



# Sorptive removal of arsenite [As(III)] and arsenate [As(V)] by fuller's earth immobilized nanoscale zero-valent iron nanoparticles (F-nZVI): Effect of Fe<sup>0</sup> loading on adsorption activity



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## ABSTRACT

Fuller's earth immobilized nanoscale zerovalent iron (F-nZVI 1–8) were synthesized by borohydride reduction method. The iron loading of fuller's earth immobilized nZVI was varied from 5 to 50% (w/w) in these F-nZVI 1–8. The F-nZVI 1–8 were characterized by FE-SEM-EDX, FTIR, BET, XRD and TGA. The FE-SEM analysis showed an increase in agglomeration of nZVI on the immobilized material with increase in the loading of Fe<sup>0</sup>. F-nZVI 1–8 were studied for adsorptive removal of As(III) and As(V) from aqueous solution, with an emphasis on the effect of Fe<sup>0</sup> loading of adsorbent on arsenic remediation. Iron loading has a significant role in adsorption of As(III) and As(V) on F-nZVI, with increase in adsorption with optimum iron loading of 20% (w/w) on fuller's earth (F-nZVI-4). However, increase in loading above 20%, resulted in no significant increase in As(III) and As(V) adsorption. The adsorption results fitted well with Langmuir and Freundlich isotherm models and the maximum adsorption capacity of F-nZVI-4 for As(III) and As(V) were observed to be 50.08 and 91.42 mg/g, respectively. The adsorption isotherm and kinetic studies indicate a rapid removal of As(III) and As(V) from the aqueous solution in the presence of F-nZVI 1–8, with a substantially high rate of removal for arsenic with F-nZVI-4.

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## 1. Introduction

Arsenic is a metalloid and natural constituent of earth's crust which is recognized as a one of the most ubiquitous pollutant in the environment [1] and bioaccumulate in marine life [2], threatening the life of human population [3]. Biochemical processes have resulted in the release of naturally occurring arsenic into groundwater whereas uncontrolled anthropogenic activities such as mining, fossil fuel burning, smelting of metal ores, wood preservatives and pesticide use, release arsenic directly into the environment [4]. In ground and surface water, the prevalent forms of arsenic are inorganic arsenite (AsO<sub>3</sub><sup>3-</sup>) and arsenate (AsO<sub>4</sub><sup>3-</sup>) [5] whereas, organic arsenical are less prevalent and formed from biomethylation processes which generally bioaccumulate in aquatic organisms [6,7]. As(III) and As(V) are both linked to energy related functions of mitochondria in a cell. As(III) has very high affinity for sulfhydryl groups in protein leading to formation of thiolated species which inhibit the enzyme activity. However, As(V) compete with phosphate and limit oxidative

phosphorylation which is key to the high bond energy of ATP molecules [8]. Further, As(III) is more toxic and mobile in environment than As(V) [9], due to its existence in neutral form (H<sub>3</sub>AsO<sub>3</sub>) under a wide range of physiological conditions. As(V)/As(III) ratio plays a significant role in our environment. The As(V)/As(III) ratio in the environment is partly explained on the basis of pH–pE conditions, as in case of sea water it lies in the range of 10<sup>15</sup>–10<sup>26</sup>. However, in the marine organisms and humans this ratio is found to decrease tremendously. A primary exposure of human body to arsenic is through the consumption of contaminated water, which leads to arsenic poisoning or arsenicosis [10]. Long term exposure to arsenicals cause severe diseases such as hyperkeratosis, skin lesions, black foot diseases and cancer of the bladder, lungs, skin, kidney and liver [11,12]. Due to its significant toxicity, World Health Organization (WHO) has established 10 µg/L as the maximum contaminant level for total arsenic in potable water [12].

Various conventional technologies have been used for arsenic remediation including oxidation and reduction [13], co-precipitation [14], membrane processes [15] and ion-exchange resins [16]. Besides these techniques, adsorption [17–19] is a common technique successfully employed for water treatment of heavy metal remediation. However, oxidation and reduction, chemical

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precipitation and electrochemical process of arsenic removal are ineffective, especially when the arsenic concentration in the aqueous solution is higher [20]. Ion-exchange and membrane technology are expensive when treating large quantity of water containing arsenic and they cannot be used at large scale [21]. But among these conventional processes, adsorption is more commonly used due to its easy operation and cost effectiveness, when the loaded adsorbent can be regenerated for repeated use [22]. Based on the nature association of arsenic with soil [23], hematite and pyrite, various synthetic adsorbents studied for arsenic removal include alum [24], alumina [25], manganese oxide [18,26], and hydrotalcite [27,28]. ZVI (iron filings) and iron oxides have shown a very good adsorption efficiencies for arsenic remediation by reductive-sorption and  $\mu$ -oxo bridging interactions, respectively [29,30]. However, the mechanism for removal of both As(III) and As(V) by ZVI, is generally characterized by adsorption on enclosing oxide layer or by co-precipitation with Fe(II)/Fe(III) produced at the interface of the material and solution during corrosion [31,32].

In an effort to enhance the removal efficiency of iron based material, nanoscale zero-valent iron (nZVI) were developed. nZVI not only remediates arsenic but has a broad range of application in reductive removal of heavy metals [33,34], nitrite [35], trichloroethylene [36] and pesticides [37] from groundwater. However, these nZVI particles tend to get oxidized by air or water and agglomerate due to their high surface energy and intrinsic magnetic interaction, which leads to constrained chemical reactivity of the material [38]. The optimum activity of nZVI is ensured using stabilizers and/or immobilizers. Stabilizers are passivators, which reduce the interaction between the surface of nZVI and water present in the immediate environment. Alternatively, immobilizers are polymers on which the particles are entrapped and entrained, leading to lower agglomeration. Various immobilizers have been used for stabilizing and increasing activity of nZVI such as PVA microspheres [39], resins [40], multiwall carbon nanotubes [41], cellulose [42], Ca-alginate [43], chitosan [44], activated carbon [45], cation exchange membranes [46] and silica [47]. Apart from these, various aluminosilicates have been reported for the immobilization of the nZVI including zeolite [48], montmorillonite [49], kaolinite [50] and bentonite [51]. These aluminosilicate immobilized nZVI show higher efficiency for arsenic adsorption in comparison of bare nZVI [52]. Thus in the present work, fuller's earth immobilized nZVI with different iron loading were characterized and studied for their arsenic adsorption efficiency. Fuller's earth is a fine-grained, naturally occurring earthy substance that has been used in many medical and cosmetics applications. It has been used as a natural adsorbent in decontamination of dyes wastewater [53] and mercury [54]. This adsorption behaviour is attributed to large surface area and negative surface charge of fuller's earth in comparison to other aluminosilicates. Thus, in continuation of our work on immobilized nZVI for water treatment [42], study of effect of iron loading on adsorption efficiency of F-nZVI was carried out.

## 2. Experimental

### 2.1. Materials

All chemicals used including fuller's earth, anhydrous ferric chloride ( $\text{FeCl}_3$ ), sodium borohydride ( $\text{NaBH}_4$ ), polyethylene glycol [ $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ ], methanol ( $\text{CH}_3\text{OH}$ ), sodium hydroxide ( $\text{NaOH}$ ) and hydrochloric acid ( $\text{HCl}$ ) were of analytical grade and used directly without further purification. The stock solution of As(III) and As(V) were prepared from sodium arsenite ( $\text{NaAsO}_2$ ), and sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ). All the solutions were prepared with

type-1 water (resistivity  $< 18.2 \text{ M}\Omega \text{ cm}$ ; total organic content (TOC)  $< 10 \text{ ppb}$ ) under ambient condition.

### 2.2. Preparation of F-nZVI

To a suspension of fuller's earth (36g) in 2% aqueous polyethylene glycol solution (500 mL), ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in varied amount (2.74–27.40 g) was added and kept under stirring for 30 min. Dropwise addition of aqueous  $\text{NaBH}_4$  (10 or 20% w/v) aqueous solution was carried over a period of 2 h with continuous stirring. The completion of reaction was characterized by the colourless solution and black coloured suspension settled to the bottom. Upon completion of the reduction, the black coloured precipitate is separated by Buchner filtration. The residue were washed with excess methanol to remove borohydride impurity and moisture retained on the surface of the material and resulting black solid was dried in-vacuo to furnish F-nZVI 1–8 with 5–50% (w/w) iron loading on fuller's earth. This material was stored in tight capped containers to prevent the aerial oxidation prior to characterization and adsorption experiment.

### 2.3. Characterization

The specific surface area of fuller's earth and F-nZVI were measured by BET- $\text{N}_2$  adsorption method (Brunauer–Emmett–Teller) using Micrometrics ASAP-2020, where the samples were dried with constant flow of  $\text{N}_2$  at  $60^\circ\text{C}$  for 24 h. The structure and surface morphology of fuller's earth and F-nZVI were studied by field emission-scanning electron microscope (FE-SEM) (CARL-ZEISS model Merlin Compact, Germany) operating at 4 kV equipped with energy dispersive X-ray (EDX) analyzer. The dried samples were coated with gold prior to FE-SEM analysis. The infrared transmittance spectra were obtained using BRUKER TENSOR 27 Fourier Transform Infra-Red (FTIR) spectrometer. Samples were prepared by mixing specimens with KBr powder in 1:20 (w/w) ratio, and pressing the mixture into a pellet. X-ray diffraction (XRD) pattern of fuller's earth and F-nZVI were performed on a Bruker D8 X-ray powder diffractometer with a high power  $\text{Cu-K}\alpha$  radioactive source ( $\lambda = 0.154 \text{ nm}$ ) at 40 kV/40 mA. Continuous scans for  $2\theta$  from  $10^\circ$  to  $70^\circ$  were collected at a scan rate of about  $3^\circ/\text{min}$ . The thermal properties of adsorbents were analysed using a DTA-TG apparatus (DTG-60H, Shimadzu, Japan) from 25 to  $550^\circ\text{C}$  at heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere.

### 2.4. Adsorption experiment

Stock solution (1000 mg/L) of As(III)/As(V) were prepared. As (III)/As(V) solutions of desired concentration (20–100 mg/L) were prepared by diluting the stock solution. Adsorption studies were performed using 100 mL of arsenic solution in determinate concentration, pH of solution adjusted between 3 and 10 using  $\text{HCl}$  and  $\text{NaOH}$ , followed by the addition of 1 g/L of synthesized F-nZVI 1–8. The flasks were maintained at constant temperature of  $25 \pm 2^\circ\text{C}$  under shaking at 150 rpm using an incubator shaker. The solutions were filtered after 24 h using Whatman filter paper and analysed on Atomic Absorption Spectrophotometer (AAS) in flame mode. All the experiments were performed in duplicate and blank were prepared under identical experimental conditions. The amount of arsenic adsorbed on to F-nZVI was calculated using the following equation:

$$q = V \frac{C_i - C_f}{M} \quad (1)$$

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