New Insight into the Oxidation of Arsenite by the Reaction of Zerovalent Iron and Oxygen. Comment on "pH Dependence of Fenton Reagent Generation and As(III) Oxidation and Removal by Corrosion of Zero Valent Iron in Aerated Water"

Zerovalent iron (ZVI) as a versatile and economical material has received much attention for the removal of arsenic from groundwater and drinking water, which involves spontaneous adsorption and coprecipitation of arsenic with iron(II) and iron(III) oxides/hydroxides formed in situ as a result of the corrosion of ZVI. However, the redox reactions between ZVI and arsenic which can result in the change of arsenic speciation including the reduction of arsenate and the oxidation of arsenite are poorly understood. In a recent article, Katsoyiannis et al. (*1*) systematically investigated the kinetics and mechanism of arsenite oxidation and removal by ZVI over a wide pH range in aerated water. The authors claimed that "arsenite was oxidized mainly in solution by the Fenton reaction and removed by sorption on newly formed hydrous ferric oxide." Based on this finding they concluded that "OH radicals are the main oxidant for arsenite at low pH, whereas a more selective oxidant oxidizes arsenite at circumneutral pH." However, for the following reasons we believe that neither of these two statements is justified by the experiments described in that paper. Meanwhile, we present the new interpretation of their good experimental data, which may provide further insight into the mechanism of arsenite oxidation and removal by ZVI in the presence of oxygen.

Comparison of Arsenite and Arsenate Adsorption on Iron Oxides/Hydroxides

The experimental data presented in that paper clearly showed that arsenite was effectively removed during the corrosion of ZVI over a wide pH range in oxygen-containing solution. In parallel to its removal, the oxidation of arsenite did occur, as evidenced by the fact that arsenic sorbed on newly formed hydrous ferric oxide (HFO) was mainly arsenate at the end of experiments. To account for these observations (Figure 1 (*1*)), the authors claimed that arsenite was first oxidized to arsenate in aqueous solution by the Fenton reaction and then removed by sorption on HFO (designated as the solution−oxidation/adsorption mechanism). We agree with them that (i) the generation of the Fenton reagent is responsible for the oxidation of arsenite over a wide pH range; and (ii) the oxidation of arsenite at acidic pH mainly occurs in aqueous solution, due to the relatively slow formation of HFO and the low affinity of arsenite for HFO as noted by these authors. However, we are very mystified by the logic behind the solution−oxidation/adsorption mechanism for arsenite removal at circumneutral pH. Numerous studies have demonstrated that at circumneutral pH, the adsorption of arsenite is comparable to and even more favorable than that of arsenate on iron oxides/hydroxides via an inner-sphere mechanism similar to arsenate (e.g., refs *2−4*), which is challenging the previously stated generalization that arsenite is more mobile than arsenate in the environment, when iron oxides/hydroxides are available as adsorbents. Moreover, the removal of arsenite at circumneutral pH can occur through coprecipitation with iron(II) and iron(III) oxides/hydroxides formed in situ during the oxidation of ZVI, which is independent of the oxidation state of arsenic. So, at circumneutral pH, the adsorption/surface-oxidation mechanism seems more reasonable, where the oxidation of arsenite after adsorption or coprecipitation takes place on or near the surface of the precipitates rather than in bulk solution. This mechanism is also consistent with the observation of several recent studies that the oxidants generated by the reaction of nano scaled ZVI and oxygen mainly locate in a region close to the ZVI surface (*5−7*).

The New Interpretation of the Effects of 2-Propanol

According to the solution-oxidation/adsorption mechanism hold by these authors, factors affecting the oxidation of arsenite in aqueous solution would impact its removal. However, as contrasted with the significant inhibition effect at acidic pH, the addition of 2-propanol (OH radical scavenger) was found to have negligible effect on the removal of arsenite by ZVI at circumneutral pH (Figure 4 (*1*)). To account for the different effects of 2-propanol at acidic and circumneutral pH, they proposed that OH radicals were the main oxidant for arsenite at low pH, whereas a more selective oxidant (e.g., ferryl ion) oxidized arsenite but exhibited no reactivity toward 2-propanol at circumneutral pH.

However, if the readers consider the change of the removal mechanism for arsenite by ZVI with pH, it is not surprising that 2-propanol present in aqueous solution would have negligible effect at circumneutral pH, where the adsorption/surface-oxidation mechanism dominates. In contrast, at acidic pH where the solution−oxidation/adsorption mechanism dominates, 2-propanol could effectively scavenge OH radicals in aqueous solution and therefore significantly inhibit arsenite oxidation and subsequently its removal. So, is it adequate to propose the pH-dependent mechanism of the Fenton reaction from the effect of 2-propanol?

In addition, we believe that the adsorption/surface-oxidation mechanism can also reasonably explain the occurrence of the oxidation of arsenite in solutions containing ferrous ions, oxygen/hydrogen peroxide, and 2-propanol at neutral pH in a previous study conducted by the same research group (ref 14 in ref *1*), which was cited by Katsoyiannis et al. (*1*) to support the pH-dependent mechanism of the Fenton reaction.

OH Radicals vs FerryI(IV) Ions as Active Intermediates in the Fenton Reaction: A Never-Ending or Already-Ended Story?

Although the Fenton reagent has been known as a powerful oxidant for more than a century, the nature of active intermediates in the Fenton reaction (OH radicals vs ferryl ions) is still a controversial issue, due partly to the limited mechanistic information available for aqueous ferryl species (e.g., ref *8*). Recently, Pestovsky and coworks have characterized aqueous ferryl species spectroscopically, theoretically, and chemically that was generated by the reaction of ozone and ferrous ion, and developed criteria that made it possible to distinguish between OH radicals and this species for the first time (*9−11*). Their criteria allow them to unambiguously rule out aqueous ferryl species as active intermediates in the Fenton reaction in acidic and neutral aqueous solution (*10*). Their excellent work further strengthens our belief that it is the pH-dependent mechanism of arsenite removal rather than the pH-dependent mechanism of the Fenton reaction that is responsible for the different effects of 2-propanol observed at acidic and circumneutral pH.

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