The Effect of Phases in Nanoparticles Produced by Electrical Wire Explosion on Arsenic(III) Removal

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Nanosized iron oxide particles were prepared by electrical wire explosion (EWE) for As(III) removal. The electrical explosion of Fe wire in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂ produced a wide spectrum of iron–oxide phases from wüstite to hematite depending on the oxygen partial pressure in the chamber. An increase in oxygen partial pressure tended to shift the iron oxides towards higher oxidation states. The major phase of the explosion product was verified as the magnetite (Fe₃O₄)–maghemite (γ-Fe₂O₃) mixture through the step scan of (311) and (440) peaks. The As(III) removal capacity and saturation magnetization were found to be proportional to the amount of zero-valent iron (ZVI) in the particles. The As(III) adsorption capacity (qmax, mg/g) calculated from the Langmuir isotherm was 19.7, 9.46, and 3.55 mg/g for particles synthesized in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂, respectively. The EWE process could be utilized to produce nano-sized adsorbent particles with a wide range of As(III) removal capability simply by varying the gas mixture. The eco-friendly nature of EWE process combined with the magnetic separation option would add to the list of the successful As(III) removal adsorbents.

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1. Introduction

Arsenic (As) contamination in drinking water has been a global concern because of As toxicity and occurrence.¹ ² In 1993, the World Health organization (WHO) recommended that the maximum contamination level (MCL) for As in drinking water should be lowered to 10 µg/L.³ Arsenic exists mainly as arsenite (As(III)) and arsenate (As(V)) in water and these forms of As have different dissociation patterns. As(V) has a negative charge at neutral pH (6–9) but As(III) is neutral. The negative charge of As(V) is utilized for As removal by adsorption, anion exchange, or a co-precipitation process.⁴ The conventional As removal process consists of the pre-oxidation of As(III) to As(V) and subsequent precipitation or adsorption.

The U.S. Environmental Protection Agency (USEPA) suggested the use of activated aluminum or iron-based sorbents in their technical handbook for As removal from small drinking water systems.⁵ Among the many candidate sorbents, iron-based sorbents have attracted environmental interest from two points of view. One point of view is that some iron oxides have a high sorption capacity for As(III) and the oxidation process would be undemanding.⁶ Another point of view is that iron oxides such as magnetite (Fe(II)Fe(III)₂O₄) and maghemite (γ-Fe₂O₃) with magnetic properties seize the spotlight because magnetic separation of As-embedded sorbents would be possible after As removal.⁷ Nano-sized magnetic iron oxides are successfully employed for the removal of toxic elements including As.⁸ ⁹ In most chemical methods, however, hazardous chemicals or solvents are indispensable for the preparation of iron oxide particles. Ball milling is proposed as an alternative solvent-free method for the preparation of iron oxide particles but a surfactant is necessary for iron oxide nanoparticles.⁸ ⁹

The electrical wire explosion (EWE) method has been performed for the synthesis of non-metal nanoparticles using pure metal wire and gas in an explosion chamber.⁹ ¹⁰ EWE has a strong advantage because it is unnecessary to use a hazardous chemical in the preparation process. In this study, eco-friendly magnetic iron oxide nanoparticles were synthesized using the EWE method, varying the partial pressure of O₂ in the chamber and examining the feasibility of using magnetic iron oxide nanoparticles as As(III) adsorbents.

2. Experimental Procedure

The explosion experiment was performed using iron wire of 0.3 mm diameter in a 30-liter chamber evacuated and flushed with pure argon gas. The explosion atmosphere was controlled by the mixture of gases: Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂. The capacitance of the exploding circuit was 3.5 μF. The applied voltage across the 20 mm-long wire was 11.4 kV. The total number of explosions for each condition was approximately 600. After the explosion, the powders were filtered through a 125 µm sieve to remove misfired portions. The specimens were examined by FE-TEM (Field-Emission Transmission Electron Microscope, model JEM-2010F, JEOL Ltd.) and X-ray Diffraction (XRD, D/MAX 2200, Rigaku Corp.) with Cu Kα radiation. The specific surface area was measured at 77 K using a Micrometrics Tristar 3000 BET surface area analyzer. Magnetic measurements were obtained in a superconducting quantum interference device (SQUID) magnetometer (MPMS-5, Quantum Design) at 6 K.

All chemicals of ACS grade were obtained from Sigma-Aldrich and used without further purification. Feasibility experiments for As(III) sorption capacity for each set of nanoparticles were performed in triplicate at constant ionic strength of 10 mM NaCl. Samples were shaken for 24 h at 25.0 ± 0.2°C in a temperature-controlled shaker at 150 rpm, and pH was maintained at 7.0 ± 0.2. Dissolved As was
analyzed using ICP-OES (Optima 5300DV, Perkin-Elmer) after filtering through a 0.2 µm membrane filter (cellulose acetate, Sartorius) and acidifying with instrumental grade HNO₃. An adsorbent dosage of iron oxide nanoparticles was varied from 0.1 to 1 g/L and As(III) concentration in the solution varied from 1 to 7 mg/L at intervals of 1 mg/L. Sorption equilibrium was reached in less than 24 h. The analytical detection limit for As was 0.01 mg/L and uncertainty was less than 15%.

3. Results and Discussion

3.1 Characterization of explosion products

The iron-oxide nanoparticles prepared by EWE revealed mostly octahedral or truncated octahedral morphology. The sizes of the nanoparticles ranged from 10 to 200 nm with the average particle size of approximately 48 nm (Fig. 1). The BET surface area of the particles produced in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂ was 9.7, 10.7, and 14.6 m²/g, respectively. This result suggests that the particles synthesized in Ar–30% O₂ may be finer than others. Actual measurement to differentiate the particle size from their FE-TEM images was not successful in revealing the differences in size between different conditions, due probably to the difficulties involved in resolving very fine particles smaller than 10 nm.

Iron oxide has a spectrum of phases ranging from wüstite (FeO), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃). The phase identification of the iron oxides using a conventional X-ray diffraction technique frequently encounters a problem simply because the lattice parameters of magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are almost identical. Figures 2(a), 2(b), and 2(c) show X-ray diffraction patterns of iron oxide nanoparticles produced by EWE in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂, respectively. The major cubic phase marked by ○ could be indexed to either magnetite or maghemite. Table 1 lists the lattice parameters of the phase in question together with those from the standard JCPDS pattern of magnetite and maghemite phases. The lattice parameters of the samples lie almost halfway between the lattice parameters of magnetite and maghemite (0.8396 and 0.83515 nm). Therefore, we could not allocate the lattice parameters to either one of the phases. Another possible way to differentiate both phases concerns the fact that the maghemite phase has two extra peaks at (210) and (211) between 20 and 30°. However, those peaks are too weak to positively confirm the identification unless it is a single phase maghemite of complete crystallinity. In the case of nanosized particles, the broadening of the peaks due to the fine particle size makes the identification of the peaks even more difficult. It is possible that the particles may be a mixture of magnetite and maghemite.

3.2 Verification of the magnetite–maghemite mixture

If the phase was a two-phase mixture, we thought that it would be possible to separate the phases through a step scan of the higher angle peaks. Figure 3 shows the step scan trace of (511) and (440) peaks for samples prepared in Ar–10%O₂. The (511) and (440) peaks obviously show doublets (delineated by ○) that correspond to the magnetite and maghemite peaks. This appearance of doublets was more apparent after we stripped Kα₂ lines (delineated by ●). The phase is obviously a mixture of magnetite and maghemite. Nevertheless, the doublets may be an artifact at high-angle peaks. We therefore applied the same procedure to a single-phase commercial magnetite and maghemite powder and found no doublets as we observed in this study. As a result, we allocate the lower angle peak to magnetite and the higher angle peak to maghemite. Theoretically, the integrated
intensity comparison of overlapping peaks after deconvolution should provide quantitative information on the relative amount of each phase. We are working on this aspect and hope to develop a simple method for the phase quantification of a magnetite–maghemite mixture through the peak deconvolution routine. In addition to the mixture phase, small amounts of wüstite (FeO) and stable hematite (α-Fe₂O₃) were produced as minor phases in Ar–5%O₂ and Ar–30%O₂, respectively.

3.3 Determination of ZVI

Except for the magnetite–maghemite mixture, the most noticeable phase was the zero-valent iron (ZVI), the main peak of which was located at 44.67°(110). The ZVI peak is found to decrease as the oxygen pressure increases (Fig. 2). It is the highest for the particles exploded in Ar–5%O₂(a) and vanishes completely for the particles produced in Ar–30%O₂(c). We later found that the presence of ZVI affected both the saturation magnetization and the As removal efficiency. This led us to determine the amount of ZVI by preparing a calibration curve from the intensity ratio of reference mixture samples containing ZVI.

The reference samples containing 20, 40, 60, and 80% ZVI were prepared by weighing and mixing ZVI with the nanopowders exploded in Ar–30%O₂. As discussed previously, the major phase was the mixture of magnetite and maghemite. If we knew the exact proportion of magnetite and maghemite in each sample, we could prepare a reference mixture using the single-phase magnetite and maghemite powders. Not knowing the proportions, however, we selected the nanoparticles produced by EWE in Ar–30%O₂ instead, which do not contain ZVI.

The integrated intensity percent of the (110)Fe peak against the six largest peaks from each sample was measured and compared with the pre-determined composition of reference samples as follows:

$$I_{Fe} (%) = 100 \times \left( \frac{I_{Fe}}{I_{total}} \right)$$

(1)

Here, $I_{Fe}$ is the integrated intensity of (110)Fe and $I_{total}$ is the sum of the integrated intensity of the six major peaks. Figure 4 is the calibration curve thus obtained, which shows the relationship between $I_{Fe}$ and the composition of the reference samples. The calculation was made assuming a two-phase (magnetite–maghemite mixture + ZVI) and neglecting the small amount of the hematite phase in samples prepared in Ar–30%O₂. From the calibration curve, the amount of ZVI in iron oxide nanoparticles prepared in Ar–5%O₂ and Ar–10%O₂ was measured to be 44 and 29%, respectively.

3.4 Magnetization of nanoparticles prepared by EWE

The magnetic property of iron oxide nanoparticles could be one of the important factors in environmental remediation because it provides the magnetic recovery option for As-embedded particles after treatment. Magnetization hysteresis loops for iron oxide nanoparticles at 6 K are shown in Fig. 5. A saturation magnetization was taken as the magnetization at a field of 1 Tesla. The measured values were 101.2, 88.9, and 70.4 emu/g for iron oxide nanoparticles prepared in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂, respectively. Theoretical values of the saturation magnetization for bulk iron, magnetite, and maghemite are given as 222, 96.4, and 87.3 emu/g, respectively. The particles produced in Ar–
Freundlich constant related to the sorption capacity, mass of adsorbent and solution at equilibrium, eqs. (2) and (3), respectively. and Freundlich sorption isotherm models can be expressed as sorption on the adsorbent. The linear forms of the Langmuir model describes a heterogeneous non-ideal multilayer independent and equivalent sorption sites. The Freundlich homogeneous monolayer sorption on the adsorbent having sorption isotherm models. The Langmuir model is applied to as an adsorbent was examined with Langmuir and Freundlich

5%O₂ possessed the highest saturation magnetization because they contain the largest amount of ZVI. The saturation magnetization of iron oxide nanoparticles prepared by EWE in this study appears to be somewhat lower than the theoretical values. The saturation magnetization can be estimated using the theoretical values for each phase and the amount of ZVI in each sample. Table 2 summarizes the result of this estimation. As we do not know the relative amount of the magnetite–maghemite mixture, an average value was used. This calculation shows that the measured values for the samples are approximately 30% lower than the theoretical values, which is in agreement with the report that the saturation magnetization of nano-sized particles was lower than the theoretical values.10–13

3.5 As(III) sorption isotherm
As(III) removal efficiency using iron oxide nanoparticles as an adsorbent was examined with Langmuir and Freundlich sorption isotherm models. The Langmuir model is applied to homogeneous monolayer sorption on the adsorbent having independent and equivalent sorption sites. The Freundlich model describes a heterogeneous non-ideal multilayer sorption on the adsorbent. The linear forms of the Langmuir and Freundlich sorption isotherm models can be expressed as eqs. (2) and (3), respectively.

\[
\frac{C_e}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \quad (2)
\]

\[
\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (3)
\]

where \(q_e\) and \(C_e\) represent the As(III) concentration per unit mass of adsorbent and solution at equilibrium, \(K\) is the Freundlich constant related to the sorption capacity, \(q_{\text{max}}\) is the maximum adsorption capacity, and \(b\) and \(n\) are constants for the adsorption energy and intensity.

The linear plots of the Langmuir and Freundlich sorption isotherms are shown in Fig. 6. Both Langmuir (\(R^2 > 0.97\)) and Freundlich (\(R^2 > 0.95\)) models match well with experimental data, suggesting that As(III) sorption may occur through monolayer or multilayer coverage. Further study is required to clarify the mechanism of As(III) adsorption on the iron oxide nanoparticles prepared by the EWE method. The reciprocal of the slope in Fig. 6(a) of the Langmuir linear curve represents the maximum sorption capacity. This maximum sorption capacity decreases as oxygen pressure increases. The same trend is also detected in the Freundlich linear curve, where the Intercept (\(\ln K\)) of the sorption capacity increases as the oxygen pressure decreases [Fig. 6(b)].

The parameters of the Langmuir and Freundlich equations and their correlation coefficients (\(R^2\)) are presented in Table 3. The maximum As(III) adsorption capacity (\(q_{\text{max}}\)) was calculated using the Langmuir equation as 19.7, 9.46, and 3.55 mg/g for nanoparticles prepared in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂, respectively. This result appears to suggest that the adsorbent containing more ZVI shows higher As(III) removal capacity. An arithmetic relationship between the amount of ZVI in the sample and the sorption capacity was therefore assumed and is depicted in Fig. 7. Figure 7 shows a linear proportionality. If one extrapolates the line to the y-axis, the line intercepts the y-axis at approximately 37 mg/g, which corresponds to the removal efficiency for the sample containing only ZVI. It would be interesting to see if the removal efficiency of 100% ZVI produced by EWE matches up with the value. Even though nanoscale ZVI has been considered to be a promising material for As(III) removal,14–19 actual data on the sorption capacity of ZVI are very scarce and conflicting (Table 4).

Table 2 Estimation of saturation magnetization of iron oxide nanopowders from the theoretical values and the amount of ZVI measured (Fe: 222 emu/g, magnetite: 96.4 emu/g, maghemite: 87.3 emu/g).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZVI (%)</th>
<th>Measured (emu/g)</th>
<th>Theoretical (emu/g)</th>
<th>% against theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% O₂</td>
<td>44</td>
<td>101.2</td>
<td>149</td>
<td>67.9</td>
</tr>
<tr>
<td>10% O₂</td>
<td>29</td>
<td>88.9</td>
<td>130</td>
<td>68.6</td>
</tr>
<tr>
<td>30% O₂</td>
<td>0</td>
<td>70.4</td>
<td>92</td>
<td>76.6</td>
</tr>
</tbody>
</table>

Table 3 Parameters for the Langmuir and Freundlich isotherms for As(III) adsorption by the adsorbents.

| Preparation condition | Langmuir constant | Freundlich | |
|-----------------------|--------------------|------------|
|                       | \(q_{\text{max}}\) | \(b\)      | \(R^2\)   |
| 5% O₂                 | 19.7               | 0.86       | 0.971     |
| 10% O₂                | 9.46               | 1.34       | 0.975     |
| 30% O₂                | 3.55               | 1.75       | 0.976     |

Fig. 6 Langmuir (a) and Freundlich (b) isotherms of As(III) adsorption on iron oxide nanoparticles prepared by EWE in the As(III) concentration range of 1–7 mg/L.
Further study is clearly needed for the proper evaluation of the sorption capacity of nanoscale ZVI.

The sorption capacities of EWE nanopowders (the magnetite–maghemite mixture and ZVI) are observed to be high (Table 4). In drinking water treatment handbook by EPA, 1 mg/L of arsenic is regarded as the maximum contaminated level and the volume of adsorbent should be increased by the safety factor.4) Our nanoparticles would be effective in treating contaminated groundwater including drinking water with high arsenic levels without the pre-oxidation of As(III) to As(V) to make the sorption easier. Our EWE nanopowders are believed to be sufficiently satisfactory for this purpose.

The EWE process has an advantage over other chemical methods. In the EWE process, hazardous chemicals are not used to prepare the adsorbent particles. There is likewise no need to remove byproducts or solvent afterwards. As the major phase was the mixture of magnetite and maghemite, As-embedded particles could be recovered by magnetic separation after As(III) removal. If anti-ferromagnetic wüstite or hematite were the major phase, recovery of the As-embedded particles would not be possible.

4. Summary

The removal of arsenic(III) from the aqueous solution of pH 7 containing 0.1–100 mg/L was investigated using nano-sized iron oxide particles. Iron oxide particles were prepared by the electrical explosion of Fe wire in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂. The major phase in the explosion products was the mixture of magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) for all conditions. The presence of this mixture phase was verified successfully through the step scan of high-angle peaks as (511) and (440). Except for the mixture phase, 44 mass% ZVI together with small amounts of wüstite was produced when the oxygen partial pressure was low (Ar–5%O₂). As the oxygen pressure increased (Ar–10%O₂), ZVI decreased to 29 mass% with the advent of a small hematite peak. At the highest oxygen pressure (Ar–30%O₂), ZVI was diminished completely with small increase of the hematite phase. The As(III) adsorption capacity (qₘₐₓ, mg/g) calculated from the Langmuir isotherm was 19.7, 9.46, and 3.55 mg/g for particles prepared in Ar–5%O₂, Ar–10%O₂, and Ar–30%O₂, respectively. The As(III) removal capacity and saturation magnetization were found to be proportional to the amount of ZVI in the particles. The EWE process could be utilized to produce nano-sized adsorbent particles with a wide range of As(III) removal capabilities simply by varying the gas mixture.

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