

BATCH STUDIES ON ARSENIC ADSORPTION ONTO LIGNITE, BENTONITE, SHALE AND IRON SAND: EFFECTS OF pH, TIME, PARTICLE SIZE AND SULFATE CONCENTRATION

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Abstract

Arsenic (As) is a toxic element found in both natural and anthropogenic sources. High concentration of this element was recently uncovered in the groundwater of Sumbawa Island, Indonesia. To mitigate this problem, As adsorption potential of natural geological materials like lignite, bentonite, shale, and iron sand obtained in Indonesia were evaluated by batch experiments. Arsenic adsorption onto these materials was investigated as a function of solution pH, particle sizes of adsorbents and coexisting sulfate concentration. In addition, batch leaching experiments were performed to elucidate the stability of geogenic As present in all adsorbents at different pHs. The results showed that among these natural materials tested, lignite was the most effective adsorbent of As(V) followed by bentonite, shale and then iron sand, and that the amounts of As(III) adsorbed onto all adsorbents were lower than those of As(V). This indicates that As(III) is more mobile in comparison to As(V). The adsorption isotherms of As(III) and As(V) conformed to non-linear types, either Langmuir or Freundlich. It was found that adsorption of As onto these natural adsorbents was pH-dependent. This could be attributed to

the changes in the surface charges of the adsorbents with pH. With respect to the adsorbent particle size, the amount adsorbed somewhat increased with decreasing particle size, which could be explained by the larger surface area of the smaller particles. Acidic (pH < 6) and alkaline (pH > 10) conditions destabilized the geogenic As content of the adsorbents, indicating that the effectiveness of these natural materials as adsorbents is greatly limited by the pH of the contaminated system.

Keywords: Adsorption, arsenic, natural geological materials, particle size, pH

1 Introduction

Arsenic (As), which is toxic to most living organisms, creates potentially serious problems throughout the world. Arsenic contamination of the groundwater has been reported in many countries in different parts of the world. For example, high concentration of As in the groundwater of many countries like India (Das *et al*, 1994; Chattarjee and Mandal, 1995), Bangladesh (Karim, 2000; Smedley and Kinniburgh, 2002), Taiwan (Chen *et al*, 1994; Hricko, 1994), Mongolia (Fujino *et al*, 2004), and China (Hricko, 1994; Niu *et al*, 1995) used for drinking and cooking has caused symptoms of chronic As poisoning like arsenicosis and keratosis to the local hu-

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man population. Recent advances in the analysis of As as well as more detailed studies of its human health effects show that As is carcinogenic even at minute concentrations; so that the World Health Organization (WHO) lowered the provisional guideline for As concentration in drinking water from 50 to 10 $\mu\text{g/L}$ that was immediately adopted by developed countries like Japan and USA (WHO, 1993; USEPA, 2002). Arsenic can be released from natural sources as well as a variety of anthropogenic activities including mining, agriculture and combustion of coal contribute to the As contamination of the surrounding soil and groundwater (Ferguson and Gavis, 1972). In addition, depending on the redox conditions, inorganic As occurs in groundwater mostly as arsenate [As(V)] or arsenite [As(III)]. Both oxidation states are often observed due to their relatively slow arsenic redox transformations (Smedley and Kinniburgh, 2002; Lai *et al*, 2004). These redox transformations of As are important because As(III) is more mobile and toxic than As(V).

Removal of hazardous elements like As from aqueous solutions can be achieved by different technological methods which include chemical precipitation, ion exchange, adsorption, reverse osmosis, modified coagulation/filtration, modified lime softening, electro deposition and oxidation/filtration (USEPA, 2002). Among them, significant attention has centered on adsorption because of its simplicity, cheaper pollution control, ease of operation and handling, sludge-free operation, and regeneration capability. Several solid materials have been employed as adsorbents for As like activated alumina, fly ash, pyrite fines, manganese greensand, amino-functionalized mesoporous silicas, clinoptilolite and other zeolites, iron oxides, activated carbon and zero-valent iron (Subramanian *et al*, 1997; Yoshitake *et al*, 2003; Elizalde-Gonzalez *et al*, 2001; Bang *et al*, 2005; Lackovic *et al*, 2000). Although these adsorbent materials are effective, most of them are expensive. It is necessary to substitute naturally occurring materials for effective but expensive adsorbents. However, investigations involving these naturally occurring materials are few and most of these studies have been conducted using min-

erals synthesized in the laboratory (Baskan and Pala, 2011; Shevade and Ford, 2004; Pena *et al*, 2005).

Although most environmental As problems are the result of mobilization under natural conditions, contamination due to mining activities is also significant. For example, high concentration of As in the groundwater of Sumbawa Island, Indonesia has recently been uncovered. To mitigate this problem, the authors envision the use of a permeable reactive barrier (PRB) for the immobilization of As. However, a suitable adsorbent for these PRBs is still not available. Therefore, this study aims to characterize several natural geological materials and to evaluate their As(V) and As(III) adsorption properties. In the present study, lignite, bentonite, shale and iron sand are used as adsorbents of As removal from aqueous solution because they are cheap and readily available and can be applied to the remediation of contaminated sites in Indonesia. The effects of solution pH and shaking time on As were also evaluated because these parameters are known to be sensitive. In addition, the effects of particle sizes of the adsorbents and SO_4^{2-} concentration on the adsorption of As were also elucidated. Special consideration was given to SO_4^{2-} because it has been reported as having a moderate negative effect on the adsorption of As onto Fe and Al oxyhydroxides and the contaminated groundwater in Sumbawa Island has substantial SO_4^{2-} concentration (ca. 1500 mg/L) (LAPI-ITB, 2009). Moreover, equilibrium isotherm models were applied to predict the adsorption capacity of each adsorbent. Finally, we elucidated the stability of geogenic As found in all adsorbents at different pH values.

2 Materials and Methods

2.1 Sample collection

The materials used as adsorbents in this research were natural geological materials collected in Indonesia: lignite from Samigaluh, Kulon Progo area; bentonite from Punung, Pacitan, East Java; shale from, Bogor, West Java; and iron sand from Glagah beach, Kulon Progo



Figure 1: Location of the sampled places of adsorbents.

area. The location of the sampled places is shown in Figure 1.

2.2 Sample preparation and characterization

Prior to experiments, the geological materials were air-dried, crushed and sieved through 0.125, 0.25, 0.5 and 1 mm aperture screens to segregate into different particle sizes. For the chemical and mineralogical analysis, parts of these materials were further ground into $<50 \mu\text{m}$. To identify the mineralogical composition, an X-ray diffractometer (XRD), Multiflex (Rigaku Corporation, Japan), was employed while the chemical composition was determined using an X-ray fluorescence spectrometer, Spectro Xepos (Rigaku Corporation, Japan). After drying the samples ($<2 \text{ mm}$) in an oven at 110°C for 24 hr, loss on ignition (LOI) was determined through gravimetry by heating the sample inside a furnace at 750°C for 1 hr. Total organic carbon (TOC) content of all adsorbents was analyzed using TOC-L Total Organic Carbon Analyzer coupled with a Solid Sample Module SSM-5000A (Shimadzu Corporation, Japan). Specific surface area and total pore volume of the adsorbents were measured by N_2 adsorption using the BET method. After degassing under vacuum at 120°C , the amount

of adsorbed N_2 was determined at constant temperature (77 K) by using Beckman Coulter SA 3100 (Beckman Coulter Inc., CA). Variations of the zeta potential with pH were obtained using NanoZS 90 (Malvern Instruments Ltd., UK). The amount of sample used in this analysis was 10 mg with particle size of $<50 \mu\text{m}$. The pH was adjusted using 0.1 M of hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions.

2.3 Adsorption experiments

Batch adsorption tests were performed to determine the adsorption performance of the geological materials to remove As. Both As(V) and As(III) solutions were prepared by dissolving reagent grade disodium hydrogen arsenate heptahydrate $[\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}]$, and diluting arsenic standard solution for atomic adsorption spectrometry (As_2O_3 and NaOH in water, pH 5.0 with HCl, Wako Pure Chemistry Industry Ltd., Japan), respectively. The adsorption experiments were carried out in 250 mL flasks. One gram of each material was added to 100 mL of As(V) or As(III) solution with concentrations of 1–50 mg/L, and then the mixture was shaken at room temperature for 24 hr at 120 rpm until adsorption equilibrium was attained. After mixing, the pH and redox

potential (ORP) of suspensions were immediately measured and the suspensions were filtered using 0.45 μ m Millex® sterile membrane filters ((Merck Millipore, USA). The suspensions of bentonite and shale samples were centrifuged at 3,000 rpm for 20–25 min before filtration. Arsenic concentrations before and after mixing were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan).

The effect of shaking time on the adsorbed amount of As(V) and As(III) were investigated using the best three adsorbents of As: lignite, bentonite and shale. This was done by using a constant As initial concentration and amount of adsorbent added. For As(V), 0.5 g of lignite, 1 g of bentonite or 1 g of shale were added to 2 mg/L of As(V) solution. On the other hand, 2 g of each adsorbent were mixed with 2 mg/L of As(III) solution. The mixing period ranged from 1 to 48 hr.

The effect of pH on As adsorption was examined by setting initial As concentration ranging 1 to 5 mg/L and adsorbent added ranging 1 to 2 g. The contact time was fixed at 24 hr. The initial pH of the solution was adjusted by dropping hydrochloric acid (HCl) or sodium hydroxide (NaOH) solution resulting in suspension pH values from 2–10.

To investigate the effects of particle size, the best two adsorbents of As(V) (i.e., lignite and bentonite) were used. In addition to these two adsorbents, shale was also used in the As(III) adsorption experiments because there were not so significant differences in the amounts of As(III) onto on these three adsorbents. The adsorption experiments were carried out with adsorbents of variable sizes (0.125–1mm) by using the same initial As concentration and adsorbent dosage. For the adsorption of As(V), 1 g of lignite or bentonite were added to 100 mL of As solution with concentrations of 5 and 3 mg/L; respectively. For As(III) adsorption, 100 mL of As(III) solution with concentration of 2 mg/L and 2 g of adsorbent were mixed.

The effects of SO_4^{2-} concentration were investigated using solutions with variable concentrations of SO_4^{2-} (500, 1000, 1500 and 2000 mg/L)

and 10 mg/L of As(V). For this experiment, 1 g of lignite and 5 g of bentonite, respectively, were mixed with 10 mg/L As(V) solution containing SO_4^{2-} .

2.4 Adsorption isotherms

Equilibrium isotherms were obtained from batch adsorption experiments. The adsorbed amount of As (q) per unit adsorbent mass was calculated using the follow equation:

$$q = \frac{(C_o - C_e) V}{m} \quad (1)$$

where, q is the adsorbed amount (mg/g), C_o is the initial As concentration (mg/L), C_e is the concentration of As at equilibrium (mg/L), m is the amount of adsorbent added (g), and V is the volume of solution (L).

To investigate the adsorption isotherms, the equilibrium data obtained in the different adsorbent-solute systems were fitted with the linear, Langmuir and Freundlich models. The linear isotherm was calculated as follows:

$$q = K_d C_e \quad (2)$$

where, K_d is the distribution coefficient (L/g). The Langmuir isotherm was fitted using the following equation:

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

A linear form of this equation is rewritten as following:

$$\frac{C_e}{q} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

where, K_L (L/mg) is the Langmuir constant related to adsorption energy expressing how strong the adsorbate is attached onto surfaces, q_m is the maximum adsorption capacity (mg/g). The Langmuir model assumes monolayer adsorption onto a surface with a finite number of identical sites.

The Freundlich isotherm is an empirical equation based on the adsorption onto heterogeneous surfaces that describes the relationship between the adsorbed amount (mg/g) and these remaining in solution (mg/L) (Limousin *et al*, 2007).

$$q = K_F C_e^n \quad (5)$$

K_F and n are Freundlich constants that are related to the adsorption capacity and adsorption intensity, respectively. According to the Freundlich equation, the isotherm does not reach a plateau as C_e increases (Limousin *et al*, 2007).

2.5 Leaching experiments

The leaching experiments were conducted by mixing 15 g of sample and 150 mL of prepared leachants. Variable concentrations of HCl and NaOH solutions were used as leachants to yield final suspension pH in the range of 2 to 13. The suspensions were shaken under the same conditions as those of the batch adsorption experiments. After 24 h, the suspensions were filtered and the filtrates were analyzed for As using ICP-AES. For As concentrations less than 0.1 mg/L, the filtrates were pretreated and analyzed using the hydride generation process coupled with the ICP-AES. For the pretreatment of filtrates with low As concentrations, 30 ml of the leachate sample was mixed with 15 ml of 12 M HCl, 2 ml of 20% potassium iodide (KI) solution, and 1 ml of 10% ascorbic acid solution and then diluted with deionized water to 50 ml.

3 Results and Discussion

3.1 Characterization of the adsorbents

The chemical compositions of geological materials used as adsorbent in this study are shown in Table 1. Although lignite contains 13.6 wt.% Fe, 9.37 wt.% is associated with pyrite and the remainder (4.18 wt.%) with Fe_2O_3 by considering its mineralogical properties (Figure 2). The As content of lignite is 1.8 mg/kg with high sulfur content of 10.8 %. Total organic carbon content (TOC) of lignite is 32.3 %, which means that it has appreciable amounts of volatile matter. The As contents of bentonite, shale and iron sand are 5, 14.5, 2 mg/kg, respectively, with low sulfur contents. The As content of shale is slightly higher than the average As concentration of sedimentary rock (around 5-10 mg/kg) (Webster, 1999).

Table 2: The BET surface area and total pore volume of adsorbents.

Sample	Surface area (m ² /g)	Total pore volume (ml/g)
Lignite	7.53	0.016
Bentonite	126	0.176
Shale	27.3	0.045
Iron sand	0.905	0.003

The mineralogical compositions of the adsorbents are shown in Figure 2. The prominent mineral phase observed in lignite is pyrite [FeS_2] as shown in Figure 2a. However, there are several smaller, but well defined peaks that correspond to orpiment [As_2S_3]. The minerals detected in bentonite are primarily silicate minerals such as, montmorillonite, halloysite, kaolinite and quartz (Figure 2b). Prominent peaks of quartz and kaolinite were also detected in shale (Figure 2c). The main minerals observed in iron sand are magnetite [Fe_3O_4] and albite [(Na,Ca)Al(Si,Al)₃O₈] (Figure 2d).

The specific surface areas and total pore volumes of the adsorbents are shown in Table 2. Among the adsorbents, bentonite exhibited the highest specific surface area (126 m²/g), followed by shale (27.3 m²/g), lignite (7.53 m²/g) and then iron sand (0.905 m²/g). Total pore volume of bentonite was the highest (0.175 mL/g), followed by shale (0.045 mL/g), lignite (0.016 mL/g) and iron sand (0.003 mL/g).

The zeta potentials of the adsorbents as a function of pH are shown in Figure 3. Lignite had two PZCs at pH 2.4 and 7.0. This means that lignite has a positively charged surface between pH 2.4 and 7.0, and has a negatively charged surface at pH less than 2.4 and greater than 7.0. In contrast, iron sand had a single PZC at pH 5.5, indicating that this adsorbent has a positive charged surface at pH less than 5.5 and a negatively charged surface at pH greater than 5.5 (Figure 3b). Bentonite and shale had negatively charged surfaces in the entire pH range without PZCs (Figures 3c-d).

Table 1: Chemical composition of adsorbents.

Sample	SiO ₂ (wt.%)	TiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	MnO (wt.%)	MgO (wt.%)	CaO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	P ₂ O ₅ (wt.%)	S (wt.%)	TOC (wt.%)	As (mg/kg)	LOI (wt. %)
Lignite	3.64	1.47	1.67	4.18	0.03	0.12	0.25	1.06	0.04	0.08	10.8	32.3	1.8	74.4
Iron sand	40.0	4.18	8.07	37.5	0.53	7.31	10.4	0.99	0.61	0.61	0.0007	0.148	2	1.29
Bentonite	62.7	1.38	24.7	9.13	0.03	2.89	1.73	0.09	0.02	0.0005	0.009	-	5	8.87
Shale	66.0	1.15	11.3	4.42	0.07	3.23	3.07	0.18	2.16	0.02	0.44	0.764	14.5	6.97

Note: In lignite, FeS₂ was calculated using wt. % of S and the remainder of Fe as calculated as Fe₂O₃.

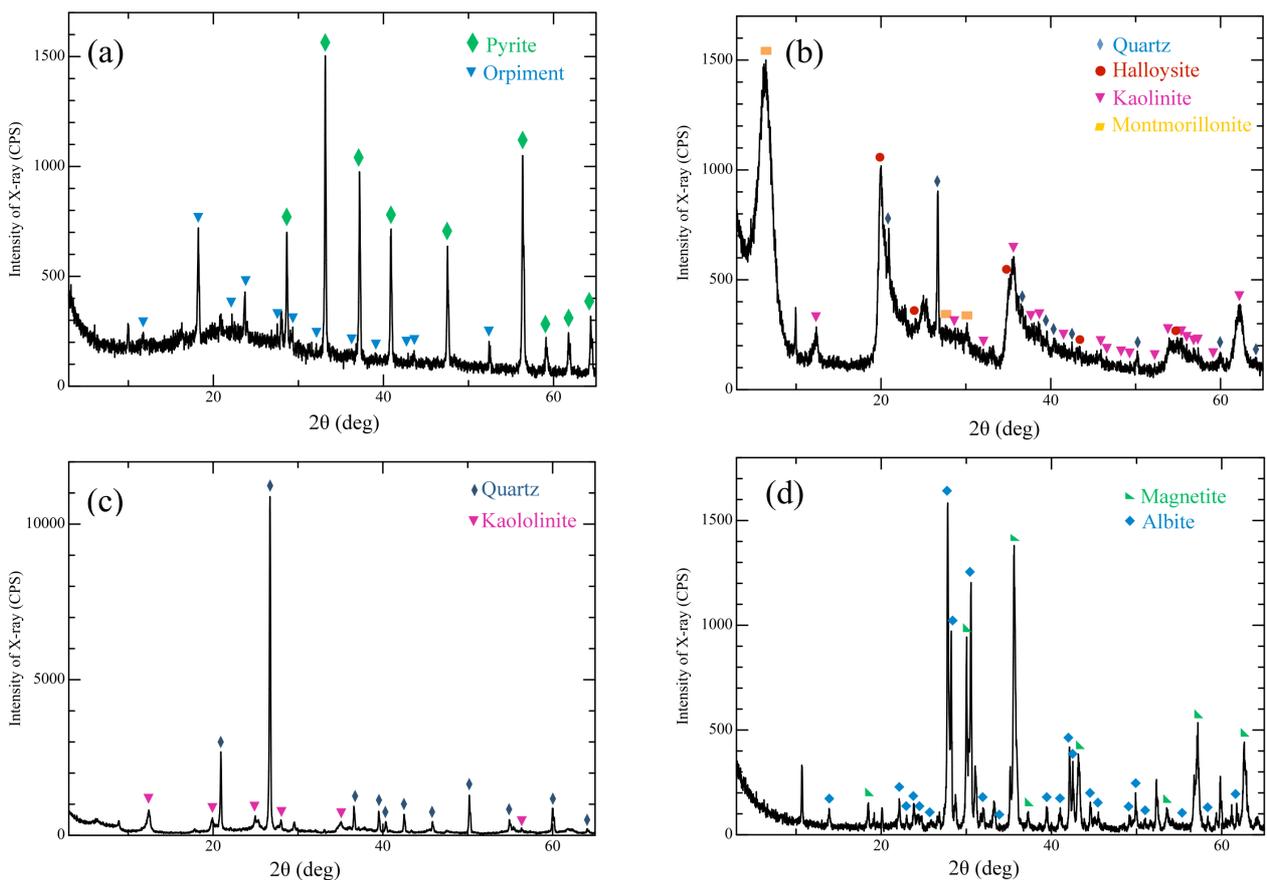


Figure 2: X-ray diffractograms of (a) lignite, (b) bentonite, (c) shale and (d) iron sand.

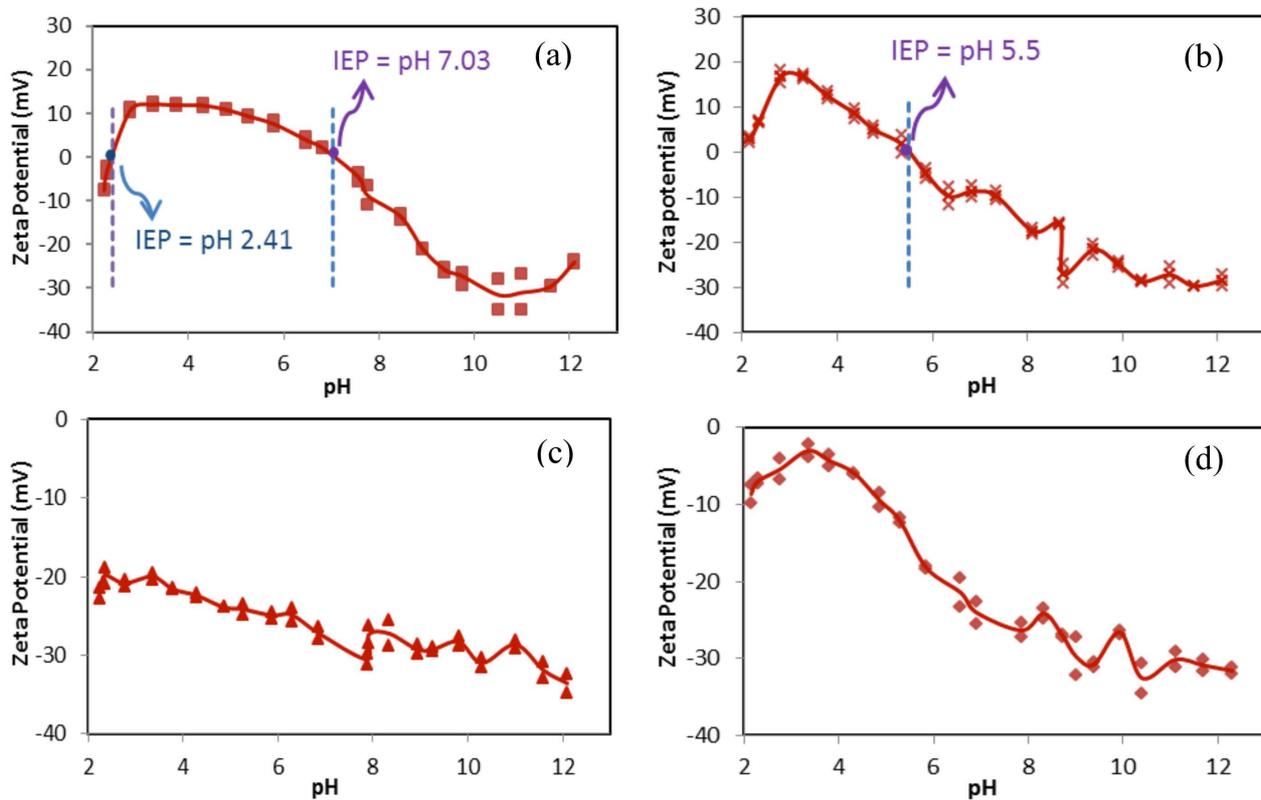


Figure 3: Zeta potential analysis of (a) lignite, (b) iron sand, (c) bentonite and (d) shale.

3.2 Effect of shaking time

Figure 4 shows the effect of shaking time on the adsorption of As(V) and As(III) onto lignite, bentonite and shale. Apparent equilibrium was reached after several hours for lignite whereas 24 to 48 hours was required to reach equilibrium for bentonite and shale.

3.3 Effect of pH

The effect of pH on the adsorption of As(V) and As(III) is shown in Figure 5. From these results, As(V) adsorption was most favorable in the pH range of 3–8 for lignite and 2–7 for bentonite and shale. However, the amount of As adsorbed decreased dramatically at $pH > 8$. In contrast, adsorption of As(V) onto iron sand was negligible in the entire pH range (Figure 5a). These indicate that arsenate adsorption was favored from pH 4 up to circumneutral pH and then gradually decreases with pH.

Thermodynamics dictates that As(V) exist in an aqueous solution in the pH range of 3 to

12 as negatively charged oxyanionic species ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) (Figure 6). On the other hand, the surface charge of adsorbents, which is controlled by the transfer reactions of proton between the solution and the mineral surface, is positive, negative or equal to zero depending on the pH (Kundu *et al*, 2004). In the pH range corresponding to the predominance of $H_2AsO_4^-$ (pH 2–7), the surface charge of lignite was positive, thus the electrostatic attraction between the anionic species and the positively charged surface sites was promoted. On the other hand, at pH values greater than 7.0, the surface of charge becomes more electronegative, resulting in the decrease of As adsorption onto lignite.

The amount of adsorbed As(V) onto bentonite and shale decreased above neutral pH value (Figure 5a). Although the surface charges of bentonite and shale were negative in the entire pH range, positive charges could be created due to edge defects, that is, protonation of broken Al-OH bonds exposed at particle edges

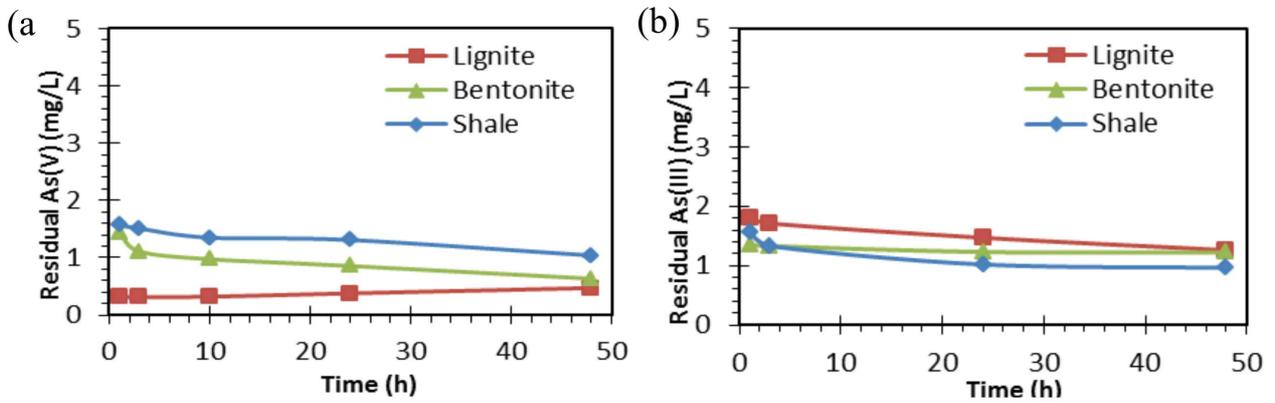


Figure 4: Effect of shaking time on the adsorption of (a) As(V) and (b) As(III).

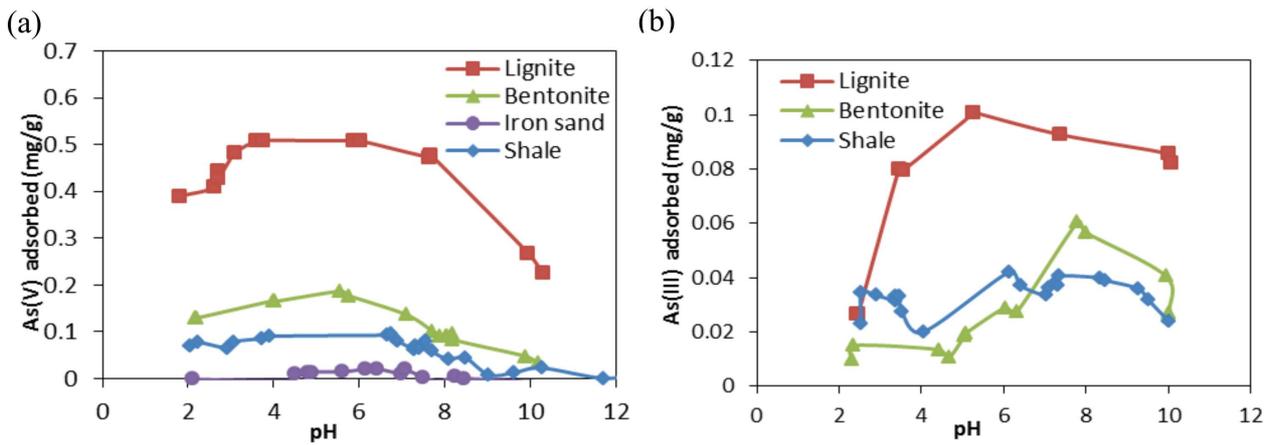


Figure 5: Effect of pH on the adsorption of (a) As(V) and (b) As(III).

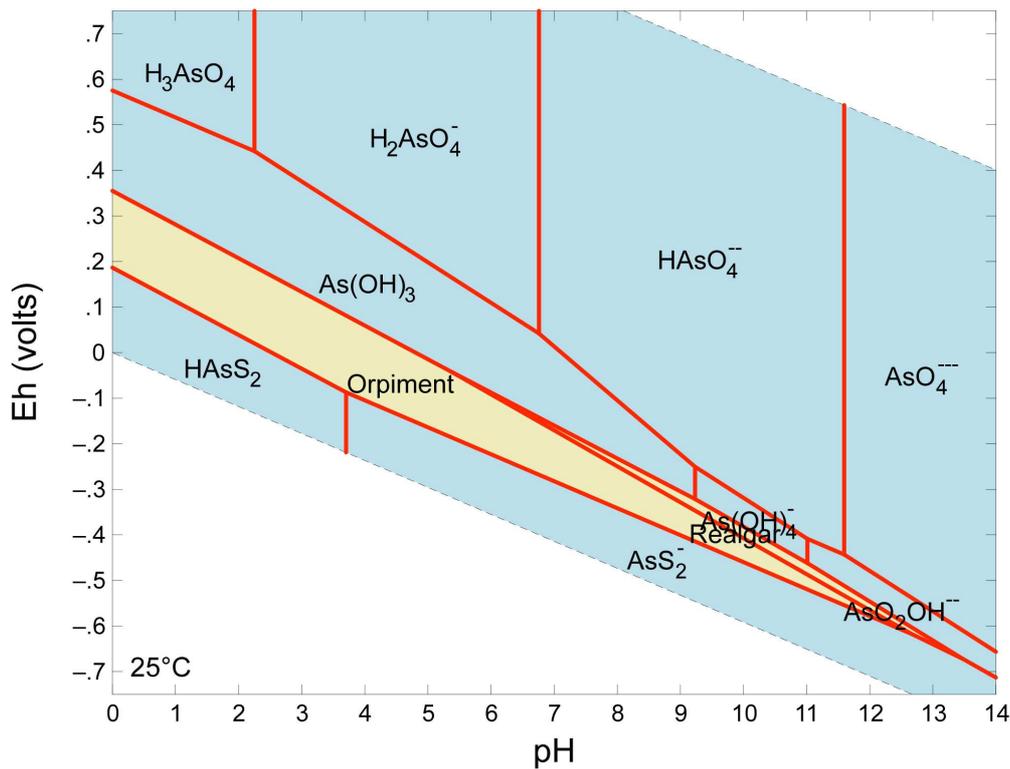


Figure 6: Eh – pH predominance diagram of As at 25°C, 1.013 bars, activity As = 10⁻⁶ and activity SO₄²⁻ = 10⁻².

leading to anion adsorption at these sites (Lin and Puls, 2000). Aluminum silicate minerals with edge defects like kaolinite and halloysite were found in substantial amounts in bentonite and shale (Figures 2b-c). Consequently, the adsorption of As may also occur due to the broken Al-OH bonds at particle edges of minerals (Lin and Puls, 2000).

In case of As(III) adsorption, the maximum amount adsorbed was observed at pH>4 for lignite, whereas favorable adsorption took place at pH 8 for bentonite and at 6–9 for shale (Figure 5b). Arsenite mainly occur as an uncharged oxyanion [H₃AsO₃] in the pH range of 2–9 (Figure 6). However, this uncharged As(III) oxyanion [H₃AsO₃] deprotonates to the charged H₂AsO₃⁻ oxyanion at pH>9. As a result, greater As(III) removal was observed at low pH value (pH 4–10) for lignite due to its positively charged surface (Figures 3 and 5).

Consequently, the amounts of As(III) adsorbed onto bentonite and shale were less than that of As(V) because of the less favorable elec-

trostatic interactions between the positively charged particle edges and the uncharged H₃AsO₃ oxyanion. In addition, the adsorbed amount on bentonite was higher than shale, which could be attributed to the higher surface area of bentonite.

3.4 Effects of particle size

The effects of the particle size of adsorbents on the adsorption of As(V) and As(III) are shown in Figure 7. It can be seen that decreasing the particle size of the adsorbents somewhat increased the amount of As adsorbed, which could be attributed to the increasing surface area of the particle with decreasing particle size. A bigger surface area means higher concentration of active sites for adsorption on the surface of the adsorbents that enhance the adsorption of As. However, the effects of the particle size were not so obvious. This means that lignite and shale are the promising adsorbents used in PRBs by considering the permeability.

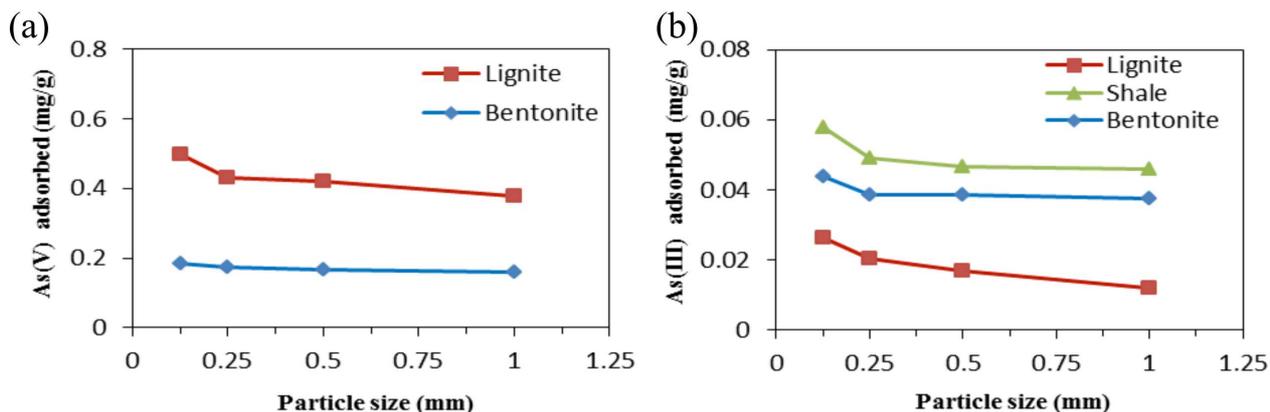


Figure 7: Effects of particle size on the adsorption of (a) As(V) and (b) As(III).

3.5 Effects of sulfate concentration

The effects of concentrations of coexisting SO_4^{2-} on the adsorption of As(V) onto lignite and bentonite are shown in Figure 8. Although SO_4^{2-} has been reported to have moderate negative effects on As adsorption at concentrations greater than 250 mg/L onto Al and Fe-oxyhydroxides (Sun *et al*, 2006; Asta *et al*, 2009), it was found that SO_4^{2-} did not have any noticeable effect on the adsorption of As onto lignite. However, SO_4^{2-} appears to have a slight positive effect on As(V) adsorption onto bentonite especially at low adsorbent dosage (1 g/100 mL) (Figure 8b). These results indicate that the effects of SO_4^{2-} on As adsorption is largely dependent on major functional groups or minerals available in the adsorbent. This could be attributed to inability of SO_4^{2-} ions to form any insoluble layers with these natural adsorbents, which could prohibit the diffusion of dissolved As species (Kundu *et al*, 2004).

3.6 Adsorption isotherms

The adsorption isotherms of As(V) are shown in Figure 9. Linear, Langmuir and Freundlich equations are applied to the obtained results. From this figure, nonlinear adsorption isotherms like Langmuir and Freundlich types fitted better with the observed results than the linear one for all adsorbents.

The linear, Langmuir and Freundlich model parameters and their corresponding statistical fits to the adsorption data are given in Table 3.

The values of R in the Langmuir and Freundlich types were higher than that of the linear type, which indicates that the adsorption of As(V) cannot be expressed by the linear adsorption isotherm. In addition, the fitted curves showed that lignite had the highest As(V) adsorption capacity at 10.9 mg As/g, followed by bentonite (0.33 mg As/g), shale (0.14 mg As/g) and iron sand (0.024 mg As/g). This means that the best adsorbent for As(V) in this study is lignite and the order of adsorption capacity is as follows: lignite > bentonite > shale > iron sand. The adsorption capacity (q_m) results mentioned above correspond to the pH interval of 2.8–3 for lignite, 6.5–7 for bentonite, 7.5–7.8 for shale and 6.7–6.8 for iron sand.

For As(III) adsorption, the amounts of adsorbed onto all adsorbents were lower than those of As(V) (Figure 10). According to R values in Table 3, nonlinear type adsorption isotherms fitted better than the linear isotherm for lignite, bentonite and shale whereas the linear type is more applicable to iron sand. Lignite had the highest adsorption capacity, followed by bentonite and shale similar to those observed in the adsorption of As (V). The maximum As(III) adsorption capacity (q_m) shown in Table 3 is limited to the pH interval of 2.5–2.7 for lignite, 6.2–6.7 for bentonite and 7.5–7.8 for shale. The better fit of the Langmuir isotherm to the experimental data indicates monolayer adsorption of As(V) and As(III) onto the adsorbents except As(III) adsorption onto iron sand. Non-linear isotherms also suggest progressive

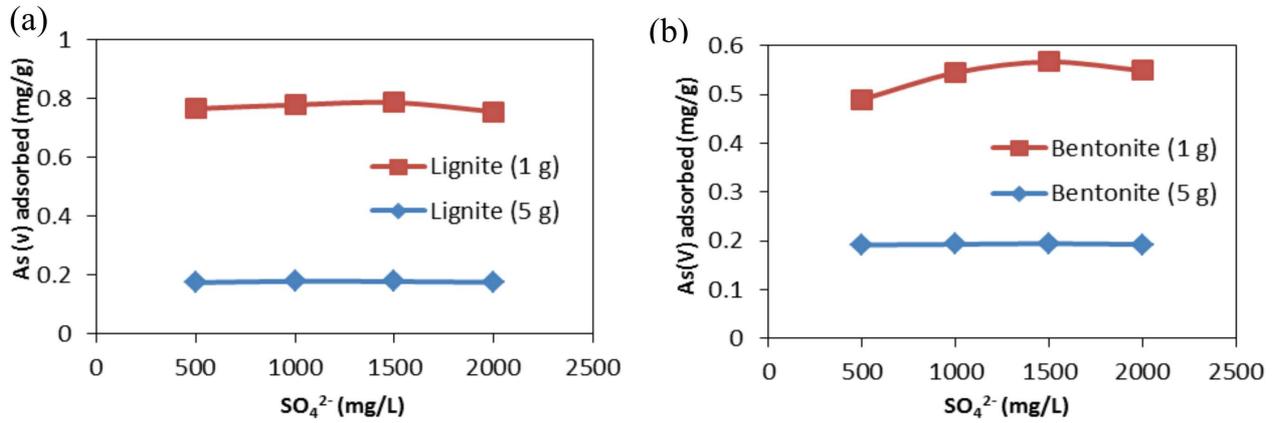


Figure 8: Effects of SO_4^{2-} on the adsorption of As(V) onto (a) lignite and (b) bentonite.

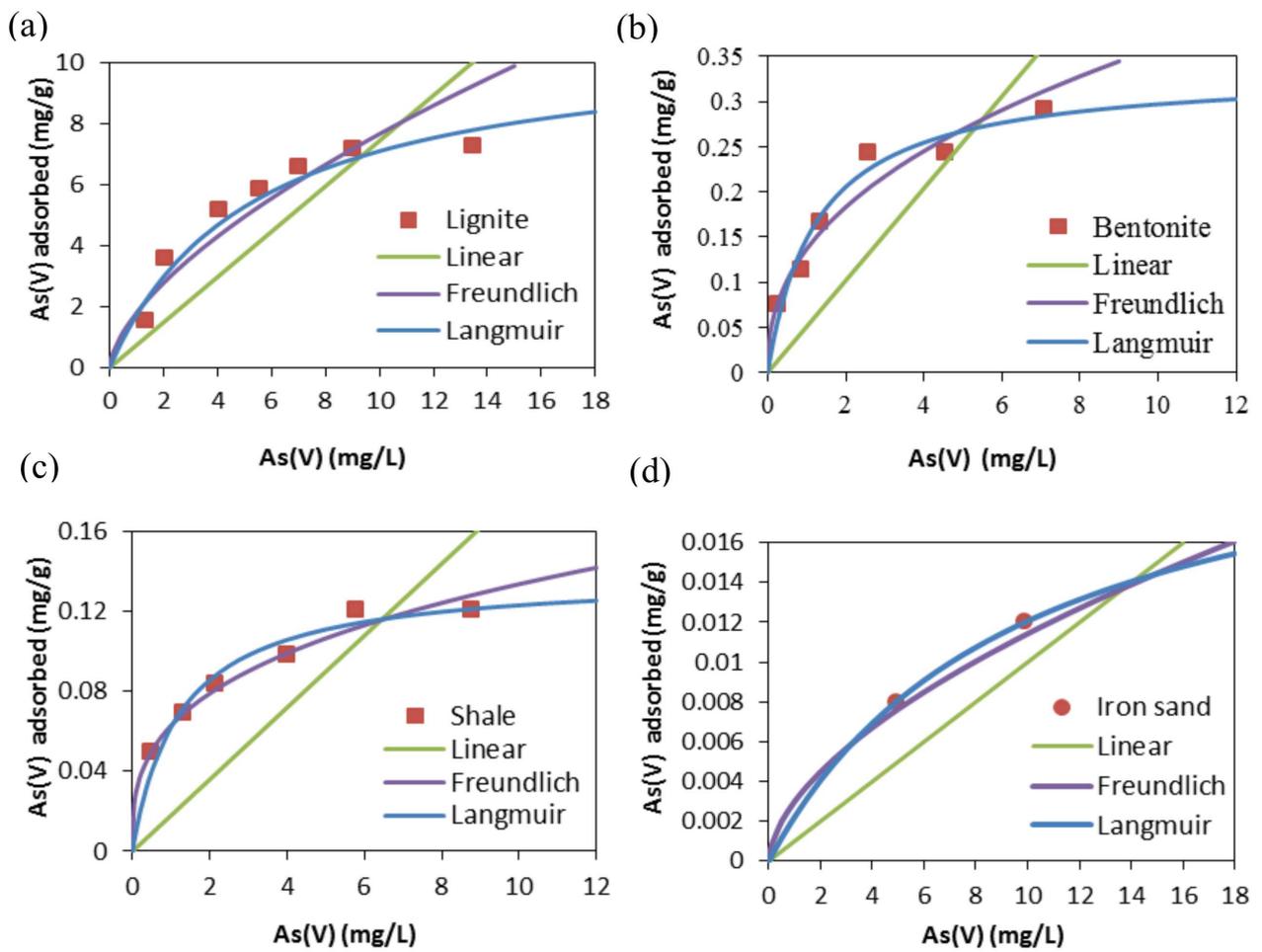


Figure 9: Adsorption isotherms of As(V) onto (a) lignite, (b) bentonite, (c) shale and (d) iron sand.

Table 3: Fitted parameters and correlation coefficients of linear, Langmuir and Freundlich isotherms calculated based on the least squares method.

Isotherm parameters	Lignite		Bentonite		Shale		Iron sand	
	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)
Langmuir								
K_L (L/mg)	0.189	0.068	0.799	0.11	0.818	0.385	0.103	-
q_{max} (mg/g)	10.9	0.324	0.334	0.317	0.138	0.181	0.024	-
R	0.946	0.748	0.99	0.997	0.995	0.995	1	-
Freundlich								
K_f (L/g)	1.799	0.022	0.137	0.032	0.063	0.049	0.003	-
n_f	0.63	0.752	0.42	0.755	0.327	0.524	0.581	-
R	0.926	0.981	0.978	0.998	0.99	0.987	1	-
Linear								
K_d (L/g)	0.745	0.013	0.052	0.020	0.018	0.019	0.001	0.005
R	0.427	0.911	-0.1	0.961	-0.98	0.632	0.768	0.982

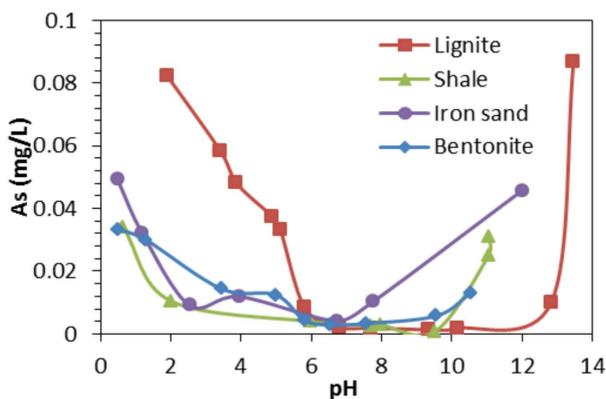


Figure 11: Leaching behaviors As from lignite, bentonite, shale and iron sand with pH.

saturation of the adsorbent, leading to the proportional decrease of adsorption with increasing As concentration (Limousin *et al*, 2007).

3.7 Leaching experiments

The leaching behavior with pH of geogenic As contained in all adsorbents is shown in Figure 11. The results show that the leaching of geogenic As was strongly pH dependent. Enhanced release of geogenic As occurred under both acidic and alkaline conditions while a minimum was observed around the circumneutral pH range.

The release of As was minimal in the pH

range of 6 to 10 for lignite, shale and bentonite and at pH 3 to 7 for iron sand. On the other hand, at pH values above 10 and below 6, the concentration of As in the leachate significantly increased. The maximum amount of As released from lignite was observed at pH 2 and 13 at 0.08 and 0.09 mg/L, respectively. For shale, the highest concentration of As was observed at pH 1 and 11 amounting to 0.03 mg/L. Similarly, the amount of As released from bentonite was highest at very acidic pH (pH = 1). For iron sand, As concentration increased at pH values below 3 and above 7 reaching a maximum at pH 1 and 12 (0.05 mg/L). The experimental results indicate that the effectiveness of these natural materials as adsorbents is greatly limited by the pH of the contaminated system.

4 Conclusion

The preliminary study was conducted to determine the As adsorption properties of several naturally occurring adsorbents. Lignite was the most effective adsorbent for As(V) and followed by bentonite, shale and then iron sand. On the other hand, the amounts of As(III) adsorbed onto all adsorbents were lower than those of As(V). This indicates that As(III) is more difficult to immobilize through adsorption in comparison to As(V). The adsorp-

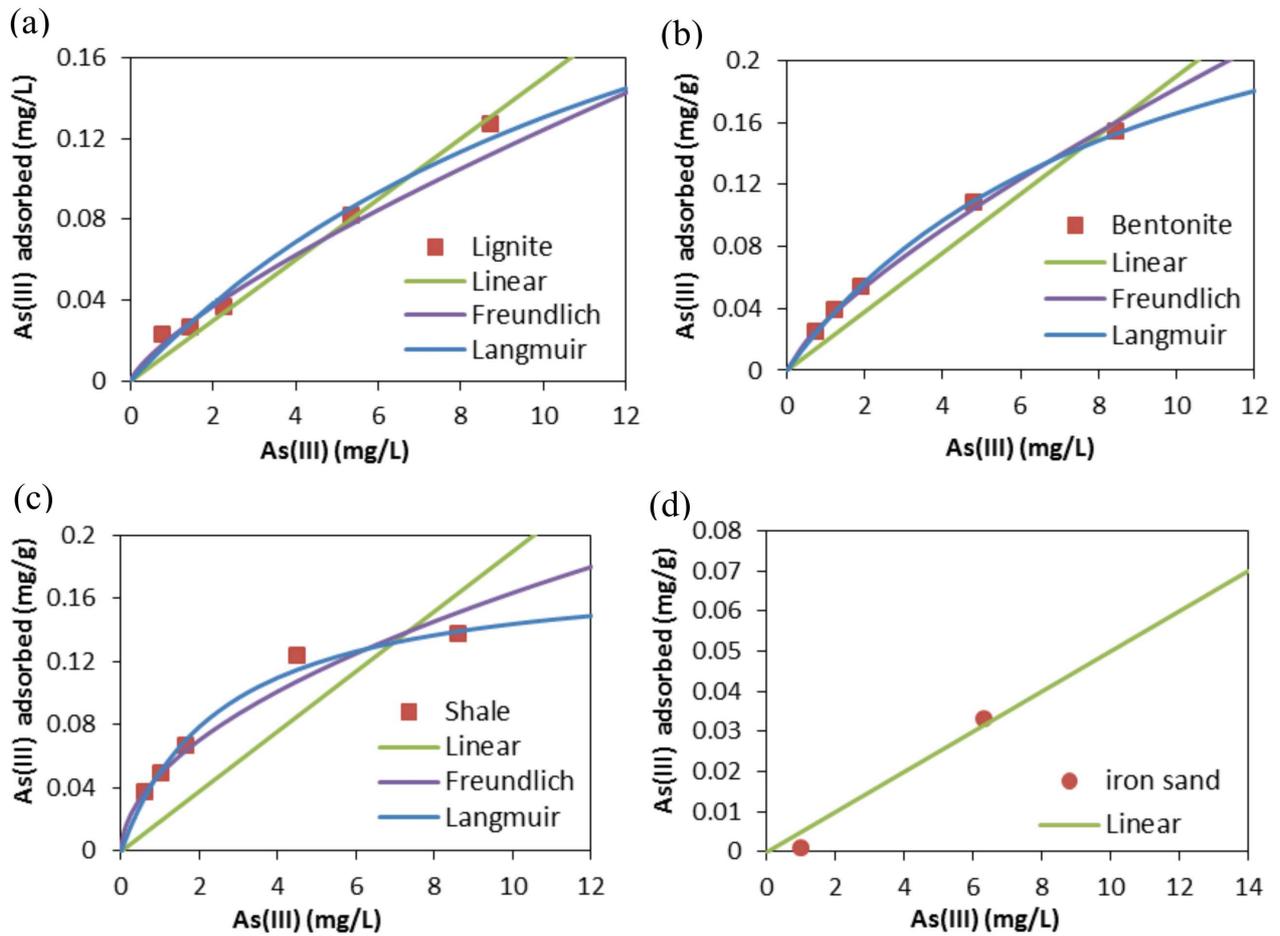


Figure 10: Adsorption isotherms of As(III) onto (a) lignite, (b) bentonite (c) shale and (d) iron sand.

tion equilibrium data fitted well with nonlinear models for all adsorbent regardless of the chemical forms of As. The amount of adsorption was pH-dependent, and the maximum amount of adsorption was observed at around circum-neutral pH regardless of the adsorbent and the chemical forms of As. The zeta potential measurements helped to explain the changes in the amounts of adsorbed As based on the electrostatic attraction/repulsion of As species and the surface of the adsorbents. The effects of particle sizes of adsorbents were not so obvious. Although SO_4^{2-} did not have any noticeable effect on the adsorption of As onto lignite, it appeared to have a slight positive effect on As(V) adsorption onto bentonite. From the results of batch leaching tests, acidic ($\text{pH} < 6$) and alkaline ($\text{pH} > 10$) conditions destabilized the geogenic As of the adsorbents, indicating that the effectiveness of these natural materials as adsorbents is greatly limited by the pH of the contaminated system.

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