Adsorptive Removal of Arsenic by Mesoporous Iron Oxide in Aquatic Systems

Jiyeol Bae 1,*, Suho Kim 2, Kwang Soo Kim 1, Hwan-Kook Hwang 1 and Heechul Choi 3,∗

1 Department of Land, Water and Environment Research, Korea Institute of Civil Engineering and Building Technology (KICT), Goyang 10223, Korea; kskim@kict.re.kr (K.S.K.); hkhwang@kict.re.kr (H.-K.H.
2 Construction Environment Engineering, University of Science and Technology (UST), Daejeon 34113, Korea; kimsuho@kict.re.kr
3 School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, Korea

* Correspondence: baejiyeol@kict.re.kr (J.B.); hcchoi@gist.ac.kr (H.C.)

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Abstract: In an effort to explore the potential for the removal of arsenic from water, mesoporous iron oxide (MI) was prepared using a sonochemical method. The surface area and average pore size of the MI sample were determined using a Brunauer Emmett Teller (BET) analysis to be 269 m²/g and 6.9 nm, respectively. Kinetic experiments revealed that more than 90% of the As(III) and As(V) were adsorbed onto the MI sample within 5 min at 0.1 g/L of MI dosage. The Langmuir equation model suited As(V), whereas As(III) related better to the Freundlich equation model due to different adsorption mechanisms. The predominant mechanism of As(V) adsorption onto MI is thought to be the electrostatic force between As(V) and MI, whereas As(III) in the solution bound to the adsorbed As(III) on the MI in a way consistent with van der Waals attraction. The removal rate of As(III) and As(V) has the highest adsorption efficiency in the pH 5–9 range. The adsorption of As(III) and As(V) was little affected by ionic strength, however the presence of H₄SiO₄₀ and PO₄³⁻ significantly reduced the arsenic adsorption capacity. Furthermore, the adsorption and regeneration efficiency of MI was maintained at around 100% for given adsorption–regeneration cycles.

Keywords: mesoporous iron oxide; arsenic removal; adsorption; ionic effects; regeneration

1. Introduction

Arsenic (As), a common constituent of the earth’s crust, is well-known as a carcinogenic element [1]. Arsenic is introduced into the environment through a combination of natural processes (i.e., weathering reactions, biological activities, and volcanic emissions) and anthropogenic activities [2] and is usually found in the form of inorganic oxyanions. In general, arsenate (As(V)) exists in aerobic conditions, whereas arsenite (As(III)) is dominant in anoxic conditions. As(III) is considerably more mobile and toxic than As(V) [3]. The valence states and chemical forms are strongly dependent on pH, redox potential, and the presence of complexing ions [3,4].

The chronic toxicity of arsenic in drinking water causes various types of cancer and Blackfoot disease [5]. For this reason, the World Health Organization (WHO) and the United States Environment Protection Agency (US EPA) have classified arsenic as a known human carcinogen, and a new maximum contaminant level (MCL) of 10 µg/L for arsenic in drinking water was enforced in 2006 [6,7]. Therefore, the development of an effective arsenic treatment process has been required to meet the tightened MCL. Among the possible treatment processes, adsorption is considered the most cost-effective, the easiest, and the safest process [3,4,8]. These benefits have attracted researchers to use adsorption for arsenic removal from drinking water; to date, various materials such as silica [9],
activated alumina (AA) [8], zeolite [4], activated carbon [7], cationic surfactant-modified activated carbon [10], activated carbon impregnated with Fe or Mn oxides [11] metal iron oxide nanoparticle [12], iron oxide [13], hybrid metal oxide [14], iron oxide-coated micro sand [15] and nanosized zero-valent iron (NZVI) [16,17] have been investigated for arsenic removal.

Among the various adsorbents, iron oxides have been rapidly concentrated in water treatment and environmental remediation as they are a widely available natural mineral and geo-catalyst and can be readily synthesized in the laboratory. For example, ferric oxide [18], hydrous ferric oxide [19], and granular ferric hydroxide [20] have been used in arsenic removal from drinking water due to their high affinity toward arsenic. Moreover, iron oxide adsorbents can be easily regenerated through chemical treatment [21]. Therefore, iron oxides are considered very effective and economical adsorbents for arsenic removal.

In addition, porous adsorbents such as micro and mesoporous materials have received significant attention due to their high specific surface area and porous structure [22]. Among them, mesoporous materials have recently gained much attention in environmental engineering due to their provision of a high surface area combined with large pore sizes, narrow pore size distributions, and well-defined pore structure within a relatively small volume of material [23,24]. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, inorganic solids that contain pores with diameters in the 2–50 nm range are considered mesoporous materials [25]. Due to the unique properties of mesoporous materials, these can be widely utilized in surface-related applications. Accordingly, various mesoporous materials such as mesoporous silica, carbon, and metal oxide were considered effective adsorbents for water treatment, and high contaminant removal efficiencies using these adsorbents are reported [26–30]. However, there are as yet few studies utilizing mesoporous iron oxide for the removal of contaminants from wastewater and drinking water (i.e., Cr(VI) removal by mesoporous γ-Fe₂O₃ [29] and Pb(II)/Cd(II) removal by mesoporous amine-functionalized mesoporous Fe₃O₄ [30]. However, these studies only investigated adsorption capability regarding removing contaminants using synthetic water, without considering the effects of authentic natural aquatic conditions such as ionic strength or competing materials.

The goal of this study was, therefore, to investigate the application of synthesized mesoporous iron oxide (MI) using a sonochemical technique for the removal of As(III) and As(V) from drinking water. Our main objectives included: (i) characterization of synthesized mesoporous iron oxide; (ii) investigation of the characteristics of arsenic adsorption using MI via kinetic, isotherm, and regeneration tests; and (iii) investigation of the effects of water chemistry (i.e., pH, ionic strength, and competing anions) on arsenic adsorption. To the best of our knowledge, this is the first study of the application of MI in the removal of arsenic from water.

2. Materials and Methods

2.1. Preparation of Mesoporous Iron Oxide (MI)

MI was prepared by a supramolecular templating method using a sonochemical technique [31]. Iron (III) ethoxide (C₆H₁₃FeO₃, Alfa Aesar, Haverhill, MA, USA) and cetyltrimethylammonium bromide (CTAB, Sigma Aldrich Chemical Co., St. Louis, MO, USA) were used as an inorganic precursor and the surfactant, respectively. The following procedure was then adopted: 477.11 mg of iron (III) ethoxide was placed in a sonication flask, and 364.45 mg of CTAB in 20 mL of ethanol was added to the solution, followed by 60 mL of double-distilled water. Furthermore, 40 mL of ammonium hydroxide (NH₄OH) was added to the prepared pH adjustment solution to 10.6. The system was then irradiated with a high-intensity ultrasonic horn (Ti-horn, 20 kHz, 40% efficiency) for 3 h. After sonication, the mixture was centrifuged at 9000 rpm to separate the precipitate from the solution, and the remaining precipitate was washed several times with DI(Deionized) water. Finally, the precipitate was dried for 1 h at 90 °C, and the surfactant was removed via extraction with ethanol at 58 °C.
2.2. Materials Characterization

X-ray diffraction (XRD) patterns of MI were obtained from a Rigaku D/MAX Ultima III diffractometer (Japan) using Cu/Kα radiation, and N₂ adsorption/desorption experiments were carried out using a Micromeritics ASAP 2010 volumetric adsorption analyzer (USA). Transmission electron microscopy (TEM) images of the materials were then acquired on a JEOL 2010 electron microscope (Japan) operating at 200 kV. The point of zero charge (PZC) of the MI was determined with an Otsuka Electronics ELS-8000 zeta potential analyzer (Japan).

2.3. Batch Experiment

Stock solutions were prepared using sodium arsenate (Na₂H₂AsO₄·7H₂O) for As(V) and sodium arsenite (NaAsO₂) for As(III) (Sigma Aldrich Chemical Co., St. Louis, MO, USA). Batch adsorptions of As(III) and As(V) were carried out in 50 mL polypropylene copolymer centrifuge tubes containing 3.75 mg of MI in 50 mL of arsenic solution in 0.01 M NaCl at pH 7. The samples were placed on a shaker and mixed continuously for 12 h. The samples in the test tubes were filtered through a 0.45 µm polyvinylidene fluoride (PVDF) filter, and the filtered solution was analyzed for total arsenic using an inductively coupled plasma-optical emission spectrometer (ICP-OES; Perkin Elmer, Waltham, MA, USA). A series of batch isotherm tests were performed for As(III) and As(V) adsorption by varying the initial arsenic concentration (1–9 mg/L) and the temperature (278, 298, 318 K) using 0.075 g/L of MI at pH 7 (total volume: 50 mL). The mixtures were shaken for 12 h at 200 rpm to reach equilibrium. Batch kinetic tests were conducted to determine the rate of arsenic removal by MI. The experiments were initiated by adding 0.05, 0.075, and 0.1 g/L of MI into 50 mL of a solution containing 1 mg/L of As(III) and As(V) at pH 7. The samples were taken out at predetermined times and then analyzed for arsenic after passing through a 0.45 µm PVDF. The rate constants (kd, g/mg min) were calculated using the pseudo-second-order kinetic model, and the intraparticle diffusion model was also used for the analysis of the rate-limiting step of the adsorption. The effect of pH (range 2–12) was studied by adding 0.1 M HCl or 0.1 M NaOH, as needed. The effect of ionic strength on arsenic adsorption was determined using inert electrolyte KCl solutions (0–50 mM). In addition, batch tests were performed to observe the effect of competitive anions using solutions of 1 ppm As(III) and As(V) in 10 mM solutions of NaH₂PO₄, Na₂SiO₃, Na₂SO₄, NaNO₃, and NaHCO₃. After a 12-h reaction time, the arsenic concentration was analyzed using ICP-OES. The regeneration test was conducted to estimate the reusability of MI. In these experiments, a NaOH solution (0.1 M) was used as the desorption solution.

3. Results and Discussion

3.1. Characterization of MI

Figure 1 shows the N₂ adsorption–desorption measurement and pore size distribution of fresh MI. According to the IUPAC classification of adsorption isotherms for gas–solid equilibrium, Figure 1 reveals that MI was classified as Type IV, indicating the pore size of MI was determined to be a mesoporous structure [32]. Moreover, by the modern classification of hysteresis loops, MI has an H-2 loop type [32]. The H-2 loop is broad, with the desorption branch being much steeper than the adsorption branch. It is accepted that this kind of loop occurs when there is a difference in the mechanism between condensation and evaporation and that this occurs in pores with narrow necks and widebodies or when the porous material has an interconnected pore network. BET specific surface area, pore volume, and mean pore size is shown in Figure 1. The pore size distribution confirms the mean pore size and volume of MI is approximately 6.9 nm and 0.44 cm³/g, respectively. The BET surface area is estimated to be 269 m²/g. In addition, a wide-angle XRD measurement was conducted to confirm the phase structure of MI. As shown in Figure S1, the main diffraction peaks for MI, observed at 20, indicate that sonochemically synthesized MI is hematite (α-Fe₂O₃). In the TEM image (Figure S2), the bright area indicates the pores, and the dark region is the solid phase, and the MI has an irregular shape with diameters in the 0.5–1 µm range. Uniformity in the pore structure is hardly visible for
mesostructures, and the structure is more likely of a wormhole-like morphology. The point of zero charge (PZC) of MI was determined to be around 8.4, which is similar to hematite [33,34], and the zeta potential of MI at pH 7 was measured to be 9.43 mV.

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]

where \( q_e \) (mg/g) is the maximum adsorption capacity, \( q_e \) (mg/g) is the amount of adsorbed arsenic, \( C_e \) (mg/L) is the equilibrium arsenic concentration, \( K_f \) and \( n \) are Freundlich constants, and \( K_L \) (L/mg) is the Langmuir constant. The linear Langmuir and Freundlich isotherms were subsequently fitted to the experimental data (Figure 2).

3.2. Adsorption Isotherms

Langmuir and Freundlich isotherms were examined to analyze the adsorption characteristics of the adsorbent. The linear forms of these equations are displayed as Equation (1) (Langmuir model) and Equation (2) (Freundlich model):

\[ \frac{1}{q_e} = \frac{1}{K_L (1/C_e)} + \frac{1}{q_m} \]  
\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]

Figure 1. adsorption-desorption isotherm for mesoporous iron oxide (MI) (Inset: Pore size distribution).

Figure 2. Isotherm for As(III) and As(V) at different temperatures (278 K, 298 K, and 318 K). The experiments were initiated by adding 0.075 g/L of MI into 1–9 mg/L of As(III) and As(V) solution at pH 7, 200 rpm.
The results of fitting the Freundlich and Langmuir equations to isotherm curves are summarized in Table S1. The maximum adsorption capacity of As(III) and As(V) calculated by the Langmuir isotherm was 136.89 mg/g and 31.82 mg/g at 298 K, respectively. Based on the adsorption isotherm analysis, adsorption of As(III) on MI was well fitted to the Freundlich model, whereas the Langmuir model agreed well with the experimental data of As(V) removal. For further comparison of the fitting of experimental data to isotherm models, a non-linear Chi-square analysis ($\chi^2$) suggested by Ho. (Ho, 2004) was also conducted. $\chi^2$ is determined using the following equation (Equation (3)):

$$ \chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{3} $$

where $q_e$ (mg/g) is the experimental equilibrium capacity, and $q_{e,m}$ (mg/g) is the equilibrium capacity calculated from the models. As Ho et al. suggested, the smaller $\chi^2$ values display a better match to the model [35].

As shown in Table S1, the $\chi^2$ values of the Freundlich isotherm for As(III) adsorption were lower than those of the Langmuir isotherm, indicating that the Freundlich isotherm is the better fitting isotherm for the adsorption of As(III) on MI. The results indicated that As(III) adsorbed onto MI in multilayer and also adsorption increases with increasing the concentration of As(III). In contrast, the $\chi^2$ values of the Langmuir isotherm were lower than the Freundlich isotherm for the As(V) cases; i.e., the Langmuir equation represents a better fit of the experimental data than the Freundlich equation. This indicates that As(V) adsorption could be characterized by a steep initial rise that approaches a plateau attributed to a complete monolayer’s formation. When the initial As(III) and As(V) concentration is below 2 mg/L, the adsorption capacities of MI for As(V) are higher than that for As(III), whereas the adsorption capacities of MI for As(III) are higher when the initial arsenic concentration is increased to more than 2 mg/L.

In general, the adsorption capacity of As(V) is higher than As(III) due to electric charge and mobility [36]. In contrast, MI show opposite arsenic adsorption tendency, and a similar trend was reported by Tang et al. when they use ultrafine $\alpha$-Fe$_2$O$_3$ nanoparticles as an arsenic adsorbent [37]. The different adsorption trends for As(III) and As(V) in this study suggest that different mechanisms outside of the existing adsorption controlled processes—not related to surface charge for arsenic adsorption—might be occurring during As(III) adsorption. In order to identify this process, the surface charge of arsenic adsorbed MI was measured. At pH 7, the surface charge of As(III) and As(V) adsorbed MI were $-0.25$ mV and $-10.95$ mV, respectively. In this neutral condition, the MI adsorbed with As(III), and the As(III) has a neutral charge. Therefore, it is posited here that MI adsorbed with As(III) was weakly bound to As(III), which can be explained using the van der Waals attraction model; this, in turn, explains why this data shows that As(III) adsorption follows the Freundlich model. In other words, As(III) was adsorbed to MI via electrostatic force until As(III) occupied the active surface of MI, at which point the As(III) in the solution bound to the adsorbed As(III) on the MI as per van der Waals attraction. Whereas the predominant mechanism of As(V) adsorption onto MI is attributed to the electrostatic force between As(V) and MI, in this case, As(V) was adsorbed onto MI via electrostatic attraction as a monolayer formation, and then electrostatic repulsion occurred between As(V) and As(V) adsorbed MI. This explains why the isotherm experiment results of As(V) adsorption follow the Langmuir model.

Thermodynamic parameters were also calculated based on Equations (4)–(6) and reported in Table S2.

$$ \Delta G = -RT \ln K \tag{4} $$

$$ \ln K = \Delta H/RT + C \tag{5} $$

$$ \Delta G = \Delta H - T\Delta S \tag{6} $$

$\Delta G$ is the Gibbs free energy change, $R$ is the ideal gas constant (4.187 J mol$^{-1}$ K$^{-1}$), $T$ is the temperature (K), $K$ is the Langmuir or Freundlich isotherm constant, $\Delta H$ is the enthalpy change, and $\Delta S$ is the entropy change.
is the entropy change. As listed in Table S2, the adsorption capacities of As(III) and As(V) are seen to rise with increasing temperatures, possibly due to the activation of more sites on the MI surface at higher temperatures. A positive value of the standard enthalpy change (ΔH°) for As(III) and As(V) adsorption on the MI surface indicates the endothermic nature of the process, a negative value of the free energy indicates the spontaneous nature of the adsorption process.

3.3. Kinetics of Arsenic Adsorption

Arsenic adsorption kinetics were examined to investigate the prepared MI’s adsorption behavior using different MI dosages with an initial pH of 7. The removal of As(III) and As(V) were then fitted to the pseudo-second-order kinetic model, which has been frequently utilized for the adsorption capacity of mesoporous materials [26,28]. The effect of MI dosages (0.05, 0.075, and 0.1 g/L) on the rate of adsorption using 1 mg/L of As(III) and As(V) are shown in Figures 3a and S3. The adsorption rate was rapid in the first 30 min and lowered considerably as the reaction approached equilibrium. Figure S3 shows that 60% and 70% of As(III) and As(V) were adsorbed within only 5 min, and the performance reached 90% and 100% in 1 h for the 0.1 g/L MI nanoparticle. Moreover, arsenic adsorption rose with an increase in the adsorbent concentration (from 0.05 to 0.1 g/L). This increase in the adsorbent dose corresponds to an increase in the number of active sites and enhancing the arsenic adsorption. Hence, an MI concentration of 0.075 g/L, at which As(III) and As(V) removal was improved with minimum MI concentration, was used in all subsequent experiments unless otherwise specified. The pseudo-second-order kinetic model (Equation (7)) [38] was applied to describe arsenic adsorption to calculate the sorption changes.

\[
\frac{t}{q_t} = \frac{1}{K_{ad}q_c^2} + \frac{1}{q_e} t
\]

where \(K_{ad}\) (g/mg min) is the rate constant of the pseudo-second-order kinetic model, \(q_e\) is the amount of adsorbate sorbed at equilibrium (mg/g), and \(q_t\) is the amount of adsorbate sorbed at t (min). Note that the pseudo-second-order rate constants \(k_{ad}\) and surface area normalized rate constants \(k_{sa}\) for arsenic removal by MI were calculated and reported in Table 1. For the initial arsenic concentration of 1 mg/L with 0.05–0.1 g/L of MI doses, the rate constant values were 0.0073–0.1443 g/mg min for As(III) and 0.0054–0.1138 g/mg min for As(V). Comparing the arsenic adsorption capacity with other nanomaterials such as nanoscale zero-valent irons, MI shows similar 1ppm As(V) removal efficiency despite using only a one-fifth of the adsorbent dosage in the literature, which is attributed to the enhanced properties in MI in this study [12,17].

![Figure 3. Kinetic rate constants (a), rate constants: The reaction is pseudo-second-order with respect to the MI concentrations) and intraparticle diffusion constants (b), 0.075 g/L MI concentration) of As(III) and As(V) adsorption. The experiments were initiated by adding 0.05, 0.075, and 0.1 g/L of MI into a solution containing 1 mg/L of As(III) and As(V) at pH 7.](image-url)
**Table 1.** Pseudo-second-order rate constants ($k_{ad}$) and their surface area normalized rate constants ($k_{sa}$) for As(III) and As(V) removal by MI.

| MI (g/L) | $k_{ad}$ (g/mg min) | $k_{sa}$ (L/m² hr) | $R^2$ | $k_{ad}$ (g/mg min) | $k_{sa}$ (L/m² hr) | $R^2$ |
|----------|---------------------|-------------------|-------|---------------------|-------------------|-------|
| 0.05     | 0.0073              | 0.0005            | 0.8532| 0.0054              | 0.0004            | 0.9196|
| 0.075    | 0.0140              | 0.0047            | 0.8715| 0.0142              | 0.0007            | 0.8596|
| 0.1      | 0.1443              | 0.0054            | 0.9105| 0.1138              | 0.0042            | 0.9620|

Experiment condition: 1 mg/L As(III) and As(V) solutions in 0.01 M NaCl, at pH 7, 25 °C and 200 rpm.

Since the general kinetics analysis could not identify the rate-limiting step of the As(III) and As(V) adsorption process on MI, the intraparticle diffusion model was used to analyze the rate-limiting step of the adsorption. The equation (Equation (8)) given by Weber and Morris can be written as [39]:

$$q_t = k_d t^{1/2}$$

$k_d$ is the intraparticle diffusion rate constant (mg/g min1/2) of the first 30 min adsorption step, estimated from the straight line of $q_t$ versus $t^{1/2}$. The well-fitted straight lines for the initial 30 min of sorption in Figure 3b indicate that intraparticle diffusion might be the rate-limiting step in the period of the first 30 min of sorption. This initial period of 30 min is the typical time used in the literature for intraparticle diffusion based on the macropore/mesopore diffusion process [40]. The high $R^2$ values in Table S3 support that the predominant adsorption process occurred in the first 30 min; also, fast arsenic adsorption is attributed to the mesopore structure of MI.

### 3.4. Effect of pH on Arsenic Adsorption

The effect of pH on As(III) and As(V) uptake by MI is presented in Figure 4. The removal rate of As(III) and As(V) was high in the pH range (5–9), and the As(III) removal rate decreased to 56.2% at a pH below 4 or above 10. In the case of As(V), after As(V) adsorption reached equilibrium, the sorption of As(V) sharply decreased at the basic condition. The pH dependency of adsorption can be explained via the ionization of both MI and arsenic. When the pH is above 9.2, H$_2$AsO$_3^-$ is the predominant As(III) species—while the MI surfaces are also negative, causing electrostatic repulsion. Similarly, this trend of pH dependence was observed during As(V) removal using MI. As(V) has pH1, pH2, and pH3 values of 2.2, 7.08, and 11.5, respectively. In a pH range of 2–7, H$_2$AsO$_4^-$ and HAsO$_4^{2-}$ are the predominant species of As(V). Because the predominant As(V) species changes in water, electrostatic attraction and repulsion between MI and As(V) occurred. The decrease in As(V) adsorption is higher than As(III) at a high pH due to the more substantial electrical charge of As(V) compared to As(III). A similar pH dependence trend in the arsenic adsorption on nanosized zero-valent iron (NZVI), hematite, and goethite has also been observed [16,17,39].

![Figure 4. Effect of pH on the adsorption of As(III) and As(V). The pH of the solution was varied in the range of pH 2 to 12.](image-url)
3.5. Effects of Ionic Strength and Anions on Arsenic Adsorption

To determine the effect of ions on arsenic removal using MI, an investigation of how the ionic strength and competing ions affect the experiment was performed. As shown in Figure 5a, the adsorption of As(III) and As(V) was little affected by different ionic strength (0–50 mM). Figure 5b shows the effect of individual anions (HCO$_3^-$, SO$_4^{2-}$, NO$_3^-$, H$_4$SiO$_4^0$, and PO$_4^{3-}$) on the adsorption of As(III) and As(V) on MI. The HCO$_3^-$, SO$_4^{2-}$, and NO$_3^-$ ions had a slight effect on the As(III) uptake in 10 mM concentrations, whereas the same concentration of PO$_4^{3-}$ and H$_4$SiO$_4^0$ reduced the adsorption by 79.6% to 11.9% and 0%, respectively. Similar results were reported by Su and Puls [41]. Adsorption of As(V) was slightly affected by NO$_3^-$ and SO$_4^{2-}$ anions, whereas HCO$_3^-$, PO$_4^{3-}$ and H$_4$SiO$_4^0$ decreased the sorption from 91.9% to 46.5%, 7.2%, and 1.3%, respectively. According to the batch experiments results, for As(III), the adsorption maximum and affinity parameters do not statistically differ among the 5mM HCO$_3^-$ concentrations, whereas HCO$_3^-$ ions exhibit a noticeable influence on the As(V) adsorption onto MI. In the case of anions, anions are well adsorbed on iron oxide adsorbents with positive charge. For anions, they are readily adsorbed onto the iron oxide adsorbents with positive charge via electrostatic attraction. In particular, it was hypothesized that As(V) arsenic is more affected because it has a greater negative charge than As(III). Similary, Suzuki explained that HCO$_3^-$ acted as a competitor for adsorption sites for As(V) but not for As(III) [42]. Whereas, in the case of PO$_4^{3-}$, not only is the amount of charge affected, but also the structural effect. When the PO$_4^{3-}$ is present, the phosphate ion has similar physical and structural properties as the arsenic ions because both ions are located in the same group of the periodic table [43]. Moreover, As(V), PO$_4^{3-}$ and H$_4$SiO$_4^0$ are all tetrahedral anions; consequently, all anions form inner-sphere complexes with the functional groups at the surfaces of iron oxides [44]. Moreover, in H$_4$SiO$_4^0$, a significant portion of silica existed in colloidal form due to low solubility (183 ppm at pH 7, 50 °C) of silica [45]. Consequently, the adsorption capacity of MI might be decreased because of the fouling of the sorbent pores/surface caused by the colloidal silica. Therefore, the phosphate ion and silicate ion act as strong competitors of arsenic adsorption.

![Figure 5. Effect of ionic strength (a) and anions (b) on the adsorption of As(III) and As(V). The solutions of 1 mg/L in inert electrolyte KCl solutions (0–50 mM) (a) and 10 mM solutions of NaH$_2$PO$_4$, Na$_2$SiO$_3$, Na$_2$SO$_4$, NaNO$_3$, and NaHCO$_3$ (b) were used, respectively.](image)

3.6. Regeneration of Arsenate Adsorbed MI

In Figure 4, the adsorption of As(V) decreased as the pH value increased, which indicates that an adsorbed As(V) ion can be desorbed from MI by alkaline media. In order to prevent the dissolution of mesoporous iron oxide, desorption experiments were conducted using As(V) adsorbed MI with 0.1 M NaOH solution, and the reaction time varied in a range of up to 6 h. As shown in Figure 6, the desorption procedure reached equilibrium within 30 min. More than 60% of the As(V) was desorbed from the MI within 30 min, and no iron ion was detected in the treated solution. In addition,
the feasibility of the adsorption–desorption cyclic operation was examined to check out the long-term performance of MI. Figure S4 shows repeated runs of As(V) adsorption in the regenerated MI, with a fresh supply of 3 mg/L As(V) added at the beginning of each cycle. In every cycle, the As(V) was completely adsorbed. In the 0.2 g/L MI dosage, an average of 2.25 ppm As(V) was adsorbed after five cyclic operations; it was thus noted that MI could undergo repeated adsorption–desorption cycles without a noticeable loss of adsorption activity.

![Figure 6. Desorption efficiency of As(V) using 0.1 M NaOH at various times.](image)

4. Conclusions

In this research, sonochemically synthesized mesoporous iron oxide (MI) showed high adsorption capacity for the removal of As(III) and As(V). Adsorption of As(III) and As(V) on MI was well fitted to the pseudo-second-order kinetic model with high rate constants compared to other types of nanomaterials. Adsorption mechanism of As(III) on MI follows the Freundlich model based on the van der Waals interaction, whereas that of As(V) on MI was well fitted to Langmuir model due to mainly electrostatic interaction between As(V) and MI or As(V) adsorbed MI. Water characteristics such as competing anions and pH affected arsenic adsorption capacity; on the other hand, ionic strength (<50 mg/L KCl) had a slight effect on MI adsorption capacity. Moreover, arsenic adsorbed MI was efficiently regenerated under basic condition, and MI showed good reusability for arsenic removal. This study suggests that MI has a great potential for field application as an arsenic adsorbent in practical and economic feasibility due to the fast adsorption/desorption rate, simple regeneration process, and high adsorbent stability.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/2073-4441/12/11/3147/s1](http://www.mdpi.com/2073-4441/12/11/3147/s1), Table S1: Related parameters for the adsorption of As(III) and As(V) on MI, Table S2: Thermodynamic parameter for adsorption of As(III) and As(V) on MI at different temperatures. (Langmuir and Freundlich isotherm), Table S3: Intraparticle diffusion rate constants for adsorption of As(III) and As(V) on MI at different MI dosage, Figure S1: Wide-angle X-ray diffraction patterns of MI (α-Fe₂O₃). (Reference: JCPDS file, No. 33-0664), Figure S2: Transmission electron microscope images of MI, Figure S3: Adsorption kinetics of As(III) (a) and As(V) (b) based on pseudo second model with various MI concentrations. The experiments were initiated by adding 0.05, 0.075 and 0.1 g/L of MI into solution containing 1 mg/L of As(III) and As(V) at pH 7, Figure S4: Regeneration cycle of As(V) adsorbed MI. The experiments were initiated by adding 0.2 g/L of MI and 3mg/L As(V) was added at the beginning of each cycle. model with various MI concentrations. The experiments were initiated by adding 0.05, 0.075 and 0.1 g/L of MI into solution containing 1 mg/L of As(III) and As(V) at pH 7.

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