

High arsenic adsorption capacity of sub-4 nanometer magnetite nanoparticles

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Abstract—Although arsenic-contaminated groundwater belongs to local scale pollution, this problem prevails all over the world. Through the long temporal contact between groundwater and rocks or sediments containing arsenic (As), the groundwater can be polluted due to the variation of pH and redox potential. Traditional treatment technologies are not effective and magnetite nanoparticle seems to be a good alternative due to its highly selective adsorption toward arsenic and feasibility on regeneration. Here, we report the result of adsorption of arsenite (As(III)) and arsenate (As(V)) using the magnetite nanoparticles (MNP) with diameter less than 4 nm. This nanomaterial exhibited high As(V) adsorption capacity, up to 206.9 mg g⁻¹, which is the highest in the literature to the authors' knowledge. The results suggested that sub-4 nm MNP is an excellent As adsorbent.

Keywords- Arsenic; Magnetite; Nanoparticle; Adsorption.

I. INTRODUCTION

Arsenic has been ranked at the top on the CERCLA Priority List of Hazardous Substances in USA for more than a decade and is also an imperative groundwater contaminant all over the world. Currently, there are still tens of millions of people suffering drinking water containing high arsenic concentration, especially in the south and east Asia.[1] In Bangladesh alone, about 50,000,000 people are at risk exposed to arsenic contaminated drinking water.

Arsenic poisoning can be either acute or chronic. Acute poisoning is usually caused by mistaken ingestion of foods or water with high As concentration. Chronic poisoning is often resulted from long-period exposure to low level As from contaminated foods, water, and air. Thus, effective removal of As from drinking water is in urgent demand.

Apart from traditional As-removal technologies, such as coagulation and flocculation followed by sedimentation and filtration, reverse osmosis [2], ion exchange [3], membrane filtration [4] and adsorption [5], recently magnetite nanoparticles has emerged as a viable alternative due to their extremely high adsorption capacity [6-8]. Magnetite nanoparticles smaller than ~16 nm will possess a unique superparamagnetic characteristic [9] which promotes their suitability for dispersed adsorbent application. This approach may have advantage over membrane filtration or fixed bed due to no fouling or plugging problems [8]. The adsorption capacities for As(III) and As(V) and the recovery of this adsorbents from treated water were investigated.

II. EXPERIMENTAL

A. Synthesis of magnetite nanoparticle

Several methods are available to prepare magnetite nanoparticle and have been well documented [11, 12]. Here, a modified coprecipitation method was employed. Briefly, ferrous chloride (FeCl₂·4H₂O, #2064-01, J.T. Baker, Taiwan Branch) and ferric chloride (FeCl₃·6H₂O, #31232, Riedel-de Haën, Taiwan Branch) were mixed at a 1 to 2 ratio in a 100-ml amber glass bottles and sodium hydroxide were added to adjust the pH to 12. These amber glass bottles were then placed into a sonication bath (Ultrasonic Cleaner DC600H, Delta New Instrument Co., Taiwan) for 30 minute for mixing and reaction. The nanoparticle products were rinsed by deionized water (Millipore, Billerica, MA, USA) at least five times before vacuum drying in an anaerobic chamber (Coy Laboratory Products, Inc., Grass Lake, Michigan, USA). The dried nanoparticles were pooled into a bigger bottle and wrapped with aluminum foil to keep in dark.

B. Characterization of magnetite nanoparticle

Dried magnetite nanoparticles were characterized by using a transmission electron microscope (TEM; JEM-1400, JEOL, Tokyo, Japan), a powder x-ray diffractometer (XRD, X'pert Pro, Panalytical, Almelo, The Netherlands), and a Brunauer-Emmett-Teller (BET) surface area analyzer (ASAP 2020, Micromeritics, Norcross, Georgia, USA). The JEM-1400 transmission electron microscope has a resolution at around 0.4 nm, however, the image cannot be clearly observed at less than 1 nm range.

C. Adsorption experiment and quantification

Stock solutions of arsenite and arsenate were prepared at 1,000 ppm and were remade weekly and monthly, respectively. Both stock solutions were kept in anaerobic conditions before use. Immediately prior to adsorption experiments, stock solutions were diluted with a 0.01 M tris(hydroxymethylamino)methane buffer (Tris buffer) to 10, 50, 100, 250, 500, 1000, 1500, 2500, 5000, 10000, and 25000 ppb at a volume of 40 ml. With a Tris buffer, the pH is maintained at pH 8.0, a typical pH in most groundwater systems. The amount of adsorbent was 0.002 g of magnetite nanoparticle. All adsorption tests lasted for six hours at 30°C to ensure the equilibrium was reached even though the equilibrium can be reached within one hour (data not shown). At the end of the adsorption tests, the magnetite

nanoparticles were recovered by sitting on a strong rare earth magnet for 30 minutes. The supernatants were then transferred to new test tubes for sample digestion and quantification by an inductively coupled plasma mass spectrometer (ICP-MS; ELAN DRC II, Perkin-Elmer, Inc., Waltham, Massachusetts, USA). All tests were conducted with triplicates and blanks.

D. Recovery test

In order to judge the feasibility of using such nanomaterial in real world application, a recovery test was undertaken to quantify the residual iron oxide possible residual arsenic concentration in the treated water. A fixed amount of MNP was added into deionized water to reach a final concentration at 0.1 g L^{-1} and mixed well. Then, the test serum bottles underwent magnetic separation by sitting on a rare earth strong magnet for 30 minutes and the supernatants were sent to ICP-MS quantification to determine the residual iron oxide concentration in treated water.

III. RESULTS

A. Synthesis and characterization of magnetite nanoparticle

The modified coprecipitation method used in this study can produce hundreds of grams of sub-two-nanometer magnetite at a time. The shape and size was obtained under TEM as shown in Figure 1 a. Due to the resolution of the camera, the exact shape cannot be effectively captured. Here, two electron micrograph showed that the aggregate of these magnetite nanoparticles was as small as $3.02 \pm 0.32 \text{ nm}$ (mean \pm CI 95%, $n=100$). The X-ray diffraction test has been performed twice, before and after the adsorption experiments (Figure 2). There was no significant difference between these two patterns and both of them clearly matched the characteristic peaks of magnetite mineral according to Powder Diffraction Files by International Centre for Diffraction Data (ICDD). The specific surface area was measured twice and the results were 62.9 and $68.6 \text{ m}^2 \text{ g}^{-1}$ giving an average of $65.8 \text{ m}^2 \text{ g}^{-1}$. This value is much less than the calculated value of that of a 3.02 nm sphere, around $386 \text{ m}^2 \text{ g}^{-1}$. This lower specific surface area may be resulted from the aggregation of the particles upon drying because the BET surface area measurement requires a dry sample.

B. Adsorption tests

Adsorption tests were carried out under two different conditions, aerobic and anaerobic, and were discussed in the following sections.

- *As adsorption by magnetite nanoparticles under anaerobic conditions:* The results of the adsorption experiments using magnetite nanoparticles were significant different for As(III) and As(V) under anaerobic condition (Figure 4). In this study, the adsorption capacity of magnetite nanoparticles on As(V) is as high as 206.9 mg g^{-1} , which is significantly higher than that on As(III), 168.8 mg g^{-1} . For As(V), for all tested concentration, the

removal ranged from 35.6 % to 93.0 %. When the initial concentration of As(V) at 100 ppb, the removal is the highest. For As(III), for all tested concentration, the removal ranged from 36.8 % to 71.3 %. For both experiment results, three adsorption isotherms, i.e., linear, Freundlich, and Langmuir, were applied and Freundlich showed the best fit.

- *As adsorption by magnetite nanoparticles under aerobic conditions:* Similarly, the results of the adsorption experiments using magnetite nanoparticles were significant different for As(III) and As(V) under aerobic condition (Figure 5). Further, the adsorption capacity under aerobic conditions is significantly lower than that under anaerobic condition. Under aerobic condition, the adsorption capacity of magnetite nanoparticles on As(V) is 138.1 mg g^{-1} , which is still higher than that on As(III), 108.6 mg g^{-1} . These adsorption capacities were about 64-67% of their counterparts under anaerobic condition. For As(V), for all tested concentration, the removal ranged from 27.6% to 79.7% with the highest removal at initial concentration at 10 ppb. For As(III), for all tested concentration, the removal ranged from 21.7% to 79.4%. For both experiment results, three adsorption isotherms, i.e., linear, Freundlich, and Langmuir, were applied and Freundlich isotherm was the best fit.

C. Recovery test

In order to judge the feasibility of applying these MNPs in real world treatment, a recovery test was undertaken. The residual iron concentration in the treated water is 602.5ppb.

IV. DISCUSSION

For the synthesis of magnetite nanoparticle, two different ways were tried, i.e., microemulsion and coprecipitation [13]. According to our experience, coprecipitation method is easier in operation and the cost is about 95% less than microemulsion method in bench scale. The small size renders the nanoparticles superparamagnetism property that allows the particles to disperse themselves in liquid. This is very favorable in adsorption applications [7, 9]. From the TEM micrograph of synthesized magnetite nanoparticles (Figure 1 a), one can see the uniform size distribution of the nanoparticles. After a mild probe sonication, the shape of the nanoparticle cannot be clearly imaged under a 120 KeV TEM. Since probe sonication usually breaks the weak chemical bonds including hydrogen, ionic bonds, and hydrophobic interactions[14], it is estimated that the actual size of the particle may be less than 1 nm. Dynamic light scattering measurement was also performed but no consistent results can be obtained. Such measurement discrepancy by dynamic light scattering has been reported by other researchers [15].

Among all the tests, under anaerobic condition, magnetite nanoparticles exhibited highest adsorption capacity on As(III) and As(V), up to 168.8 mg g^{-1} and 206.9 mg g^{-1} , respectively,

which is one of the highest in the literature [6-9, 18]. A comparison of the adsorption capacity is tabulated as shown in Table 1. According to the reported adsorption capacity of iron oxide nanoparticles with size less than 20 nm at pH around 8.0, they appeared to have higher adsorption capacity than larger particles. Even though the measured specific surface area of the synthesized nanoparticle in this study was not as high as those in other studies at similar or slightly larger sizes, the adsorption capacity appeared to have no negative impact. One plausible reason is that the actual specific surface area may differ from that measured by BET instrument. In other words, the dried aggregates in solid phase for the measurement may have smaller specific area than the dispersed nanoparticles in the liquid phase for adsorption reaction.

Considering the potential adverse health effects of magnetite nanoparticle in human, a recovery test was performed (Table 2). By using a strong rare earth magnet for the magnetite nanoparticles with a 0.1 g L^{-1} concentration in water (an intent application concentration for this nanoparticle), there were about 602.5 ppb remained in the water indicating a 99.4 % recovery. With such high recovery, it appeared that this nanoparticle will be more favorable when being applied to water with arsenic levels less than 1500 ppb. Since the arsenic levels are usually less than 1000 ppb in As-contaminated groundwater, it appears that this MNP is a promising alternative treatment technology for As-contaminated drinking water.

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TABLE I. COMPARISON OF THE AS(III) AND AS (V) ADSORPTION CAPACITY BY DIFFERENT IRON OXIDE ADSORBENTS

Absorbent	Size (nm)	pH	SSA (m ² g ⁻¹)	q _e , max		References
				As(III) (mg g ⁻¹)	As (V) (mg g ⁻¹)	
Magnetite	3.02±0.32	8.0	65.8	168.8	206.9	This study (anaerobic)
Magnetite				108.6	138.1	This study (aerobic)
Maghemite	6	7	174	172.5	-	Auffan <i>et al</i> , 2008
Magnetite	12	8.0	-	-	~200	Yavuz <i>et al.</i> , 2006;
Magnetite	11.72	8.0	98.8*	114.9	172.5	Yean <i>et al</i> , 2005
	20	8.0	60	29.2	5.9	
	300	6.1	3.7	1.5	0.75	
Maghemite	3.8±0.8	7.0	203.2	-	20.0	Tuutijärvi <i>et al.</i> , 2009
		9.0			12.5	

* Calculated by Yean *et al*, 2005

** Calculated

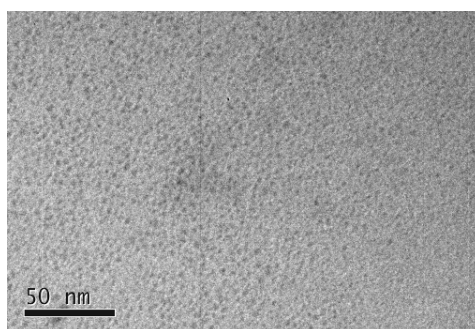


Figure 1. TEM micrograph of magnetite nanoparticles (a) and magnetite nanoparticle composite (b) before adding Silica Gel. The bars represent 50 nm and 100 nm in panel a and b, respectively.

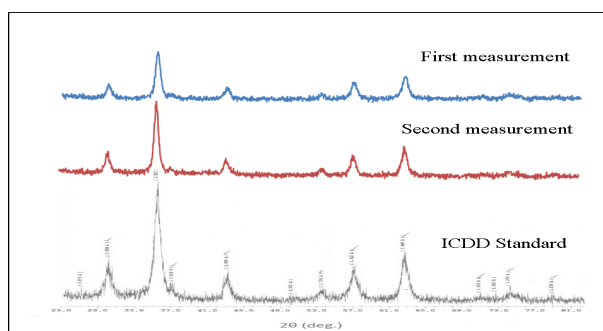


Figure 2. Powder XRD histograms generated from two measurements of the synthesized magnetite nanoparticles. The top and middle profiles were measured more than 30 days apart showing no significant difference. The bottom profile is from the ICDD standard file for magnetite crystals.

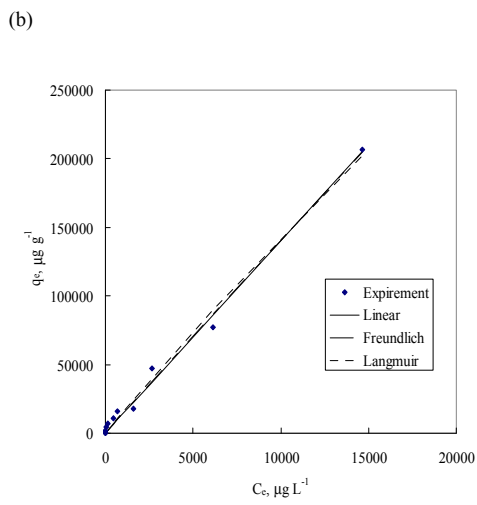
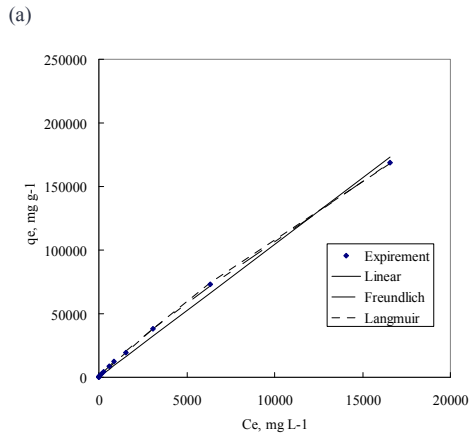


Figure 4. Adsorption of As(III) (a) and As(V) by magnetite nanoparticle under anaerobic condition. The experimental data were fitted by three adsorption isotherms where Freundlich isotherm showed the best fit for both

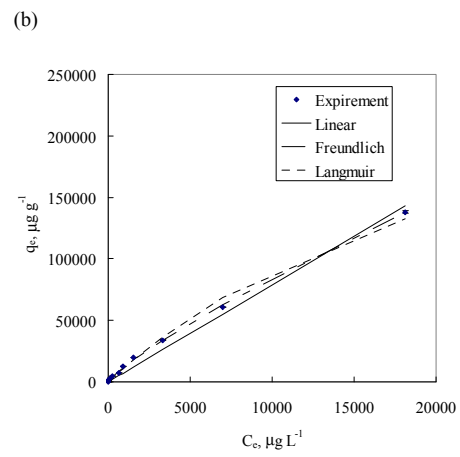
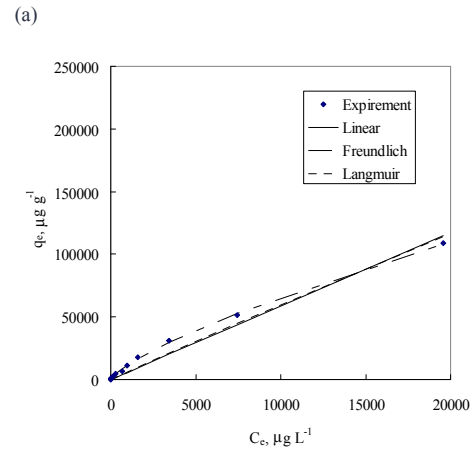


Figure 5. Adsorption of As(III) (a) and As(V) (b) by magnetite nanoparticle under aerobic condition. The experimental data were fitted by three adsorption isotherms where Freundlich isotherm showed the best fit for both.