



Modeling arsenic removal by nanoscale zero-valent iron

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Abstract Arsenic removal by nanoscale zero-valent iron (NZVI) was modeled using the USGS geochemical program PHREEQC. The Dzombak and Morel adsorption model was used. The adsorption of As(V) onto NZVI was assumed to happen because of the hydrous ferric oxide (Hfo) which was the surface oxide for the model. The model predicted results were compared with the experimental data. While the experimental study reported that 99.57% arsenic removal by NZVI, the model predicted 99.82% removal which is about 0.25% variation. All the arsenic species have also been predicted to be significantly removed by adsorption onto NZVI surface. The effect of pH on As(V) removal efficiency was also evaluated using the model and it was found that above point-of-zero-charge (PZC), the adsorption of As(V) decreases with the increase of pH. The authors conclude that PHREEQC can be used to model contaminant adsorption by nanomaterials.

Keywords Nanomaterials · PHREEQC · Dzombak and Morel · Arsenic · Zero-valent iron · Hydrous ferric oxide

Introduction

Arsenic is one of the most toxic contaminants present in groundwater throughout the world. It exists as arsenate [As(V), $\text{H}_2\text{AsO}_4^{1-}$ and HAsO_4^{2-}] under oxidizing conditions and as arsenite [As (III), H_3AsO_3] under mildly reducing conditions (Kanel et al. 2005). The maximum contaminant level (MCL) for arsenic in drinking water is 10 $\mu\text{g/L}$ (USEPA 2001). Even at lower concentrations, long-term ingestion of water containing arsenic may result in adverse chronic health problems (Shiber 2005). Long-term exposure to arsenic causes cancer and skin lesions and may lead to cardiovascular disease and diabetics (WHO 2019). Arsenic exposure has been linked with high occurrence of ischemic stroke rates (Lisabeth et al. 2010) and uterine function damage (Akram et al. 2010). People who regularly consume water with even 3 $\mu\text{g/L}$ arsenic have about a 1 in 1000 risks of developing lung or bladder cancer during their lifetime (NRC 2001); the risk is more than 3 in 1000 when arsenic concentration is 10 $\mu\text{g/L}$ (NRC 2001). The World Health Organization also reported negative impacts of arsenic on cognitive development and death in children (WHO 2019).

The most commonly used treatment technologies for arsenic removal from drinking water include adsorption, ion exchange, membrane processes, chemical precipitation, and coagulation and filtration (USEPA 2004). In recent years, the use of nanoscale zero-valent iron (NZVI) for arsenic treatment has also been proposed as an effective method (Tang and Lo 2013). Several studies have reported that NZVI and their corrosion

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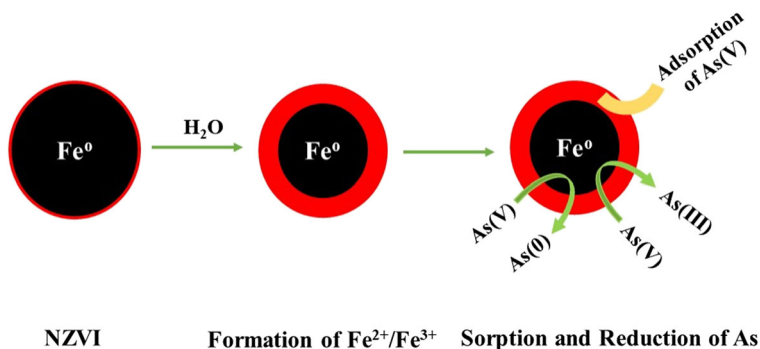
products are suitable materials for remediation of both As (III) and As(V) (Kanel et al. 2005, 2006; Bezbaruah et al. 2013; Deng et al. 2018). NZVI can treat contaminant plumes and the source significantly because of their high surface area to volume ratio and high reactivity (Tang and Lo 2013). While laboratory-based experiments can yield valuable data, they are time-consuming and resource-intensive. It would be useful to have modeling tools to predict the behavior of an adsorptive medium (such as NZVI) used for arsenic removal.

PHREEQC is a public domain computer program that can do a wide variety of aqueous geochemical calculations using a number of in-built models (Parkhurst and Appelo 2013). This program can simulate different types of batch-reaction and one-dimensional (1D) transport with reversible and irreversible reactions. The program's capabilities include the ability to simulate surface complexation, kinetically controlled reactions, effects of pressure and temperature changes on reactions, ion-exchange equilibria, and effects of mixing of solutions. Sorption and desorption of different ions can be modeled in PHREEQC using surface complexation reactions. PHREEQC uses two models for surface complexation: (1) Dzombak and Morel and (2) CD-MUSIC models. Dzombak and Morel (1990) model is used for simulation of surface complexation of heavy metal ions on hydrous ferric oxide (Hfo) or ferrihydrite which binds metals onto strong and weak sites (Dzombak and Morel 1990). The model assumes that Hfo or ferrihydrite is the primary iron oxide surface with large surface area and, hence, contains a large number of binding sites. In the model, chemical binding occurs at strong sites (typical value: 0.005 mol/mol Hfo) as well as at weak sites (0.2 mol/mol Hfo).

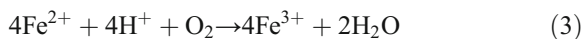
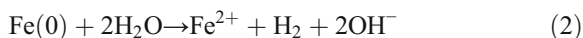
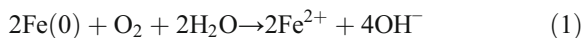
Rozell (2010) used experimental data from a study by Joshi and Chaudhuri (1996) to model arsenic removal by iron-coated sand using PHREEQC. The sand grains were coated with a layer of Hfo that participated in arsenic adsorptions. Joshi and Chaudhuri (1996) achieved breakthrough in their column at 165 bed volumes (BV) as As(V) reduced from 1 mg/L to 10 µg/L (breakthrough concentration) and the model by Rozell (2010) predicted the breakthrough volume as 168 BV (1.8% error). Again, when the breakthrough concentration was set at 5 µg/L, breakthrough was achieved at 210 BV in the lab and the model by Rozell (2010) predicted it as 228 BV (8.6% error). It can be seen that the model was capable of predicting the experimental data fairly accurately (it overpredicted the experimental results by 1.8 to 8.5%).

In this work, we have used NZVI as the adsorptive medium and modeled its arsenic removal behavior. NZVI particles have a core-shell structure (Fig. 1) where the core is Fe(0) and the shell is a thin iron oxide layer (Krajangpan et al. 2012). The oxide layer is generated due to corrosion of Fe(0) by dissolved oxygen (DO) present in water (Eq. 1). Even when no DO is present, water can oxidize Fe(0) to Fe²⁺, and the Fe²⁺ reacts with OH⁻ to produce ferrous hydroxide Fe(OH)₂ (Eq. 2) (Kanel et al. 2005). This Fe²⁺ is also oxidized to Fe³⁺ and ferric hydroxide Fe(OH)₃ is formed (Eqs. 3–4). Both the surface oxide layer and the core Fe(0) of NZVI participate in arsenic remediation (Fig. 1). While iron hydroxide layer sorbs As(V) and As(III), the core Fe(0) reduces the sorbed As(V) to As(III) and then to very stable As(0) (Yan et al. 2010). While the remediation of arsenic by NZVI involves both adsorption and reduction, the removal of arsenic from the bulk solution is still controlled by the adsorption onto the surface oxide

Fig. 1 Schematic of the mechanisms of arsenic removal by NZVI (modified after Bezbaruah et al. 2013)



layer. It should, therefore, be possible to model the arsenic removal by NZVI using PHREEQC.



In this study, we used laboratory experiment generated As(V) removal data from a NZVI study to model the system in PHREEQC and verified whether the model could predict the removal efficiency accurately.

Methodology

The current study is based on the data generated in an As(V) removal experiment conducted by Bezbaruah et al. (2013) using bare and calcium alginate entrapped NZVI. The data from only the bare NZVI experiments were used for modeling. The original batch experiment done with 500 mL bulk solution had an initial As(V) concentration (C_0) of 10 mg/L and used 0.5 g of NZVI. The detailed NZVI synthesis process and experimental procedure are described elsewhere (Bezbaruah et al. 2013). Based on As(V) removal data collected at specified time intervals, the final As(V) removal efficiency (after 2 h) was reported as 99.57% (Bezbaruah et al. 2013).

In this study, the adsorption of As(V) onto NZVI was modeled using PHREEQC's Dzombak and Morel model (1990) for surface complexation. The 0.5 g of NZVI used in 500 mL As (V) solution in the reported study (Bezbaruah et al. 2013) translates to 0.00895 mol of NZVI for use in the model. The composition of oxide on NZVI surface varies from Fe (III) oxide near the particle-water interface to mixed Fe (II)/Fe (III) oxides

Table 2 Input values used in the current model

Parameter	Value
As(V)	0.0001335 mol
NZVI	0.00895 mol
Weak sites	0.000893 mol
Strong sites	0.0000223 mol
Total Hfo	0.3975 g
pH	7.0
Temperature	25 °C

closer to the core (Wang et al. 2009). After being exposed to water, these oxides become hydrous iron [Fe (II)/Fe (III)] oxides (Hfo) and arsenic can be adsorbed to this Hfo (Wang et al. 2009). It was assumed in this study that all the oxides present on NZVI surface is Hfo. The oxide (Hfo) coating on fresh (virgin) NZVI is typically ~ 5 nm (Bezbaruah et al. 2013) but increases due to continuous corrosion. In our model, we assumed this oxide layer (Hfo) to be between 10 and 50% of the total volume of each NZVI particle. When Hfo is taken as 50% of the particle volume, the thickness of the Hfo layer will be 3.6 nm on a 35-nm-diameter NZVI particle, and for 10%, it will be 0.6 nm (Table 1). The As(V) removal efficiency was compared for different percentages (10, 15, 20, 25, and 50%) of Hfo. With a NZVI particle containing 50% Hfo, the test bed (adsorptive surface) will have 0.3975 g of Hfo (Eq. 1). The adsorptive surface has 0.0008935 mol of weak sites and 0.00002233 mol of strong sites (given 0.005 mol of strong sites per mole of Hfo and 0.2 mol of weak sites per mole of Hfo and the molecular weight of Hfo is 89). Similarly, the amount of weak sites and strong sites were calculated for other percentages of Hfo (Table 1). The arsenic solution was assumed to have a temperature of 25 °C and a pH of 7.0. The original study by Bezbaruah et al. (2013) was done in anaerobic conditions and the redox potential played a role in arsenic removal. There is

Table 1 Surface composition of NZVI at different percentage of Hfo

% Hfo	Thickness of oxide layer (nm)	Amount of Hfo (gm)	Amount of Hfo (mole)	Weak sites (mol/mol of Hfo)	Strong sites (mol/mol of Hfo)
10	0.6	0.0795	0.000893	0.000179	4.46629×10^{-06}
15	0.9	0.11925	0.00134	0.000268	6.69944×10^{-06}
20	1.25	0.159	0.001787	0.000357	8.93258×10^{-06}
25	1.60	0.19875	0.002233	0.000447	1.11657×10^{-05}
50	3.61	0.3975	0.004466	0.000893	2.23315×10^{-05}

Table 3 Reaction and thermodynamic constants for surface complexation reactions used in the current model (Allison et al. 1990)

Adsorption reaction	LogK (KJ/mol)
$\text{Hfo_sOH} + \text{H}_3\text{AsO}_4 = \text{Hfo_sOHAsO}_4^{3-} + 3\text{H}^+$	- 10.12
$\text{Hfo_wOH} + \text{H}_3\text{AsO}_4 = \text{Hfo_wOHAsO}_4^{3-} + 3\text{H}^+$	- 10.12
$\text{Hfo_wOH} + \text{H}_3\text{AsO}_4 = \text{Hfo_wHAsO}_4^- + \text{H}^+ + \text{H}_2\text{O}$	2.81
$\text{Hfo_wOH} + \text{H}_3\text{AsO}_4 = \text{Hfo_wH}_2\text{AsO}_4 + \text{H}_2\text{O}$	8.61

a set initial redox potential in the model. In this study, the set redox potential was used in the model. The model was also run at different pH (4 to 9) to investigate the effect of pH on arsenic removal. The input values for this simulation were based on the original study (Bezbaruah et al. 2013) and some assumptions made (Table 2). The WATEQ4F.dat database was used as this database includes the surface complexation reactions and reaction constants for arsenic from literature (Table 3). Steps to model the system are shown in Fig. 2. The results from the current work should be read with a caveat that these constants (Table 3) were derived for iron oxide-coated sand/rock. There is no reported work on modeling the adsorption of arsenic onto NZVI surfaces, and so, the surface complexation constants of iron oxide surfaces of NZVI are unknown. It was assumed that surface complexation constants for iron oxide surfaces of NZVI particles will be the same as those for iron oxide coated sand/rock.

Results and discussion

Modeling results indicate that As(V) removal efficiency increases with the increase in percent Hfo (Table 4). Maximum removal efficiency (99.82%) was obtained for 50% Hfo and the minimum (41.12%) was for 10% Hfo. The experimental study performed by Bezbaruah et al. (2013) found 99.57% removal of As(V) by NZVI. The model predicted value (with 50% Hfo) is very close to the experimental value with a variation of only 0.25%. Based on our calculations (Table 1), 50% Hfo is associated with an oxide coating of 3.6 nm which is very close to the reported value of 5 nm (Bezbaruah et al. 2013). It is safe to say that 50% Hfo represents the experimental conditions. The results from Bezbaruah et al. (2013) also indicated that mainly Hfo layer of NZVI particles participates in As(V) adsorption process. Similar results were reported by others. Suazo-Hernández et al. (2019) reported in their study that As(V) is preferentially removed by the NZVI due to the presence of iron oxyhydroxides on the NZVI surface and these oxyhydroxides are formed due to the oxidation of NZVI. Babaee et al. (2017) also proposed in their study that the hydroxyl group attached to the iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$) on NZVI surface participated in arsenic adsorption. In a most recent study, Bae et al. (2018) reported the formation of various iron oxides on the shell part of the NZVI and these oxides include $\text{Fe}^{\text{II}}\text{O}$, $\text{Fe}^{\text{II}}(\text{OH})_2$, $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$, and $\text{Fe}^{\text{III}}\text{OOH}$. Liu et al. (2018)

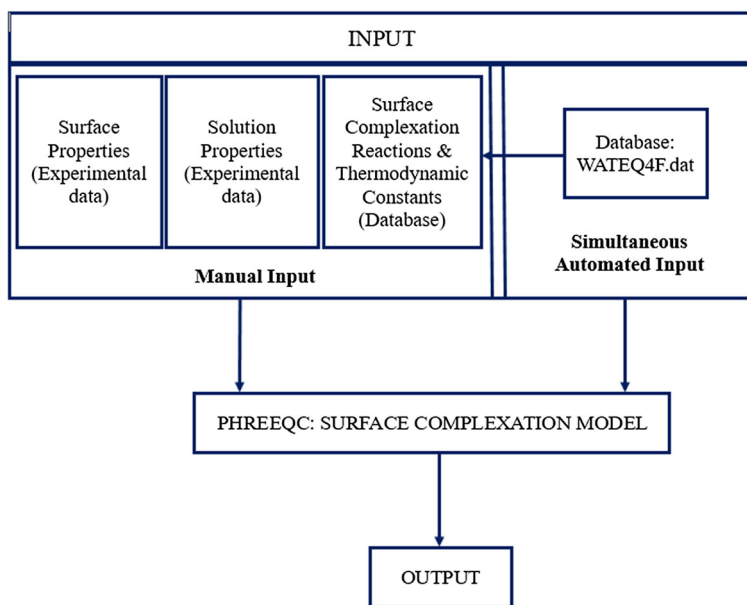
Fig. 2 Schematic representing the modeling steps in PHREEQC for arsenic removal by NZVI

Table 4 As(V) removal efficiency predicted by the model in the presence of different amount of Hfo on the nanoparticle surface

% Hfo	Initial As(V) concentration (molality)	Final As(V) concentration (molality)	% As(V) removal
10	1.335×10^{-04}	7.856×10^{-05}	41.12
15	1.335×10^{-04}	5.558×10^{-05}	58.37
20	1.335×10^{-04}	3.613×10^{-05}	72.94
25	1.335×10^{-04}	2.066×10^{-05}	84.5
50	1.335×10^{-04}	2.395×10^{-07}	99.82

also reported a spherical shape for NZVI and reported that iron species in NZVI are well stratified with Fe^{3+} in the outermost periphery and a mixture of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the next inner layer; Fe^{2+} is present in the next layer followed by pure Fe^0 at core. They further reported that As(V) reacts with NZVI because of a well-structured redox environment in the shell layer and the redox gradient thermodynamically favors transfer of electron from the Fe^0 core to the surface-bound arsenic; because of this effective electron transfer As(V) reduces to As(III) and then to As(0) as arsenic travels from oxide shell-water interface to the Fe^0 core (Liu et al. 2018). These results vindicate our basic assumptions about the iron species present in NZVI and how arsenic is removed by NZVI.

Based on solution properties (pH, redox, temperature), the arsenic may be present in different forms (species). In PHREEQC, the Dzombak and Morel model (1990) has the capability to predict arsenic species in solution before and after adsorption. We explored the removal of all possible arsenic species by NZVI with 50% Hfo. All the arsenic species were predicted to be removed significantly by adsorption onto NZVI surface (Table 5). The model was not only capable of predicting the overall As(V) removal efficiency but also could

Table 5 Model predicted removal efficiencies of different arsenic species by NZVI

As(V) species	Initial As(V) concentration (molality)	Final As(V) concentration (molality)	% As(V) removal
HAsO_4^{-2}	7.905×10^{-05}	1.418×10^{-07}	99.82
H_2AsO_4^-	5.444×10^{-05}	9.769×10^{-08}	99.82
AsO_4^{-3}	6.089×10^{-09}	1.091×10^{-11}	99.82
H_3AsO_4	8.290×10^{-10}	1.488×10^{-12}	99.82

Table 6 Composition of iron oxide surface (on NZVI)

Binding sites	Mole fraction
Hfo_sOHAso_4^{-3}	0.139
Hfo_wOHAso_4^{-3}	0.139
Hfo_wHAsO_4^-	0.006
$\text{Hfo_wH}_2\text{AsO}_3$	0.000

predict the possible removal efficiency of different arsenic species by NZVI. It is worth noting that it is still a major challenge to find out the removal efficiency of different As(V) species experimentally. This model can be a good starting point for determining the concentration of different As(V) species before and after adsorption, and potentially experiments can be designed based on such predictions.

The model also predicted the possible composition of Hfo surface after adsorption of arsenic. Only 13.9% binding sites of Hfo surface were used for the As(V) removal (Table 6).

We also used the model to predict the effect of pH on As(V) removal, and the results showed that As(V) removal efficiency decreased from 99.99 to 60.31% with the increase of pH from 4 to 9 (Table 7). The point-of-zero-charge (PZC) of NZVI was reported as 7.7 (Almeelbi and Bezbaruah 2012; Suazo-Hernández et al. 2019) indicating that at this pH, the net surface charge will be zero. Below PZC, the surface is positively charged which will facilitate the As species (HAsO_4^{-2} , H_2AsO_4^- , AsO_4^{-3}) adsorption on NZVI surface. Above PZC, the surface is negatively charged, and adsorption of arsenic species will not be favorable. Suazo-Hernández et al. (2019) reported ~ 100% As(V) removal efficiency at $\text{pH} < 7.0$, but a slight decrease was observed at $\text{pH} > 7.0$. Tucek et al. (2017) also found that acidic pH ($\text{pH} < 7$) was more favorable for As(V)

Table 7 Effect of pH on As (V) removal

pH	Final concentration (molality)	% removal
4.0	2.492×10^{-10}	99.99
5.0	1.368×10^{-09}	99.99
6.0	1.236×10^{-08}	99.99
7.0	2.395×10^{-07}	99.82
8.0	8.645×10^{-06}	93.52
9.0	5.298×10^{-05}	60.31

adsorption than alkaline pH ($\text{pH} > 7$). Our model also predicted that below PZC (7.7), the As(V) removal efficiency is $> 99\%$. However, above PZC (7.7), the removal efficiency decreases to 93.52% (pH 8) and 60.31% (pH 9) (Table 7). So, the model predicted results conform to the PZC theory and also matched with the experimental results from the literature.

Conclusion

Modeling of adsorption of As(V) onto NZVI assuming Hfo as the surface oxide matched experimental results. A Dzombak and Morel adsorption model yielded 99.82% removal of arsenic by NZVI whereas the experimental results reported 99.57% removal of arsenic by NZVI. The model predicted arsenic removal results matched with the reported data from pH studies and showed that the point-of-zero-charge (PZC) theory holds here. This model was also able to predict the removal efficiency of different arsenic species by NZVI. To our knowledge, this is the first study on modeling the adsorption of arsenic by NZVI particles. The model outputs can be improved by incorporating the actual K (surface complexation constant) values for NZVI and the reduction processes $[\text{As(V)} \rightarrow \text{As(III)} \rightarrow \text{As(0)}]$ in the model.

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Compliance with ethical standards

Ethical approval This article does not contain any studies with human participants performed by any of the authors.

Conflict of interest The authors declare that they have no conflict of interest.

Disclaimer Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the NSF and NDWRRI.

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