

# ARSENIC ADSORPTION PERFORMANCE OF LIGNITE IN LABORATORY COLUMN EXPERIMENTS UNDER SATURATED FLOW CONDITIONS

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## Abstract

This paper presents the adsorption behavior of arsenic (As) onto lignite in saturated column experiments under various flow rates and adsorbent thicknesses. The lignite sample originated from Indonesia is predominantly composed of organic matter with minor amounts of pyrite (FeS<sub>2</sub>). Arsenic content of lignite is 1.8 mg/kg with high sulfur content of 10.8 wt. %. The experiments were performed at room temperature using a glass column with an inner diameter of 2.4 cm and total length of 30 cm. Different lignite bed thicknesses (6 and 12 cm) at a constant flow rate of 0.85 cm<sup>3</sup>/min and a fixed lignite bed thickness of 12 cm with different flow rates (0.85 and 0.22 cm<sup>3</sup>/min) were conducted. All effluents had acidic pH (1.04 to 3.36) and were under oxidizing conditions (Eh: +554 – +629 mV) regardless of the flow rate and lignite bed thickness. The breakthrough of As indicated both leaching and adsorption regions. The leaching of As could be attributed to very high concentration of dissolved organic carbon (DOC) that competes with As for Adsorption sites. Leaching region occurs until ca. 69 mL (ca. 1.35 h) at a thinner lignite bed. After this, the concentration of As in the effluent slowly increased and then reached the influent As concentration. In contrast, the retardation of As observed until ca. 159 mg/L (ca. 3.15 h) at a thicker lignite bed, indicating that the As adsorption increased substantially at thicker lignite bed. Decreasing the flow rate (0.22 cm<sup>3</sup>/min) had a similar effect with case 2, that is, the As adsorption increased substantially. Based on these results, As removal efficiency under flow-through conditions is strongly influenced by thickness of adsorbent but not the flow rate.

**Keywords:** Arsenic, Adsorption, Flow rate, Lignite, Thickness of adsorbent bed

## Introduction

Arsenic (As), which is toxic to most living organisms, causes potentially serious environmental problems throughout the world because of the contamination of soils and groundwater. The use of As contaminated groundwater for drinking and cooking in many parts of the world, including Bangladesh [1][2], Taiwan [3][4], China [4][5], Mexico [6], Argentina [7], Chile [8], India [9][10][11] and Mongolia [12] has been linked to increase the incidence of keratosis, cardiovascular illnesses and certain types of cancers. Numerous technologies and processes are now available for the removal of liquid-phase As like chemical precipitation, ion exchange, adsorption onto activated alumina and Fe-(oxy)hydroxides, reverse osmosis, modified coagulation/filtration, modified lime softening, electro deposition and oxidation/filtration [13]. Among them, significant attention has centered on adsorption because of its simplicity, cheap pollution control, ease

of operation and handling, sludge free operation, and regeneration capability. Several materials have been utilized as adsorbents for As including activated alumina, fly ash, pyrite fines, manganese greensand, amino-functionalized mesoporous silicas, clinoptilolite and other zeolites, iron oxides, activated carbon and zero-valent iron [14][15][16][19][20]. Although these adsorbents are effective, most of them are expensive. Cheaper alternatives are essential especially in the remediation and mitigation of As contaminated groundwater found in rural areas of less developed countries like Indonesia. High concentration of As was recently uncovered in the groundwater of Sumbawa Island, Indonesia. To mitigate this problem, the author has envisioned the use of permeable reactive barrier (PRB) using natural geological materials to remove As. A PRB is defined as an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation goals down-gradient of the barrier [21][22]. This mitigation approach was chosen because of its simplicity and low overall cost.

In our previous papers, natural geological materials such as, lignite, bentonite, shale and iron sand were evaluated for their ability to remove As from aqueous solution [21][22]. These materials were chosen because they are relatively cheap and locally available. Our previous results showed that lignite was the best adsorbent among these four materials and was chosen for this present study [23][24]. Adsorption of As onto lignite fitted well with the Langmuir isotherm, indicating monolayer adsorption with progressive saturation of adsorption sites. The maximum adsorption capacity ( $q_m$ ) of lignite was 10.9 mg/g at the pH interval of 2.8-3. In addition, adsorption of As onto lignite was highly pH dependent and was more favorable around the acidic to circumneutral pH (3 – 8) where lignite had a net positively charged surfaces [23][24]. Based on these previous results, lignite was chosen for column studies. Although batch laboratory adsorption studies have provided useful information regarding about the adsorption affinity and capacity of adsorbents, these data are still insufficient in the understanding of the long term migration of As through the adsorbent close to field conditions. Thus, continuous flow-through studies were conducted to provide additional insights into the parameters and processes important in the retardation and transport of As in lignite under conditions close to the actual setting.

In this study, the adsorption characteristics of As onto lignite were evaluated under saturated flow conditions. Specifically, the effects of lignite-bed thickness and flow rate on the adsorption and migration of As were elucidated. In addition, changes in the pH, Eh and concentrations of coexisting ions like iron (Fe), sulfate ( $\text{SO}_4^{2-}$ ) and dissolved organic carbon (DOC) were monitored throughout the duration of the experiments. Finally, the effects of coexisting ions like Fe and  $\text{SO}_4^{2-}$  on As adsorption under flow conditions were investigated.

## **Materials and Methods**

### **Chemical, Mineralogical and Physical Properties of Lignite**

The lignite sample evaluated in this study was collected in Samigaluh, Kulon Progo area, Java island, Indonesia, which is the same adsorbent used in our previous researches [21][22]. It was air dried, crushed and sieved into several particle sizes. The particle size between 0.5 – 1 mm was chosen for column experiments. Lignite is composed predominantly of organic carbon (32.3 wt.%) with minor amounts of pyrite ( $\text{FeS}_2$ ). Arsenic content of lignite is 1.8 mg/kg with high sulfur content of 10.8 wt. %. [23].

The measured specific surface area and total pore volume of the lignite sample were 7.53 m<sup>2</sup>/g and 0.016 mL/g, respectively [24]. The specific gravity and water content of the sample were 1.87 g/cm<sup>3</sup> and 23.5 wt.%, respectively.

### Column Experiments

The influent solution with As concentration of 10 mg/L As was prepared from reagent grade disodium hydrogen arsenate heptahydrate (Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O) (Wako Pure Chemical Industries Ltd., Japan). The columns used were made of glass with an inner diameter of 2.4 cm and length of 30 cm. Three cases were conducted at room temperature using a constant influent As concentration with different thicknesses of adsorbent bed and flow rates. Details of the column experimental conditions are shown in Table 1. The adsorbent bed was packed between two baffle layers to minimize the formation of dead zones and flow variations around the ends of the columns. These baffles are composed of spherical glass beads with diameters of ca. 2 mm. Glass filters with a thickness of ca. 1 mm were placed between the baffles and adsorbent bed. The influent solution was introduced underneath the column and forced to flow upwards using a peristaltic pump (Eyela cassette tube pump SMP-21, Tokyo Rikakikai Co., Ltd., Japan). The outflow was connected to a fraction collector (Eyela fraction collector DC-1200, Tokyo Rikakikai Co., Ltd., Japan), which collected effluent samples at fixed time intervals. The column experiments were continued until the As concentration of the effluent was almost equal to the influent concentration. Effluents were taken from the fraction collector after the predetermined time intervals, and immediately weighed. This was followed by measurements of the effluent pH, oxidation-reduction potential (Eh) and electrical conductivity (EC). Then, the effluents were filtered through 0.45 µm Millex<sup>®</sup> sterile membrane filters (Merck Millipore, USA) and stored in glass containers prior to the chemical analyses.

**Table 1. Lists of Column Experimental Conditions**

Column	Flow Rate (cm <sup>3</sup> /min)	Thickness of Adsorbent Bed (cm)	Bulk Density (g/cm <sup>3</sup> )	Particle Density (g/cm <sup>3</sup> )	Total Mass of Adsorbent (g)	Porosity (%)
Case 1	0.85	6	0.639	1.87	17.35	0.658
Case 2	0.85	12	0.673	1.87	36.5	0.640
Case 3	0.22	12	0.673	1.87	36.5	0.640

### Chemical Analyses

Arsenic concentrations of the influent solution and effluent samples were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan). Major coexisting ion (e.g. Fe) was also determined using the ICP-AES. Sulfur in the effluent samples from the first column were found to be mostly in the form of SO<sub>4</sub><sup>2-</sup> based on the results of anion chromatography (ICS-1000, Dionex Corporation, USA). Thus, for faster and easier determination of SO<sub>4</sub><sup>2-</sup>, the ICP-AES was used in the later experiments. DOC was analyzed using TOC-L Total Organic Carbon Analyzer (Shimadzu Corporation, Japan).

## Geochemical Modeling

Saturation indices (*SI*) of important precipitates/minerals like Fe hydroxides/oxides, Fe arsenate and arsenic oxides were calculated from measured effluent chemistries using the equilibrium modeling software PHREEQC [25]. In the calculation of *SI* the database distributed with the program (*wateq4f.dat*) in PHREEQC (version 2) was applied.

## Results and Discussion

### Evolution of pH, Eh, EC and Concentrations of As, Fe, SO<sub>4</sub><sup>2-</sup>, and DOC

The changes in the effluent pH and Eh with the cumulative volume (*Q*) under saturated conditions for all cases are shown in Figure 1. The shapes of the pH curves were similar in all cases, that is, the pH increased gradually with cumulative volume. In case 1, the measured pH gradually increased from 1.21 to 2.04 until ca. 83 ml (ca. 1.65 h) (Figure 1(a)). This was then followed by pH stabilization, which indicates apparent equilibrium with respect to the effluent pH. Similarly, the measured pH values in cases 2 and 3 increased with cumulative volume approaching the apparent equilibrium pH as observed in case 1. Although the pH increased gradually with time/*Q*, all effluents collected had acidic pHs regardless of the flow rate and lignite bed thickness. This could be attributed to the substantial pyrite content of the sample and its very low acid buffering capacity. Oxidation of pyrite produces acidity as explained by the following equations:

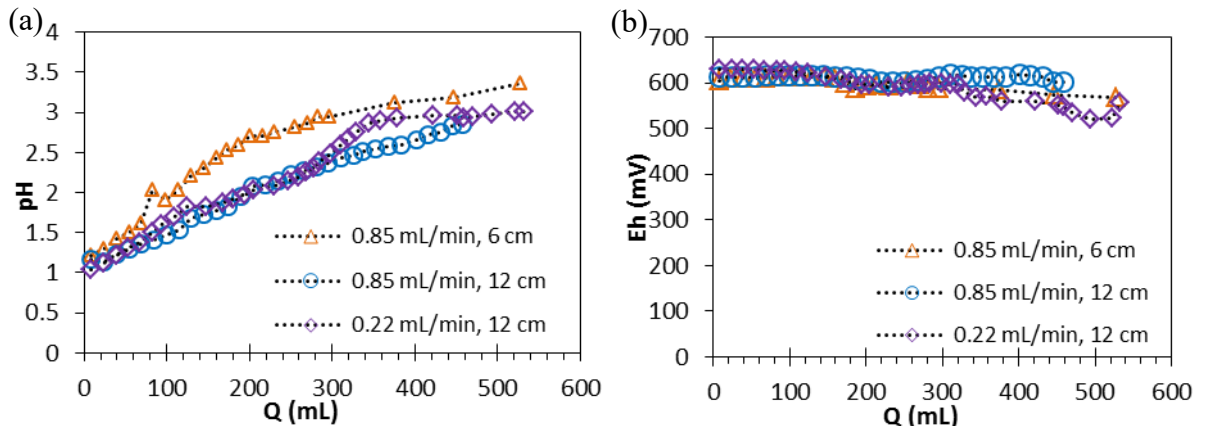
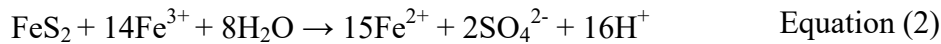
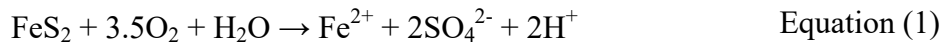


Figure 1. Evolution of pH and Eh under saturated –column conditions of all cases; (a) pH change with cumulative volume (*Q*), and (b) Eh change with cumulative volume (*Q*)

Although the average pH in case 1 (pH = 2.37) was also slightly higher in comparison to that in case 2 (pH = 2.12) and case 3 (pH = 2.13), the average pH in case 2 is similar to case 3. These results imply that the pH of the effluent is sensitive to the amount of adsorbent used, but not to the flow velocity. In addition the results showed that the pH of the effluents was a function of cumulative volume. On the other hand, the Eh values of the effluents did not change dramatically in all cases as illustrated in Figure 1(b). The measured Eh ranged from +605 to +568 mV, +613 to +592 mV and +629 to +557 in cases

1, 2 and 3, respectively, which indicates that the saturated lignite adsorbent bed system was under oxidizing conditions throughout the duration of the experiments.

The EC and DOC curves of all cases are illustrated in Figure 2. The EC value of a liquid sample roughly shows the total amount of dissolved ions, that is, very low EC values indicate almost pure water while very high EC values means relatively high concentrations of dissolved ions. In case 1, the highest EC value (ca. 32,100  $\mu\text{S}/\text{cm}$ ) was measured in the first effluent sample, which decreased rapidly with the cumulative volume and stabilized in the range of 1278 - 203  $\mu\text{S}/\text{cm}$  after ca. 185 mL (ca. 4 h) (Figure 2(a)). A similar trend in the EC curves was also observed in cases 2 and 3, that is, the EC values were initially very high, decreased rapidly and then stabilized. These flushing-out trends of the EC in all cases indicate that substantial amounts of soluble phases is found in the lignite adsorbent bed, which is the source of most of the dissolved ions in the effluent.

The DOC curves in the effluents of all cases also had flushing-out trends similar to EC (Figure 2(b)). The highest concentrations of DOC values were observed at the start of the experiments which decreased rapidly and stabilized with cumulative volume (Figure 2(b)). The DOC values of effluent samples at the start of the experiments were 300, 364 and 630 mg/L in cases 1, 2 and 3, respectively. These values decreased rapidly with the cumulative volume and stabilized in the range of 12.8 - 9.9 mg/L after ca. 170 mL (ca. 3.45 h), 35.6 - 8.7 mg/L after ca. 190 mL (ca. 3.75 h) and 65.9 - 16.4 mg/L after ca 180 mL (ca. 15 h) in cases 1, 2, and 3, respectively. Higher amount of DOC values in all cases could be due to the high content of organic matter in lignite which contains easily soluble organic compounds.

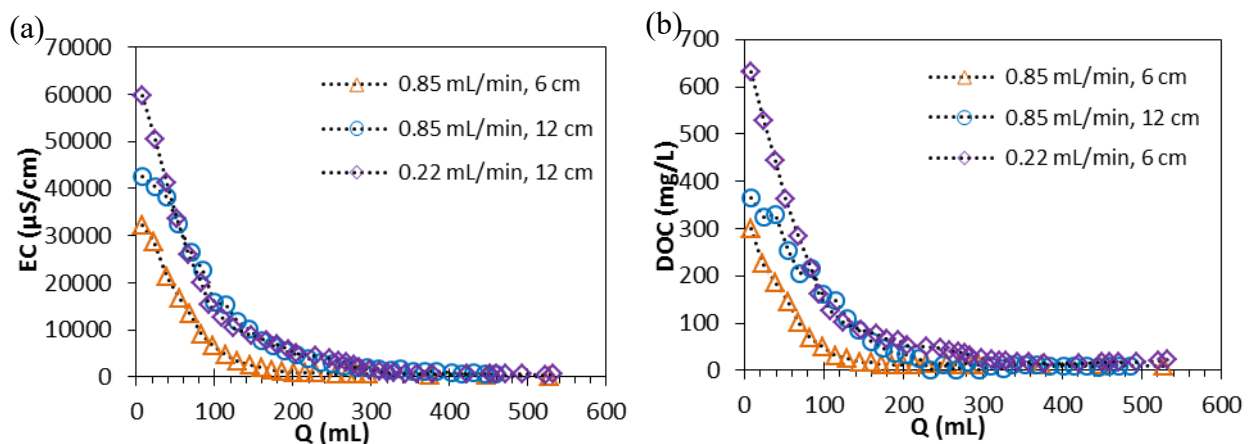


Figure 2. EC change with cumulative volume ( $Q$ ), and (b) DOC change with cumulative volume ( $Q$ )

Figure 3 illustrates the concentrations of  $\text{SO}_4^{2-}$  and Fe as a function of cumulative volume in all cases. The  $\text{SO}_4^{2-}$  and Fe concentration trends with cumulative volume were similar to those of the EC and DOC, that is, both of these ions had flushing-out trends. The highest  $\text{SO}_4^{2-}$  and Fe were observed at the beginning of the experiments in all cases.  $\text{SO}_4^{2-}$  concentrations measured in the first effluent samples were very high at 24,200, 55,800 and 41,000 mg/L in cases 1, 2, and 3, respectively. These values decreased rapidly and were nearly constant after ca. 130 mL (ca. 2.5 h), ca. 203 mL (ca. 4 h) and ca. 205 mL (ca. 18 h), in cases 1, 2 and 3, respectively (Figure 3(a)).

Similarly, Fe concentrations at the start of the experiments were very high at 8,830, 12,000 and 15000 mg/L in cases 1, 2 and 3, respectively, and decreased rapidly and stabilized after ca. 130 mL (ca. 2.5 h) in case 1, ca. 219 mL (ca. 4.35 h) in case 2 and ca.

230 mL (ca. 18 h) in case 3 (Figure 3(b)). In all cases, very high concentrations of Fe and  $\text{SO}_4^{2-}$  were observed at the pH range between 1.04 and 2.08. Over this pH values, Fe and  $\text{SO}_4^{2-}$  concentrations were decreased dramatically and stabilized. High concentrations of Fe and  $\text{SO}_4^{2-}$  could be attributed to the pyrite content of lignite. When pyrite oxidizes at low pH, the secondary soluble minerals like Fe-sulfates will form as shown in Equation (1). Dissolution of these soluble phases releases Fe,  $\text{SO}_4^{2-}$  and  $\text{H}^+$  (Equation (2)).

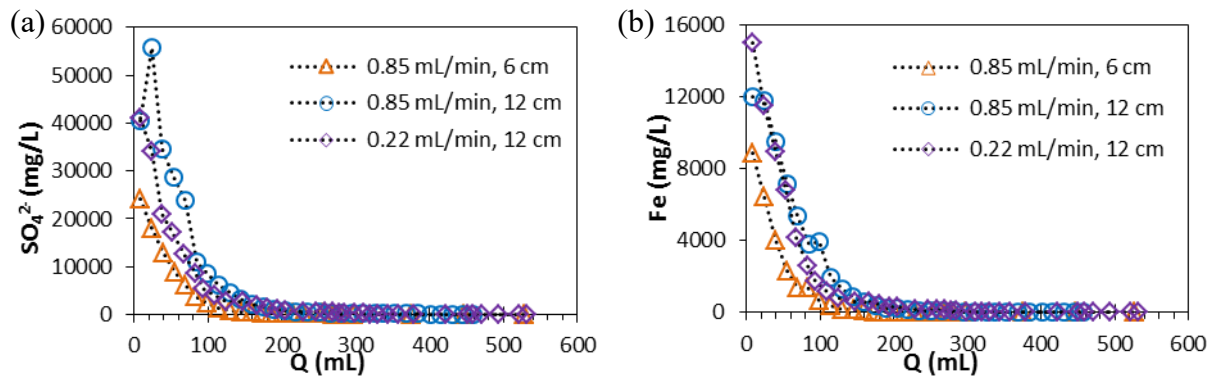


Figure 3. Changes in major ions (a)  $\text{SO}_4^{2-}$ , and (b) Fe concentrations under saturated-column conditions in all cases

Figure 4 shows the As concentration as a function of cumulative volume in all cases. As illustrated in the figure, the behavior of As in all cases could be divided into two parts: a leaching and an adsorption regions. The leaching regions were observed at the start of the experiments until ca. 69 mL (ca. 1.35 h), ca. 159 mg/L (ca. 3.15 h) and ca. 147 mL (ca. 12.6 h) in cases 1, 2 and 3, respectively. The leaching concentration of As in case 1 (6.28 – 2.56 mg/L) was relatively higher than that in case 2 (2.66 – 1.63 mg/L) and case 3 (3.03 – 0.834 mg/L). Adsorption regions were observed after the end of leaching regions in all cases. After leaching part, ca. 69 mL (ca. 1.35 h), the concentration in the effluent slowly increased and approached the influent As concentration in case 1. The slow increase of As concentration after retardation could be due to the saturation of adsorption sites. Arsenic concentrations in the effluent samples in case 2 with higher lignite thickness bed (12 cm) was 1.38 mg/L in the first ca. 174 mL (ca. 3.45 h) and increased slowly to the influent As concentration, indicating the As adsorption increased substantially. Mass balance of As in all cases were calculated to estimate the amount of As adsorbed (Table 2). In the case of same flow rate and different lignite thickness beds; the adsorbed amount of As in case 1 (37 %) was lower than that of case 2 (56 %).

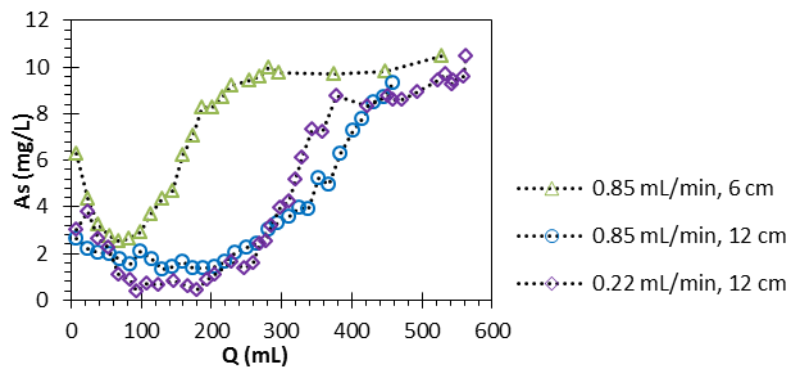


Figure 4. Change in As concentration under saturated-column conditions in all cases

**Table 2. Mass Balances of As in All Cases**

Column	Total Mass of As in the Influent (mg)	Total Mass of As in the Effluent (mg)	Total Mass of Adsorbed of As Adsorbed (mg)	Total Mass of Adsorbed of As Adsorbed (%)
Case 1	3.71	2.34	1.37	37
Case 2	5.17	2.28	2.90	56
Case 3	5.88	2.68	3.21	55

In case 3 at lower flow rate ( $0.22 \text{ cm}^3/\text{min}$ ) but same lignite thickness bed with case 2, the detected As concentration in the effluent samples was  $0.61 \text{ mg/L}$  in the first ca.  $167 \text{ mL}$  (ca.  $14 \text{ h}$ ) and gradually increased to the influent As concentration. It means that the adsorption performance of lignite is almost the same with case 2. As can be seen in table 4.4, in the cases of same lignite thickness bed and different flow rates; the adsorbed amount of As in case 2 (56 %) and that of case 3 (55 %) were almost the same.

### Effects of pH, DOC, and Coexisting Ions

During the experiments the pH gradually increased with time/ $Q$  in all cases (Figure 1). However, the pH values of all effluents were acidic regardless of the flow rate and lignite thickness bed. The leaching regions were observed at  $\text{pH} < 2$  in all cases. At the end of the leaching regions ( $\text{pH} > 2$ ), the adsorption regions started in all experiments indicating that As leaching and adsorption were influenced by pH. The DOC values were very high initially in the leaching regions and after DOC values decreased to a certain amount, As adsorption became substantial. It may be contributed to the very high DOC concentration in the lignite sample is competing with As for adsorption sites. Fe and  $\text{SO}_4^{2-}$  don't have effects on the adsorption of As. The pH values were acidic during experiments in all cases, which prevented the precipitation of Fe. Sulfate was reported to be insensitive to As adsorption onto lignite [24]. These suggest that both Fe and  $\text{SO}_4^{2-}$  do not affect the As adsorption significantly.

To better understand the effects of these parameters on the concentrations of As under saturated conditions, statistical analysis was used to compute the correlations of As with each of the parameters. In case 1, As concentrations had a strongly positive and statistically significant correlations with pH indicating that As adsorption increase with increasing pH during the experiments (Table 3). On the other hand, strongly negative and statistically significant correlations were found between the concentrations of As and that of Fe,  $\text{SO}_4^{2-}$  and DOC, which means that the adsorption of As tend to increase with decreasing Fe,  $\text{SO}_4^{2-}$  and DOC (Table 3).

Similarly in case 2, the concentrations of As had strong positive correlation with pH and strong negative correlations with that of Fe and  $\text{SO}_4^{2-}$  (Table 4). However, moderate negative correlation was found between the concentrations of As and that of DOC. As shown in Table 5, there is a moderate positive correlation between the concentration of As and pH in case 3. In contract, concentration of As and that of Fe,  $\text{SO}_4^{2-}$  and DOC had moderately negative and statistically significant correlations. Based on these results, in case 2 and 3, As adsorption is enhanced at higher pH and it tends to increase with decreasing Fe,  $\text{SO}_4^{2-}$  and DOC like case 1.

**Table 3. Correlation of pH, Fe, SO<sub>4</sub><sup>2-</sup> and DOC with As in Case 1**

Relationship	a	b	R	N
As vs pH	2.058	1.298	0.77*	23
As vs Fe	12.87	-0.169	0.85*	23
As vs SO <sub>4</sub> <sup>2-</sup>	23.18	-0.212	0.832*	23
As vs DOC	18.27	-0.337	0.758*	23

$y = ax^b$ , y = As concentration in the effluent, x = Fe, SO<sub>4</sub><sup>2-</sup> or DOC concentrations in the effluent, a, b = constant, R = correlation coefficient, N = number of samples. \*: significant at  $p < 0.005$ .

**Table 4. Correlation of pH, Fe, SO<sub>4</sub><sup>2-</sup> and DOC with As in Case 2**

Relationship	a	b	R	N
As vs pH	0.913	1.71	0.738*	33
As vs Fe	9.00	-0.212	0.771*	33
As vs SO <sub>4</sub> <sup>2-</sup>	14.8	-0.233	0.733*	33
As vs DOC	6.89	-0.249	0.580*	33

$y = ax^b$ , y = As concentration in the effluent, x = Fe, SO<sub>4</sub><sup>2-</sup> or DOC concentrations in the effluent, a, b = constant, R = correlation coefficient, N = number of samples. \*: significant at  $p < 0.005$ .

**Table 5. Correlation of pH, Fe, SO<sub>4</sub><sup>2-</sup> and DOC with As in Case 3**

Relationship	a	b	R	N
As vs pH	1.17	1.40	0.532*	34
As vs Fe	9.05	-0.202	0.627*	34
As vs SO <sub>4</sub> <sup>2-</sup>	14.3	-0.225	0.583*	34
As vs DOC	13.9	-0.358	0.497*	34

$y = ax^b$ , y = As concentration in the effluent, x = Fe, SO<sub>4</sub><sup>2-</sup> or DOC concentrations in the effluent, a, b = constant, R = correlation coefficient, N = number of samples. \*: significant at  $p < 0.005$ .



## Mechanisms of Arsenic Removal on Lignite

The saturation indices (*SI*) of the precipitates/minerals of interest during the column experiments were calculated using PHREEQC [25]. The calculated *SI*s with time for case 1, 2, and 3 are presented in Figure 5. In the effluent samples collected from all cases of column, the *SI* values of Fe oxyhydroxides/oxides such as goethite FeO(OH) and hematite (Fe<sub>2</sub>O<sub>3</sub>) were greater than zero, which means that the pore water is supersaturated with respect to these minerals and they thermodynamically favored to precipitate throughout the experiments. In the cases of shorter water residence time at a thinner lignite bed (case 1) or higher flow rate (case 2), and lower flow rate (case 3), the *SI* values of magnetite (Fe<sub>3</sub>O<sub>4</sub>) were greater than zero after ca. 3 h, ca. 6 h, ca. 28 h, respectively, indicating that the precipitation of this mineral was not thermodynamically possible at the start of the experiments, but becomes favorable with time. In all columns, *SI* values of Fe hydroxides/oxides like Fe(OH)<sub>3</sub>, arsenic oxides, arsenolite (As<sub>2</sub>O<sub>3</sub>) and iron arsenate, scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) were less than zero, indicating that the precipitation of these minerals that are important in the immobilization of As are not thermodynamically favorable. This indicates that a portion of As is sequestered in the column experiments (Figure 4) due to the precipitation of Fe-oxyhydroxides (Figure 5). In addition, the result indicates that the mechanism of As removal with lignite is not only adsorption alone but also other processes like precipitation/co-precipitation of iron-bearing minerals.

## Conclusions

The removal of As was investigated under saturated-column experiments with different flow rates and lignite bed thicknesses. The breakthrough curves of As in all three cases were characterized by two distinct regions: a leaching and an adsorption regions. Adsorption of As onto lignite only effectively occurred after the end of the leaching region. The leaching of As could be attributed to very high concentrations of DOC that competes with As for adsorption sites. Adsorption of As at the start of the experiment was less effective most likely due to the combined effects of very low pH and very high DOC concentration. After the DOC decreased substantially, the adsorption of As onto lignite became significant. The acidic pH of the effluent was due to the oxidation of pyrite contained in the sample. In addition, the very high concentrations Fe and SO<sub>4</sub><sup>2-</sup> at the beginning of the experiments were a consequence of the dissolution of the soluble secondary minerals formed by pyrite oxidation. At the same flow rate with different lignite bed thicknesses of cases 1 and 2, greater adsorbed amount of As was occurred in a higher thickness, whereas at the same lignite bed thickness with different flow rates of cases 2 and 3, As adsorption was almost the same. Based on these results, As removal efficiency under flow-through conditions is strongly influenced by thickness of adsorbent bed but not the flow velocity. Based on the experimental and calculated results with PHREEQC, the mechanism of As removal with lignite is not only adsorption alone but also other processes like precipitation/co-precipitation of iron-bearing minerals.

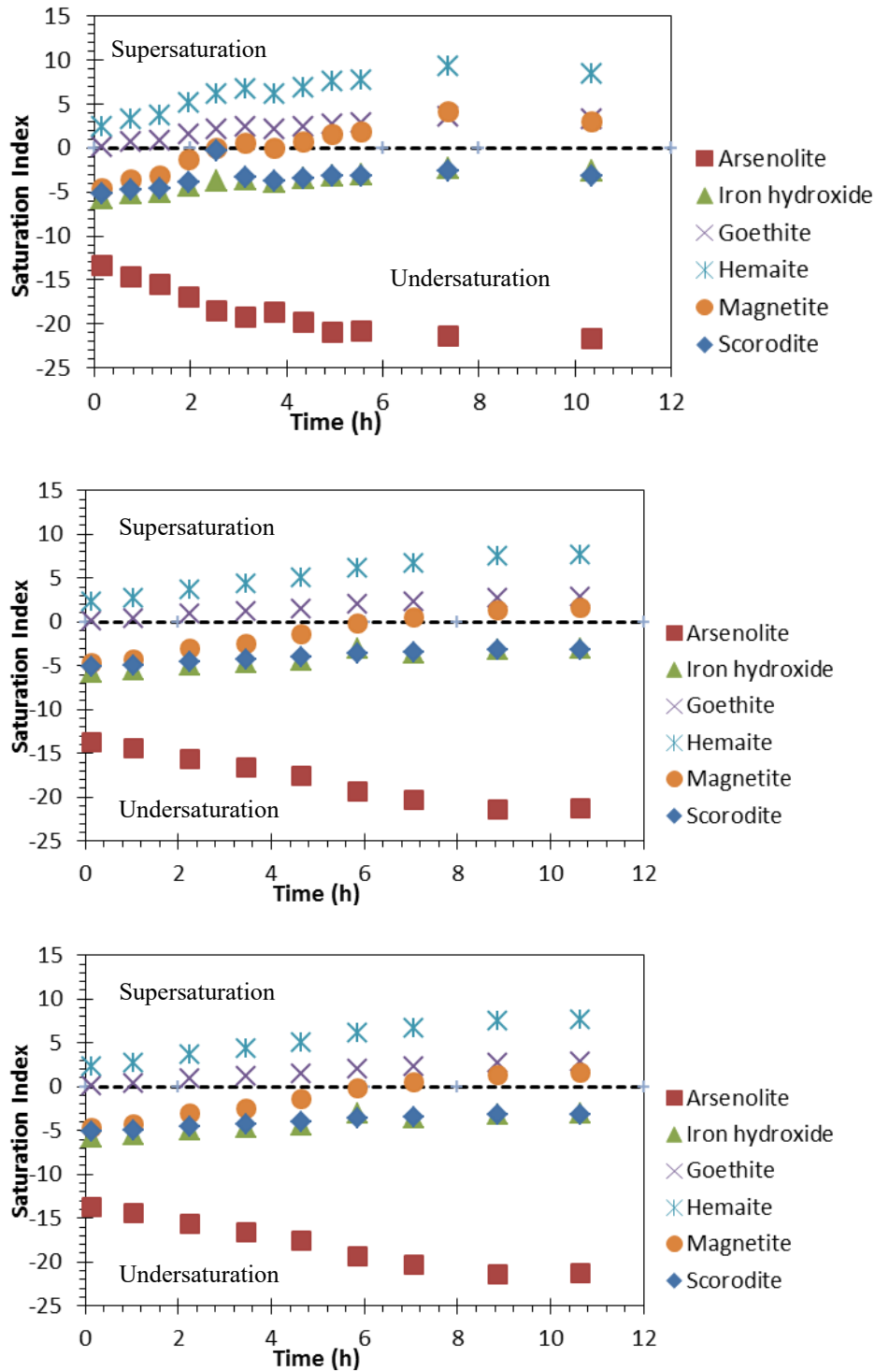


Figure 5. Saturation indices of arsenolite,  $\text{Fe}(\text{OH})_3$ , goethite, hematite, magnetite and scorodite in the column experiments (a) case 1, (b) case 2 and (c) case 3

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