Effect of Water Hardness and pH on Adsorption Kinetic of Arsenate on Iron Oxide

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Abstract. The adsorption of arsenate on iron oxide particles was studied as a function of pH and hardness concentrations. Morphology of the studied iron oxide surface was rough and irregular. The major chemical composition of iron oxide particles was Fe\textsubscript{2}O\textsubscript{3} (96%). The optimal solution pH for adsorption was 8.0. The equilibrium of arsenic concentration was reached after 1 hour of contact time. The adsorption capacity ($q_e$) increased with increasing iron oxide particles. Freundlich isotherm and pseudo-second order reaction were best descriptors of arsenate adsorption behavior. Calcium or magnesium concentrations did not significantly affect the adsorbed concentration of arsenic at equilibrium. However, arsenate adsorption was higher at low pH and decreased significantly with increasing pH.

Keywords: Arsenate, adsorption kinetics, isotherm, groundwater.
1. Introduction

Arsenic in groundwater is a major problem in many Asian countries such as Laos, Cambodia, India, China, and Bangladesh [1-4]. An exposure to high concentrations of dissolved arsenic can lead to acute arsenic poisoning, with symptoms including nausea, vomiting, abdominal pain, and severe diarrhoea [5]. Long term arsenic exposure from drinking water and food can cause skin cancer, lesions, cardiovascular effects, neurotoxicity, and diabetes [5]. High concentration of arsenic can be found in the north eastern and southern regions of Thailand [6]. For example, villagers in the Ronpibhhun Subdistrict of Nakhon Srithammarat Province are exposed to high concentrations of arsenic in groundwater due to mining activities [6]. The highest total arsenic concentration these villagers were reportedly exposed to was as high as 583 µg/L [6], compared to the World Health Organization’s (WHO) recommended maximum control limit (MCL) of 10 µg/L [7], and Thailand’s Pollution Control Department’s (PCD) set maximum of arsenic concentration in drinking water of 50 µg/L [8].

Unfortunately, groundwater is the main source of drinking water in many of these affected regions. Different technology have been identified to reduce arsenic concentrations in groundwater [9-21]. Coagulation with alum can be used to reduce arsenic concentrations to a certain level [22], and adsorption has been found to be effective in removing several metals in groundwater including arsenic while using less chemicals and generating less waste [11, 12, 15]. Iron oxides have been studied for their adsorption abilities [11, 12, 15]. For example, copper, lead, and chromium were found to adsorb well on iron oxide under various chemical conditions [23-26]. Researchers also used iron oxide in treating arsenic in water [27, 28]. Both chemical and physical interactions were found to play important roles in the adsorption of arsenic on iron oxides [15, 27, 29]. This study chose to investigate the adsorption mechanism of arsenic on iron oxide in the presence of high hardness concentrations which is common in groundwater. The objective of this study is to investigate adsorption kinetics of inorganic arsenate on iron oxide particles in different pH conditions. Adsorption kinetic models and isotherms will be calculated and identified from the experiment. The effect of water hardness as calcium and magnesium concentrations on arsenic adsorption will also be studied.

2. Materials and Methods

2.1. Iron Oxide Characterization

Iron oxide particles were obtained from milling iron rods to small particles at a Mechanical Shop at the Department of Mechanical Engineering, Chulalongkorn University. Surface morphology of the resultant iron oxide particles was studied by Scanning Electron Microscope (SEM, JEOL, JSM-6610LV). Chemical composition of the particle surface was measured by X-ray Fluorescence Spectrometry (XRF, BRUKER, S4 Pioneer). Particle size distribution was determined by sieving analysis.

2.2. Preparation of Water Sample

Synthesized groundwater was used in this experiment. The synthesized groundwater used in this experiment was prepared by adding Na,HAsO₄.7H₂O to deionized water to make a stock solution of 1000 mg/L of arsenate. Next, nitric acid (2%) was added to the solution. The stock was further diluted to prepare a solution of 1 mg/L arsenate. NaHCO₃ was used as a buffer to maintain a water pH of 8.0-8.5. For pH-dependent experiments, 1.0 N HCl or 1.0 N NaOH was added to adjust the pH. Total arsenic concentration was measured by Inductively Coupled Plasma-Quadrupole Mass spectrometry (ICP-QMs, iCAP Qc21) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University. Total arsenic concentration was interpreted to represent arsenate concentration. The detection limit of the instrument is 0.2 µg/L.

2.3. Adsorption Kinetics of Arsenate on Iron Oxide

Batch tests were conducted to study the kinetics of arsenate adsorption on iron oxide particles as a function of pH and water hardness. Jar testing was performed at 130 rpm for 1 hour for all batch tests.
2.3.1. Adsorption capacity of iron oxide particles

Batch tests were conducted to determine the optimal amount of iron oxide particles needed in arsenate adsorption. A 2, 4, 6, 8, 10, and 20 mg of iron oxide particles were added to 250 mL of synthesized groundwater (pH 8.0-8.5 with 1 mg/L arsenate). Suspensions were stirred at 130 rpm for 1 hour to reach equilibrium. An aliquot from each batch was taken and filtered for arsenic concentration analysis of the filtrate. The adsorption capacity of the iron oxide particle ($q_e$) was calculated using Eq. (1).

$$ q_e = \frac{(C_0 - C_e)V}{M} \tag{1} $$

where, $q_e$ is adsorption capacity of the iron oxide particle (µg Arsenic/mg iron oxide), $C_0$ and $C_e$ are the initial and equilibrium arsenic concentrations (µg Arsenic/L), $V$ is the suspension's liquid volume (L), and $M$ is the total mass of iron oxide particle in suspension (g).

2.3.2. Optimum pH for adsorption experiment

Batch tests were conducted to determine the optimal pH for arsenic adsorption by iron oxide particles. The amount of iron oxide particles optimal to arsenic adsorption as determined from 2.3.1 was added to 250 mL of synthesized groundwater containing 1 mg/L arsenate. Solution pH was adjusted with either 1.0N HCl or 1.0N NaOH. Suspensions were stirred at 130 rpm for 1 hour to reach equilibrium. An aliquot from each batch was taken and filtered for arsenic concentration analysis of the filtrate.

2.3.3. Effect of Ca, Mg on adsorption

CaCl$_2$ or MgCl$_2$ were added to 1L amounts of deionized (DI) water to make Ca or Mg solutions of 50, 100, 150, 200, and 250 mg/L. 1 mL of arsenate stock was added to each Ca or Mg solution, and NaHCO$_3$ was added as a buffer to maintain pH of 8.0-8.5. Adsorption testing was conducted using the amount of iron oxide particles and pH optimal for arsenic adsorption as determined from 2.3.1 and 2.3.2.

2.4. Isotherm Models

Different kinetic models such as pseudo-first order and pseudo-second order models were applied to describe the rate constant of adsorption.

2.4.1. Langmuir isotherm

Equation (2) is the equation for the Langmuir isotherm [30]:

$$ \frac{C_e}{q_e} = \frac{1}{ab} + \left(\frac{1}{a}\right)C_e \tag{2} $$

where, $C_e$ is the equilibrium concentration of arsenic in µg/L, and $q_e$ is the adsorption capacity of arsenic at equilibrium (µg$_{As}$/gFe$_{2O_3}$). 1/a is the slope of a fitted linear regression between $C_e$ (as x axis) and $q_e$ (as y axis).

2.4.2. Freundlich isotherm

Equation (3) is the equation for the Freundlich isotherm [30]:

$$ \log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \tag{3} $$
where, $C_e$ is equilibrium concentration of arsenic in µg/L, and $q_e$ is the adsorption capacity of arsenic at equilibrium (µgAs/gFe₂O₃). $K_f$ is an indicator of adsorption capacity ((µg/g)(L/g)⁻¹/n, and 1/n is a measure of intensity of the adsorption.

2.5 Kinetic Models

2.5.1 Pseudo-first order

Equation (4) is the pseudo-first order adsorption equation [30]:

$$\ln(q_e - q_t) = \ln q_e - kt$$

where $q_t$ and $q_e$ are the amounts of arsenic adsorbed on iron oxide particles (µgAs/gFe₂O₃) at time $t$ and at equilibrium. $k_1$ is the first-order adsorption rate constant (min⁻¹).

2.5.2 Pseudo-second order

Equation (5) is the pseudo-second order adsorption equation [30]:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

where $q_t$ and $q_e$ are the amounts of arsenic adsorbed on iron oxide particles (µgAs/gFe₂O₃) at time $t$ and at equilibrium. $k_2$ is the second-order adsorption rate constant (g/µg.min).

3. Results and Discussion

3.1. Iron Oxide Characteristics

The chemical composition of iron oxide used in this study is shown in Table. 1. The main compound, Fe₂O₃, on the particle surface is what plays the important role of adsorption in the removal of heavy metals in wastewater [23].

Table 1. Chemical compositions of iron oxide particles.

| Chemical Compositions | Percent by Mass (%) |
|-----------------------|---------------------|
| Fe₂O₃                 | 96.08               |
| SiO₂                  | 2.7                 |
| CuO                   | 0.422               |
| Cu₂O                  | 0.166               |
| SO₃                   | 0.144               |
| Cr₂O₃                 | 0.142               |

SEM capture of the iron oxide particles is shown in Fig. 1. Iron oxide precipitated onto the particle surface as seen in Fig. 1. The observed iron oxide particle surface was rough and amorphous, concurring with previous studies conducted by other researchers [31].
3.2. Adsorption Capacity of Iron Oxide Particles

Adsorption capacity of arsenic on iron oxide particle is shown in Fig. 2. An increase in the amount of iron oxide led to a quick decrease in arsenic concentration at equilibrium ($C_e$). Specifically, the $C_e$ at 2 g iron oxide/250 mL water was 14.45 µg/L, and 1.17 µg/L at 4 g iron oxide /250 mL water. Adsorption capacity ($q_e$) decreased from 123.19 to 12.49 µg arsenic/g iron oxide for 2 and 20 g iron oxide added. From the results of this experiment, 4 g iron oxide /250 mL was chosen for subsequent experiments because this amount of iron oxide was able to reduce the arsenic concentration to below the WHO Drinking Water Standard’s MCL of <10 µg/L [7].

3.3. The effect of pH on arsenic adsorption

The effect of pH on arsenic adsorption is shown in Fig. 3. Arsenic concentration at equilibrium decreased from 59.44 to 2.31 µg/L when pH increased from 2 to 8. At pH > 8, equilibrium arsenic concentration in water increased to 512.82 and 905.52 µg/L at pH 10 and 12. Two studies, Mustafa et al., and Parks and Bruyn [32, 33] which measured the surface charge of iron oxide as a function of pH may explain the results of our study. At pH 8, iron oxide has a negative surface charge [32, 33]. At pH > 8, arsenic exists as HAsO$_4^{2-}$ [34], which adsorbs on positive iron oxide [32, 33]. These two effects leads to electrostatic repulsion between the negatively charged iron oxide and arsenic oxide particles [35]. Other studies [28, 36] have suggested that
adsorption capacity of arsenic on iron oxide minerals decrease when pH is higher than 9. Our experimental result suggests that the adsorption of arsenic on iron oxide particle is optimal at pH 8.

Fig. 3. Concentration of arsenic at equilibrium as a function of pH (batch test, 1 mg/L arsenic, 4 mg of iron oxide particle in 250 mL water, 130 rpm, 1 hour).

3.4. Adsorption Isotherm of Arsenic on Iron Oxide Particles

Figure 4. expresses iron oxide’s adsorption capacity of arsenic as a function of time at pH 8.0. During the first 10 min of interaction, adsorption capacity rapidly increased with time as reflected by the graph’s steep slope. After 10 min, the adsorption capacity rate keeps increasing but more slowly until equilibrium was reached, mostly after 30 min. An increase in iron oxide led to faster approach to equilibrium. For example, it required 60 minutes for 2 g Fe₂O₃/250 mL to reach equilibrium, and only 30 minutes for 4 g Fe₂O₃/250 mL.

Fig. 4. Arsenic concentration as a function of time. Iron oxides were varied from 2 to 20 mg in 250 mL water. (pH 8.0, 1 hour of equilibration, 1 mg/L of As, 135 rpm)

Adsorption isotherms of arsenic on iron oxide are shown in Fig. 5. Linear regression model was used to fit the data, and the correlation coefficient (R²) was used to compare and determine the model that best fitted
with the data. Fig. 5a and 5b show the $R^2$ for the Langmuir and Freundlich isotherm at 0.9934 and 0.994, respectively, which suggests that both of these isotherms explain the adsorption of arsenic on iron oxide particle fairly well.

Fig. 5. Adsorption isotherm of arsenic on iron oxide particles using a) Langmuir isotherm, b) Freundlich isotherm.

To determine the arsenic adsorption rate constant on iron oxide particles, the data obtained from adsorption capacity (Fig. 4) was fitted to pseudo-first order and pseudo-second order kinetic models. The adsorption rate constant ($k$) was calculated from the slope of linear regression obtained from fitted data. To determine the best fitted model for each kinetic model, root mean square ($R^2$) was used as a correlation coefficient. The constant ($k$) of the pseudo-second order reaction was calculated from the ratio between (slope)$^2$ and $y$-intercept. Comparison of $R^2$ values suggested that the pseudo-second order model with $R^2$ values ranging from 0.9198 to 1, shown in Fig. 6, was a better fit than the pseudo-first order model (not shown). Furthermore, an increase in the amount of iron oxide particles used in adsorption led to higher adsorption rates. Specifically, $k_{1g} = 2g$ is 0.0062 g/µg.min, while $k_{1g} = 10g$ is 0.04 g/µg.min.
3.5. Effect of Ca and Mg on Arsenic Adsorption

Figure 7 shows arsenic concentration at equilibrium as a function of calcium and magnesium concentrations. 0 and 50 mg/L CaCO$_3$-equivalence of Ca or Mg concentrations showed an inverse of the amount of arsenic adsorbed by iron oxide versus Ca or Mg concentrations (less arsenic was adsorbed at 50 mg/L CaCO$_3$-equivalence). However, further increases in Ca or Mg concentrations did not change the equilibrium concentration of arsenic significantly ($P<0.05$). It could be concluded from these results that Ca or Mg concentrations do not have significant effects on the adsorption of arsenic by iron oxide particles.

4. Conclusions

The adsorption of arsenic on iron oxide particles was investigated as a function of pH, and calcium and magnesium concentrations. Iron oxide particles have an irregular shape and rough surface. The optimal pH for adsorption is around 8.0, which indicated that electrostatic repulsion between arsenic and iron oxide particles was lowest at this point [32, 33]. Iron oxide particles required at least 30 min of contact time to fully
adsorb arsenic to reach equilibrium. Adsorption capacity \((q)\) decreased from 123.19 to 12.49 µg arsenic/g iron oxide for 2 to 20 g of iron oxide added to 250 mL amounts of arsenic solution. The adsorption isotherm of arsenic on iron oxide could be described by either the Langmuir or Freundlich isotherms due to equally high correlation coefficients \((R^2)\). The adsorption kinetic was best fitted by a pseudo-second order reaction with a rate constant \((k_2)\) between 0.0062 to 0.0801 g/µg.min for 2 g to 20 g of iron oxide particles used. Adsorption occurred more rapidly with an increase amount of iron oxide adsorbent. Finally, adsorption capacity was independent of calcium or magnesium concentrations.

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