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Adsorptive removal of arsenite from water using nanomagnetite

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ABSTRACT

This paper describes a study of the sorptive removal of arsenite (As(III)) from aqueous solutions by commercial nanomagnetite (NM). We also investigated the adsorption mechanism of arsenite (As(III)) onto the NM. The influences of solution pH, initial arsenite (As(III)) concentration and sorbent concentration were investigated in multiple kinetic runs. The adsorption rates and isotherms were investigated in batch experiments. We evaluated fits to the experimental data of the pseudo-first-order and pseudo-second-order kinetic models and determined that our system was best described by the second-order model. Langmuir and Freundlich isotherms were used to fit the adsorption data from equilibrium experiments. According to results of As removal measurements, NM has a high arsenite removal efficiency, with the ability to reduce the concentration of arsenite in the aqueous solution from an initial value of 300 to <5 μg/L.

Keywords: Arsenite; Adsorption; Kinetics; Isotherm; Commercial nanomagnetite

1. Introduction

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters. Arsenic contamination of groundwater and surface water occurs naturally through weathering and dissolution of arsenic-containing minerals and ores such as realgar, orpiment and arsenopyrite [1]. Although environmental restrictions and regulations have limited the production and uses of arsenic and its compounds, they are still extensively used in various industries including metallurgy, agriculture, forestry, electronics, pharmaceuticals and glass and ceramic industry [2].

In aqueous environments, arsenic is predominantly present as arsenite (+3) and arsenate (+5) [3–5]. The As(III) species, which exists predominantly as nonionic H_3AsO_3 in natural waters, is more difficult to remove than As(V) [6–8]. Arsenite is about 60 times more poisonous than arsenate and 70 times more toxic than the methylated species [9]. Inorganic arsenic can combine with sulfhydryl groups in proteins and accumulate in human bodies. Arsenite has higher affinity for proteins than arsenate [10,11]. The chronic effects commonly include skin diseases and many other cardiovascular, neurological, hematological, respiratory diseases [12].

Due to high toxicity of arsenic, the World Health Organization (WHO), the European Union, the United States and many other countries' governments have established a value of 0.01 mg/L as the maximum contaminant level for total arsenic in potable water [3]. This low As drinking water standard requires the development of simple, cost effective methods for As removal from drinking water. Many methods have been developed to remove arsenic from water. These include adsorption [13,14], coagulation [15], precipitation [16], ion exchange [17] and reverse osmosis [18].

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The adsorption technique is becoming more and more popular because of its simplicity, potential of regeneration and sludge-free operation [19].

Although a large variety of adsorbents are available for the adsorptive removal of arsenic from the contaminated waters, iron based adsorbents e.g. zero valent iron, iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite (α-FeO-OH), hematite (Fe_2O_3) and magnetite (Fe_2O_3) are the most widely used adsorbents owing to their high removal efficiency and availability at low cost [20]. Among the iron-based adsorbents, nanometer-sized iron oxides are promising adsorbents due to their high capacity for adsorption of arsenic, apparently associated with their large surface area [21–26]. Nanomagnetite (Fe_3O_4) was reported to exhibit different chemical and physical properties from large-sized magnetite due to their extremely small size and large specific surface area [21]. In addition to surface area, the surface properties of iron oxides including nanomagnetite (NM) are also key factors in the adsorption of arsenic, which could occur through mechanisms such as ion exchange, complexation and precipitation [20]. The sorption behavior of arsenic is also strongly influenced by solution pH and the oxidation state of arsenic [21,22].

Previous studies have shown that the particle size of NM exerts a profound effect on its adsorption capacity for As(V) and As(III), which increases with decreasing the size of NM [21,22,24]. Mayo et al. [24] observed a dramatic effect of nanoparticle size on the adsorption of arsenic. They found that the adsorption capacities for both As(III) increased nearly 200 times as the particle size decreased from 300 to 12 nm. Shipley [24] reported using a low solid concentration of NM to remove >90% of arsenic in solution. Türk et al. [26] showed that a 5 g/L concentration of magnetite nanoparticles was sufficient to remove >90% of arsenic (As(V)) from solution.

In the present study, NM (<50 nm) was used as adsorbent for arsenite removal from water. The adsorption mechanisms of arsenite onto the adsorbent were examined. The tests of As(III) adsorption with NM were performed under different initial As concentrations, contact time, initial pH levels, and NM dosages.

2. Material and methods

Commercially available NM obtained from Sigma Aldrich was used in this study. Earlier studies [26] on XRD analysis of the sample using a Rigaku D/max-IIIC X-ray diffractometer confirmed the presence of a single phase of cubic Fe_3O_4.

Table 1
A summary of the experimental conditions used in this study

Parameter	Range
Contact time (min)	15–30–60–120–180
Initial pH	3–5–7–9–12
Initial As Concentration (μg/L)	100–300–500–1000–2000
Adsorbent dosage (g/L)	0.05–0.1–0.5–1–5
Temperature (°C)	25
Agitation speed (rpm)	200

Analytical-grade dehydrated sodium arsenite ($NaAsO_2$, Sigma, Germany) was used to prepare As(III) stock solution (100 mg/L) from which working solutions for experiments were freshly prepared. Distilled and deionized water was used in the preparation of all the solutions. Hydrochloric acid (1 M HCl) or sodium hydroxide (1 M NaOH) was added to adjust pH of the solutions. A pH meter equipped with a combined glass electrode (Orion 81-75) was used to measure pH. The electrode was calibrated using buffer solutions of pH 4.0, 7.0 and 10.0 before any measurement.

The adsorption tests were carried out in a temperature controlled shaker (Wiggen Hauser SI-100T), which was operated at 200 rpm and maintained at room temperature (298°K). The influences of As(III) concentration (100–2,000 μg/L), contact time (15–180 min.), adsorbent dosage (0.05–5 g/L) and pH (3–12) on the adsorptive removal of As(III) were investigated (Table 1). Adsorption tests were performed in triplicate. The data generated at different initial concentrations of As(III) (100–2,000 μg/L) were used for the equilibrium and kinetics modeling studies. pH was kept constant at pH 9 in the adsorption tests under standard conditions due to the alkaline nature of the polluted waters targeted in the current study [14]. 50-mL solutions of As(III) of known concentration (e.g. 300 μg/L) at the required adsorbent dosage (e.g. 0.25 g) were prepared in 100 mL Erlenmeyer flasks. Flasks were then shaken for an equilibration period of 180 min. At predetermined time intervals, the flasks were sampled by removing 3 mL samples, which were then centrifuged at 4,000 rpm for 1 min. to obtain a clear supernatant for analysis. Analysis of arsenic from the solutions was performed by a flow-injection, hydride generator atomic adsorption spectrophotometer (model, Perkin Elmer, FIAS 100) at a wavelength of 193 nm.

NM was found to have a pH_{pzc} (point of zero charge) of 7.1, which was determined by equilibrating NM with 0.1 M NaCl solutions at different pH values (3–12). Details of the procedure can be found elsewhere [14,26].

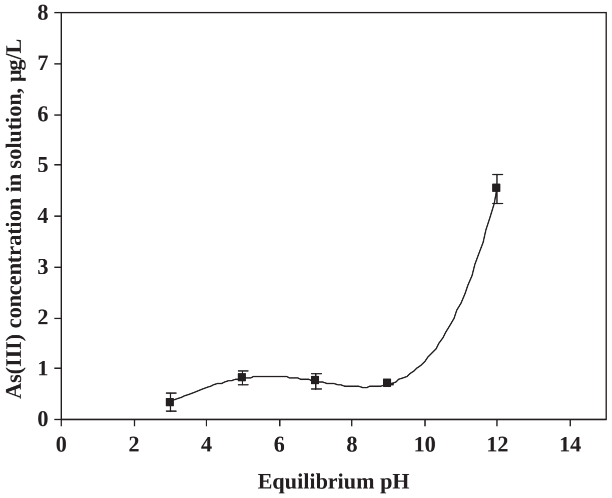

Fig. 1. Effect of pH on As(III) removal by NM (T: 25°C, C_0: 300 μg/L, D: 5 g/L, t: 180 min).

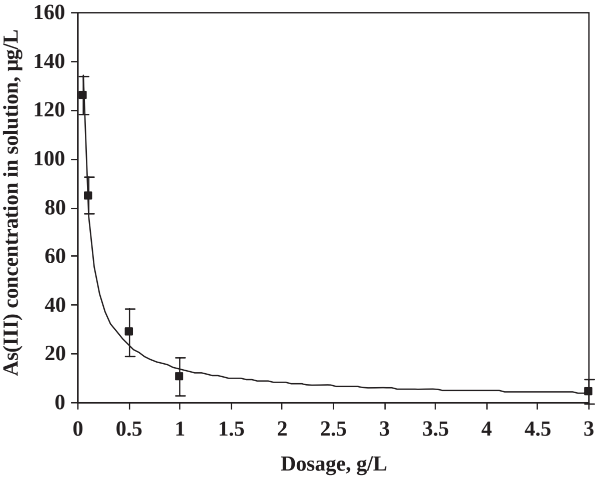

Fig. 2. Effect of adsorbent dosage on As(III) removal by NM (T: 25°C, C_0: 300 μg/L, pH: 9, t: 180 min).

3. Results and discussion

3.1. Factors affecting the adsorption of As(III)

Fig. 1 shows the effect of initial pH values on the efficiency of As(III) adsorption by NM at an initial As(III) concentration of 300 μg/L. The results indicated that NM was more effective at initial pH values of ≤9 in that the removal of As(III) was faster and more extensive at ≤ pH 9 than at pH 12 (Fig. 1). Over an adsorption period of 180 min., the residual arsenic in solution was determined to be 0.34–0.7 μg/L at pH 3–9 compared with 4.33 μg/L at pH 12. The adverse effect of high pH may be attributed to the predominance of negatively charged arsenic species and the increase in negative surface sites of NM with increasing pH [26]. NM sample was determined to have a pHpzc value of pH 7.1 and at pH > pHpzc, NM surface is negatively-charged. In this study, arsenite adsorption on NM was observed to be maximum at pH 3 (Fig. 1).

Fig. 2 shows that the arsenite removal efficiency increased with the dosage of NM. After a contact time of 180 min, the residual concentration of As(III) in solution was 125.8 μg/L at a NM dosage of 0.05 g/L compared with 4.37 μg/L at 5 g/L NM. This suggested that NM at a dosage of 5 g/L could be suitably used to reduce the level of As(III) from 300 μg/L to below the limit value of 10 μg/L set for drinking water by WHO. In the subsequent studies, the adsorbent dosage was, therefore, set to be 5 g/L NM.

The effect of the concentration of As(III) in the range of 100–2,000 μg/L on the adsorption process was also studied at 5 g/L NM dosage and pH 9 (Fig. 3). The concentration of As(III) in solution at low initial levels tested (100–500 μg/L) decreased rapidly to <10 μg/L over the initial 15 min of adsorption. However, at high initial concentrations tested (1,000–2,000 μg/L) the decrease in the level of As(III) from the solution was relatively slow approaching a limit value after 120 min. of adsorption. This adsorption behavior at high As(III) concentrations was attributed to the saturation of active sites on NM surface with As(III). The adsorption capacity of NM was determined to be ~209 μg As(III) per g NM.

3.1. Adsorption isotherms

Since the residual concentration of As(III) was observed to almost level off after 120 min, the equilibrium data collected over a period 180 min were used in the isotherm studies. The adsorption capacity of NM was also determined from the equilibrium data (Fig. 4),

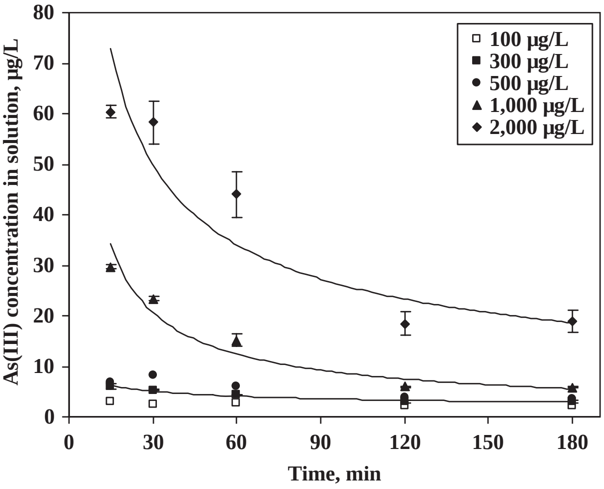

Fig. 3. Arsenite adsorption on NM at 25°C, pH 9, D: 5 g/L and initial arsenite concentration range 100–2,000 μg/L.

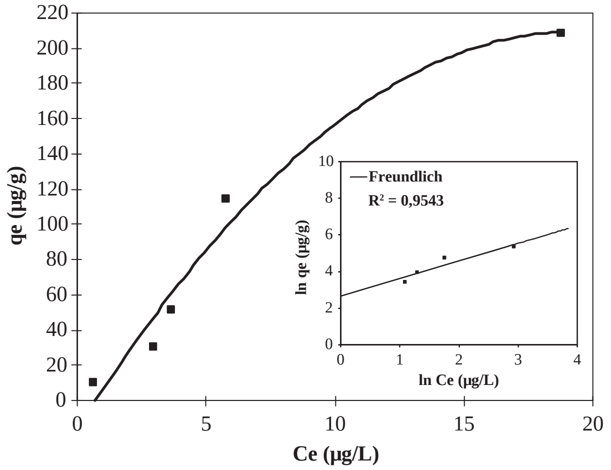

Fig. 4. Equilibrium isotherm for As(III) adsorbed on NM at pH 9 and 298 K and Freundlich adsorption isotherm models for As(III) adsorption.

which were studied by Langmuir and Freundlich isotherms as the most commonly used models in batch adsorption studies [27]. The Freundlich isotherm (Eq. (1)) is used for modeling the adsorption on heterogeneous surfaces. It also indicates the exponential distribution of active sites and their energies [28].

$$q_e = K_f\, C_e^{1/n}, \tag{1}$$

where C_e is the equilibrium concentration (µg/L), q_e is the amount adsorbed under equilibrium (µg/g), K_f and n are Freundlich isotherm constants representing the adsorption capacity and intensity, respectively.

The Langmuir isotherm models the monolayer coverage of adsorbent surface by adsorbate. This model assumes that the surface of adsorbent is homogenous with an infinite number of identically active sites available for adsorption [29]. Langmuir isotherm equation (Eq. (2)) is given as:

$$q_e = \frac{QbC_e}{1 + bC_e}, \tag{2}$$

where Q (µg/g) the adsorption capacity and b (L/µg) is a Langmuir constant.

The Freundlich adsorption isotherm is presented in Fig. 4. The Freundlich isotherm values obtained from the linear plots, as manifested by linear regression coefficient ($R^2 = 0.9543$). The K_f and n values for As(III) adsorption on NM were found to be 14.42 and 1.04, respectively. The Langmuir adsorption isotherm is presented in Fig. 5. The Q and b values for As(III) adsorption on NM were found to be 467.90 and 0.03, respectively. Although the equilibrium data is in agreement with both models, the Langmuir model with a higher correlation coefficient ($R^2 = 0.99$) describes better the As(III) adsorption isotherm.

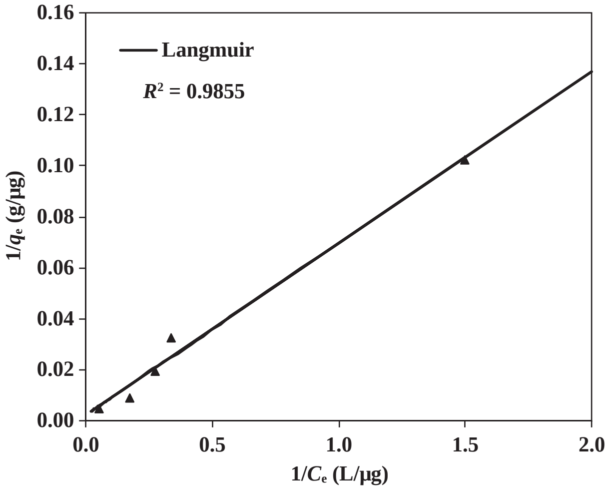

Fig. 5. Langmuir adsorption isotherm models for As(III) adsorption on NM.

3.2. Kinetics of adsorption

The adsorption of As(III) on NM was observed to be a fast process in that >95% of As(III) was removed from solution over an initial adsorption period of only 15 min (Fig. 3). However, the time required to reach eqilibrium seemed to depend on the initial concentration of As(III), i.e., As(III) to NM ratio since the equilibrium was approached over an extended period of > 120—180 min at high initial As(III) levels.

Kinetics of As(III) removal by NM were examined using the pseudo-first-order and second-order kinetic models, which are commonly used to describe the rate of adsorption of arsenic on various adsorbents [26,30]. The pseudo-first- and second-order rate equations are expressed, respectively, as [30]:

$$\frac{dq_t}{dt} = k_1\,(q_e - q_t), \tag{3}$$

$$\frac{dq_t}{dt} = k_2\,(q_e - q_t)^2, \tag{4}$$

where k_1 and k_2 are the equilibrium rate constant of pseudo- first- and second-order equations, respectively (g/µg min), q_e and q_t are amount of metal ions adsorbed at equilibrium and at time t, respectively. Integrating Eqs. (3) and (4) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives

$$In\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t, \tag{5}$$

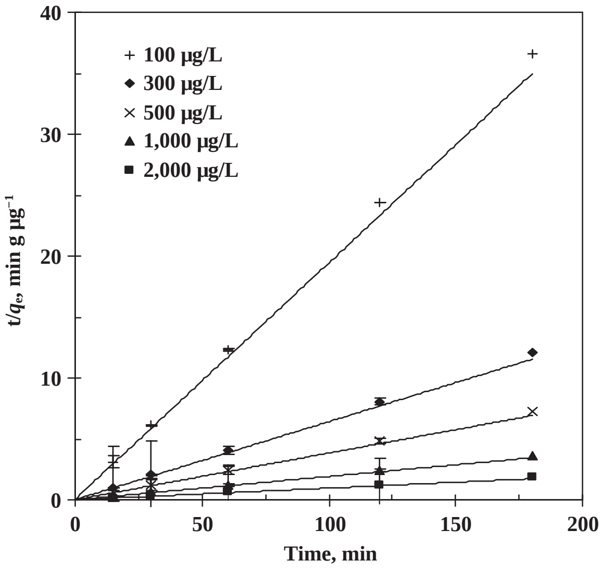

Fig. 6. Linear plot of t/q_t vs. t of the pseudo-second-order rate equation for As(III) adsorption onto NM.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t. \tag{6}$$

Eq. (7) may be to rearranged to a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}. \tag{7}$$

The curves in the plot of t/q_t against t are linear and the k_2 rate constants can be calculated from the slope of these curves (Fig. 6). The estimated kinetic parameters for both models with the linear regression coefficients (R^2) are shown in Table 2. The present kinetic adsorption data for As(III) on NM appeared to be best described by the pseudo-second order model (Table 2), which agrees with chemisorption as the rate-controlling mechanism [30].

4. Conclusion

This study have shown that NM can be suitably used as an effective adsorbent for arsenite (As(III)). NM was able to reduce the arsenite concentration from ~300 μg/L to a final value of <5 μg/L, which is below the limit value (10 μg/L) for drinking water as suggested by WHO and the regulatory bodies in many countries. The results indicated that the adsorption of As(III) by NM were affected only slightly at initial pH values of ≤9. However, further increase in alkalinity (pH 12) produced an adverse affect on the adsorption of As(III) as indicated by relatively slow adsorption and high residual As(III) in solution. This could be ascribed to the increased negativity of NM surface as drifted from its $\mathrm{pH_{pzc}}$ (i.e., pH 7.1) coupled with the negatively charged As(III) species predominating at high pHs. An adsorbent dosage of 5 g/L (i.e. >1 g/L) was found to be required to reduce As(III) levels to <10 μg/L. The equilibrium capacity of NM was determined to be ~209 μg/g at the initial As(III) concentrations in the range of 100–2,000 μg/L. Equilibrium data were shown to be described best by the Langmuir model. Although the adsorption of As(III) occurs, to a large extent, over an initial 15 min an extended period of >120 min appeared to be required to reach the equilibrium. Kinetics of the adsorption of As(III) are consistent with the pseudo-second-order model.

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Table 2
Adsorption kinetic model parameters on adsorption of As(III) by NM at different initial concentrations (T: 25°C, pH: 9, D: 5 g/L)

		Initial As(III) loads (μg/L)				
Kinetic model	Parameter	100	300	500	1,000	2,000
Pseudo-first-order	k_1 (min^{-1})	0.017	0.014	0.015	0.013	0.011
	q_e (μg g^{-1})	0.14	0.29	0.39	1.51	3.39
	R^2	0.9487	0.994	0.972	0.9681	0.9928
Pseudo-second-order	k_2 (g μg^{-1} min^{-1})	0.20	0.07	0.04	0.01	0.007
	q_e (μg g^{-1})	5.16	15.63	26.09	52.36	104.46
	R^2	0.9999	0.9999	0.9999	0.9999	0.9999

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