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Adsorptive removal of arsenate from aqueous solutions by biochar supported zero-valent iron nanocomposite: Batch and continuous flow tests

Shengsen Wang [a], Bin Gao [a,*], Yuncong Li [b], Anne Elise Creamer [a], Feng He [c]

[a] Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States
[b] Tropical Research and Education Center, University of Florida, Homestead, FL 33031, United States
[c] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, China

HIGHLIGHTS

- Biochar supported nZVI (nZVI/BC) was synthesized.
- nZVI/BC showed excellent As(V) removal efficiency in batch and CMR experiments.
- 100% removal efficiency was achieved in CMRs.
- Surface adsorption was the dominant removal mechanism.

GRAPHICAL ABSTRACT
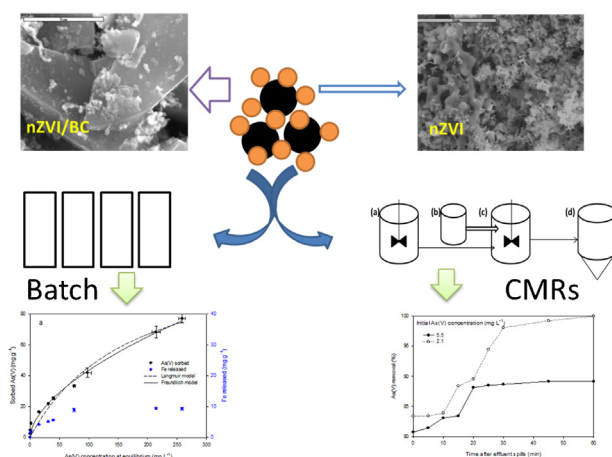
ABSTRACT

Arsenate (As(V)) removal ability by nanoscale zero-valent iron (nZVI) is compromised by aggregation of nZVI particles. In this work, pine derived biochar (PB) was used as a supporting material to stabilize nZVI for As(V) removal. The biochar supported nZVI (nZVI/BC) was synthesized by precipitating the nanoparticles on carbon surfaces. Experiments using batch and continuous flow, completely mixed reactors (CMRs) were carried out to investigate the removal of As(V) by the nZVI/BC from aqueous solutions. Batch experiments showed that nZVI/BC had high As(V) removal capacity in a wide range of pH (3–8). Kinetic data revealed that equilibrium was reached within 1 h and the isotherm data showed that the Langmuir maximum adsorption capacity of the nZVI/BC for As(V) at pH 4.1 was 124.5 g kg^{-1}. As(V) (100 mg L^{-1}) adsorption in anoxic condition was about 8% more than in oxic conditions, where As(V) reduction was observed in anoxic condition. The performance of the nZVI/BC in flowing condition was evaluated in CMRs at influent As(V) concentrations of 2.1 and 5.5 mg L^{-1} and the adsorbent removed 100% and 90% of the As(V), respectively. Furthermore, the nZVI/BC composite is magnetic which facilitates collection from aqueous solutions.

* Corresponding author. Fax: +1 3523924092.
  E-mail address: bg55@ufl.edu (B. Gao).

1. Introduction

Arsenic (As) is a carcinogenic metalloid and thus long-term consumption of As contaminated water may cause serious health problems. Arsenate (As(V)) along with arsenite As(III) is the primary inorganic form in the environment and in natural pH, exists in oxyanionic form [1]. Although many As(V) removal technologies e.g., precipitation and redox reaction, have been well documented, adsorption is still a more preferable approach due to its easy operation and satisfactory removal efficiency [2,3]. ZVI has recently attracted increased interest because of good removal capacity of a wide array of organic and inorganic hazardous materials including As(V) and As(III) [4–6]. Nanoscale ZVI (nZVI) outperforms large-sized ZVI in environmental remediation due to higher reactivity of surface and surface area [4,7].

Arsenic removal from aqueous solutions by nZVI involves several mechanisms such as reduction, reduction–oxidation, adsorption and co-precipitation, mainly depending on redox potential of sorbates and availability of O_2 of ambient medium [8,9] and aging of iron particles [10], and ratio of adsorbents and sorbates [11]. As(V) can be reduced to As(III) or As(0) by nZVI [8,10,11]. Furthermore, As(V) in anaerobic condition mainly reacts with iron filings through surface complexation and is removed via adsorption process [12]. In aqueous solution, nZVI can instantaneously be passivated to form Fe oxide such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), lepidicrocite (γ-FeOOH), and ferrihydrite ($Fe_2O_3 \cdot 0.5H_2O$), which forms a core–shell structure with ZVI as nuclei and Fe oxyhydroxide as coating [11,13–16]. In the core–shell structure, the metallic Fe (Fe^0) core offers strong reduction capacity and the shell (oxy) hydroxide accommodates adsorption [11]. Numerous studies revealed the adsorption of As by Fe oxide and hydroxide. For example, magnetite [17] and maghemite [17,18] are common iron oxides and extensively used adsorbents for As reclamation. Thus, arsenic species can be retained by adsorption onto Fe oxides layer of the core-shell configuration. Another possible mechanism is co-precipitation, when ferrous and ferric iron species derived from corrosion of ZVI may co-precipitate with As species [13,14].

Although nZVI is more reactive than ZVI, it tends to aggregate due to its high surface energy and strong magnetic attraction, which reduces its effective surface area and contact area for targeted pollutants [19,20]. Thus, different techniques have been explored to increase stability of nZVI [21]. Immobilization of nZVI onto supporting materials has been proposed to stabilize nZVI. This technique gains popularity because it not only increases stability of nZVI but retains the properties of both support materials and nZVI [21,22]. It is documented that supporting frameworks facilitate dispersion of nZVI and enhance performance of nZVI for environmental reclamation. For example, nZVI shows better adsorption capacity for lead (Pb), As, and uranium with the support of graphene [23,24], activated carbon (AC) [16,25], Na-bentonite [26], montmorillonite [27], polymer [20], and mesoporous silica [28].

Biochar is a pyrolytic carbonaceous material that is produced by thermal conversion of lignocellulose material. It has been used as supporting materials for Fe and manganese oxides in the removal of As(V) from aqueous solutions [29,30]. Biochars have also been used as matrix to support ZVI. Zhou et al. [31] soldered ZVI on biochar with chitosan and found the prepared adsorbent has excellent adsorption for Pb, chromium, As(V), phosphate, and methylene blue. However, the ZVI is not nano-sized and not closely attached onto the carbonaceous surface of biochars. nZVI was supported by biochar and served as an activator to degrade organic contaminants such as trichloroethylene [32] and acid orange 7 (Azo dye) [33]. Using biochar as a support material has several advantages including: biochars are inexpensive carbonaceous materials and more readily available than activated carbon; biochars are sta-

ble for long term; biochars themselves are good adsorbents for some contaminants; and biochars have many attracting properties for environmental uses [34]. It is anticipated that the nZVI would be more effective than other Fe/mineral particles, such as natural hematite (α-Fe_2O_3) [30], maghemite (γ-Fe_2O_3) [35], birnessite (MnO_2) [29], manganese ferrite ($MnFe_2O_4$) [36], and aluminum oxide (Al_2O_3) [37] in modifying biochars because of its excellent magnetic property and outstanding As(V) removal ability. In addition to reducing self-aggregation of ZVI, the nZVI and biochars composites are magnetized and can be easily separated from aqueous solution. Because of all these advantages, it is necessary to develop a novel method to prepare the nZVI/BC for environmental applications, particularly with respect to the removal of As(V) from water. Furthermore, the development and use of low-cost adsorbents from waste materials are of great interest recently [38–40]. The development of the nZVI/BC would also satisfy this need.

Most of previous studies used batch studies to evaluate performance of nZVI adsorbents in contaminants removal. The performance in continuously flowing conditions is not well understood. The completely mixed reactors (CMRs) are commonly used as a method for organic and inorganic contaminant removal in more realistic conditions [41–43]. CMRs are advantageous as they provide continuous contaminant removal capacity, constant contamination concentration in effluent, and constant removal efficiency. To the best of the authors' knowledge, nZVI supported by biochar has not been up-scaled in CMRs. In this study, results from batch studies was up-scaled with bench scale continuous CMRs experiment, in order to provide guideline in As(V) remediation in the real world.

In this work, nZVI was prepared by wet chemistry method and immobilized by biochar. Batch and CMRs approaches were adopted to evaluate the performance of the nZVI/BC for the removal of As(V) from aqueous solutions under static and flow conditions. The objectives of this work were to: prepare and characterize nZVI/BC composites, evaluate As(V) adsorption capacity at different operation conditions in batch experiments, investigate As(V) removal efficiency in CMRs, and explore governing mechanisms of As(V) adsorption.

2. Materials and methods

2.1. Reagents

Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$), concentrated hydrochloric acid (HCl), sodium borohydride ($NaBH_4$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) of analytical grade were purchased from Fisher Scientific and Sigma–Aldrich companies. Deionized (DI) water (18.2 MΩ) was used to prepare all chemicals.

2.2. Preparation of adsorbents

To prepare pristine pinewood derived biochars (PB), crushed loblolly pine (*Pinus taeda*) wood of 0.425–1 mm size was oven dried at 80 °C and then pyrolyzed at 600 °C for one hour in a tube furnace (MTI, Richmond, CA) under continuously flowing N_2 gases. The biochars were rinsed with tap water for 1 h and DI water for 10 min, and oven dried overnight at 80 °C. The nZVI/BC composites were synthesized according to methods proposed by Jabeen et al. [23] with modification. The reduction reaction took place by the following equations:

$$2Fe^{3+} + BH_4^- + H_2O \rightarrow 2Fe^0 + BO_2^{2-} + 2H_2 + H^+ \qquad (1)$$

Briefly, 5 g biochar was added into 300 mL DI water and suspension was sonicated for 1 h. $FeCl_3 \cdot 6H_2O$ of 0.01 mol (2.703 g) was