



Montmorillonite-supported nanoscale zero-valent iron for removal of arsenic from aqueous solution: Kinetics and mechanism

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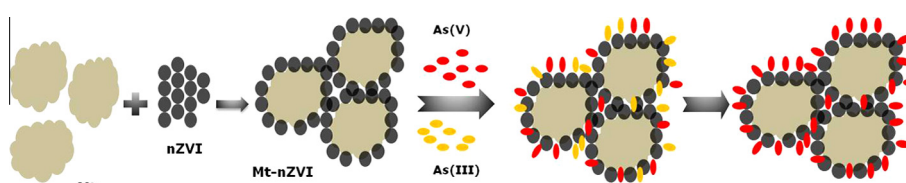
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HIGHLIGHTS

- Novel adsorbent consisting of montmorillonite-supported nZVI have been synthesized.
- Mt-nZVI consists of core shell Fe(0) structure with an outer oxide/hydroxide shell.
- Mt-nZVI showed higher affinity for As(III) than As(V).
- As(V) was not reduced but As(III) was oxidized to As(V) on reaction with Mt-nZVI.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 October 2013

Received in revised form 16 December 2013

Accepted 18 December 2013

Available online 28 December 2013

Keywords:

Arsenic
Montmorillonite
Nano zero valent iron
Adsorption

ABSTRACT

Montmorillonite-supported nanoscale zero-valent iron (Mt-nZVI) has been synthesized to remove inorganic arsenic (As) from aqueous solutions. BET, SEM, EDX, XRD and XPS were used to characterize the clay-supported material which consists mainly of core shell Fe(0) structure with an outer oxide/hydroxide shell. The dispersion of nZVI onto montmorillonite was found to be increased with decreasing tendency to agglomerate into larger particles. Batch experiments revealed that adsorption kinetics followed pseudo-second order rate equation with high affinity towards both As(III) and As(V) over a wide pH range (4–8) which was decreased at pH > 9. The maximum adsorption capacity calculated from the Langmuir adsorption isotherm was found to be 59.9 and 45.5 mg g⁻¹ for As(III) and As(V) respectively at pH 7.0. Although the presence of competing anions like SO₄²⁻, HCO₃⁻ and NO₃⁻ did not show pronounced effect, PO₄³⁻ had an inhibitory action on the adsorption. The XPS analyses of As-reacted Mt-nZVI indicated the occurrence of surface catalyzed oxidation of As(III) to As(V). The possible regeneration using 0.1 M NaOH and performance of Mt-nZVI was investigated by repeating adsorption-elution process. This study has great significance for demonstrating Mt-nZVI as potential adsorbent to reduce elevated levels of As in groundwater.

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1. Introduction

Arsenic (As) is a naturally occurring metalloid and common constituent of earth crust [1]. However As is one of the toxic and

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carcinogenic elements and is categorized as the first priority toxic substances by WHO [2]. The inorganic species, arsenate [As(V)] and arsenite [As(III)] are the predominant forms of As in groundwater and surface water [1]. As(V) exists as oxyanions (H₂AsO₄⁻ and HAsO₄²⁻) at neutral pH, while As(III) remains protonated as H₃AsO₃ below pH 9.2 [3]. Thus the mobility of As is dependent upon the oxidation state which in turn depend upon the redox

environment where As(III) predominates under reducing condition [4].

Chronic exposure to As via drinking water is the major cause of As poisoning and currently millions of people are at risk from consuming As contaminated water [5]. The grave of the problem lies in the fact that exposure to low concentration ($<50 \mu\text{g L}^{-1}$) can cause chronic toxicity of As. Thus various environmental protection agencies and National Standards are lowering the permissible level of As below $10 \mu\text{g L}^{-1}$ in drinking water. It is therefore necessary to develop simple, fast and low cost methods for removal of As from aqueous environment. Currently, there are various technologies that are being used to reduce the concentration of As from aqueous environment [6], but among them, adsorption is more common because of its simplicity, treatment stability and cost effectiveness [7]. Moreover, the process can be sludge free when the loaded adsorbent can be regenerated for repeated use. As a consequence, novel adsorbent are continuously being researched for the practicability of its application in removing not only As but also other toxic chemical contaminants from aqueous solution [8–12].

Elemental iron and iron hydroxides have a high affinity for As and these materials have extensively been used for As removal [7]. Zero-valent iron is one such material that has been effective to reduce the concentration of As and has successfully been applied to field scale permeable reactive barrier system [13–15]. Recently, nanoscale zero-valent iron (nZVI) has been used for treatment of As contaminated groundwater [16–19]. Because of its large active surface area and high As adsorption capacity, nZVI acts as promising material for removal of As from aqueous solution [20]. However, tiny particle size and powder state along with lack of durability and mechanical strength restricts the direct use of nZVI [21]. The intrinsic characteristics of nZVI to agglomerate during preparation decreases the reactivity of the particle and also results in poor mobility and successful transport of nZVI to the contaminated area for *in situ* remediation [22]. Moreover, agglomeration of iron particles in fixed bed column or any other dynamic flow system results in high-pressure drop, thus restricting the direct use of nZVI for field scale application. Hence, loading nZVI onto supporting material may be a potential method to decipher the problem [21]. Clay is an abundant natural resource and can be a suitable supporting material due to its potential applicability in catalysis and various composites [23,24]. Clay-nZVI is known to remove heavy metals (Cr, Pb, Co) from aqueous solution [25–27]. However little is known about the use of such material for removal of As from aqueous solution.

Thus the present study aims to characterize the montmorillonite-supported nanoscale zero-valent (Mt-nZVI), synthesized by borohydride reduction method and to test the adsorption capability towards inorganic As in aqueous solution. Sorption kinetics, isotherm and the effect of solution pH and chemical competition on the adsorption were studied in details. Open atmospheric conditions were chosen in all experiments in order to have reaction condition compatible with the natural system. Finally, a mechanism of As removal and method for regeneration of Mt-nZVI after repetitive use have also been proposed.

2. Experimental

2.1. Materials and chemicals

The natural Na-Montmorillonite (SWy-2, abbreviated as Mt in this study) obtained from Source Clay Mineral Repository, University of Missouri, Columbia, USA was used without any pre-chemical treatment. The X-ray diffraction pattern showed that the clay consists primarily of Mt with minor impurities of quartz and muscovite.

All the chemicals were analytical grade and used without further purification. Sodium borohydride (NaBH_4), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and absolute ethanol (99%) were obtained from Panreac (Spain). Stock solutions of As(V) and As(III) were prepared by dissolving appropriate amount of di-sodium hydrogen arsenate-heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) (Merck) and sodium (meta) arsenite (NaAsO_2) (Fluka) respectively in deionized water (Millipore Milli-Q 18 M Ω).

2.2. Preparation of Mt-nZVI

Montmorillonite-supported nanoscale zero-valent iron (Mt-nZVI) was synthesized under N_2 atmosphere by conventional method of reducing Fe(III) with NaBH_4 in presence of Mt as a supporting material [26,27]. An excess of NaBH_4 was used to ensure complete reduction of Fe(III). nZVI without supporting clay were also prepared in similar way. The protocol of synthesis is provided in Supporting information (S1). After the synthesis, Mt-nZVI and nZVI were dried in vacuum and stored under N_2 atmosphere to prevent aerial oxidation prior to experiment.

2.3. Characterization and measurement

Zero point charge pH (pH_{ZPC}) of the Mt-nZVI was determined by acid–base titration method as described by Stumm and Morgan [28]. The surface morphology images of Mt-nZVI were taken by scanning electron microscope (SEM) (CARL-ZEISS model DSM 960 A, Germany) operating at 30 kV and equipped with energy dispersive X-ray (EDX) analysis. The dried samples were coated on gold and carbon for SEM and EDX analyses respectively. X-ray diffraction (XRD) pattern of Mt and Mt-nZVI were performed in a Bruker X-ray powder diffractometer (model D8) using $\text{Cu-K}\alpha$ radiation source operating at 40 kV and 40 mA. The specific surface area was measured by Brunauer–Emmett–Teller (BET) N_2 adsorption method using a Micromeritics Gemini V2.00 (Model 2380) instrument where the samples were dried with a constant flow of N_2 at 60 °C for 24 h.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of Mt-nZVI within a depth of $<10 \text{ nm}$. The analysis was performed with an upgraded ESCALAB 220i-XL spectrometer using monochromatic Al - $\text{K}\alpha$ radiation operated at 15 kV and 150 W. Charge corrections were applied on the spectra using the C1s line (284.6 eV) of adventitious aliphatic carbon as an internal reference. Data acquisition and processing was done using Advantage Data Spectrum Processing Package (Thermo VG Scientific, UK).

2.4. Adsorption experiments

The adsorption experiments were performed in batch method at room temperature ($22 \pm 1 \text{ }^\circ\text{C}$) under open (aerobic) laboratory conditions. In a typical kinetic experiment, Mt-nZVI (1 g L^{-1}) was added to a 50 ml centrifuge tube and an aqueous solution of either As(III) and As(V) was added so as to make a final concentration of 5 mg L^{-1} . The pH of the solution was adjusted to 7.00 using an aqueous solution of HCl and NaOH and was shaken in a rotating shaker. Solutions were withdrawn at selected interval of time and were filtered using $0.45 \mu\text{m}$ filter (Minisart-GF, Sartorius Stedim Biotech). The filtrate was stored with acidification at 4 °C until analysis of total As concentration by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7500C). Based on preliminary kinetic experiment, equilibration time was set at 4 h.

In order to investigate the effect of pH on adsorption, initial pH was varied from 4 to 10. Five mg L^{-1} of As(III) and As(V) were equilibrated for 4 h and were filtered using $0.45 \mu\text{m}$ filter for As

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