Characterization of Natural Geological Materials; Lignite, Bentonite, Shale and Sand for Arsenic Removal

Kyu Kyu Mar, D. Karnawati, D.P.E. Putra, Sarto, T. Igarashi, C.B. Tabelin

Abstract— Natural geological materials such as lignite, bentonite, shale and sand were collected from Java Island, Indonesia. The mineralogical, chemical and physical properties of these materials were characterized by XRD, XRF, N_2 adsorption using BET method, zetasizer, TOC-L coupled with a Solid Sample Module. In addition, batch leaching experiments were performed to elucidate the stability of geogenic arsenic (As) present in the natural geological materials at different pHs. Finally, As adsorption potential of lignite, bentonite, shale and sand were evaluated by batch experiments. The results showed that acidic (pH < 6) and alkaline (pH >10) conditions destabilized the geogenic As content of the adsorbents. It means that the effectiveness of these natural materials as adsorbents is greatly limited by the pH of the contaminated system. Among these natural geological materials, lignite was the most effective adsorbent of As(V) followed by bentonite, shale and then sand whereas 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 nonlinear types, either Langmuir or Freundlich.

Keywords— Adsorption isotherm, Adsorption, Arsenic, Leaching, Natural geological materials

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1. INTRODUCTION

ARSENIC (As) is a very toxic element which is naturally found in nature only in trace amount. However, elevated As concentration can occur in soils and water due to the release of As from As-bearing sediments. In addition, numerous anthropogenic sources including mining, agriculture and combustion of coal contribute to the As contamination of the surrounding soil and groundwater [1]. Arsenic contamination of the groundwater has been reported in many countries in different parts of the world like India [2], [3], Bangladesh [4], [5], Taiwan [6], [7], Mongolia [8] and China [7], [9]. When utilized as drinking and cooking purposes, groundwater contaminated with As has caused symptoms of chronic As poisoning like arsenicosis and keratosis to the local human population [10], [11], [12], [13]. Due to its highly toxicity, the World Health Organization (WHO) lowered the provisional guideline for As concentration in drinking water from 50 to 10 µg/L that was immediately adopted by developed countries like Japan and USA [14], [15]. Therefore, As-contaminated groundwater should not be used for drinking and cooking purposes without proper pre-treatment to remove As.

Removal of hazardous elements like As from aqueous solutions can be achieved by different technological

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methods which include ion exchange, chemical precipitation, adsorption, reverse osmosis, modified coagulation/filtration, modified lime softening and oxidation/filtration [15]. Among these methods, significant attention has centered on adsorption because of its simplicity, cheaper pollution control and ease of operation and handling. 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 [16], [17], [18], [19], [20]. Although these adsorbent materials are effective, most of them are expensive. It is necessary to substitute naturally occurring materials for effective but expensive adsorbents.

Recent hydro-geochemical surveys in Sumbawa Island, Indonesia observed that As concentrations in the groundwater were ca. 10- to 100-fold higher than the WHO provisional drinking water guideline. It may be due to the several decades of mining activities in this area. 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 so that As-adsorption potential of naturally occurring geological materials obtained near the contaminated area were investigated. Therefore, this study aims to characterize natural geological materials and As adsorption properties of these materials. Characterization also includes batch leaching experiments to elucidate the stability of geogenic As present in the natural geological materials at different pHs. In this research, lignite, bentonite, shale and sand were 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 shaking time on As were also evaluated to investigate the equilibrium

time. Finally, equilibrium isotherm models were applied to predict the adsorption capacity of each adsorbent.

2 MATERIALS AND METHODS

2.1 Sample Collection and Preparation

The natural geological materials used as adsorbents in this study were collected in Java Island, Indonesia: lignite from Samigaluh, Kulon Progo area, Central Java and bentonite from Punung, Pacitan, East Java, shale from, Bogor, West Java; and iron sand from Glagah beach, Kulon Progo area. (Fig. 1). After collecting, these samples were brought back to the laboratory, air-dried, crushed and sieved through 18 mesh (particle size of <2 mm) aperture screens. For the chemical and mineralogical analysis, parts of these materials were further ground into < 50 µm. The prepared samples were stored in airtight containers to minimize its exposure to moisture.

2.2 Sample Characterization

The mineralogical composition of the geological materials was investigated using an X-ray diffractometer (XRD), Multiflex (Rigaku Corporation, Japan), while the chemical composition was determined using an X-ray fluorescence spectrometer, Spectro Xepos (Rigaku Corporation, Japan). Both analyses were done using pressed powders of the geological materials. After drying the samples (< 2 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 h. 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). For this analysis, the container were heated in oven at 900 °C about 20 min. After heating the container, it was cool down and then about 0.05 to 0.1 g of < 50 µm particle size of sample was put to the container and ready for analysis.

Specific surface area and total pore volume of the adsorbents were measured by N_2 adsorption using the BET (Brunauer-Emmett-Teller) 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). 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 µm. The pH was adjusted using 0.1 M of hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions.

Fig. 1. Location of the sampled places of adsorbents.

2.3 Batch Leaching Experiments

It is important to evaluate the leaching properties of natural geological materials before the adsorption experiments because some materials, though good adsorbents, tend to increase the concentrations of unwanted solutes in the final effluent or lower/raise its pH to undesirable values. 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 at room temperature for 24 h at 120 rpm. After mixing, the suspensions were filtered and As concentrations in the filtrates were analyzed by using an inductively couples plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Japan). 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.

2.4 Batch Adsorption Experimetnts

Batch adsorption tests were conducted to determine the adsorption performance of the geological materials to remove As. While As(V) solutions were prepared by dissolving reagent grade disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4.7H_2O$), As(III) solutions were prepared by 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).

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 µm Millex® sterile membrane filters (Millipore Corporation, USA). The suspensions of bentonite and shale samples were centrifuged at 3,000 rpm for 20-25 min before filtration. After filtration, the solutions were stored in the containers and ready for analysis. Arsenic concentrations in the solution before and after experiments were analyzed by using the ICP-AES.

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 adsorbed amount of As (q) per unit absorbent mass was calculated using the follow equation:

$$q = (C_0 - C_e)V/m \qquad (1)$$

where, q is the adsorbed amount (mg/g), C_0 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:

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

where, K_d is the distribution coefficient (L/g).

3 RESULT AND DISCUSSION

3.1 Mineralogical, Chemical and Physical Properties of the Adsorbents

The mineralogical and chemical compositions of geological materials: lignite, bentonite, shale and sand used as adsorbent in this study are shown in Fig. 2 and Table 1, respectively. As can be seen in Fig. 2, the prominent mineral phase observed in lignite is pyrite (FeS_2) (Fig. 2(a)). 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, hallosite, kaolinite and quartz (Fig. 2(b)). Prominent peaks of quartz and kaolinite were also detected in shale (Fig. 2(c)). The main minerals observed in sand are magnetite (Fe_3O_4) and albite (($Na,Ca)Al(Si,Al)_3O_8$) (Fig. 2(d)).

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 (Table 1 and Fig. 2). The As content of lignite is 1.8 mg/kg with high sulfur content of 10.8 wt.%. Total organic carbon content (TOC) of lignite is 32.3 wt.%, which means that it has appreciable amounts of volatile matter. Bentonite contains substantial amounts of amorphous Al and Fe phases (Al_2O_3 24.7 wt.% and Fe_2O_3 9.13 wt.%) which are higher than that contains in shale (Al_2O_3 11.3 wt.% and Fe_2O_3 4.42 wt.%) as shown in Table 1. The As contents of bentonite, shale and sand are 5, 14.5, and 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) [21].

N_2 adsorption using BET method results showed that bentonite exhibited the highest specific surface area (126 m²/g), followed by shale (27.3 m²/g), lignite (7.53 m²/g) and then sand (0.905 m²/g) (Table 2). Similarly, 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 sand (0.003 mL/g).
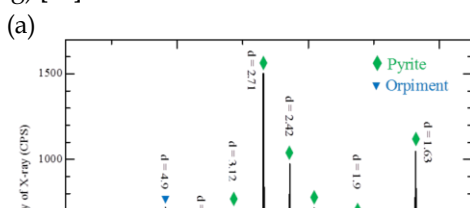
(a)

TABLE 1

CHEMICAL COMPOSITION OF GEOLOGICAL MATERIALS

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
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
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

TABLE 2

THE BET SURFACE AREA AND TOTAL PORE VOLUME OF ADSORBENTS

Sample	Surface area (m2/g)	Total pore volume (mL/g)
Lignite	7.53	0.016
Bentonite	126	0.176
Shale	27.3	0.045
Sand	0.905	0.003

Fig. 3. Zeta potential analyses of (a) lignite, (b) bentonite, (c) shale and (d) sand.

Fig. 3 represents the zeta potentials of the adsorbents as a function of pH. Lignite had two PZCs (point of zero charge) at pH 2.4 and 7.0 (Fig. 3(a)). This means that lignite had 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, bentonite and shale had negatively charged surfaces in the entire pH range without PZCs (Fig. 3(b) and (c)). On the other hand, 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 (Fig. 3(d)).

3.2 Batch Leaching Experiments

The leaching behavior with pH of geogenic As contained in all adsorbents is shown in Fig. 4. Enhanced release of geogenic As occurred under both acidic and alkaline conditions while a minimum was observed around the circumneutral pH range. The results show that the leaching of geogenic As was strongly pH dependent.

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 sand. On the other hand, at pH values above 10 and below 6, the concentration of As in the leachate significantly increased.
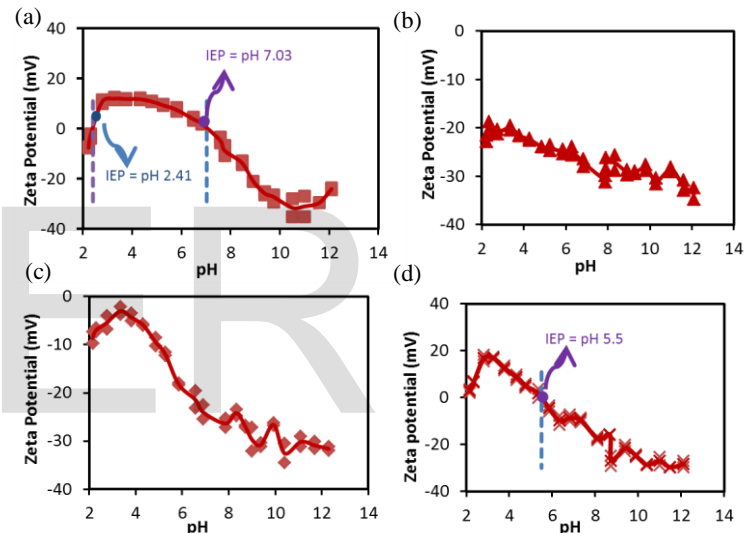
The maximum amount of As released from lignite was observed at pH 2 and 13 with the concentrations of 0.08 and 0.09 mg/L, respectively. For bentonite, the highest concentration of As was observed at very acidic pH (pH = 1) amounting to 0.03 mg/L. Similarly, the amount of As released from shale was highest (0.03 mg/L) at pH 1 and 11. For 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.

3.3 Batch Adsorption Experiments

1) Effect of shaking time: Fig. 5 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 on both As(V) and As(III) adsorbtion.
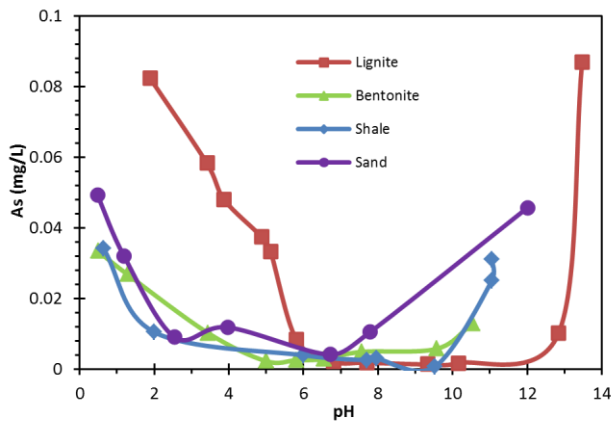
Fig. 4. Leaching behaviors As from lignite, bentonite, shale and sand at different pHs.
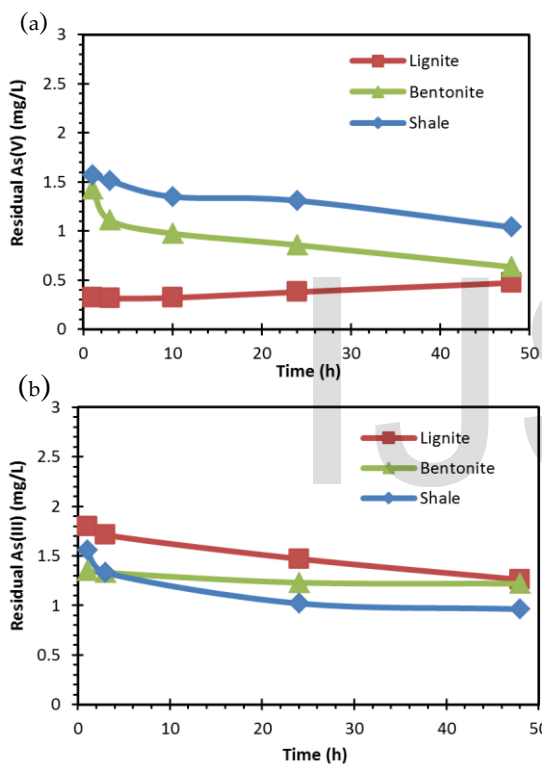

Fig. 5. Effect of shaking time on the adsorption of (a) As(V) and (b) As(III).

2) Adsorption Isotherms: Linear, Langmuir and Freundlich equations are applied to the obtained results. As shown in Fig. 6, As(V) adsorption onto all adsorbents fitted better with nonlinear adsorption isotherms like Langmuir and Freundlich types than the linear one. As shown 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. The maximum adsorption capacity (q_m) of As(V) were found to be 10.9, 0.33, 0.14 and 0.024 mg/g onto lignite, bentonite, shale and sand, respectively. 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 > sand. For As(III) adsorption, the amounts of As adsorbed onto all adsorbents were lower than those of As(V) (Fig. 7). Similar to As(V), the adsorption of As(III) onto lignite, bentonite and shale fitted better with nonlinear type whereas the linear type is more applicable for sand. The adsorption capacity of the samples was dependent on the relative abundance of the functional component/mineral responsible for As adsorption. These functional components are carbon and FeS_2 in lignite and amorphous/crystalline Al and Fe bearing phases in bentonite, shale and sand. The adsorption of As(V) and As(III) onto lignite could be attributed to the incorporation of arsenic in FeS_2, and precipitated as arsenic sulfide [22], [23]. In addition, the aqueous oxyanions (such as $H_2AsO_4^-$ or $HAsO_4^{2-}$) undergo a ligand exchange reaction with iron speciation on the carbon surface and form an inner-sphere monodentate or bidentate surface complex [24], [25]. Moreover, the ability of adsorbents to sequester As is primarily dependent on their net surface charge. Lignite has higher As adsorption capacity than bentonite even though bentonite has a larger surface area. This is due to the zeta potential distribution with pH, lignite has positive charge the pH value between 2.4 and 7.03 whereas bentonite have negative charge at the entire pH range (Fig. 3(a) and (b). Moreover, the major chemical form of As(V), $H_2AsO_4^-$ species is dominant at pH range between 2 and 7. Therefore, the electrostatic attraction between the anionic species and the positively charged surface sites was promoted. On the other hand, As(III) mainly occur as an uncharged oxyanion (H_3AsO_3) in the pH range of 2-9. Consequently, the adsorption of As(III) on lignite was decreased. Bentonite has negative charge at the entire pH range (Fig. 3(b)). As a result, the adsorbed amount of As on bentonite was lower than that of lignite. Because the main mechanism by which As attaches to the adsorbent is via electrostatic attraction (i.e., negative charges are attracted to positive charges and vice versa).

In the cases of bentonite and shale, both of them have net negative charge during adsorption (Fig. 3(b) and (c)). However, bentonite contains more clay minerals like montmorillonite than shale (Fig. 2(b) and (c)). The mineral phases that adsorbed arsenic in both of these materials are the clays such as kaolinite and montmorillonite. Therefore, the higher adsorbed amount of As on bentonite than that of shale could be due to the higher contents of clays in bentonite relative to shale. In addition, specific surface area and total pore volume should be considered in the adsorption capacity of the material which has same functional components. For example, bentonite and shale have same functional components, but the adsorption capacity of As(V) and As(III) on the former was slightly higher than the later. These differences could be attributed to the larger surface area and greater total pore volume of bentonite compared to shale. However, in the present study the adsorbed amount of sand was very low (0.024 mg/g). This could be attributed to the lower content of Al and Fe bearing phases in sand and it's very low specific surface area (0.905 m²/g).
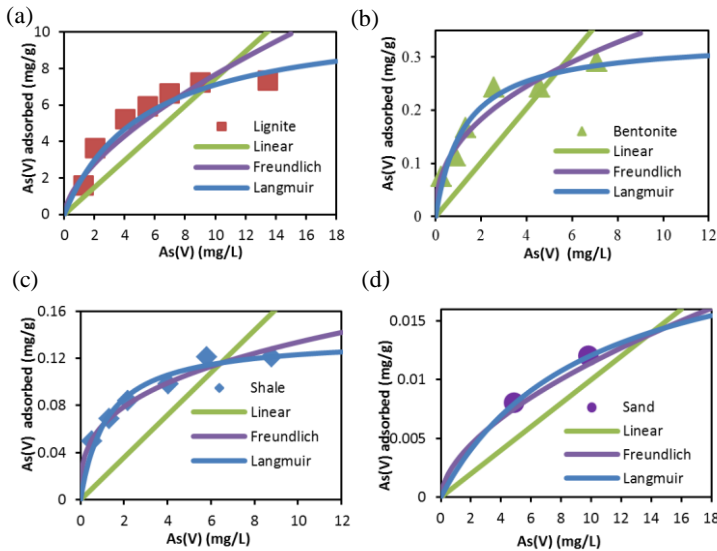
Fig. 6. Adsorption isotherms of As(V) onto (a) lignite, (b) bentonite, (c) shale and (d) sand.
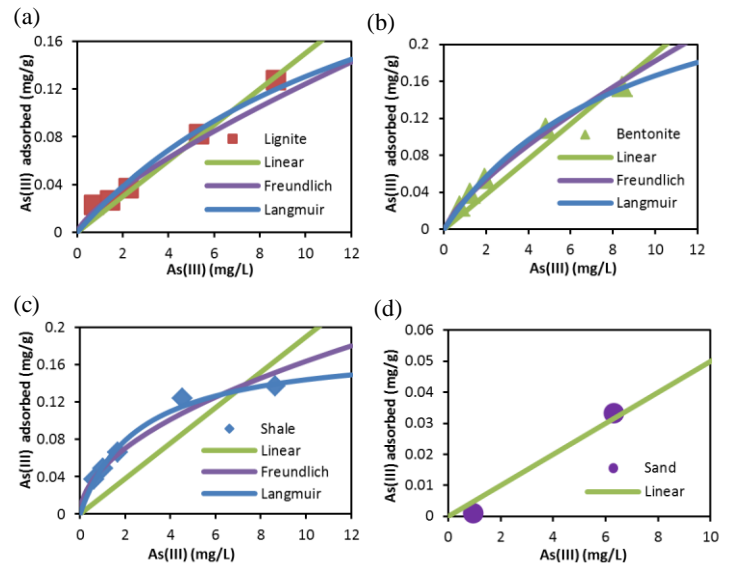

Fig. 7. Adsorption isotherms of As(III) onto (a) lignite, (b) bentonite, (c) shale and (d) sand.

TABLE 3
FITTED PARAMETERS AND CORRELATION COEFFICIENTS (R) OF LINEAR, LANGMUIR AND FREUNDLICH ISOTHERMS CALCULATED BASED ON THE LEAST SQUARE METHODS

	pH	Langmuir			Freundlich			Linear	
		K_L	q_{max}	R	K_f	n_f	R	K_d	R
Lignite									
As(V)	2.8 - 3	0.189	10.9	0.947	1.799	0.63	0.926	0.745	0.427
As(III)	2.5 - 2.7	0.068	0.324	0.748	0.022	0.752	0.981	0.013	0.911
Bentonite									
As(V)	6.5 - 7	0.799	0.334	0.99	0.137	0.42	0.978	0.052	-0.1
As(III)	6.2 - 6.7	0.11	0.317	0.997	0.032	0.755	0.998	0.020	0.961
Shale									
As(V)	7.5 - 7.8	0.818	0.138	0.995	0.063	0.327	0.99	0.018	-0.98
As(III)	7.5 - 7.8	0.385	0.181	0.995	0.049	0.524	0.987	0.019	0.632
Sand									
As(V)	6.7 - 6.8	0.103	0.024	1	0.003	0.581	1	0.001	0.768
As(III)	6.5 - 6.7	-	-	-	-	-	-	0.005	0.982

4 CONCLUSIONS

The preliminary study was performed to determine the As adsorption properties of lignite, bentonite, shale and sand. Lignite was the most effective adsorbent for As(V) and followed by bentonite, shale and then sand. Lignite was suitable adsorbent for As removal technologies, considering that it is naturally abundant and relative low cost materials. The amounts of As(III) onto both adsorbents were lower than that of As(V). This indicates that As(III) is more difficult to immobilize through adsorption in comparison to As(V). The adsorption equilibrium data fitted well with nonlinear models for all adsorbents regardless of the chemical forms of As. From the results of batch leaching tests, acidic (pH < 6) and alkaline (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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