Simulation of antimony adsorption on nano-zero valent iron and kaolinite and analyzing the influencing parameters
Setareh Saeidnia, Gholamreza Asadollahfardi, Ahmad Khodadadi Darban and Mehdi Mohseni

ABSTRACT
Antimony is one of the most toxic pollutants in industrial and mineral wastewaters threatening the life of humans and other creatures. We simulated the adsorption of antimony in the presence of nano-zero valent iron (nZVI) adsorbent, on kaolinite and in the presence of nZVI coated on kaolinite from mineral wastewater using VISUAL MINTEQ 3.1 software. Our aim was to determine the factors affecting the adsorption of antimony by applying simulation. The simulation was performed using an adsorption model of a diffuse layer model. The results of the simulation indicated that the nZVI concentration, initial concentrations of antimony and pH factor are effective on the adsorption of antimony. In the conducted stimulation, the optimum pH was 2–5 and the highest adsorption occurred in an acidic state. With increasing initial concentrations of antimony in the simulation, we concluded that nZVI had absorbed various concentrations above 90% and, by increasing the concentration of nZVI, antimony adsorption rate increased. The increased surface area of nZVI and the expansion of more interchangeable surfaces available for reaction with antimony ions causes more antimony ions to be adsorbed. In all cases, the coefficient of determination between the laboratory results and the model predictions that was obtained was more than 0.9.

Key words | adsorption, antimony, mineral wastewater, MINTEQ, nano-zero valent iron, VISUAL

INTRODUCTION
Gold processing plants’ wastewater contains high amounts of antimony. This metal is very toxic and soluble in water. Solubility in water causes an extended polluted area (Esanlou 2001). Antimony is a metalloid that is detrimental to human and plant health. Breathing an antimony in composition with oxygen in the gas phase is considered to be a health risk (Tabrizi 2001).

Therefore, assessment of the environmental impact and reduction or removal of it from mineral water by applying appropriate methods is essential (Hantson et al. 1996). Antimony in the oxidation state mainly takes three types of redox states which include 3,–3, and 5. Sb(III) is called antimonite and antimony, Sb(V), is called antimonate. This metalloid is sensitive to oxidation-reduction reactions. Mobility of the species depends on various factors, such as pH in the environment, the presence of other ionic species, and the chemistry of the solution. Antimony is infrequently observed in nature as a pure element and antimony(III) and antimony(V) are readily hydrolyzed in aqueous solutions (Wardell 1978).

For freshwater and seawater, dissolved Sb concentration has been found to be in the range of 0.1–2 μg L−1 (Filella et al. 2002). Numerous techniques can be used to remove antimony from water and wastewater. Among these methods, the adsorption method has attracted the attention of many researchers in recent years because it is a simple, low cost and effective method of eliminating heavy metal ions and organic compounds at low and average concentrations (Deliyanni et al. 2003). Factors affecting adsorption include the type and characteristics of the absorbent and the adsorbed, and the degree of mixing in the liquid phase, the pH and temperature (Djeribi & Hamdaoui 2008).

Nanotechnology is considered a priority and strategic technology in all countries because of the diverse application areas and direct impact on most industries and sciences.
Nanomaterials have very extensive surfaces compared to normal materials (Aragay & Merkoci 2012). Zero valent iron nanoparticles are capable of decomposing organic pollutants and adsorbing inorganic pollutants. Some of these nanoparticles may be covered by different surface modifiers to control their reactions and mobility (Dorjee et al. 2014). Modified iron nanoparticles have been produced to increase adsorption capacity. Kaolinite is an industrial mineral found in clay soil, which plays an important role in controlling pollutants through geochemical processes, especially adsorption (Rakshit et al. 2014). Kaolinite has the ability to act as an absorbent and with easy access through structural stability in geochemical conditions. Owing to these properties, the clay can be used to host nano-zero valent iron (nZVI) in clearing systems (Üzüm et al. 2009).

Anjum & Datta (2012) studied the trivalent antimony adsorption kinetics on montmorillonite and achieved a reaction time of 10 to 180 minutes. They concluded that about 99% of synthesis solution antimony, 100 mg/L, was removed by applying an adsorbent. Adsorption of Sb(V) on kaolinite has been reported using macroscopic and spectroscopic studies; however, to date, no surface complexation modeling of Sb(V) adsorption on kaolinite has been published (Rakshit et al. 2014). Salam & Mohamed (2015) removed trivalent antimony using multi-walled carbon nanotubes. Sari et al. (2012) used expanded perlite as a trivalent antimony and obtained an optimal capacity of 54.4 milligrams per gram of adsorbent. Leng et al. (2012) removed trivalent antimony using graphene. The optimal capacity of 8.056 mg per gram of adsorbent was obtained. Xi et al. (2010) removed pentavalent antimony using kaolinite. They obtained an optimal pH of 3.6 for the removal. Vithanage et al. (2015) investigated surface complexation modeling and spectroscopic evidence of antimony adsorption in iron-oxide-rich red earth soils. Successful data modeling using the 2-pK diffuse double layer model (DDLM) with the FITEQL revealed that adsorption occurred through the formation of bidentate mononuclear and binuclear complexes. Model simulations indicated the highest adsorption of Sb(V) occurred in a pH of about 4 to 6. Safavi (2014) conducted a simulation of the adsorption process of cyanide on titanium dioxide nanoparticles using VISUAL MINTEQ software. Also, the coefficient of determination between the results of simulation and experiments was equal to 0.9 which indicates that the model was acceptable. The results obtained from the use of 2-pK CCM and 2-pK DLM surface complexes presented the same results.

The aim of this study was to simulate the adsorption of antimony in the presence of nZVI, adsorption of antimony on kaolinite, and the adsorption of antimony in the presence of nZVI coated with kaolinite from mineral wastewater using the VISUAL MINTEQ 3.1 software. The second objective was to determine the factors affecting the adsorption rate using a diffuse layer model (DLM).

**METHODS**

MINTEQ is a geochemical software based on chemical equilibrium. The code, originally built using USEPA’s MINTEQA2 software, has been maintained by Jon Petter Gustafsson at KTH, Sweden, since 2000. Types of adsorption patterns, mass balance between solid or liquid and gas phases and equations for mass interplay are available in this software. In addition, this software contains algorithms to check and correct equilibrium constants. In this model, no time is available and the circumstances are not kinetic and it is assumed that maximum adsorption took place at the time of equilibrium (Geoscience 1998).

Owing to the high possibility of interactions between the ions and inorganic and organic solids in natural systems, the models are used as a tool to quantify and predict the behavior of ions in solution and their interactions with other particles. For this reason, in recent decades, several models have been proposed for the analysis of chemical reactions. A DLM is one of the various models that are available to explain ion adsorption data (Davodi 2010).

The DLM was first proposed by Stumm et al. (1970) and then revised by Dzombak & Morel (1990). In this model, all the ions are located at the surface and just within the core complex. The double-layer model typically considers two adsorption sites with a low adsorption affinity and a high adsorption affinity (Dzombak & Morel 1990). The ionic strength of this model affects the charge in the d layer and the I parameter. The double double-layer models may be used for ionic strengths up to 0.1 M, the upper limit for using the Davies correction for computing the activity coefficients. However, as described below, based on theoretical consideration, the DLM and constant capacitance model (CCM) are often limited to lower and higher ionic strength conditions, respectively (Dzombak & Morel 1990). Consequently, this model can be used in varying conditions of low ionic strength. Equation (1) describes the relationship between the load (load is the surface charge density) in layer (d) and ionic strength (I) (M) (Hayes et al. 1999):

\[
\sigma_d = -0.1174 \times \sqrt{I} \times \sinh \left( \frac{Z \times F \times \Psi_d}{2 \times R \times I} \right) \left[ \text{C/m}^2 \right]
\]  

where \(\sigma_d\) is the diffusion layer load (C/m²); \(Z\) is the electrolyte capacity assumed to be 1 and \(I\) is the ionic strength.
(M). $F$ is the Faraday constant (J/volt equiv); $R$ is the gas constant (J/K.mol); $T$ is the absolute temperature (K); and $\Psi_d$ (volt) is the electrostatic potential of d layer. $\Psi_d$ is the potential at the surface of the absorbent.

The assumptions of the model are as follows (Dzombak & Morel 1990):

1. The surface sites are amphoteric (a site can be positive, neutral, or negative).
2. Surface complexes are monodentate and within the sphere (only one atom is connected to the central metal atom).
3. Two electrostatic plates are available in this model:
   - (a) the surface electrostatic adsorbs H, OH, and other ions;
   - (b) the d electrostatic surface for the ions with opposite charge.
4. The relationship between the charge and electrostatic potential in the diffuse layer is explained by the Gouy–Chapman theory. Gouy & Chapman’s theory described the effect of surface charge on ion adsorption by using an electric double layer theory, which was then reviewed by Stern (1924) and (Safavi 2014).
5. The base state of the model is a zero load for the surface forms and a very dilute solution for the solution forms.

In the MINTEQ, based on the above assumption, the Sb adsorption percentage is calculated based on cation exchange capacity, specific surface area of the adsorbents, pH and temperature of others ions presence in the solution.

The reasons for selecting this software were availability of various adsorption models, an organic material, a powerful database, and an acceptable agreement with experimental data (Safavi 2014). In this simulation, we used the experimental data which were researched by Rakshit et al. (2014), Dorjee et al. (2014), and Nosrati (2013). Creating chemical equilibrium (reversible reaction), time independent (there are no kinetic reactions), temperature restriction (0–99 °C), and limited ionic strength are among the limitations of this software.

### Simulation of surface complexation of antimony on kaolinite

To simulate the antimony adsorption process and study the pH effect, we used the experimental data from Rakshit et al. (2014). Table 1 indicates the data at a constant temperature of 25 °C and an initial concentration of antimony at 4.11 μmol/L, and ionic strength of 0.1 M, clay particle size of less than 2 μm, 66 g/L of adsorbent concentration and a particle surface area of 20 m²g⁻¹. We used a pH between 3 and 9 for the adsorption of antimony on clay adsorbents.

### Simulation of antimony adsorption by nZVI

To simulate the antimony adsorption process, we applied the experimental data from Dorjee et al. (2014). Table 2 indicates the data at a constant temperature of 25 °C and different concentrations of Sb (0.5, 2.5, 5, 10, 25, and 50 μg L⁻¹), with different masses of nZVI (0.025 to 1.00 mg), a particle surface area of 45 m² g⁻¹ and nZVI with diameters of 50 to 70 nm.

### Simulation of antimony adsorption by nZVI coated on kaolinite (K-nZVI)

To simulate the antimony adsorption process, the experimental data of Nosrati (2013) was used. Tables 3 and 4 indicate the data at a constant temperature of 25 °C and an initial concentration of antimony at 31.82 mg/L and nZVI with diameters of 40 to 100 nm and specific surface of 43.34 m²g⁻¹. We used a pH between 1 and 2 for adsorption of antimony on the absorbents. The absorbent values were considered to be 7.5–12.5 as the optimal values and the tests were conducted at these intervals (Kraepiel et al. 1998). 1-pK and 2-pK formulations exist in surface complexation theory with respect to the description of basic

### Table 1

<table>
<thead>
<tr>
<th>pH</th>
<th>Antimony adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>nZVI concentration (mg)</th>
<th>Percent adsorption of Sb</th>
<th>Sb(V) concentration (μg L⁻¹)</th>
<th>Percent adsorption of Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>97</td>
<td>0.5</td>
<td>90</td>
</tr>
<tr>
<td>0.05</td>
<td>98</td>
<td>2.5</td>
<td>99</td>
</tr>
<tr>
<td>0.1</td>
<td>100</td>
<td>5</td>
<td>97</td>
</tr>
<tr>
<td>0.2</td>
<td>99</td>
<td>10</td>
<td>96</td>
</tr>
<tr>
<td>0.5</td>
<td>98</td>
<td>25</td>
<td>92</td>
</tr>
<tr>
<td>1</td>
<td>97</td>
<td>50</td>
<td>91</td>
</tr>
</tbody>
</table>
charging behavior of (hydr)oxide electrolyte interfaces. The 2-pK approach has been commonly used with at least four different electrostatic models, whereas the 1-pK model has been primarily used with only one of those electrostatic models. A purely DLM generally gave the poorest fit to experimental data when combined with the 1-pK approach and was only slightly better when combined with the 2-pK formula. Either the 1-pK basic strength model (BSM) or the 2-pK CCM gave the best fit to the data in all the examples. However, it was found in two cases that some arbitrary constraint was necessary to define a unique (and thus meaningful) parameter set for the 2-pK CCM. The 1-pK triple-layer model (TLM) version allowed, in more than half of the examples, a unique parameter set to be determined, which is impossible with the 2-pK TLM. It is concluded that the 1-pK BSM should be considered as the first choice model with respect to the goodness of fit and the uniqueness of the estimated parameters. The 2-pK CCM is still a good choice for a constant ionic strength case when the experimental data allow a determination of unique parameters and if only goodness of fit is used as a criterion (Lützenkirchen 1998). Figures 1 and 2 indicate scanning electron microscope (SEM) of kaolinite before and after coating with nVZI (Nosrati 2013).

The chemical equilibrium constants of Sb retention on the surface sites were calculated by the nonlinear least squares optimization program using the DDLM. Assuming that the natural red earth (NRE) surface hydrolysis is described by the 2-pK charging mechanism, the amphoteric products of the surface hydrolysis were considered as follows, and because the composite is rich in both Fe and Al, two different surface sites were used:

\[ \equiv XOH + H^+ \rightarrow \equiv XO^{-} + H^+ \quad \text{(Reaction 1)} \]

\[ \equiv XOH \rightarrow \equiv XOH^+ \quad \text{(Reaction 2)} \]

where X in Reactions (1) and (2) represents both Fe and Al surface sites. Protonation constants for the surface hydroxyl

<table>
<thead>
<tr>
<th>pH</th>
<th>Percent antimony adsorption on K-nZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65.77</td>
</tr>
<tr>
<td>1.25</td>
<td>73.74</td>
</tr>
<tr>
<td>1.5</td>
<td>80.8</td>
</tr>
<tr>
<td>1.75</td>
<td>87.68</td>
</tr>
<tr>
<td>2</td>
<td>93.06</td>
</tr>
</tbody>
</table>

Table 3 | Experimental data on pH values of 1-2 (Nosrati 2013)

<table>
<thead>
<tr>
<th>Adsorbent concentration (g L(^{-1}))</th>
<th>Percent antimony adsorption on K-nZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>93.06</td>
</tr>
<tr>
<td>8.5</td>
<td>93.4</td>
</tr>
<tr>
<td>9.5</td>
<td>93.8</td>
</tr>
<tr>
<td>10.5</td>
<td>94.5</td>
</tr>
<tr>
<td>11.5</td>
<td>95.31</td>
</tr>
<tr>
<td>12.5</td>
<td>95.5</td>
</tr>
</tbody>
</table>

Table 4 | Experimental data on adsorbent concentrations of 7.5-12.5 g L\(^{-1}\) (Nosrati 2013)

Figure 1 | SEM of kaolinite before coating with nZVI (Nosrati 2013).
groups were applied as described in the literature (Vithanage et al. 2013). For a description of the surface complexation reactions used for modeling the sorption edge of both Sb(III) and Sb(V) on composite, readers should refer to Vithanage et al. (2013).

RESULTS AND DISCUSSION

Simulating the effect of pH on antimony adsorption on kaolinite

The results of the simulation indicated that increasing the pH from 3 to 9 resulted in antimony adsorption decreasing from 95% to 2%. Figure 1 presents the simulated and experimental values of antimony adsorption at different pH in the presence of kaolinite in the surface complexation model 2-pK DLM. Also, the results of model 2-pK DLM show that the simulation value of antimony adsorption at its highest value at pH = 3 was 95%. The maximum adsorption based on Rakshit’s et al. (2014) experiment at pH = 3 was 90%. The coefficient of determination between the simulated and experimental data was $R^2 = 0.96$ and the index of agreement was $d = 0.98$. Several approaches were used to fit the pH data of kaolinite (Nosrati 2013). Xi et al. (2010) removed pentavalent antimony using kaolinite. They observed that the optimal pH for removing 75% of the antimony was a pH of 5.6. As indicated in Figure 3, by increasing the pH from 3 to 9, the amount of Sb adsorption decreased sharply.

Simulating the effect of different amounts of nZVI on antimony adsorption

We simulated the effect of nZVI concentrations in an initial concentration of antimony at 20 mg L$^{-1}$ on antimony adsorption. Figure 4 presents the simulated and experimental values of antimony adsorption at different concentrations of nZVI in the surface complexation model 2-pK DLM. By increasing the concentration of nZVI in simulation from 0.025 to 1 mg, the antimony adsorption rate was over 90%. The simulation value of antimony adsorption was at its highest value in an adsorbent
concentration of 0.1 mg. Antimony adsorption in a concentration above 0.1 mg nZVI is constant. A high adsorption rate of 90% Sb by 0.1 nZVI was caused by the high effect of nZVI in adsorption and even with a slight presence of nZVI the adsorption rate was still high. Also, the constant adsorption of antimony in concentrations greater than 0.1 mg is because there are enough sites for antimony adsorption in this concentration. Although more sites exist at a higher concentration, there is no unadsorbed antimony left. The coefficient of determination between the simulated and experimental data was $R^2 = 0.94$ and the index of agreement was $d = 0.96$ (Figure 4).

**Simulating the effect of increasing Sb(V) concentrations on antimony adsorption**

We simulated the effect of an initial concentration of Sb(V) solution ranging between 1 and 50 μg L$^{-1}$ by using 250 mg of nZVI on antimony adsorption. The result of 250 mg nZVI interaction with different concentrations of Sb(V) demonstrates that nZVI could rapidly adsorb Sb(V) of various concentrations. The simulation value of antimony adsorption was more than 90% on the surface of nZVI. Figure 5 illustrates the simulated and experimental values of antimony adsorption in different concentrations of Sb(V) in the surface complexation model 2-pK DLM. The coefficient of determination between the simulated and experimental data was $R^2 = 0.94$ and the index of agreement was $d = 0.95$.

**Simulating the effect of pH of the antimony adsorption on K-nZVI**

To simulate antimony adsorption, the adsorbed value was considered to be 7.5 g/L. Figure 6 indicates the simulated and experimental values of antimony adsorption at different pH in the presence of K-nZVI in the surface complexation model 2-pK DLM. By increasing the pH from 1 to 2, antimony adsorption was increased by 60 to 92.3%. Also, the results of model 2-pK DLM demonstrated that the simulation value of antimony adsorption was at its highest value at pH = 2 which was 92.3%. The maximum adsorption which happened based on Nosrati’s (2013) experiment at pH = 2 was 93.06%. The coefficient of determination between the simulated and experimental data was $R^2 = 0.92$ and the index of agreement was $d = 0.97$. Rakshit et al. (2014) studied the adsorption of antimony on kaolinite and obtained a maximum adsorption at pH = 3 with the value of 95%. Sarkar et al. (1999) studied the adsorption of mercury on kaolinite and obtained a maximum adsorption at pH = 4.4. In the conducted simulation,
the optimum pH was 2 and the highest adsorption occurred in an acidic state. As indicated in Figure 6, by increasing the pH from 1 to 2, the amount of Sb(V) adsorption increased.

The effect of K-nZVI concentrations on antimony adsorption

Since adsorption is primarily a surface phenomenon, the amount of surface area available for adsorption and thus the adsorbent mass can significantly affect the adequacy and performance of adsorption (Safavi 2014). Therefore, we simulated the effect of K-nZVI concentrations on antimony adsorption at pH = 2. Figure 7 presents the simulated and experimental values of antimony adsorption in different concentrations of K-nZVI in the surface complexation model 2-pK DLM. By increasing the concentrations of nZVI from 7.5 to 12.5 g/L, the antimony adsorption rate increased by 92 to 95.5%. The above 90% adsorption may be due to the high effect of K-nZVI on adsorption. The reason is the increased surface area of nZVI and the expansion of more interchangeable surfaces available for reaction with antimony ions in increased concentrations. The simulation value of antimony adsorption is at its highest value in an adsorbent concentration of 7.5 g/L. The coefficient of determination between the simulated and experimental data was $R^2 = 0.97$ and the index of agreement was $d = 0.99$.

According to the Nosrati (2013) experiment, the highest antimony adsorption on K-nZVI was 93.06% at pH = 2 with an adsorbent concentration of 7.5 g/L and the antimony adsorption capacity was 3.94 mg/g. The results of our simulation presented the highest adsorption of 92.33% at pH = 2 with an adsorbent concentration of 7.5 g/L and an adsorption capacity of 3.92 mg/g.

Adsorption capacity of adsorbent agent is affected by surface properties and its porosity, and it also depends on contact time, the amount of absorbent, pH, and the amount of pollutants. Improving the surface of absorbent characteristic causes a rise in its adsorption capacity. If we compare nZVI surface characteristic with kaolinite, nZVI contains a higher specific surface which means that, in the same situation, nZVI adsorbs more pollutants than kaolinite. Wang et al. (2014) studied the removal of Ni(II) by kaolinite supported by nZVI, nZVI, kaolinite and ZVI. They indicated that kaolinite-nZVI was more useful and had a better adsorption capacity (9.24 mg/g) than nZVI (8.69 mg/g), kaolinite (1.61 mg/g), and ZVI (4.58 mg/g).

CONCLUSIONS

The results of simulation of antimony adsorption on nZVI, kaolinite, and kaolinite coated with nZVI from mineral wastewater using VISUAL MINTEQ 3.1 software are as follows:

1. The simulation results using VISUAL MINTEQ 3.1 software and using a surface complexation model 2-pK DLM were consistent with laboratory results.

2. By analyzing the effect of nanoparticles in a zero-valent iron concentration, initial concentrations of Sb and pH, we reached a coefficient of determination between the experimental data and the simulation value of 0.9, which indicates the acceptability of simulation.

3. By increasing the pH from 3 to 5 the adsorbed antimony on kaolinite reached a maximum value and then decreased rapidly, which is consistent with Rakshit et al. (2014). Also, by increasing the pH from 1 to 2 the adsorption rate of zero-valent iron nanoparticles coated on kaolinite increased and at pH = 2 the highest value was obtained, which is consistent with Nosrati (2013).

4. By increasing the concentrations of antimony on nZVI from 0.025 to 1 mg in the antimony adsorption model, the antimony adsorption rate was over 90%, which is consistent with Dorjee et al. (2014). Also, by increasing the K-nZVI adsorbent from 7.5 to 12.5 g/L, the adsorption rate slowly increased and reached above 90%, which is consistent with Nosrati (2013).

5. By increasing the initial concentration of antimony from 0.5 to 50 μg L$^{-1}$, we concluded that nZVI absorbed various concentrations above 90%, which is consistent with Dorjee et al. (2014).

6. Based on the experimental results and our simulation of antimony adsorption, we may state that pH, initial concentrations of Sb, and concentrations of nZVI have a high performance in antimony adsorption.
ACKNOWLEDGEMENT

We wish to acknowledge Mr Ernest Rammel’s assistance in editing our paper.

REFERENCES


Nosratí, N. 2015 Antimony adsorption from Zarshouran Gold Mineral processing plant wastewater by nZVI coated on industrial minerals. MSc thesis, Tarbiat Modares University, Tehran, Iran.


Safavi, B. 2014 Mathematical study for determination of effective parameters for removal of cyanide from artificial wastewater using nanoparticle titanium dioxide. MSc thesis, University of Kharazmi, Karaj, Iran.


First received 3 December 2015; accepted in revised form 5 February 2016. Available online 27 February 2016