Efficient Removal of Arsenic Using Magnetic Multi-Granule Nanoclusters

Seung-Ho Lee, Jinmyung Cha, Kyunjong Sim, and Jin-Kyu Lee

Interdisciplinary Program in Nanoscience and Technology, Seoul National University, Seoul 151-747, Korea
1Department of Chemistry, Seoul National University, Seoul 151-747, Korea. *E-mail: jinklee@snu.ac.kr

Received December 4, 2013, Accepted December 9, 2013

Magnetic multi-granule nanoclusters (MGNCs) were investigated as an inexpensive means to effectively remove arsenic from aqueous environment, particularly groundwater sources consumed by humans. Various size MGNCs were examined to determine both their capacity and efficiency for arsenic adsorption for different initial arsenic concentrations. The MGNCs showed highly efficient arsenic adsorption characteristics, thereby meeting the allowable safety limit of 10 μg/L (ppb), prescribed by the World Health Organization (WHO), and confirming that 0.4 g and 0.6 g of MGNCs were sufficient to remove 0.5 mg/L and 1.0 mg/L of arsenate (AsO₄³⁻) from water, respectively. Adsorption isotherm models for the MGNCs were used to estimate the adsorption parameters. They showed similar parameters for both the Langmuir and Sips models, confirming that the adsorption process in this work was active at a region of low arsenic concentration. The actual efficiency of arsenate removal was then tested against 1 L of artificial arsenic-contaminated groundwater with an arsenic concentration of 0.6 mg/L in the presence of competing ions. In this case, only 1.0 g of 100 nm MGNCs was sufficient to reduce the arsenic concentrations to below the WHO permissible safety limit for drinking water, without adjusting the pH or temperature, which is highly advantageous for practical field applications.

Key Words: Arsenic, Iron oxide, Adsorption, Multi-granule nanoclusters, Magnetic nanoparticle

Introduction

Arsenic is highly toxic element known for its deleterious influences on both the environment and human health. High levels of arsenic uptake by humans have led to health problems such as skin-, kidney-, lung-, liver cancer, and neurological damage in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan, Nepal, Vietnam, and India. The largest at-risk population to groundwater arsenic pollution is in Bangladesh, followed by the inhabitants of West Bengal in India. Because of its toxicity and carcinogenic effects on human health, the World Health Organization (WHO) reduced the allowable safety limit of arsenic in drinking water from 50 to 10 μg/L in 1993, and strictly regulated the quality of water. The European Union has amended all drinking water supply systems according to this updated limit. The United States Environmental Protection Agency (USEPA) has also adopted the WHO prescribed maximum level of arsenic contamination (10 μg/L) in drinking water; this has been put to effect since 2006.5

There is an urgent need to improve the prevailing water treatment technology because arsenite (AsO₂³⁻) and arsenate (AsO₄³⁻) are the two predominant arsenic species found in groundwater. Adsorption has become an attractive and promising technology for arsenic extraction because of its simplicity, safety, ease of operation, maintenance, and handling, sludge-free operation, potential for regeneration, and possibility for the use of inexpensive adsorbent. In general, it is open considered to be the most effective treatment process for the removal of arsenic from aqueous environments at relatively low costs. Furthermore, to be effective and practical, an arsenic removal method should be easily applicable at individual sites serving households or small communities. Various types of iron-based nanoparticle adsorbents have been developed for arsenic removal because of their high affinity for and adsorption capacity of the anionic form of arsenic oxyacids. Some of the representative examples of these types of compounds are Fe₃O₄@NiO hierarchical nanostructures, ordered meso-porous carbon encapsulating a wide range of metal oxide nanoparticles, Fe₂O₃ and Fe₃O₄ obtained through a precipitation method, and mechanically ball-milled Fe₂O₃ nanopowder. Many methods have been developed to increase the size of magnetite nanoparticles, which would result in a fast response to the external magnetic field particles, while keeping them stably dispersed in solution. To this end, it is sometimes misunderstood that large-sized superpara-magnetic nanoparticles having negligible remanence (residual magnetism) and coercivity (the field required to reduce magnetization to zero) at room temperature is the most effective material. However, this is not the most effective way. We recently reported that ferromagnetic materials could be made more useful when they could be dispersed in the solution by a strong interaction between solvent molecules and surface functional groups. The magnetic saturation (Mₛ) values measured at 70 kOe (300 K) were 73.9, 80.3, and 84.6 emu/g for MGNCs of 100, 200, and 400 nm, respectively. The relatively high Mₛ value of multi-granule nanocluster (MGNC) samples at 100 nm was very close to the reported Mₛ values for Fe₂O₃ nanoparticles. The zero-field cooling/field cooling (ZFC/FC)
measurements clearly showed the ferromagnetic behavior of MGNCs with various diameters. Although the MGNCs used in our experiments are ferromagnetic are very stable in aqueous solution and are homogeneously dispersed because of multi-granule structure resulting an increased numbers of the surface functional groups (–OH). Therefore, it is of interest to use this new type of magnetite in MGNC for arsenic removal application.

In the present research, MGNCs were prepared in a large scale, as reported in our previous work, and examined for their capacity to remove the AsO\textsubscript{4}\textsuperscript{3−} anion from water. We find out that contaminated water could be easily remediated with magnetic MGNCs, which could effectively and practically be applied at individual sites serving households or small communities.

**Experimental**

**Materials.** Iron(III) chloride hexahydrate (FeCl\textsubscript{3}·6H\textsubscript{2}O, > 97%, Sigma-Aldrich), sodium arsenate dibasic heptahydrate (Na\textsubscript{2}HAsO\textsubscript{4}·7H\textsubscript{2}O, > 98%, Sigma-Aldrich), sodium acetate anhydrous (NaO\textsubscript{2}CCH\textsubscript{3}, > 98.5%, Samchun Chemicals), and ethylene glycol (HOCH\textsubscript{2}CH\textsubscript{2}OH, > 99.5%, Samchun Chemicals) were purchased and utilized as received. An arsenic stock solution of 100 mg/L was prepared by dissolving appropriate amount of sodium arsenate Na\textsubscript{2}HAsO\textsubscript{4}·7H\textsubscript{2}O in deionized water. Working solutions for each experiment were freshly prepared from the stock solution.

**Preparation of MGNCs.** MGNCs were prepared by following the procedure published in the literature. In a typical MGNC synthesis, FeCl\textsubscript{3}·6H\textsubscript{2}O (27 g, 0.1 mol), NaO\textsubscript{2}CCH\textsubscript{3} (100 g, 1.2 mol) and distilled water (100 g, 5.6 mol) were completely dissolved in ethylene glycol (1.5 L) by vigorous mechanical stirring to form a yellowish-brown turbid solution. After heating the solution at 70 °C for various lengths of time, the reaction temperature was increased to the refluxing temperature to complete the reaction, leading to the formation of MGNCs. At this point, the reaction solution turned reddish-brown and then slowly became black. After being cooled down to room temperature, the black sediment was separated magnetically by attaching a strong permanent magnet to the outside of the reaction flask and then washed with ethanol and distilled water several times to eliminate any organic and inorganic byproducts. The specific surface area of magnetic MGNCs was characterized using the Brunauer-Emmett-Teller (BET) method by measuring the nitrogen adsorption/desorption surface area (TriStar II 3020, Micromeritics, USA operated at 77 K).

**Adsorption Experiments and Analysis.** MGNCs having sizes of 100, 200, and 400 nm were used for arsenic removal. Adsorption studies were conducted with aqueous solutions having arsenic concentrations of 0.5 and 1.0 mg/L, which corresponds to the range of arsenic concentrations in contaminated groundwater. The amounts of the MGNCs used were 0.2, 0.4, 0.6, 0.8, and 1.0 g/L for each size. The solutions of arsenic mixed with MGNCs were shaken in an orbital shaker at 200 rpm, at 298 K for 24 h; the solutions occupied a total volume of 20 mL within the 30 mL glass vial. The MGNCs in the mixture were removed by magnetic decantation with a permanent magnet and the remaining water was evaluated to determine the adsorption capacity. The arsenic concentrations before and after the adsorption experiments were analyzed by means of an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7510).

**Results and Discussion**

**Characterization of MGNCs.** The MGNCs were prepared as previously reported by the simple reaction of FeCl\textsubscript{3} and sodium acetate in ethylene glycol, which served as both the solvent and reductant. Simple refluxing in glassware at atmospheric pressure allowed us to easily monitor changes in the color of the reaction mixtures and control the sizes of the MGNCs. The sizes of the MGNC were selected to be 100, 200, and 400 nm for experiments, as shown in Figure 1, because MGNCs with these features exhibited a fast response to the applied external magnetic field after arsenic removal from the aqueous solutions.

The specific surface area of the MGNCs was estimated using the BET method as shown in Table 1. As expected the surface area decreased significantly as the size of MGNC was increased; the surface area for the 400 nm size MGNC was still larger (about 2 times) than that of the bulk (< 5 μm) magnetite powder, confirming the characteristic multi-granular shape of MGNC.

**Effect of Initial Arsenic Concentration and Amount of MGNCs of Each Size.** The maximum capacity of adsorption can be increased when the initial arsenic concentration is relatively high with respect to the values found in groundwater; however, we measured adsorption capacity at arsenic concentration of 0.5 and 1.0 mg/L because these values are more representative of contaminated groundwater. As shown in Figure 2(a), when the initial concentration of As(V) was 0.5 mg/L, 100 nm MGNC could remove more than 90% of the arsenic at a concentration of 0.2 g/L. At the same initial

![Figure 1. TEM images of MGNCs prepared from the molar ratios of FeCl\textsubscript{3}:NaOAc:H\textsubscript{2}O = 0.1:1.2:5.6 in 1.5 L of ethylene glycol after heating at 70 °C for (a) 1 h, (b) 12 h, and (c) 35 h. (scale bar: 400 nm)](image1)

**Table 1. BET surface areas of various size MGNCs and commercial iron oxide (< 5 μm)**

<table>
<thead>
<tr>
<th>MGNC Size (nm)</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>&lt; 5 μm Bulk Fe\textsubscript{3}O\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area (m\textsuperscript{2}/g)</td>
<td>29</td>
<td>14</td>
<td>9.3</td>
<td>5.1</td>
</tr>
</tbody>
</table>
arsenic concentration and the same size of MGNC, 0.4 g/L of the MGNC (residual arsenic was actually measured as 1 μg/L) was efficient to remove arsenic to satisfy the WHO’s allowable limit of 10 μg/L. When 200 nm MGNC was used, although the adsorption efficiency appeared to be slightly decreased, the WHO’s allowable limit could still be achieved at conditions of 0.4 g/L (residual arsenic was actually measured as 3 μg/L). The largest size MGNC (400 nm), used in the adsorption experiments, showed the lowest arsenic removal efficiency, as expected. At this size, 0.8 g/L MGNC was needed to satisfy the WHO limit. These trends can be explained by the differences in the surface areas of MGNCs as shown in Table 1.

When the initial concentration of As(V) was increased to 1.0 mg/L, a larger amount of MGNCs was needed to remove the arsenic, and the residual arsenic concentrations were measured as 1.5 and 6 μg/L at the conditions of 0.6 g/L of 100 and 200 nm MGNCs, respectively (Fig. 2(b)). However, for 400 nm MGNC, the WHO’s limit could not be achieved even at 1.0 mg/L of the MGNC.

**Adsorption Isotherm.** Data for the equilibrium arsenate adsorption onto various size MGNCs, as shown in Figure 2, were fitted against the two-parameter Langmuir and Freundlich isotherm models and the three-parameter Sips isotherm model, as shown in Figures 3(a)-3(c). The Langmuir isotherm model assumes that the adsorption occurs at specific homogeneous sites within the adsorbent. This means that once an adsorbate molecule adheres to a site, no additional
adsorption can occur at that site. We can assume that at low adsorbate concentrations, it effectively reduces to a linear isotherm, and thus obeys Henry’s law. Alternatively, at high adsorbate concentrations, it leads to a constant monolayer sorption capacity. The Freundlich isotherm model can be applied to nonideal sorption on heterogeneous surfaces, as well as multilayer sorption. Frequently, the fundamental thermodynamic basis is required because the Freundlich isotherm model does not reduce to Henry’s law at low concentrations. The Sips model, also known as the combined Langmuir-Freundlich isotherm, is a three-parameter isotherm model developed to enhance the performance of the individual two-parameter models. The Langmuir-Freundlich name originates from the restraining performance of the equation and the resulting model has characteristics of both the contributing models. At low adsorbate concentrations, it effectively reduces to the Freundlich isotherm, and thus does not obey Henry’s law. At high adsorbate concentrations, it predicts the monolayer sorption capacity aspect of the Langmuir isotherm.

The mathematical descriptions for the isotherm models are shown as follows: Langmuir (Eq. 1), Freundlich (Eq. 2), and Sips (Eq. 3)

\[
q_e = \frac{(b \cdot Q_o \cdot C_e)}{(1 + b \cdot C_e)} \quad (1)
\]

\[
q_e = K_F \cdot C_e^{1/n} \quad (2)
\]

\[
q_e = \frac{[Q_s \cdot (a_s \cdot C_e)^n]}{[1 + (a_s \cdot C_e)^n]} \quad (3)
\]

\( q_e \) is the equilibrium adsorption capacity (mg·g\(^{-1}\));
\( b \) is the Langmuir constant related to adsorption intensity (L·mg\(^{-1}\));
\( Q_o \) is the Langmuir constant reflecting the theoretical maximum adsorption capacity;
\( C_e \) is the equilibrium arsenic concentration after adsorption process (mg·L\(^{-1}\));
\( K_F \) is the Freundlich constant related to adsorption capacity;
\( a_s \) is the Sips isotherm constant; and
\( s \) is the Sips isotherm exponent.

The estimated parameters derived from each isotherm model are summarized in Table 2, with the measured experimental data calculated by a non-linear optimization method. The three-parameter Sips model produced a better fit to the experimental data compared to two-parameter isotherm model, as clearly shown by the value of the correlation coefficient (R\(^2\)). The correlation coefficient for the Sips isotherms models varied from 0.916 to 0.990, showing a good fit of the measured data. Conversely, for the Langmuir and Freundlich models, the parameters were obtained with a relatively low correlation coefficient: R\(^2\) = 0.978-0.821 and 0.897-0.967, respectively.

All of the models for the 100 nm MGCN generated very good correlation coefficient values (in the range of 0.928-0.981). Furthermore, the maximum arsenic adsorption capacity derived from both the Langmuir and Sips models were rather consistent. These values (2.3-2.4 mg As(V)/g MGCNs) were higher than those of previously reported for nanoparticle adsorbents such as hematite coated Fe\(_3\)O\(_4\) particles (2.1 mg/g),

 \[
K_F = 0.20 \text{ mg/g}
\]

and magnetite nanoparticles supported on Fe-hydrotalcite (1.3 mg/g). The Freundlich isotherm provides an “n” value that is related with adsorption intensity. A high “n” value indicates good adsorption over the entire range of concentrations studied; a low “n” value means that adsorption ability is increased at high concentrations, but is decreased at lower concentrations. The “n” values of the MGCNs were 4.3-6.3 for different size MGCNs, which were higher than the “n” values of previously reported nanoparticle adsorbents such as commercial nanomagnetite (1.8), magnetic Fe\(_3\)O\(_4\) @NiO hierarchical structures (2.2), and magnetite-reduced graphene oxide composites (2.9-3.0).

Based on the results of the arsenic removal experiments and the adsorption isotherm model studies, the MGCNs studied in this work seem to have several advantages including: (i) quick, simple, and straightforward preparation, which can be easily scaled-up for mass production; (ii) neither pH nor temperature dependence that is usually needed during the adsorption process (yet they maintain high adsorption capacity which is beneficial for efficient field applications); and (iii) a simple magnetic separation and recovery system that takes advantage of the strong magnetic property of MGCNs.

**Arsenic Removal from Artificial Arsenic-contaminated Groundwater.** In order to emphasize the applicability of our new MGCN adsorbent to remove arsenate from the natural system, As(V)-contaminated groundwater was artificially prepared from distilled water spiked with arsenate and other commonly found cations and anions, as previously described in the literatures (Table 3). and the remediation process was tested. One liter of artificial contaminated groundwater...
spiked with arsenate (0.6 mg/L) along with the various cations and anions was treated with 1.0 g of 100 nm MGNCs in the Erlenmeyer flask, as shown in Graphical Abstract. The treated water was then separated from the MGNCs by magnetic decantation and the remaining arsenic concentration in the purified water was determined by ICP-AES. The remaining arsenic concentration was lower than 10 μg/L, implying that our MGNCs successfully adsorbed the arsenate from the artificial arsenic-contaminated groundwater to achieve the WHO prescribed safety limit of arsenic concentration in drinking water.

Conclusions

Ferromagnetic multi-granule nanoclusters which can be synthesized on a large scale with reasonably high magnetic saturation values of 74-85 emu/g and good dispersion properties in water despite their relatively large size in the range of 100-400 nm, were successively employed as new adsorbents for removing arsenic contaminant from water. Adsorption equilibrium data were fitted to the Langmuir, Freundlich, and Sips isotherm models and the various resulting parameters were evaluated. The findings of this work are significant because they show that 1 L of artificial arsenic contaminated groundwater (0.6 mg/L of arsenate) could be effectively remediated with 1.0 g of 100 nm MGNCs, which complied with the WHO permissible arsenic limit of 10 μg/L in drinking water. From these results, we expect that magnetic MGNCs can effectively remove arsenic from contaminated groundwater at a considerably low cost that will make it suitable for application in household- or small-scale water treatment system, after a more precise kinetic investigation of the adsorption processes is conducted.

Acknowledgments. This study was supported by the Nano R&D Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science, and Technology (2009-0082736). J.-M. Cha and K. Sim gratefully acknowledge the BK21 fellowship.

References


Table 3. Composition of artificial arsenic-contaminated groundwater

<table>
<thead>
<tr>
<th>Ion</th>
<th>Na⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>HCO₃⁻</th>
<th>SiO₃²⁻</th>
<th>PO₄³⁻</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>145</td>
<td>8</td>
<td>51</td>
<td>363</td>
<td>1.93</td>
<td>32</td>
<td>90.3</td>
<td></td>
</tr>
</tbody>
</table>