

Stabilized chitosan/Fe⁰-nanoparticle beads to remove heavy metals from polluted sediments

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ABSTRACT

Sediment contamination by heavy metals has become a widespread problem that can affect the normal behaviors of rivers and lakes. After chitosan/Fe⁰-nanoparticles (CS-NZVI) beads were cross-linked with glutaraldehyde (GLA), their mechanical strength, stability and separation efficiency from the sediment were obviously improved. Moreover, the average aperture size of GLA-CS-NZVI beads was 20.6 μm and NZVI particles were nearly spherical in shape with a mean diameter of 40.2 nm. In addition, the pH showed an insignificant effect on the removal rates from the sediment. Due to the dissolution of metals species into aqueous solutions as an introduction of the salt, the removal rates of all heavy metals from the sediment were increased with an increase of the salinity. The competitive adsorption of heavy metals between the sediment particles and GLA-CS-NZVI beads became stronger as the sediment particles became smaller, leading to decreased removal rates. Therefore, the removal efficiency could be enhanced by optimizing experimental conditions and choosing appropriate materials for the target contaminants.

Key words | chitosan (CS), glutaraldehyde (GLA), heavy metals, nanoscale zero-valent iron (NZVI), sediment

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INTRODUCTION

In the last few decades, sediment contamination by heavy metals, such as Cr(VI), Cd(II), Pb(II), etc., has been a major concern to environmental safety and public health (Arienzo *et al.* 2013). The interaction of heavy metals with sediment is complex (Hsieh *et al.* 2007; Orecchio & Giuseppe 2013; Bo *et al.* 2015), and sediment sorption can inhibit or limit the removal of heavy metals by sorption agents. Moreover, heavy metals cannot be degraded but are easily accumulated in human tissue (Akcil *et al.* 2015). Biological magnification through the food chain is a major concern for human health and environmental safety (Singh *et al.* 2000). Thus, remediation technologies are required to understand this matter more fully.

Recently, nanoscale zero-valent iron (NZVI) has been introduced into reducing various contaminants from soil and wastewater (Li & Zhang 2006; Zhang *et al.* 2011). However, the delivery and mobility of NZVI in soil limited the application of NZVI (He *et al.* 2007). NZVI in an aggregate state prevented its movement through sand and soil (Kanel & Choi 2007). To improve the delivery and mobility of NZVI in soil, various surfactants, such as starches (He &

Zhao 2005) and carboxymethyl cellulose (He *et al.* 2009), have been explored. Compared to non-stabilized NZVI, the stabilized NZVI displayed much improved soil mobility (Zhang *et al.* 2011).

Most reported studies have focused on the modification of NZVI to improve its delivery and mobility in soil. Due to their small size, NZVI was hardly separable from sediments after the remediation. However, the knowledge of the separation of NZVI from sediment after remediation has been lacking.

In recent years, environmentally friendly materials have been used in wastewater treatment (Barreca *et al.* 2014a, b). Chitosan (CS) was also used to modify and support NZVI (Geng *et al.* 2009). The CS beads, especially, were porous and effective in removing heavy metal, because of their special structural properties and high adsorption capability (Lasko & Hurst 1999; Li *et al.* 2005). However, the mechanical strength of CS beads needs to be improved (Candy & Sharma 1993). The mechanical strength of CS beads was obviously enhanced by glutaraldehyde (GLA) (Dambies *et al.* 2009; Wan-Ngah *et al.* 2002). However, the information

on chemical modification of CS-NZVI beads by GLA is limited.

The present study has therefore been established not only to enhance the mechanical strength of CS-NZVI beads but also to improve the separation of NZVI from sediment after remediation. Multiple heavy metals solutions were used as test contaminants to examine the effectiveness of GLA-CS-NZVI beads to remediate polluted sediment.

EXPERIMENTAL METHODS

The sediment collected from River Haihe (Tianjin, China) was air-dried at room temperature and then gently ground to pass through mesh screens. The properties of the sediment are shown in Table 1. It can be seen that the main part of the sediment was sand and the concentrations of heavy metals were much lower than those of the prepared sediment. A total of 20 g of the sediment was mixed with 100 mL of deionized water. A known mass of K₂Cr₂O₇, CdCl₂ and PbCl₂ was added into the prepared sediment-water mixture. The concentrations of Cr(VI), Cd(II) and Pb(II) in the sediment were 40 mg/kg, 46 mg/kg and 54 mg/kg, respectively.

CS-NZVI beads were prepared according to the procedures described in detail elsewhere (Li & Bai 2005). Recently prepared CS-NZVI beads were suspended in 2.0 g/L GLA solution for 24 h (Wan-Ngah *et al.* 2002). The GLA-CS-NZVI beads were then intensively washed with deionized water and stored in deoxygenated deionized water for further use.

GLA-CS-NZVI beads were added into the prepared sediment-water mixture at room temperature with mechanical agitation for 48 h. The sediment-water mixture was then withdrawn using a 10 mL dispensable syringe and filtered through a 30 µm filter. In this process, the GLA-CS-NZVI beads were purposefully excluded from the mixture.

Table 1 | Characterization of the sediment

Property of sediment	Content or concentration
Sand content	93.8%
Silt content	4.6%
Clay content	1.6%
Organic matter content	1.8%
pH value	6.7
Concentrations of heavy metals	Cr (0.2 µg/kg), Cd (0.1 µg/kg), Pb (0.2 µg/kg), Cu (0.2 µg/kg), Fe (20 µg/kg), Zn (12.8 µg/kg)

The remainder on the filter was frozen for the following freeze drying and microwave digesting treatment in accordance with a previously reported procedure (Hoffmann & Patzold 2002; Sandroni *et al.* 2003). All experiments were performed in duplicate.

Before the GLA-CS-NZVI beads were added into the sediment-water mixture, the mass of the beads was measured, named M_1 . After the remediation of sediment-water mixture, the mass of the separated beads from sediment was also measured, named M_2 . The separation efficiency (SE) was calculated using the following equation:

$$SE (\%) = \frac{M_2}{M_1} \times 100\% \quad (1)$$

Characterization and analytical methods

The morphological analysis of GLA-CS-NZVI beads was performed using a scanning electron microscope (SEM) (SEM, FEI Nova NanoSEM 230). The morphological analysis of NZVI was performed using a transmission electron microscope (TEM, FEI Tecnai G2 F20). The concentrations of heavy metals were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Elan-9000, PE). The concentration of Cr(VI) in the solution was determined using a UV/visible spectrophotometer and by the diphenyl-carbazine method (Ponder *et al.* 2000). Fourier transform infrared (FTIR) spectra for the CS-NZVI beads before and after being exposed to GLA were obtained using a Nexus FTIR spectroscopy.

RESULTS AND DISCUSSION

The stability of GLA-CS-NZVI beads

The stability of GLA-CS-NZVI beads was tested using mechanical properties and solubility in the solution. The mechanical strength of CS-NZVI and GLA-CS-NZVI beads was determined using a similar procedure described by Guo *et al.* (2004). The results are shown in Table 2.

It can be seen from Table 2 that crumpling ratios of GLA-CS-NZVI beads were markedly reduced after CS-NZVI beads were cross-linked with GLA, indicating that the mechanical strength of GLA-CS-NZVI beads was obviously enhanced. The blending of GLA in CS improved the mechanical strength of the hydrogel beads (Li & Bai 2002). A Schiff's reaction occurred between GLA and CS

Table 2 | Comparison of the mechanical strength of CS-NZVI beads and GLA-CS-NZVI beads

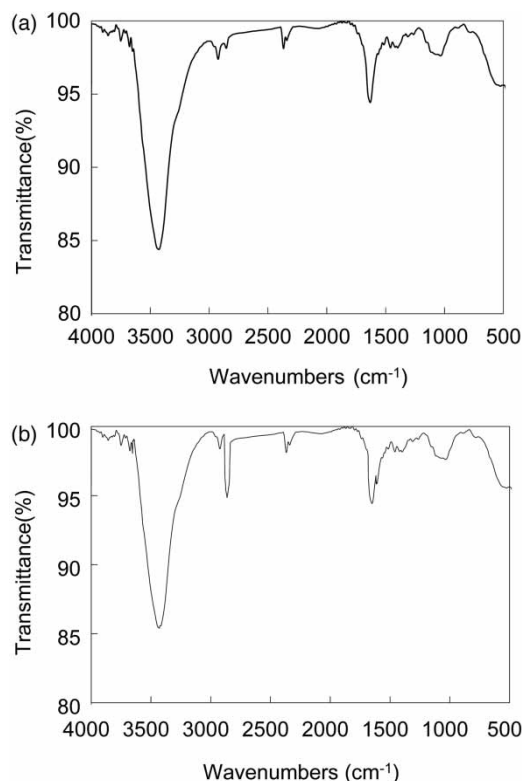
Beads	Stirring speed (rpm)			
	100	200	400	800
CS-NZVI	0	2	24	48
GLA-CS-NZVI	0	0	0	2

beads (Dambies *et al.* 2001), which could increase the stability of CS beads (Hsien & Rorrer 1997). Crumpling ratios of GLA-CS-NZVI beads were smaller than those of ECH-CS-NZVI beads (Liu *et al.* 2012), meaning that the mechanical strength of GLA-CS-NZVI beads was greater than that of ECH-CS-NZVI beads.

It was shown that the cross-linked beads (GLA-CS-NZVI beads) were found to be insoluble in alkaline and neutral solutions especially, as well as in acidic solution (Table 3). Due to a primary amine group on CS, CS beads could be dissolved in acid solutions (Wan-Ngah *et al.* 2002). A Schiff's reaction occurred between aldehyde groups on GLA and amine groups on the CS beads, which could enhance the stability in acidic media (Dambies *et al.* 2001). A chemical cross-linking reaction between GLA and CS was found to enhance the stability of CS beads in acid solutions (Li & Bai 2005). As a result, GLA-CS-NZVI beads could be used in acidic, alkaline and neutral solutions, which would extend its applicable field for *in situ* remediation of environmental pollution.

FTIR analysis

To identify possible cross-linking reactions between GLA and CS-NZVI beads, FTIR spectra were obtained for the CS-NZVI beads before and after being exposed to GLA (Figure 1). The characteristic peak at 1,631 cm⁻¹ was from the N-H bending vibration and the new peak at 3,426 cm⁻¹ contributed to the N-H and O-H stretching vibration (Figure 1(a)), indicating the existence of amide(II) and hydroxyl groups on CS chain (Wan *et al.* 2006). The FTIR

**Figure 1** | FTIR spectra for the CS-NZVI beads before (a) and after (b) the cross-linking reaction between GLA and CS-NZVI beads.

spectrum for GLA-CS-NZVI beads (Figure 1(b)) shows that the characteristic peaks at 1,631 and 3,426 cm⁻¹ became weaker, which indicated that amide(II) groups worked in the cross-linking reaction. Furthermore, new strong peaks at 2,864 and 1,648 cm⁻¹ appeared in Figure 1(b). The peaks at 2,864 were attributed to the stretching vibration of symmetric -CH₂ groups (Wan-Ngah *et al.* 2008). A Schiff's reaction occurred between aldehyde groups on GLA and amine groups on CS (Wan-Ngah *et al.* 2002), so the peak at 1,648 cm⁻¹ would be indicative of C=N chains. The results indicated that the number of symmetric -CH₂ groups and C=N chains was increased after the reaction. Therefore, the conclusion could be drawn that GLA could be used to promote the mechanical strength of CS-NZVI beads by the cross-linking reaction.

SEM and TEM characterization

SEM and TEM images were used to understand the morphology of GLA-CS-NZVI beads and NZVI in GLA-CS-NZVI beads (Figure 2). The aperture size of CS-NZVI beads ranged from 9.5 to 108.8 μm with an average size of 42.6 μm (Liu *et al.* 2012). After cross-linking of GLA, the

Table 3 | Solubility effect of CS-NZVI beads and GLA-CS-NZVI beads

Beads	Solubility effect		
	6% (v/v) acetic acid	Distilled water	0.1 M NaOH
CS-NZVI	Soluble	Insoluble	Insoluble
GLA-CS-NZVI	Insoluble	Insoluble	Insoluble

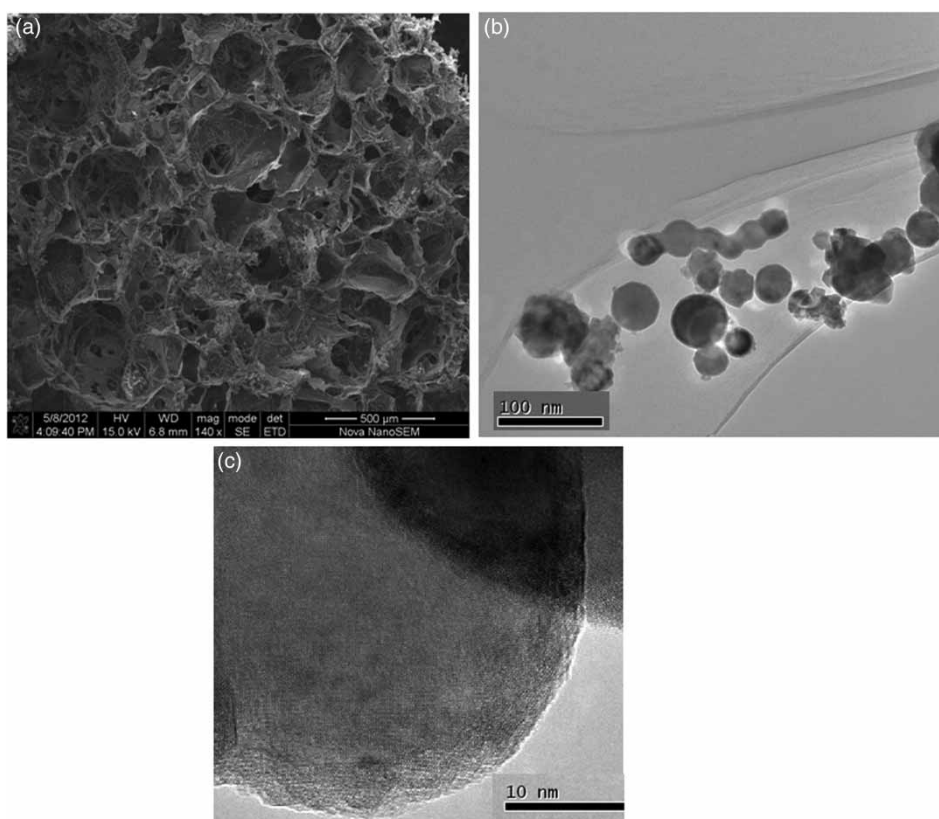


Figure 2 | The morphology of GLA-CS-NZVI beads and NZVI was analyzed: (a) SEM image of the cross-section of GLA-CS-NZVI beads; (b) TEM image of NZVI in GLA-CS-NZVI beads; and (c) higher magnification of TEM image of NZVI.

average aperture size of GLA-CS-NZVI beads became smaller and was 20.6 μm (Figure 2(a)). This indicated that CS-NZVI beads modified by GLA would be favourable for enhancing the mechanical strength of CS-NZVI beads. GLA-CS-NZVI beads showed an interconnected flow-through polymeric network with irregular pores, which could promote the transfer of electrons and flows of mass between these beads and sediment (Liu *et al.* 2012). NZVI particles were nearly spherical in shape with a mean diameter of 40.2 nm (Figure 2(b)). It can be noted that NZVI particles were found with an obvious lattice structure in Figure 2(c). Other researchers also found the lattice structure in iron oxide (Lian *et al.* 2014).

The separation efficiency

The SE of GLA-CS-NZVI beads from the sediment-water mixture after remediation was studied and the results are shown in Table 4. The SE of CS-NZVI beads and GLA-CS-NZVI beads from the sediment-water mixture was enhanced to 95.8 and 96.5%, respectively (Table 4).

Table 4 | SE of GLA-CS-NZVI beads and NZVI from the sediment-water mixture

Kinds of NZVI	SE
NZVI	Nonseparable
CS-NZVI beads	95.8%
GLA-CS-NZVI beads	96.5%

However, NZVI was nonseparable from the sediment-water mixture (Table 4). This meant that NZVI supported on GLA-CS beads could enhance its SE from the sediment. The sterically hindered effect was the main driving force that resulted in the separation of GLA-CS-NZVI beads from the sediment (Kurahashi *et al.* 2006). Sterically hindered substrates enjoyed a broad scope and wide functional group tolerance (Yin *et al.* 2002). Steric hindrance was shown to control CO₂-amine reactions (Sartor & Savage 1983). The efficiency of the carbon dioxide cycling process could be improved by a series of amino acid salts with sterically hindered amine groups (Hook 1997). Faster reaction rates have now been achieved with sterically hindered chelating alkyl phosphine ligands (Hamann & Hartwig 1998). Furthermore,

GLA-CS-NZVI beads could remain suspended and floated in or on the sediment-water mixture due to the effect of the buoyancy force (Rani *et al.* 2010).

Effect of pH values

The dominant forms of heavy metals in sediment and aqueous solution were affected by pH (Mohan & Pittman 2006). A change of pH could influence the reaction rate of iron oxidation (Alowitz & Scherer 2002), which could be used to remove heavy metals (Melitas *et al.* 2001). Thus, the effect of pH on heavy metals removal was conducted and the results are shown in Figure 3(a). It is noted that with an increase of pH, removal rates of Cr(VI) from sediment decreased but removal rates of Cd(II) and Pb(II) from the sediment increased (Figure 3(a)). Due to the protonation of amino groups, these beads were positively charged at lower pH while Cr(VI) existed mostly as an anion, which led to the electrostatic attraction between Cr(VI) and these beads (Boddu *et al.* 2003). Thus, Cr(VI) removal rate decreased with an increase in pH. However, as an increase in hydroxyl groups, the number of negatively charged sites on GLA-CS-NZVI beads was improved, leading to an enhanced attraction force between metallic cations (Cd²⁺ and Pb²⁺) and these beads. As a result, the removal amount of Cd²⁺ and Pb²⁺ was increased. In general, heavy metals activities in environmental media depended on

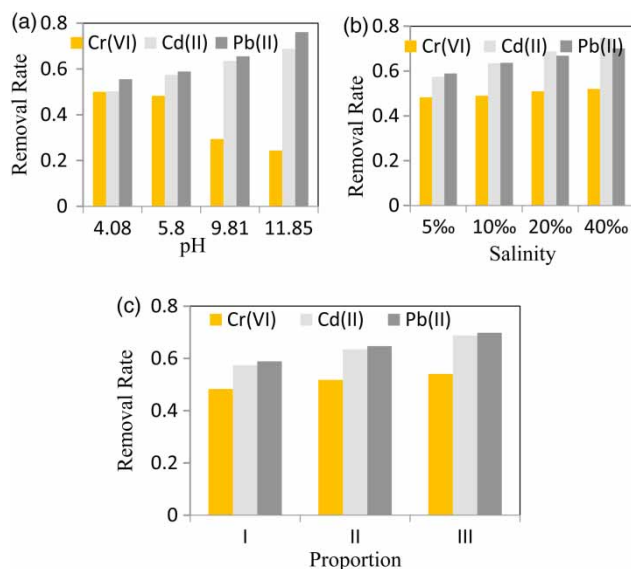


Figure 3 | Effect of experimental factors on the removal efficiency of heavy metals from sediment. (a) pH values, (b) the salinity and (c) the proportion of the sediment with different sizes: I: 40% (100–200 mesh): 25% (40–100 mesh): 35% (40 mesh); II: 35% (100–200 mesh): 25% (40–100 mesh): 40% (40 mesh); III: 10% (100–200 mesh) 40% (40–100 mesh): 50% (40 mesh).

their forms and the environmental factors (Bo *et al.* 2015). The sediment was a complex and heterogeneous matrix of many different components and phases (Usero *et al.* 1998; Brils 2008; Gao *et al.* 2013), as a result, heavy metals were easily accumulated in the sediment (Haroun *et al.* 2007). When water environment conditions change, heavy metals in the overlying water can be accumulated in the sediments (Long *et al.* 2009). Furthermore, due to the physical properties of the sediment, i.e. size, magnetism and surface hydrophobicity, heavy metals could be adsorbed on the sediment (Peng *et al.* 2009).

Effect of salinity

Very often, variation in the salinity might lead to the release of heavy metals back to the aqueous phase (Singh *et al.* 2000; Jain 2004), which would influence the concentration distribution of heavy metals in sediment and wastewater. As mentioned above, the effect of salinity on the removal efficiency was introduced and the results are shown in Figure 3(b). The removal rates of all heavy metals from sediment were higher than 48.5% and increased with an increase of salinity (Figure 3(b)).

Because of an increase in the salinity, the release of heavy metals back to the aqueous phase was enhanced (Jain 2004), leading to more heavy metals ions in the solution which were easily captured by GLA-CS-NZVI beads. This analysis was well verified by our experiment and the results are shown in Figure 4. As the salinity was increased from 0 to 40‰, the concentrations of heavy metals in the sediment reduced gradually, however, the concentrations of heavy metals in wastewater (the aqueous phase) were enhanced gradually (Figure 4). Heavy metals were adsorbed in the sediment by several mechanisms: surface adsorption, ion exchange and complexation with organic substances (Wang *et al.* 2010). When salt (NaCl) was introduced, the physicochemical properties of the sediment were changed

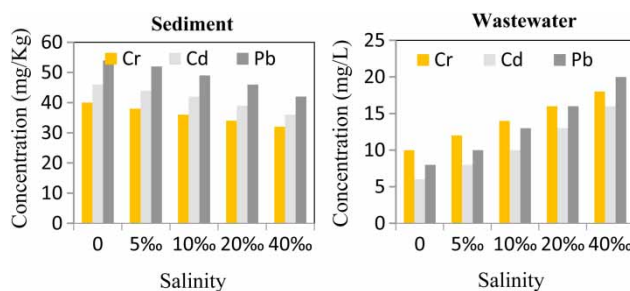


Figure 4 | Effect of salinity on the concentration distribution of heavy metals in sediment and wastewater.

(Usero *et al.* 1998; Brils 2008), which would favour microbial activity and dissolution of metals species into aqueous solutions (Erust *et al.* 2013).

Effect of the proportion of the sediment with different sizes

The effect of the particle size of the sediment on the removal efficiency of heavy metals was studied and the results are shown in Figure 3(c). The removal rates of heavy metals decreased with an increasing proportion of the smaller particles in the sediment (Figure 3(c)). NZVI was an adsorbent with higher sorption ability than the other material (Bolan *et al.* 2014), however, heavy metals could be easily adsorbed by the sediment particles. As a result, the competitive adsorption of heavy metals between the sediment particles and GLA-CS-NZVI beads became stronger as the sediment particles were smaller. Therefore, the decreased removal rates were observed as the proportion of smaller particles in sediment increased.

The results clearly indicate that GLA-CS-NZVI beads with an improved mechanical strength and stability in the solution were efficient to remove heavy metals from sediment. GLA-CS-NZVI beads may possibly offer a way to effectively use NZVI in many surface water or groundwater remediation situations.

CONCLUSIONS

GLA-CS-NZVI beads were successfully prepared and resulted in being effective in removing heavy metals from the sediment. After cross-linking with GLA, the mechanical strength, stability and SE of CS-NZVI beads were clearly improved. Different experimental conditions played a rather important role in the removal efficiency of heavy metals from the sediment. According to the results, the removal rates of heavy metals from sediment-wastewater mixture could be increased by changing the environmental conditions for the *in situ* remediation of contaminated sediment or wastewater.

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