International Journal of GEOMATE, Oct., 2020, Vol.19, Issue 74, pp.22–30
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2020.74.9176
Geotechnique, Construction Materials and Environment

EXAMINATION OF CRUSHED LATERITE BRICK FOR REMOVAL OF CHROMIUM AND ARSENIC FROM WASTEWATER

*Arachchillage Buddhika Priyadarshani Bandara[1], Gajanayaka Mudalige Pradeep Kumara[2], Akihiro Matsuno[3], Takeshi Saito[4], Tran Thi Viet Nga[5], and Ken Kawamoto[6]

[1-4]Science and Engineering, Saitama University, Japan
[5,6]National University of Civil Engineering, Vietnam

*Corresponding Author, Received: 16 June 2019, Revised: 03 May 2020, Accepted: 17 May 2020

ABSTRACT: Adsorption is one of the highly efficient methods to treat heavy metals in wastewater. Due to their economic feasibility, the use of locally available low-cost adsorbents has received much attention, especially in developing countries. The objective of this study was to investigate the applicability of laterite grains made from crushing laterite brick in Vietnam (0.105–2 mm) for the removal of chromium (Cr) and arsenic (As) from wastewater. For comparison, commercially available zeolite and Autoclaved Aerated Concrete (AAC) grains were tested. A series of laboratory tests for examining the effects of the initial metal concentration, initial solution pH, background ion concentration (ionic strength), and solid-to-liquid (S:L) ratio on adsorption and desorption characteristics were carried out. The test results showed that the Langmuir model captured well all obtained data in concentration range of 0–2,000 mg/L for laterite grains, suggesting that monolayer adsorption dominantly occurred. The measured maximum adsorption capacities of laterite grains were 8.2 mg/g and 1.3 mg/g for As and Cr, and the laterite grains gave a relatively high As adsorption compared to previously reported materials. The removal efficiencies of Cr and As were dependent on initial pH and S:L ratio, and lower initial pH and S:L ratio gave higher removal % for all tested adsorbents. Based on the results for desorption tests, laterite grains gave a higher hysteresis index for As (480%) compared to those from zeolite (128%) and AAC (176%), indicating that the tested laterite in this study possessed a strong irreversibility for adsorbed As (i.e. As immobilization). Consequently, laterite grains have a high potential as a low-cost adsorbent for As removal from wastewater.

Keywords: Wastewater, Chromium, Arsenic, Adsorption, Laterite

1. INTRODUCTION

Rapid industrialization and economic growth trigger significant population increases, especially in developing countries, inducing many serious environmental issues including contamination of the water on the earth. One of the most harmful contaminants in water is heavy metals, and these contaminants often affect human health adversely through serious biological accumulation. Among the heavy metals, chromium (Cr) and arsenic (As) are considered more hazardous contaminants to human health. Approximately 200 million people in the world suffer from As-contaminated drinking water [1]. The harmful metal shows some negative risks to human health, causing serious damages to digestive, respiratory, circulatory organs, and neural systems. For example, cancers in lung, skin, kidney, and bladder are induced by As uptake [2]. Cr contamination of water is generally derived from leather tanning, metal industry, electroplating, and mining of the metal [3]. The carcinogenic effect of Cr on human body is also strong. Dermatitis, lung cancer, and rhinitis are possible in the case of Cr uptake. Therefore, it is highly essential to treat the contaminated water before discharging it into the environment. Especially in developing countries, insufficient treatment of industrial wastewater causes deterioration of water quality. Hence, development of effective and efficient treatment technologies are markedly essential resolving this serious environmental issue.

Chemical precipitation, coagulation, membrane technologies, and ion exchange [4-6] are utilized as common wastewater treatment methods. However, high initial, maintenance, and operation costs are needed for applying these high-technology methods. Recently, adsorption treatment techniques for heavy metal removal have received considerable attention due to their high efficiency [7]. Various adsorbent materials applied and evaluated in previous studies include geomaterials [2,8-11], biosorbents [12-16], and metal oxides/hydroxides [17,18]. Development of low-cost adsorbents is highly essential to improve the economic feasibility and user friendliness, specially in developing countries. Even though cationic metals can be successfully removed from wastewater by adsorption, removal of anionic metal contaminants, including Cr and As, is insufficient yet.

According to previous studies, adsorptions onto Fe and Al oxides/hydroxides are mainly responsible for Cr and As removal [2,7,19]. Laterite produced under strong oxidizing conditions is a common product in tropical and subtropical areas. The material consists mainly of Fe, Al, and Si, creating a positive surface charge which promotes adsorption of anionic metals [12]. There are few previous studies investigating the adsorption of As and Cr as anionic chemical forms by locally available geological materials such as laterite.

The objective of this study was therefore to investigate the applicability of laterite grains from Vietnam as a locally available and low-cost adsorbent for Cr and As removal from wastewater. A series of batch adsorption and desorption experiments were performed under different initial metal concentrations, initial solution pH, background ion concentrations (ionic strength), and solid-to-liquid ratio conditions using highly concentrated Cr and As synthetic wastewater. The performance of laterite was compared with that of commercially available zeolite (common adsorbent) and Autoclaved Aerated Concrete (AAC) (adsorbent from industrial by-products) grains, both from Japan.

2. MATERIALS AND METHODS

2.1 Adsorbent Preparation and Physicochemical Characterization

Laterite brick (hereafter, laterite) from Vietnam was selected to investigate Cr and As adsorption characteristics. Commercially available AAC and zeolite from Japan were used as reference materials to characterize the adsorption properties of laterite. All tested materials were crushed by hand and sieved, and finally 0.105–2 mm grains were used for all the following experiments. Determinations of basic physicochemical properties such as pH, Electrical Conductivity (EC), gravimetric water content of air-dried grains, specific gravity, Loss Of Ignition (LOI), and Brunauer-Emmett-Telle (BET) surface area (TriStar II, Micromeritics, USA) were carried out for all three tested materials. The Point-of-Zero Charge (PZC) was determined by the potentiometric titration method. All three materials were titrated with H^+ (0.1M HCl) and OH^- (0.1M NaOH) at four different KCl concentrations, 1, 0.1, 0.05, and 0 M (Fujifilm Wako Pure Chemical Corp., Japan). Further characterization of chemical and mineralogical compositions was performed by energy-dispersive X-ray spectroscopy (X-Max Extreme, Oxford Instruments, UK) and X-ray diffractometry (XRD-7000, Shimazu Corp., Japan) analyses.

2.2 Batch Adsorption Experiments

Adsorption experiments under full contact conditions were carried out according to a standard batch method recommended by the Organization of Economic Cooperation and Development (OECD) [20]. Chemical grade reagents K_2CrO_4 and H_3AsO_4 (Fujifilm Wako Pure Chemical Corp.) with more than 98% purity were used to prepare Cr and As adsorbates (i.e. synthetic wastewater), respectively. Triplicate samples of each adsorbent (material) and each adsorbate (metal) mixed as 1:10 solid-to-liquid (S:L) ratio were prepared in 50 mL centrifuge tubes (Violamo centrifuge tube, Sigma-Aldrich, USA). They were shaken by a reciprocating shaker for 24 h at 100 rpm and 20°C. Subsequently, the tubes were centrifuged at 8,000 rpm for 15 min. The supernatants were filtered using a 0.22 µm membrane filter (GSWP02500, Millipore Sigma, USA), and they were diluted and analyzed for each metal (Cr and As) concentration based on atomic adsorption spectrophotometry (AA-6200, Shimadzu Corp., Japan). Before and after the adsorption process, pH and EC values were measured by a portable pH and EC meter. All experimental conditions are summarized in Table 1.

2.3 Effect of Initial Metal Concentration on Cr and As Adsorption

Batch experiments for adsorption of each metal onto all three materials were performed at natural pH by applying different initial metal concentrations of 0–2,000 mg/L to estimate the adsorption intensity of metals onto adsorbents and maximum metal adsorption capacity. Observed experimental results were evaluated using two classical isotherm models, Langmuir [Eq. (1),21] and Freundlich [Eq. (2),22].

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{1}$$

Table 1 Summary of all batch experiments and their test conditions.

Metal solution	Type of experiment	Particle size (mm)	Solid to liquid ratio	Initial metal concentration C_i (mg/L)	Initial pH	Background solution
Single metal solution (Cr or As)	Isotherm	0.105-2	1:10	0-2000	Natural pH*	Deionized water
	pH	0.105-2	1:10	500	2-10	$NaNO_3$ (0-0.1 M)
	Ionic strength	0.105-2	1:10	500	2-10	$NaNO_3$ (0-0.1 M)
	Desorption	0.105-2	1:10	500	Natural pH*	Deionized water

*Observed adsorbent pH when it dissolved in deionized water.

$$\text{Log}Q_e = \text{Log}K_f + \frac{1}{n}\text{Log}C_e \quad (2)$$

where C_e is the equilibrium metal concentration (mg/L), Q_e is the amount adsorbed per adsorbent at equilibrium (mg/g), b is the Langmuir constant related to binding strength (g/L), Q_m is the maximum adsorption capacity (mg/g), K_f is the Freundlich adsorption capacity (L/g), and $1/n$ is the adsorption intensity.

2.4 Effect of Initial pH and Background Ion Concentration on Cr and As Adsorption

Batch adsorption experiments were performed for each metal at 500 mg/L under several pH conditions from 2 to 10 adjusted by either 1 M HCl or 1 M NaOH. Each metal adsorbate was prepared in four different background solutions (ionic strengths: 0.1, 0.01, 0.001, and 0 M) produced by a reagent of $NaNO_3$. All tested tubes were maintained as a 1:10 S:L ratio. The removal % for each metal was calculated based on [Eq. (3),23].

$$\text{Removal \%} = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

where C_i is the initial metal concentration (mg/L) and C_e is the equilibrium metal concentration (mg/L).

2.5 Effect of Solid-to-Liquid Ratio on Cr and As Adsorption

The effect of S:L ratio on each metal adsorption was investigated by using three different ratios, 1:5, 1:10, and 1:30. In this experiment, the initial concentration of 500 mg/L for each metal was applied under natural pH condition.

2.6 Desorption Experiments for Adsorbed Metals

Desorption experiments were performed to evaluate reversibility and irreversibility of adsorption of metals onto all three materials according to the sequential decant-refill technique [24]. After the batch adsorption experiment under the natural pH condition, 10 mL of the supernatant was immediately removed. Then, the tested tubes were refilled with 10 mL of deionized water to maintain the S:L ratio of 1:10. The sequential desorption process was repeated more than three times to complete the desorption evaluation.

Data acquired in this experiment were evaluated by the Freundlich model [Eq. (2)], and the adsorption-desorption hysteresis was quantified based on the hysteresis index [Eq. (4)].

$$\omega = \left[\left(\frac{n_a}{n_d}\right) - 1\right] \times 100 \quad (4)$$

where ω is the hysteresis index (%), n_a is the adsorption intensity, and n_d is the desorption intensity according to the Freundlich model [Eq. (2)]. Reversible and irreversible metal adsorptions are theoretically characterized by $n_a = n_d$ or $n_a < n_d$ and $n_a > n_d$, respectively. Higher irreversibility of the adsorbed metals represents a higher ω value [25].

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Adsorbents

The basic physicochemical properties of tested adsorbents highly affect adsorption of metals from the liquid to solid phase. These properties of laterite, AAC, and zeolite were investigated, and the results are shown in Tables 2 and 3. Laterite is specially characterized by the relatively low pH value of 4.2 and slightly high BET surface area of 29 m^2/g among all three tested materials. A higher BET surface area can be an important indicator of higher adsorption capacity. Based on the chemical and mineralogical analyses, laterite consists mainly of Fe_2O_3, Al_2O_3, and SiO_2, which may be due to the presence of quartz, $Al_2Si_2O_5(OH)_4$, goethite, and hematite. Hematite and goethite are Fe-rich minerals, and they likely improve the positive surface charge governed by lower pH conditions, suggesting high potential for adsorption of As and Cr as anionic chemical forms [13]. Actually, the PZC for laterite was around pH 6 to 9 as determined by potentiometric titration in this study.

The adsorbent, AAC has an alkaline pH, probably due to significant OH- release in an aqueous solution. The main mineral compositions of quartz, tobermorite, anhydrite, gypsum, and illite were observed in AAC. Based on a previous study, AAC showed positive ζ-potential under pH 4, while the potential was negative over pH 7 [26].

Table 2 Basic physicochemical properties of laterite, AAC and zeolite.

Properties	Laterite	AAC	Zeolite
Particle size (mm)	0.105-2	0.105-2	0.105-2
Water content (%)	0.7	10.2	0.04
Natural pH	4.2	10	8.4
EC (mS/cm)	0.02	1.8	5.6
LOI (%)	24	10.8	1.1
Specific gravity	3	2.5	2.7
BET surface area (m^2/g)	29	23.6	22.2
Point of zero charge (pH)	6-9	—	7.5-9.5
ζ-potential pH4 (mV)	—	1.3*	—
ζ-potential pH7 (mV)	—	-6.4*	—

*Taken from a previous study [26].

Table 3 Chemical compositions of laterite, AAC, and zeolite (wt. %).

Adsorbent	Composition (wt. %) – XRF								Mineral Composition – XRD
	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MnO	CaO	H_2O	Other	
Laterite	28.22	27.91	25.59	3.66	0.12	0.09	11.67	2.74	SiO_2 (quartz), $Al_2Si_2O_5(OH)_4$, FeO(OH), Fe_2O_3 (hematite), TiO_2 (anatase), TiO_2 (rutile), TiO_2
AAC	48.61	1.89	2.76	0.20	1.00	33.76	9.19	2.59	SiO_2 (quartz), $Ca_5Si_6(O,OH,F)_{18}\cdot 5H_2O$ (tobermorite), $CaSO_4$ (anhydrite), $CaSO_4\cdot 2H_2O$ (gypsum), $(K, H_3O)\ Al_2Si_3AlO_{10}(OH)_2$ (illite)
Zeolite	20.54	14.01	4.56	0.22	0.15	20.83	15.82	23.87	$CaSO_4\cdot 2H_2O$ (gypsum), $CaSO_4\cdot 0.5H_2O$ (bassanite), $CaCO_3$ (calcite), $CaAl_2Si_{10}O_{24}\cdot 7H_2O$ (mordenite), $Na(Si_3Al)O_8$ (albite)

Zeolite showed a slightly alkaline pH, but the positive surface charge at lower pH due to the PZC value at pH 7.5 to 9.5 as estimated by potentiometric titration in this study. The material is composed mainly of gypsum, bassanite, calcite, mordenite, and albite (Table 3). Relatively high percentages of Fe_2O_3 and CaO were detected in zeolite, but AAC is generally characterized as a CaO rich material.

3.2 Effect of Initial Metal Concentration on Cr and As Adsorption

Fig.1 represents measured adsorption isotherms for Cr and As onto laterite, zeolite, and AAC. The measured data were evaluated using the Langmuir model [Eq. (1)] in the figure. Especially for laterite, the Langmuir model well captured all obtained data in the entire concentration range up to 2,000 mg/L with high r^2 values, suggesting that predominantly monolayer adsorption occurred [18].

The measured maximum adsorption capacities (Q_m) of laterite were 8.2 mg/g for As and 1.3 mg/g for Cr, as shown in Table 4. These values were lower than those of zeolite (14.6 and 5.4 mg/g for As and Cr, respectively) but clearly higher than those of AAC (4.0 mg/g for As). The Q_m value onto each adsorbent for Cr was always much lower than that for As, and especially AAC did not completely adsorb Cr.

The tested laterite in this study showed comparatively higher Q_m, especially for As, and it can adsorb Cr, indicating that the laterite has high potential as a low-cost adsorbent to remove As and Cr. The measured adsorption isotherms were also fitted to the Freundlich model [Eq. (2)], and the calculated adsorption parameters are shown in Table 5 (discussed later).

3.3 Effects of Initial pH and Background Ion Concentration on Cr and As Adsorption

Solution pH and background ion concentration can be considered important governing factors for the adsorption process, for example, inducing changes in the surface charge of adsorbent, chemical forms of adsorbate, and degree of ionization [27].

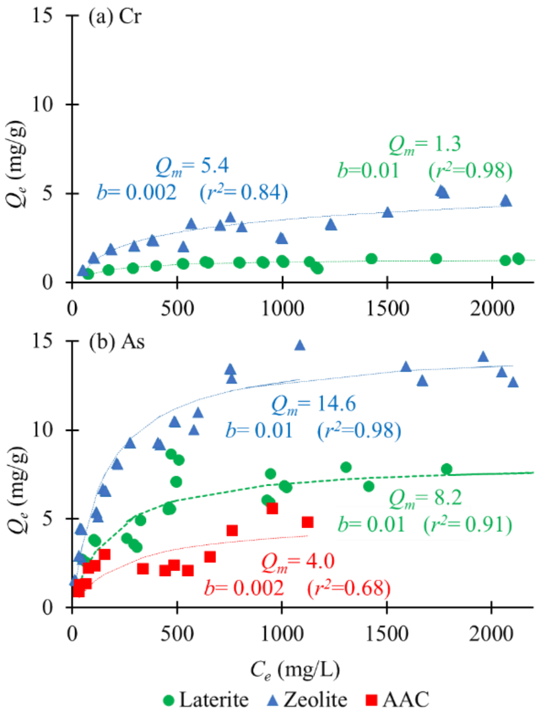

Fig.1 Measured adsorption isotherms fitted to the Langmuir model for (a) Cr and (b) As onto laterite, zeolite, and AAC. No adsorption of Cr onto AAC was noted.

Figs.2(a)–2(f) illustrate the relationships between ΔpH [= pH after adsorption (equilibrium pH, pH_e) - pH before adsorption (initial pH, pH_i)] and pH_i for Cr and As by laterite, AAC, and zeolite under different ionic strength conditions. Positive ΔpH indicates an increase in pH at equilibrium may be due to significant OH^- release during the adsorption reaction. On the other hand, negative ΔpH means a decrease in pH after adsorption. One of the possible reasons for this is the reaction

Table 4 Comparison of maximum adsorption capacity (Q_m) estimated for Cr and As onto different types of adsorbents from previous studies.

Category	Adsorbent	Particle size (mm)	S:L ratio	Cr		As		Reference
				C_i range (mg/L)	Q_m (mg/g)	C_i range (mg/L)	Q_m (mg/g)	
Natural geomaterials	Laterite	0.105-2	1;10	0-2000	1.3	0-2,000	8.2	This study
	Natural Laterite	0.165 - 0.385	1:50	-	-	0.5-20	0.57	[2]
	Illite	<0.075	1:10	-	-	10-200	0.52	[8]
	Montmorillonite	<0.075	1:10	-	-	10-200	0.64	[8]
	Kaolinite	<0.075	1:10	-	-	10-200	0.86	[8]
	Illite	-	1:250	0.1-16	0.28	-	-	[9]
	Kaolinite	-	1:250	0.1-16	0.57	-	-	[9]
	Laterite	<0.149	1:20	100-300	2.5	-	-	[10]
Modified geomaterials	Zeolite	0.105-2	1:60	0-2000	14.6	0-2,000	5.4	This study
	Iron-modified zeolite	<0.841	1:0.1	-	-	0.05-2	0.1	[28]
	Zeolite from coal fly ash	-	1:2	-	-	0-5.2	3	[29]
	Fe(III)-coated zeolite	1.4-2.4	1:5	2.5-50	0.08	-	-	[30]
	Fe(II)-modified zeolite	1.4-2.4	1:5	2.5-350	0.3	-	-	[31]
	Zeolite	<0.1	1:40	30-350	1.52	-	-	[11]
Metal oxides/ hydroxides	β-FeO(OH)	Powder	-	-	-	5-20	0.13	[32]
	Mn-FeOOH	Powder	1:500	-	-	0-50	5.72	[33]
	Goethite	<0.1	1:250	0.1-16	1.96	-	-	[18]
	α-Alumina	<0.1	1:250	0.1-16	2.16	-	-	[18]
	Hematite	<0.1	1:250	0.1-16	2.3	-	-	[18]
Bio-sorbents	Activated carbon (AC)	0.45-0.71	1:200	-	-	-	1.18	[12]
	Iron-Modified bamboo charcoal	0.063-0.125	1:67-1000	-	-	2-38	7.94	[13]
	Coir pith ash	<2	1:200	-	-	7.5-225	36.5	[14]
	Coconut tree sawdust AC	0.125-0.25	-	5-20	3.46	-	-	[34]
	Sunflower head waste	<0.3	1:250	10-70	7.9	-	-	[15]
	Rubber wood sawdust AC	<0.074	1:1000	50-200	44.05	-	-	[16]
CDW	AAC	0.105-2	1:10	-	-	0-2000	4	This study

between a hydroxyl group (R-OH) as the dominant reactive group and added metals, demonstrating significant H^+ release (deprotonation) to the solution, followed by a decrease in equilibrium pH during the adsorption process. For laterite, pH_e did not change significantly compared to AAC and zeolite, and it was less than pH 8 even after adding the initial solution at pH 10. In other words, the equilibrium pH highly depends on the initial solution pH. In contrast, both AAC and zeolite strongly increased the pH after adsorption, maybe due to being relatively rich in CaO. The pH_e for these adsorbents always showed a pH higher than around 7; however, the degree of alkalinity in the equilibrium solution was clearly lower in zeolite.

The relationships between removal % for Cr and As by the three tested adsorbents and the initial solution pH under different ionic strengths are presented in Figs.2(g)-2(l). All tested adsorbents showed similar trends in pH_i dependency on removal % for both metals. A higher removal % was commonly observed under lower pH_i conditions, and then the removal % slightly decreased with increasing pH_i. Under the pH and oxidative conditions that were applied in this study, anionic chemical forms for As ($H_2AsO_4^-$ and $HAsO_4^{2-}$) and Cr ($HCrO_4^-$ and CrO_4^{2-}) might be predominant. Also, based on the surface charge characteristics for all three adsorbents discussed above, active adsorption sites on the three tested adsorbents are likely to be positively charged at lower pH. Since a higher initial solution pH clearly gave a higher equilibrium solution pH, both metals could indicate higher removal percentages at lower pH_i. The slight decrease in removal efficiencies with increasing pH_i may have been derived from the repulsion between negatively charged surface sites and added anionic metals [10]. The active adsorption sites on AAC are likely negatively charged after pH 7 and thus, lower removal % was observed for AAC compared to laterite and zeolite, which may have alkaline PZC values at (higher) pH, as discussed above. On the other hand, background ion concentration (ionic strength) had a small effect on metal removal (adsorption) for each adsorbent in these applied pH ranges.

3.4 Effect of Solid-to-Liquid Ratio on Cr and As Adsorption

One of the other important factors governing the adsorption process besides solution pH and background ion concentration is the solid-to-liquid ratio. The results of removal percentages for both Cr and As under three different S:L ratios (1:5, 1:10, and 1:30) are presented in Fig.3. For both metal adsorptions onto each adsorbent, completely identical trends were observed, and a lower S:L

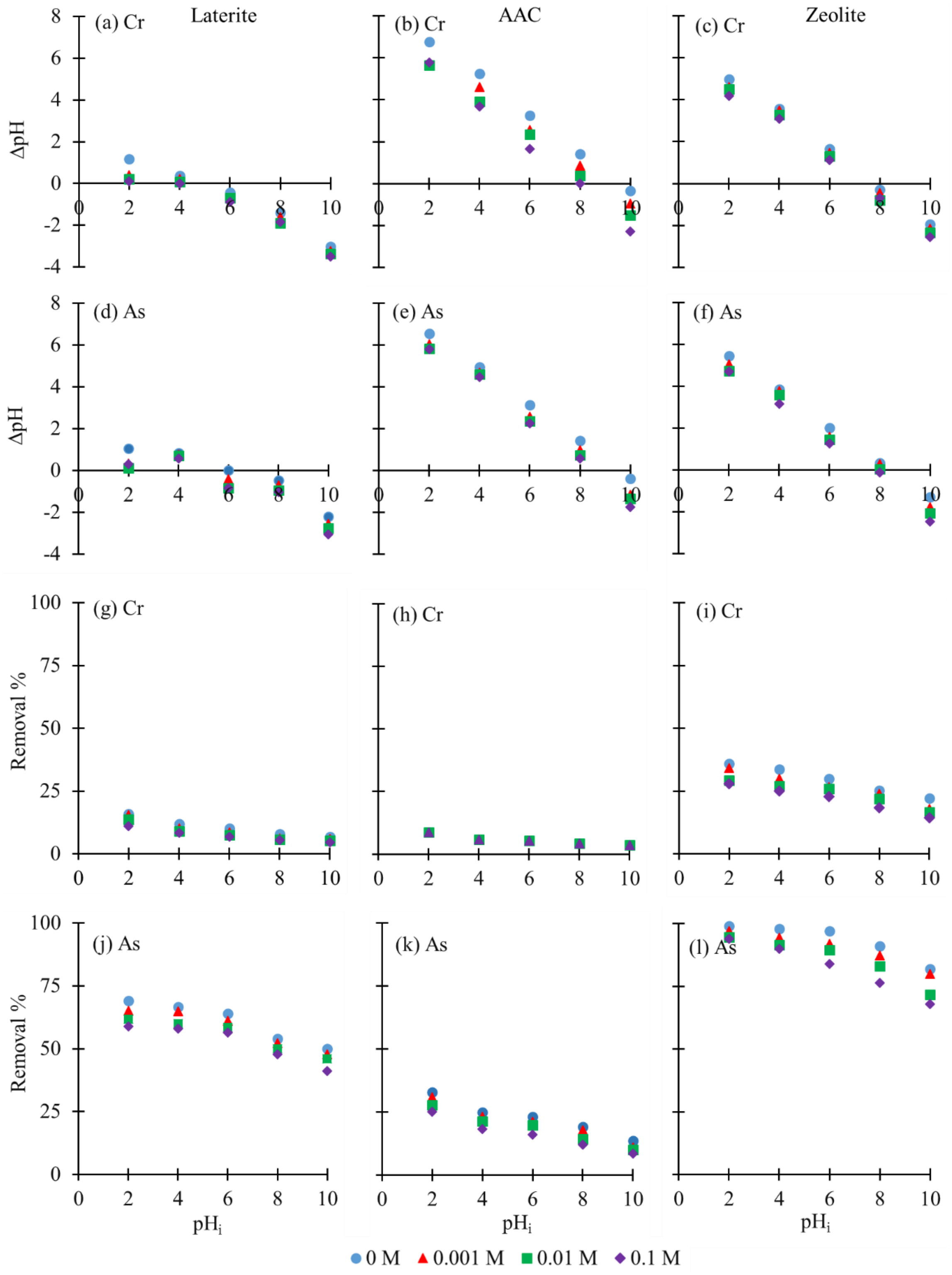

Fig.2 Relationship between ΔpH (= pH after adsorption (equilibrium pH) – pH before adsorption (initial pH)) and the initial solution pH for removal of Cr and As by laterite, AAC, and zeolite under different ionic strength conditions (a, b, c, d, e, and f). Relationship between removal % for these two metals by three tested adsorbents and the initial solution pH (pH_i) under different ionic strength conditions (g, h, i, j, k, and l).

ratio represents higher removal %. The removal % for laterite was slightly lower than that for zeolite but clearly higher than that for AAC, which are commonly observed results in this study. For example, the removal efficiencies were 7.9% for laterite and 69% for Cr and As, respectively, under the S:L ratio of 1:10 and natural pH conditions. The removal % of each adsorbent was slightly increased with decreasing pH, as illustrated in Fig. 2. Therefore, there may be a possibility of improving the adsorption efficiency by controlling several conditions such as initial solution pH and S:L ratio.

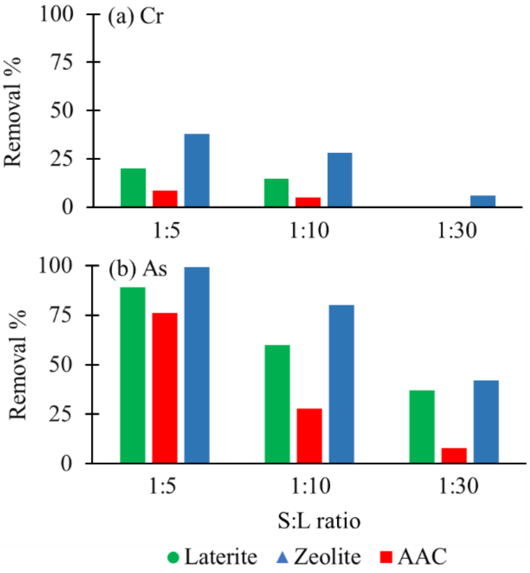

Fig. 3 Effect of S:L ratios on removal % for (a) Cr and (b) As onto laterite, AAC, and zeolite.

3.5 Desorption Experiments for Adsorbed Metals

Fig.4 presents measured adsorption and desorption isotherms for As onto laterite, AAC, and zeolite. All measured data were fitted to the Freundlich model Eq. (2) to obtain adsorption and desorption parameters, including the estimated hysteresis index (ω) Eq. (4). These parameters for Cr and As are shown in Table 5. All three tested materials showed relatively higher regression coefficients for As desorption, while the Freundlich model did not capture well the measured data for Cr.

The desorption intensity (n_d) values for As from laterite, AAC, and zeolite were significantly lower than the adsorption intensity (n_a) values, implying that As is strongly bonded onto these three materials. According to Eq. (4), a higher ω value represents higher irreversibility of the adsorption. Especially, the ω value in laterite was 480% and relatively higher than those in zeolite (128%) and AAC (176%). Therefore, laterite has better irreversibility for adsorbed As, and this metal is comparatively difficult to desorb, suggesting that laterite has better potential for As immobilization. Future studies are strongly needed to investigate, for example, the effect of solution pH, background ion (ionic strength), and S:L ratio on the immobilization of adsorbed metals.

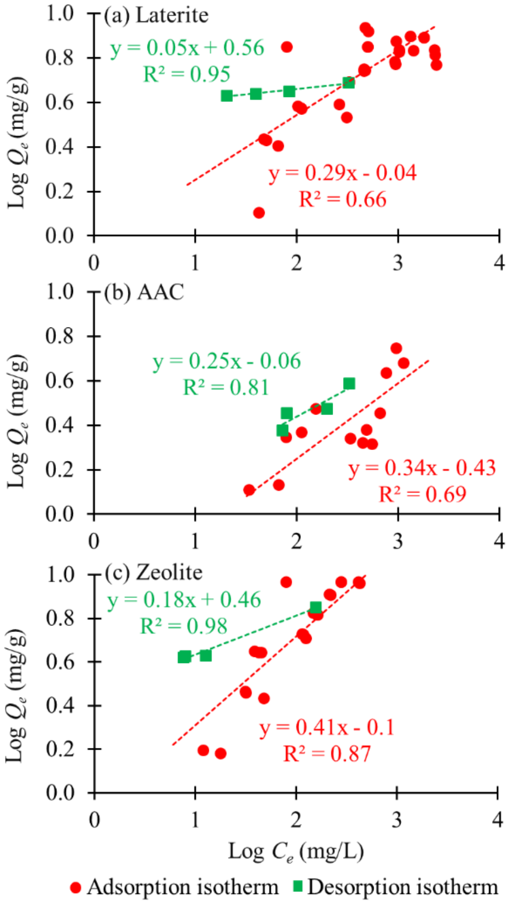

Fig.4 Measured adsorption and desorption isotherms fitted with Freundlich model for As onto (a) laterite, (b) AAC, and (c) zeolite.

4. CONCLUSIONS

The applicability of laterite grains as a low-cost adsorbent for Cr and As removal from wastewater was investigated, and the performance was compared with commercially available zeolite and AAC grains. All tested materials gave higher maximum adsorption capacities for As than for Cr. Especially, the tested laterite in this study gave a high maximum As adsorption capacity and showed high irreversibility, suggesting a good potential as a low-cost adsorbent for As removal from wastewater.

5. ACKNOWLEDGMENTS

This research was supported by the Science and Technology Research Partnership for Sustainable Development (SATREPS) of the Japan Science and Technology Agency (JST) and Japan International Cooperation Agency (JICA) (No. JPMJSA1701). We acknowledge Mr. Yuki Yoshida, a former master's degree student of Saitama University, for his dedicated effort on the laboratory tests.

Table 5: Fitted Freundlich model parameters for Cr and As adsorption and desorption (K_f, n, and r^2) and hysteresis index (ω) in laterite, AAC, and zeolite.

Metal	Adsorbent	Adsorption			Desorption			ω (%)
		K_{fa} (mg/g)	n_a	r^2	K_{fd} (mg/g)	n_d	r^2	
Cr	Laterite	0.24	0.24	0.69	2.16	0.07	0.28	242
	AAC	$1.5*10^{-4}$	1.38	0.78	2.8	0.03	0.06	4500
	Zeolite	0.22	0.4	0.74	0.84	0.17	0.67	135
As	Laterite	0.92	0.29	0.66	3.65	0.05	0.95	480
	AAC	0.37	0.69	0.69	0.87	0.25	0.81	176
	Zeolite	0.8	0.41	0.87	2.86	0.18	0.98	128

6. REFERENCES

[1] George C.M., Sima L, Arias M.H.J., Mihali J., Cabrera L.Z., Danz D., Checkley W., and Gilman R.H., Arsenic Exposure in Drinking Water: An Unrecognized Health Threat in Peru. Bulletin of the World Health Organization Vol. 92, Issue 8, 2014, pp.565-572.

[2] Maiti A., DasGupta S., Basu J.K., and De S., Batch and Column Study: Adsorption of Arsenate Using Untreated Laterite as Adsorbent. Journal of Industrial & Engineering Chemistry Research, Vol. 47, Issue 5, 2008, pp.1620-1629.

[3] Wang Q., Cissoko N., Zhou M., and Xu X., Effects and Mechanism of Humic Acid on Chromium (VI) Removal by Zero-Valent Iron (FeO) Nanoparticles. Physics and Chemistry of the Earth, Vol. 36, 2011, pp.442–446.

[4] Bissen M., and Frimmel F.H., Oxidation of Arsenic and Its Removal in Wastewater. Clean Soil Air Water, 31, Issue 2, 2003, pp.97-107.

[5] Yoon J., Amy G., Chung J., Sohn J., and Yoon Y., Removal of Toxic Ions (Chromate, Arsenate, and Perchlorate) using Reverse Osmosis, Nanofiltration, and Ultrafiltration Membranes. Chemosphere, Vol. 77, 2009, pp 228-235.

[6] Rengaraj S., Yeon K., and Moon S., Removal of Chromium from Water and Wastewater by Ion Exchange Resins. Journal of Hazardous Materials B87, 2001, pp.273-287.

[7] Owlad M., Aroua M.K., Daud W.A.W., and Baroutian S., Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review. Water Air Soil Pollut, Vol. 200, 2009, pp.59-77.

[8] Mohapatra D., Mishra D., Chaudhury G.R., and Das R.P., Arsenic Adsorption Mechanism on Clay Minerals and its Dependence on Temperature. Korean J. Chem. Eng., Vol. 24, Issue 3, 2007, pp.426-430.

[9] Ajouyed O., Hurel C., and Marmier N., Evaluation of the Adsorption of Hexavalent Chromium on Kaolinite and Illite. Journal of Environmental Protection, Vol. 2, 2011, pp.1347-1352.

[10] Yu X., Zhu L., Guo B., and He S., A Study on the Adsorption of Chromium on Laterite from Guizhou Province, China, Chin. J. Geochem, Vol. 28, 2009, pp.220-226.

[11] Zeng Y., Woo H., Lee G., and Park J., Adsorption of Cr (VI) on Hexadecylpyridinium Bromide (HDPB) Modified Natural Zeolites. Microporous and Mesoporous Materials, Vol. 130, 2010, pp.83-91.

[12] Dang S.V., Kawasaki J., Abella L.C., Auresenia J., Habaki H., Gaspillo P.D., and Kosuge H., Removal of Arsenic from Synthetic Groundwater by Adsorption Using the Combination of Laterite and Iron Modified Activated Carbon. Journal of Water and Environment Technology, Vol.6, Issue 1, 2008, pp.43-54.

[13] Liu X., Ao H., Xiong X., Xiao J., and Liu J., Arsenic Removal from Water by Iron-Modified Bamboo Charcoal. Water Air Soil Pollut, Vol. 223, 2012, pp.1033-1044.

[14] Bahar M.M., Mahbub K.R., Naidu R., and Megharaj M., As(V) Removal from Aqueous Solution using a Low-Cost Adsorbent Coir Pith Ash: Equilibrium and Kinetic Study. Environmental Technology & Innovation, Vol. 9, 2018, pp.198-209.

[15] Jain M., Garg V.K., and Kadirvelu K., Equilibrium and Kinetic Studies for Sequestration of Cr (VI) from Simulated Wastewater using Sunflower Waste Biomass. J. Haz. Materials, Vol. 171, 2009, pp.328-334.

[16] Karthikeyan T., Rajgopal S., and Miranda L.R., Chromium (VI) Adsorption from Aqueous Solution by Hevea Brasilinesis Sawdust Activated Carbon. J. Haz. Materials, Vol. B124, 2005, pp.192-199.

[17] Adegoke H.I., Adekola F.A., Fatoki O.S., and Ximba B.J., Sorptive Interaction of Oxyanions with Iron Oxides: A Review. Pol. J. Environ. Stud., Vol. 22, Issue 1, 2013, pp.7-24.

[18] Ajouyed O., Hurel C., Ammari M., Allal L.B., and Marmier N., Sorption of Cr (VI) onto Natural Iron and Aluminum (Oxy)Hydroxides: Effects of pH, Ionic Strength and Initial Concentration. J. Haz. Materials, Vol. 174, 2010, pp.616-622.

[19] Maji S.K., Pal A., Pal T., and Adak A., Modeling and Fixed Bed Column Adsorption of

As (V) on Laterite Soil. Journal of Environmental Science and Health: Part A, Vol. 42, 2007, pp.1-9.

[20] Organization for Economic Co-Operation and Development Publications (OECD), Guidelines for the Testing of Chemicals, 2000. <http://www.oecd.org/env/ehs/testing/oecdguidelines-forthetestingof-chemicals.htm>

[21] Langmuir I., The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. J. Am. Chem. Soc., Vol. 40, Issue 9, 1918, pp.1361-1403.

[22] Freundlich H.M.F., Over the Adsorption in Solution. J. Physical Chem., Vol. 57, 1906, pp.385-471.

[23] Qiu Q., Jiang X., Lv G., Chen Z., Lu S., Ni M., Yan J., and Deng X., Adsorption of Heavy Metal Ions using Zeolite Materials of Municipal Solid Waste Incineration Fly Ash Modified by Microwave-Assisted Hydrothermal Treatment. Powder Technol., Vol. 335, 2018, pp.156-163.

[24] Mon E.E., Hirata T., Kawamoto K., Hiradate S., Komatsu T., and Moldrup P., Adsorption of 2,4-Dichlorophenoxyacetic Acid onto Volcanic Ash Soils; Effects of pH and Soil Organic Matter. Environ. Asia, Vol. 1, 2009, pp.1-9.

[25] Kumara G.M.P., and Kawamoto K., Applicability of Crushed Clay Brick and Municipal Solid Waste Slag as Low-Cost Adsobents to Refine High Concentrate Cd (II) and Pb (II)-Contaminated Wastewater. Int. J. GEOMATE, Vol. 17, Issue 63, 2019, pp.133-142.

[26] Kumara G.M.P., Kawamoto K., Saito T., Hamamoto S., and Asamoto S., Evaluation of Autoclaved Aerated Concrete (AAC) Fines for Removal of Cd (II) and Pb (II) from Wastewater. J. Envir. Engin., Vol. 145, Issue 11, 2019.

[27] Park J.H., Ok Y.S., Kim S.H., Cho J.S., Heo J.S., Delaune R.D., and Seo D.C., Competitive Adsorption of Heavy Metals onto Sesame Straw Biochar in Aqueous Solutions. Chemosphere, Vol. 142, 2016, pp.77-83.

[28] Jiménez-Cedillo M.J., Olguín M.T., Fall C. and Colín A., Adsorption Capacity of Iron- or Iron–Manganese-Modified Zeolite-Rich Tuffs for As (III) and As (V) Water Pollutants. Applied Clay Science, Vol. 54, 2011, pp.206-216.

[29] Shukl E.A., Johan E., Henmi T., and Matsue N., Arsenate Adsorption on Iron Modified Artificial Zeolite Made from Coal Fly Ash. Procedia Environmental Sciences, 17, 2013, pp.279 -284.

[30] Du G., Li Z., Liao L., Hanson R., Leick S., Hoeppner N., and Jiang W., Cr (VI) Retention and Transport through Fe (III)-Coated Natural Zeolite. J. Haz. Materials, Vol. 221– 222, 2012, pp.118-123.

[31] Lv G., Li Z., Jiang W., Ackley C., Fenske N., and Demarco N., Removal of Cr (VI) from Water using Fe (II)-Modified Natural zeolite. Chem. Eng. Res. and Design, Vol. 92, 2014, pp.384-390.

[32] Deliyanni E.A., Bakoyannakis D.N., Zouboulis A.I., and Matis K.A., Sorption of As (V) Ions by Akaganeite-Type Nanocrystals. Chemosphere, Vol. 50, 2003, pp.155-163.

[33] Lakshmipathiraj P., Narasimhan B.R.V., Prabhakar S., and Bhaskar Raju G., Adsorption Studies of Arsenic on Mn-Substituted Iron Oxyhydroxide. J. Colloid Interface Sci, Vol. 304, 2006, pp.317-322.

[34] Selvi K., Pattabhi S., and Kadirvelu K., Removal of Cr (VI) from Aqueous Solution by Adsorption onto Activated Carbon. Bioresource Technol., Vol. 80, 2001, pp.87-89.

Copyright © Int. J. of GEOMATE. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors.