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

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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
Concrete (AAC) charge (PZC) was determined by the other parameters such as pH, conductivity (EC), gravimetric water content, and 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 K₂CrO₄ and H₂AsO₄ (Fujifilm Wako Pure Chemical Corp.) with more than 98% purity were used to prepare Cr and As solutions (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].

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

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 (mg/L) | Initial pH | Background solution |
|----------------|-------------------|--------------------|----------------------|-------------------------------------|------------|---------------------|
| Single metal solution | Isotherm | 0.105–2 | 1:10 | 0-2000 | Natural pH* | Deionized water |
| pH | 0.105–2 | 1:10 | 500 | 2-10 | NaNO₃ (0-0.1 M) |
| (Cr or As) | Ionic strength | 0.105–2 | 1:10 | 500 | 2-10 | NaNO₃ (0-0.1 M) |
| Desorption | 0.105–2 | 1:10 | 500 | Natural pH* | Deionized water |

*Observed adsorbent pH when it dissolved in deionized water.
Log\(Q_e\) = \(\log K_f + \frac{1}{n} \log C_e\) \hspace{1cm} (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 NaNO₃. All tested tubes were maintained as a 1:10 S:L ratio. The removal % for each metal was calculated based on [Eq. (3)].

Removal % = \(\frac{C_i - C_f}{C_i} \times 100\) \hspace{1cm} (3)

where \(C_i\) is the initial metal concentration (mg/L) and \(C_f\) 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 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)].

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

where \(\omega\) 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 \(n_d=n_a\) or \(n_d<n_a\) and \(n_d>n_a\), respectively. Higher irreversibility of the adsorbed metals represents a higher \(\omega\) 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 m²/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 Fe₂O₃, Al₂O₃, and SiO₂, which may be due to the presence of quartz, Al₂Si₂O₅(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 \(\zeta\)-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 (m²/g)     | 29       | 23.6  | 22.2    |
| Point of zero charge (pH)   | 6-9      |       | 7.5-9.5 |
| \(\zeta\)-potential pH4 (mV)| —        | 1.3*  | —       |
| \(\zeta\)-potential pH7 (mV)| —        | -6.4* | —       |

*Taken from a previous study [26].
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 Fe₂O₃ 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].

Figs. 2(a)–2(f) illustrate the relationships between ΔpH [= pH after adsorption (equilibrium pH, $pH_e$) - pH before adsorption (initial pH, $pH_0$)] and pH, 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
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 decreased 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 of these adsorbents always showed a pH higher than 10. Thus, 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 strength are presented in Figs. 2a-g, 2f-l. All tested adsorbents showed similar trends in pH dependency on removal % for both metals. A higher removal % was commonly observed under lower pH conditions, and then the removal % slightly decreased with increasing pH. Under the pH and oxidative conditions that were applied in this study, anionic chemical forms for As (H₂AsO₄⁻ and HAsO₄²⁻) and Cr (HCrO₄⁻ and CrO₄³⁻) 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. The slight decrease in removal efficiencies with increasing pH may have been derived from the repulsion between negatively charged surface sites and added anionic metals. 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 ratio led to a higher removal %.
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.

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 (\( \omega \)) 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 \( \omega \) value represents higher irreversibility of the adsorption. Especially, the \( \omega \) 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.

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 (Kf, n, and r²) and hysteresis index (ω) in laterite, AAC, and zeolite.

| Metal | Adsorbent | Adsorption | Desorption | ω (%) |
|-------|-----------|------------|------------|-------|
|       |           | Kf (mg/g)  | n, m      | r²    | Kf (mg/g)  | n, m      | r²    |       |
| Cr    | Laterite  | 0.24       | 0.24, 0.69| 2.16  | 0.07       | 0.28      | 0.24  | 0.24  |
|       | AAC       | 1.5*10⁴    | 1.38, 0.78| 2.8   | 0.03       | 0.06      | 1.5   | 1.5   |
|       | Zeolite   | 0.22       | 0.4, 0.74  | 0.84  | 0.17       | 0.67      | 0.22  | 0.22  |
| As    | Laterite  | 0.92       | 0.29, 0.66| 3.65  | 0.05       | 0.95      | 0.92  | 0.92  |
|       | AAC       | 0.37       | 0.69, 0.87 | 0.87  | 0.25       | 0.81      | 0.37  | 0.37  |
|       | Zeolite   | 0.8        | 0.41, 0.87 | 2.86  | 0.18       | 0.98      | 0.8   | 0.8   |

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