., 2017). There are various types of cryogels/hydrogels based on different monomers used, such as poly (acrylamide) (P (AAm)) cryogel, poly (vinyl alcohol) (PVA) cryogel, poly ((3-Acrylamidopropyl)trimethylammonium chloride) (p (APTMACl)) cryogel, poly (4-vinylpyridine) (p (4-VP)) cryogel, poly (sodium acrylate) (PSA) cryogel, poly (2-acrylamido-2-methyl-1-propansulfonic acid) (p (AMPS)) hydrogel and others, whose monomers are acrylamide, vinyl alcohol, (3-Acrylamidopropyl)trimethylammonium chloride, 4-vinylpyridine, sodium acrylate and 2-acrylamido-2-methyl-1-propansulfonic acid, respectively (Ozay et al., 2009; Dobritoiu and Patachia, 2013; Loo et al., 2013; Sahiner and Yildiz, 2014; Seven and Sahiner, 2014; Sahiner et al., 2016). They have been widely used as adsorbents for efficient separation and purification of biomacromolecules in biotechnology and bioseparation process, as well as carriers for various research fields based on the presence and the extent of functional groups such as $-NH_2$, -OH, -COOH, $-CONH_2$, SO_3H (Ozay et al., 2009; Andrabi et al., 2016). Recently, cryogels are initially introduced into environment domain, and some researchers have stabilized metal particles into cryogel carriers to enhance their reactivity and diminish secondary pollution (Ozay et al., 2009; Önnby et al., 2014; Andrabi et al., 2016; Sahiner et al., 2016). Nevertheless, to our best knowledge, no study has been reported on stabilizing nZVI particles into supermacroporous cryogels.

In this study, supermacroporous PSA cryogel is adopted to synthesize PSA supported nZVI composites for its ionogenic functional group (-COONa) which can exchange with Fe^{2+} ions. PSA cryogel may act as a reactive supporting material to prevent uncontrollable growth of nZVI particles and then control its size and growth rate. At the same time, the introduction of nZVI particles makes the composites possess magnetic property. In addition, we hypothesize that the ionogenic functional group $-COO^-$ of PSA cryogel could act as a pH buffering agent to maintain the solution pH at weak alkaline condition suitable for Cr(III) precipitation. So the aims of this study are: (1) to investigate the removal performance and reaction mechanisms of Cr(VI) and total Cr with PSA-nZVI composites; (2) to explore the ability of PSA cryogel to prevent nZVI from leaching during reaction; (3) to verify whether PSA cryogel can act as pH buffering agent and then pH adjusting for Cr(III) precipitation is unwanted. The design of the PSA-nZVI composites may provide an easier and more sustainable way to apply nZVI for Cr removal in practical application.

2. Experimental details

2.1. Chemicals and materials

The monomer, sodium acrylate (SA, 98%, Xiya reagent), the crosslinker, *N*,*N*′-methylenebis (acrylamide) (MBA, 98%, Macklin), ammonium persulfate (APS ≥ 98%, Macklin) as an initiator, and