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Steel Slag and Autoclaved Aerated Concrete Grains as Low-Cost Adsorbents to Remove Cd$^{2+}$ and Pb$^{2+}$ in Wastewater: Effects of Mixing Proportions of Grains and Liquid-to-Solid Ratio

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Abstract: This study investigated the applicability of industrial by-products such as steel slag (SS) and autoclaved aerated concrete (AAC) grains (<0.105, 0.105–2, 2–4.75 mm) as low-cost adsorbents for simultaneous removal of Cd$^{2+}$ and Pb$^{2+}$ in wastewater. A series of batch adsorption experiments was carried out in single and binary-metal solutions of Cd$^{2+}$ and Pb$^{2+}$ by changing the mixing proportions of SS and AAC grains. In addition, the effect of the liquid-to-solid ratio (L/S) on the removal of Cd$^{2+}$ and Pb$^{2+}$ in multi-metal solution was examined. Results showed that SS grains had a high affinity with Cd$^{2+}$ in the single solution, while AAC grains had an affinity with Pb$^{2+}$. In the binary solution, the mixtures of SS and AAC grains removed both Cd$^{2+}$ and Pb$^{2+}$ well; especially, the tested adsorbents of SS+AAC [1:1] and SS+AAC [1:4] mixtures achieved approximately 100% removal of both metals. Based on the results in the multi-metal solutions, the metal removal % and selectivity sequence varied depending on the mixed proportions of SS and AAC grains and L/S values. It was found that the SS+AAC [1:1] mixture of SS and AAC grains showed 100% removals of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ simultaneously at L/S = 10 and 60.

Keywords: industrial by-products; steel slag (SS); autoclaved aerated concrete (AAC); heavy metals; metal adsorption; selectivity sequence; wastewater

1. Introduction

Due to rapid urbanization and industrialization, the discharge of wastewater containing toxic heavy metals from various sources such as industries, mines, vehicles, batteries, and metal-containing paints is increasing all over the world, especially in developing countries [1,2]. Heavy metal ions are non-biodegradable and tend to accumulate in living organisms, and those are considered toxic or carcinogenic ions [3,4]. Over the past few decades, for example, the annual global release of heavy metals reached 22,000 tons for cadmium, 939,000 tons for copper, 783,000 tons for lead, and 1,350,000 tons for zinc [5]. Inadequate treatments of toxic heavy metals such as Cd$^{2+}$ and Pb$^{2+}$ can cause not only serious surface and groundwater pollutions and soil contamination [6–8] but also various human diseases including acute or chronic poisoning, dermatitis, brain damage in children, and digestive tract cancer [9–11]. Furthermore, the direct discharge of Cd$^{2+}$ and Pb$^{2+}$ into the sewage system causes a negative impact on the effectiveness of biological wastewater treatment [12]. Thus, Cd$^{2+}$ and Pb$^{2+}$ can be considered the most commonly available and most harmful heavy metals to humans as well as the environment. Thus, proper treatment of these heavy metals in wastewater is essential to protect public health and the environment.

Numerous efforts are being made to develop cost-effective innovative methods of wastewater treatment, such as hydroxide precipitation [13], membrane filtration [14], re-
verse osmosis \([15]\), phytoextraction \([16]\), ion exchange \([17]\), electrokinetic remediation \([18]\), and adsorption \([19]\). When developing new methods, economic feasibility and sustainability are given high priority. However, adsorption has received a great deal of attention because of its high efficiency and cost effectiveness \([20]\). At present, a number of adsorbents are used for heavy metal removal on experimental as well as industrial levels. Out of those, activated carbon is the most widely used adsorbent due to its high adsorption capacity \([21]\). However, activated carbon is still in limited use because of economic reasons, mostly in developing countries \([22]\). Therefore, the evaluation of the effective use of low-cost and locally available adsorbents is receiving much attention. Low-cost adsorbents are classified generally as geo-sorbents \([23–27]\), bio-sorbents \([28–32]\), industrial wastes \([33–35]\), industrial by-products (IBPs) and construction and demolition waste (CDW) \([36–42]\), and modified low-cost adsorbents \([19,21,43–46]\). Many adsorption experiments have been performed to examine their adsorption capacities and characteristics \([47]\). However, among these low-cost adsorbents, IBPs and CDW are still marginalized in adsorption studies as well as industrial applications, although those materials have the same potential as other low-cost adsorbents to adsorb heavy metals from wastewater \([36–39,48–50]\). Therefore, more studies on the effective use of IBPs and CDW are required.

The growing industrialization in developing countries, on the other hand, generates large amounts of IBPs such as steel slag (SS) by the steel-making industry, coal ash by coal-fired power plants, and mining waste by extracting and processing mineral resources \([51,52]\). Along with the rapid generation of IBPs, improper treatment and uncontrolled dumping of IBPs are becoming a major environmental issue in many developing countries \([53,54]\). Moreover, with increasing production of non-fired bricks such as cement blocks and autoclaved aerated concrete (AAC) all over the world, the amount of scrap waste has also been increasing in developing countries \([55,56]\). The AAC scrap waste is not fully reused in most of the countries but dumped on-site without any treatment. Proper management is vital for sustainable development, and effective utilizations of IBPs and scrap waste of non-fired bricks are required for circulating those materials in society. Hence, it is timely and important to promote the reuse of these abundantly available waste materials as a cost-effective adsorbent for wastewater treatment process to give added value to IBPs and AAC scrap waste.

Until now, many studies have investigated the applicability of IBPs and other types of low-cost adsorbents for heavy metal treatment processes, but most of the studies mainly target the treatment of heavy metals at low concentrations (typically, heavy metal concentrations <200 mg/L) \([21,57–59]\). Furthermore, most of these studies examined the adsorption capacities of target adsorbents in single and/or binary-metal solutions at a constant liquid-to-solid (L/S) ratio \([50]\). Because actual industrial wastewater might be contaminated by multi-species heavy metals like Pb\(^{2+}\), Cd\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\), further studies are needed to examine the simultaneous removal of heavy metals fully considering the co-existence of competitive metals in wastewater \([19,60]\). For example, it has been reported that Cd\(^{2+}\) adsorption onto cementitious adsorbents, including AAC grains, was hampered by the co-existence of Pb\(^{2+}\) and Cu\(^{2+}\) due to their high affinities with the tested adsorbents \([61–64]\). In addition, Kumara et al. 2019c \([65]\) examined the simultaneous removal potential of Cd\(^{2+}\) and Pb\(^{2+}\) in the multi-metal solutions by AAC, SS, and AAC+SS \([1:1]\) grains and revealed selectivity sequences of Pb\(^{2+}\) > Cu\(^{2+}\) > Ni\(^{2+}\) > Zn\(^{2+}\) > Cd\(^{2+}\) for AAC, Pb\(^{2+}\) > Cu\(^{2+}\) > Cd\(^{2+}\) > Ni\(^{2+}\) > Zn\(^{2+}\) for SS, and Pb\(^{2+}\) > Cu\(^{2+}\) > Cd\(^{2+}\) > Zn\(^{2+}\) > Ni\(^{2+}\) for AAC+SS \([1:1]\) under an L/S ratio 60. Thus, many researchers have concluded that the simultaneous removal of Cd\(^{2+}\)-like metals using a low-cost adsorbent is impossible. Therefore, it is worthwhile to discover low-cost adsorbents that have potential for simultaneous removal of commonly available heavy metals in wastewater. In order to examine the simultaneous removal of Cd\(^{2+}\) and Pb\(^{2+}\) in wastewater, therefore, this study investigated the adsorption characteristics of those metals onto the mixtures of SS and AAC grains in single and binary-metal solutions. Especially, the selectivity sequence on metal adsorption
was carefully investigated in the multi-metal solutions (coexistence of Ni$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$) at different L/S ratios ranging from 5 to 250.

2. Materials and Methods
2.1. Adsorbents Preparation and Characterization

Commercially available steel slag (SS) for civil engineering applications (Nippon Steel Cooperation and Sumitomo Metal Industries, Ltd., Saitama, Japan) and autoclaved aerated concrete (AAC) (Asahi Kasei Construction Material Corp., Tokyo, Japan) were used. General information on the manufacturing and characteristics of SS and AAC are given in Nippon Slag Association [66] and Trong et al. [67]. After crushing by hand in the laboratory, the tested samples were sieved to three grain fractions of <0.105, 0.105–2, and 2–4.75 mm. The dataset of material properties and the adsorption tests for AAC grains analyzed in this study were obtained from Kumara et al., 2019a [61].

The basic physical and chemical properties of SS and AAC grains are summarized in Table 1. The Brunauer–Emmett–Teller (BET) surface area (SSA) was measured by a ASAP2020 adsorption analyzer (Micromeritics, Norcross, GA, USA). Measured specific gravity ($G_s$) values of SS grains were higher compared to AAC grains, and pH values showed that SS grains are alkaline in water due to the hydration reaction of CaO with a release of OH$^-$. The SSA values of SS grains were lower than those of AAC grains and decreased with decreasing grain size. This implied that SS grains had fewer inter-grain pores compared to AAC grains, and the outer-grain surface controlled the SSA of SS grains.

Table 1. Basic physical and chemical properties of tested adsorbents.

| Adsorbent | Particle Size (mm) | pH DI | pH KCl | EC (mS/cm) | LOI (%) | $\omega_{AD}$ (%) | $G_s$ | SSA (m$^2$/g) | Reference |
|-----------|-------------------|-------|--------|------------|---------|------------------|------|--------------|-----------|
| SS        | <0.105            | 12.9  | 13.1   | 6.1        | 14.5    | 2.5              | 8.0  | This study   |           |
|           | 0.105–2           | 12.4  | 12.6   | 6.9        | 4.8     | 1.9              | 3.05 | 4.9          |           |
|           | 2–4.75            | 13.1  | 13.1   | 5.0        | 4.8     | 1.9              | 2.6  |              |           |
| AAC       | <0.105            | 10.0  | 8.7    | 1.7        | 10.3    | 4.4              | 23.6 |              |           |
|           | 0.105–2           | 10.0  | 8.3    | 1.8        | 10.8    | 3.9              | 2.49 | 23.6         | [61]      |
|           | 2–4.75            | 9.9   | 8.9    | 1.4        | 9.8     | 4.0              | 21.9 |              |           |

The chemical composition of tested adsorbents was characterized by energy-dispersive X-ray spectroscopy (EDX; X-Max Extreme, Oxford Instruments, High Wycombe, UK) and X-ray diffractometry (XRD; XRD-7000, Shimadzu Cooperation, Kyoto, Japan). The EDX test data are shown in Table 2. Higher CaO (41.7%) and Fe$_2$O$_3$ (22.5%), and lower SiO$_2$ (16.8%) were found for SS grains compared to those of AAC grains, indicating a potential for the ion exchange (Ca$^{2+}$) reaction with heavy metals in wastewater like other calcium silicate materials [68,69]. The XRD analysis showed that magnetite (Fe$_3$O$_4$), iron oxidate (FeO), calcite (CaCO$_3$), calcium hydroxide (Ca(OH)$_2$), and halloysite (Al$_2$Si$_2$O$_5$(OH)$_4$) were the main minerals in SS grains. Both EDX and XRD analyses confirmed the existence of high amounts of metal oxides and hydroxides in SS grains, implying that SS grains favored the adsorption of heavy metals such as Cd$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ [70–72].

Table 2. Chemical composition of tested adsorbents.

| Adsorbent | SiO$_2$ | CaO | Al$_2$O$_3$ | Fe$_2$O$_3$ | K$_2$O | MgO | Others | Reference        |
|-----------|---------|-----|-------------|-------------|-------|-----|--------|------------------|
| SS        | 16.8    | 41.7| 3.2         | 22.5        | 0.2   | 3.5 | 12.1   | This study       |
| AAC       | 48.6    | 33.8| 2.8         | 1.9         | 0.5   | 0.4 | 12.0   | [61]             |

2.2. Procedures of Batch Experiments

Stock solutions of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ (synthesized wastewater) were prepared by dissolving CdCl$_2$, PbCl$_2$, CuCl$_2$, NiCl$_2$, and ZnCl$_2$, respectively, in deionized
water (DI). The solutions’ pH and ionic strength were controlled using 1N HCl, 1N NaOH, and NaNO₃. All chemicals used for this study were analytical grade from Wako Pure Chemical Industries, Ltd., Osaka, Japan, with more than 98% chemical purity. A standard batch method recommended by the Organization of Economic Cooperation and Development [73] was used for all batch adsorption experiments. The concentrations of heavy metals and other ions were measured using a flame atomic absorption spectrophotometer (AAS; AA 6200, Shimadzu, Japan), the exact pH and EC values for each metal solution were measured before the experiment, and their changes were observed during the experiments using a pH/EC meter.

Test conditions of adsorption experiments are summarized in Table 3. The types of batch adsorption experiments in this study were categorized into four groups to investigate: (1) adsorption isotherm in a single-metal solution with L/S = 60 for Cd²⁺ and 10 for Pb²⁺, (2) % removal in a binary-metal solution (Cd²⁺, Pb²⁺) with L/S = 60, (3) % removal in multi-metal solution (Cd²⁺, Pb²⁺, Cu²⁺, Ni²⁺, Zn²⁺) with L/S = 60, and (4) the effect of L/S ratios on % removal in a multi-metals solution with different L/S ratios = 5–250.

### Table 3. Summary of batch adsorption experiments and testing conditions.

| Adsorbent | Types of Experiment | Liquid-to-Solid Ratio (L/S) | Initial Metal Concentration, (Cᵢ = mg/L) |
|-----------|---------------------|-----------------------------|----------------------------------------|
| SS        | 1. Adsorption isotherm in single-metal solution (Cd²⁺, Pb²⁺) | 60 (Cd²⁺), 10 (Pb²⁺) | 0–5000 (Cd²⁺), 0–1500 (Pb²⁺) |
| SS        | 2. Removal % in binary-metal solution (Cd²⁺ + Pb²⁺) | 60 | 1000 |
| SS+AAC [4:1] | 3. Removal % in multi-metal solution (Cd²⁺ + Pb²⁺ + Cu²⁺ + Ni²⁺ + Zn²⁺) | 60 | 1000 |
| SS+AAC [1:1] | 4. Effect of L/S ratio on removal % in multi-metal solution | 5, 10, 60, 100, 250 | 1000 |

Note: Deionized water (DI) with natural pH was used as a background solution for all experiments.

Three grain sizes of adsorbents of <0.105, 0.105–2, and 2–4.75 mm were used for the adsorption isotherm experiments in a single-metal solution, and an adsorbent grain size of 0.105–2 mm was used for other adsorption experiments. All test conditions were carried out with triplicate measurements, and the averaged values were given in the paper because of a small variation of measured data.

#### 2.2.1. Adsorption Isotherms for Cd²⁺ and Pb²⁺ in a Single-Metal Solution

Adsorption isotherm experiments for Cd²⁺ and Pb²⁺ onto SS and AAC grains were carried out at natural pH with the initial metal concentration (Cᵢ) of 0–5000 mg/L for Cd²⁺ and 0–1500 mg/L for Pb²⁺ (19 different concentrations, fully considering the actual metal concentration range in industrial wastewater [74]) at L/S = 60. To determine the maximum adsorption capacity and intensity of Cd²⁺ and Pb²⁺ onto the tested adsorbents, Langmuir (Equation (1)) and Freundlich (Equation (2)) models were used to fit the obtained experimental data:

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}
\]

(1)

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]

(2)

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

#### 2.2.2. Effect of Competitive Metal Ions on Cd²⁺ and Pb²⁺ Adsorption in Binary Metal Solution

To examine the effect of competitive metal ions on Cd²⁺ and Pb²⁺ adsorption, batch experiments were carried out in a binary-metal solution of Cd²⁺ and Pb²⁺ at natural pH
with $C_i = 1000 \text{ mg/L}$. Five different mixtures of SS and AAC grains, i.e., mixing proportions of SS (alone), SS+AAC [4:1], SS+AAC [1:1], SS+AAC [1:4], and AAC (alone), were used as tested adsorbents. The ratios in brackets show the mixing proportions in weight % (e.g., (1:1) means a mixture of 50% SS and 50% AAC). In binary-metal adsorption experiments, the mixed solutions of Cd$^{2+}$ to Pb$^{2+}$ were used at metal molar ratios of 1:0, 1:0.25, 1:0.5, 1:0.75, 1:1, 1:2, and 1:5 to investigate the effect of Pb$^{2+}$ concentrations on Cd$^{2+}$ adsorption. Vice versa, the same mixing solutions of Pb$^{2+}$ and Cd$^{2+}$ solutions were used to investigate the effect of Cd$^{2+}$ on Pb$^{2+}$ adsorption. In each experiment, the metal removal percentage ($R$, %) was calculated using Equation (3) [46]:

$$R = \frac{[C_i-C_e]}{C_i} \times 100$$  \hspace{1cm} (3)

2.2.3. Effect of Competitive Metal Ions on Cd$^{2+}$ and Pb$^{2+}$ Adsorption in Multi-Metal Solutions

To examine the effects of competitive metals on Cd$^{2+}$ and Pb$^{2+}$ adsorption onto tested adsorbents with different L/S, batch adsorption experiments in multi-metal solutions were carried out using a mixed metal solution of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ at natural pH with $C_i = 1000 \text{ mg/L}$. Like the adsorption experiments of binary-metal solutions, five different mixtures of SS and AAC grains (SS, SS+AAC [4:1], SS+AAC [1:1], SS+AAC [1:4], and AAC) were used with five different L/S values of 5, 10, 60, 100, and 250. In each experiment, the $R$ value of each metal was calculated using Equation (3).

3. Results and Discussion

3.1. Adsorption Isotherms for Cd$^{2+}$ and Pb$^{2+}$ in Single Metal Solution

The measured adsorption isotherms for Cd$^{2+}$ and Pb$^{2+}$ onto SS grains with different grain sizes are shown in Figure 1. In the figures, the Langmuir model (Equation (1)) was well-fitted to the measured data except for the Cd$^{2+}$ adsorption onto SS grains with <0.105 mm (Figure 1a). The SS grain with <0.105 mm showed a very high Cd$^{2+}$ adsorption and did not show the maximum adsorption capacity ($Q_m$) in the range of $C_i = 0$–5000 mg/L. For both Cd$^{2+}$ and Pb$^{2+}$ adsorptions, the adsorption decreased with increasing grain size. This can be understood to indicate that the adsorption surface area of tested adsorbents controlled the adsorption capacity, and the sample of <0.105 mm with higher SSA imposed a higher adsorption capacity compared to the samples with lower SSA of the grain sizes of 0.105–2, 2–4.75 mm (Table 1). The Freundlich model (Equation (2)), on the other hand, fitted well with all tested adsorbents in the range of $C_i = 0$–5000 mg/L for Cd$^{2+}$ and 0–1500 mg/L for Pb$^{2+}$. This suggests that a monolayer adsorption is predominant at the early stage of the adsorption process (typically, $C_i < 1500 \text{ mg/L}$) and the adsorption process shifts to a multilayer adsorption, especially at higher than $C_i > 1500 \text{ mg/L}$, for both Cd$^{2+}$ and Pb$^{2+}$ [75,76].

The fitted adsorption parameters by Freundlich and Langmuir models for tested SS grains are summarized in Table 4 with the reported data for AAC grains [61]. It shows clearly that the SS grains have higher affinities (higher $Q_m$ and $K_f$) to Cd$^{2+}$ compared to AAC grains while the AAC gains have higher affinities to Pb$^{2+}$ compared to SS grains. These results imply that the mixing of SS and AAC grains would be effective for the simultaneous adsorption of Cd$^{2+}$ and Pb$^{2+}$, as discussed in the following sections. For reference, the measured $Q_m$ values in this study were compared to the previously reported values for different types of adsorbents such as IBPs (including construction and demolition waste) and geo- and bio-sorbents and are summarized in Table 5. It is noticeably shown that SS has the highest $Q_m$ of Cd$^{2+}$ adsorption compared to those of other adsorbents.
Figure 1. Measured adsorption isotherms and fitted Langmuir and Freundlich models for Cd\(^{2+}\) (a,b) and Pb\(^{2+}\) (c,d) onto three grain sizes of SS.

Table 4. Fitted Langmuir and Freundlich model parameters for Cd\(^{2+}\) and Pb\(^{2+}\) adsorption onto tested adsorbents.

| Adsorbent | Metal   | Particle Size (mm) | Langmuir | Freundlich | Reference |
|-----------|---------|-------------------|----------|------------|-----------|
|           |         |                   | \(Q_e\) (mg/g) | \(b\) (L/mg) | \(r^2\) | \(K_f\) (mg/g) | \(1/n\) | \(r^2\) | |
| SS        | Cd\(^{2+}\) | <0.105            | 313\(^1\)  | -          | -        | 105  | 0.27  | 0.98 |
|           |         | 0.105–2           | 244      | 0.18  | 0.99  | 114  | 0.17  | 0.89 |
|           |         | 2–4.75            | 130      | 0.09  | 0.99  | 92.0 | 0.04  | 0.77 |
|           | Pb\(^{2+}\) | <0.105            | 17.5     | 0.02  | 0.97  | 57   | 0.67  | 0.97 |
|           |         | 0.105–2           | 8.6      | 0.01  | 0.91  | 0.15 | 0.70  | 0.96 |
|           |         | 2–4.75            | 8.2      | 0.01  | 0.93  | 0.13 | 0.72  | 0.94 |
| AAC       | Cd\(^{2+}\) | <0.105            | 16.5     | 1.72  | 0.99  | 8.89 | 0.11  | 0.91 |
|           |         | 0.105–2           | 16.5     | 0.91  | 0.99  | 9.92 | 0.10  | 0.93 |
|           |         | 2–4.75            | 15.2     | 0.69  | 0.99  | 8.82 | 0.11  | 0.89 |
|           | Pb\(^{2+}\) | <0.105            | 258\(^1\) | -      | -      | 137  | 0.20  | 0.97 |
|           |         | 0.105–2           | 257\(^1\) | -      | -      | 121  | 0.24  | 0.98 |
|           |         | 2–4.75            | 250      | 0.05  | 0.99  | 74.3 | 0.22  | 0.98 |

Note: \(^1\)\(Q_m\) values were estimated by the measured maximum adsorption amount. Langmuir and Freundlich parameters for SS were determined fitting the adsorption isotherm of Cd\(^{2+}\) at \(0 \leq C_i \leq 5000\) mg/L and the adsorption isotherm of Pb\(^{2+}\) at \(0 \leq C_i \leq 1500\) mg/L. Langmuir and Freundlich parameters for AAC were determined fitting the adsorption isotherms of Cd\(^{2+}\) and Pb\(^{2+}\) at \(0 \leq C_i \leq 2000\) mg/L.

Figure 2 shows the relationship between the amounts of Ca\(^{2+}\) and adsorbed metal released onto SS grains sized 0.105–2 mm in the measured C\(_i\) range. For both Cd\(^{2+}\) and Pb\(^{2+}\) adsorptions, the Ca\(^{2+}\) was released linearly along with the metal adsorption \((r^2 \geq 0.88)\). The correlation regression showed that the ratios of released Ca\(^{2+}\) became greater than 1 (2.24 for Cd\(^{2+}\) and 6.37 for Pb\(^{2+}\)). This means that approximately 2 and 6 times of Ca\(^{2+}\) were released when the one metal was adsorbed, indicating the adsorption mechanism was not controlled by a simple 1:1 ion exchange process of Ca\(^{2+}\) and Cd\(^{2+}\)/Pb\(^{2+}\) on the adsorbent surface of SS grains in the single-metal solution system. On the other hand, Kumara et al. 2019a [61] observed an almost 1:1 relationship between the released Ca\(^{2+}\) amount and adsorbed Cd\(^{2+}\)/Pb\(^{2+}\) for AAC grains, and the hydrated adsorbent surface was the dominant metal adsorption mechanism [77,78].
Table 5. Comparison of the maximum adsorption capacity ($Q_m$) of tested adsorbents with reported values.

| Category                        | Adsorbent                  | Particle Size (mm) | BET Surface Area (m$^2$/g) | Liquid-to-Solid Ratio (L/S) | pH Range          | $\text{Cd}^{2+}$ | $\text{Pb}^{2+}$ |
|--------------------------------|-----------------------------|--------------------|-----------------------------|-----------------------------|-------------------|----------------|----------------|
| **Industrial by-products**      | Steel slag (SS)            | 0.105-2            | 4.9                         | 60                          | 10-12             | 0-5000         | 130-313        |
|                                | Fly ash                    | 0.01-0.02          | 2.8                         | 50-10,000                   | 2-10              | 0-5            | 3.8            |
|                                | Blast furnace slag         | 0.15-0.3           | 1.1                         | 50-10,000                   | 2-10              | 0-5            | 5.1            |
|                                | Arc furnace slag           | 0.9-2              | 3.42                        | 100                         | 2-8               | 22.5-360       | 6.5            |
|                                | Autoclaved aerated concrete| 0.105-2            | 23.6                        | 60                          | 8-10              | 25-2000        | 16.5           |
|                                | Crushed concrete fines     | 0.105-2            | 11.2                        | 60                          | 6-11              | 25-2000        | 22.8           |
|                                | Crushed clay bricks        | 0.105-2            | 15.9                        | 10                          | 6-7               | 0-2000         | 3.2            |
|                                | Municipal solid waste slag | 0.105-2            | -                           | 10                          | 8-9               | 0-2000         | 2.3            |
|                                | Carbon concrete            | 1.5-2.5            | 177                         | 1428                        | 6.5-7.2           | 10-2000        | 28.7           |
| **Geo-sorbents**               | Zeolite                    | -                 | 15.4                        | 40-1000                     | 6.5-6.7           | 0-50           | 6.72           |
|                                | Ca-bentonite               | <0.063            | 87                          | 1000                        | ≈5                | 1-100          | 31.3           |
|                                | Sepiolite                  | <0.1              | 100                         | -                           | ≈5                | 50-600         | 19.2           |
|                                | Limestone                  | Powder            | 119                         | 6667                        | 2-6               | 1-200          | 52.9           |
|                                | Montmorillonite            | -                 | 100                         | 6667                        | ≈2                | 10-500         | 1.2            |
| **Bio-sorbents**               | Coconut coir husk          | <0.35             | 1.83                        | 400                         | ≈7                | 2.5-2000       | 47.3           |
|                                | Coconut husk/shell         | 0.075             | 212                         | 10                          | ≈8.8              | 100-2000       | 3.5            |
|                                | Biochar                    | 0.15              | 51.2                        | 500                         | 5-7               | 50-900         | 75             |
|                                | Green algae                | 1-1.5             | -                           | 125                         | 2-6               | 22-382         | 39.2           |
|                                | Lemon berry                | 0.15              | -                           | 100                         | 4.8-5             | 110-2800       | 129            |

Figure 2. Relationship between released $\text{Ca}^{2+}$ amount and adsorbed metal amount of SS grain (0.105-2 mm). Measured from adsorption isotherms in single-metal solution of $\text{Cd}^{2+}$ ($0 \leq C_i \leq 2000$ mg/L) at L/S = 60 and $\text{Pb}^{2+}$ ($0 \leq C_i \leq 1500$ mg/L) at L/S = 10.

3.2. Removal of $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ in Binary Metal Solution

Measured values of the percentage of metal removed, $R$ % (Equation (3)) for $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ in the binary-metal solution by tested adsorbents, were plotted against the $\text{Cd}:\text{Pb}$ and $\text{Pb}:\text{Cd}$ molar mixed ratios in Figure 3. Like the test results in a single-metal solution for the removal of $\text{Cd}^{2+}$, SS had a strong affinity with $\text{Cd}^{2+}$ and became independent of the existence of $\text{Pb}^{2+}$ in binary-metal solution, SS, and its mixtures (SS, SS+AAC [4:1], SS+AAC [1:1], SS+AAC [1:4]) gave approximately $R = 100\%$ (Figure 3a–d,f–i). In contrast, the removal of $\text{Pb}^{2+}$ in the binary-metal solution was controlled by AAC, and AAC and its mixtures (AAC, SS+AAC [1:4], and SS+AAC [1:1]), which gave approximately $R = 100\%$ (Figure 3c–e,h–j). Previous studies reported that geo- and bio-adsorbents had difficulty achieving the sufficient removal of $\text{Cd}^{2+}$ in the presence of $\text{Pb}^{2+}$ in the binary-metal solution [30,31]. In this study, however, the tested results suggested strongly that the mixing of SS and AAC grains was effective to simultaneously remove $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ in a binary-metal solution; the mixtures of SS+AAC [1:1] and SS+AAC [1:4] were especially able to absorb $\text{Cd}^{2+}$ (or $\text{Pb}^{2+}$) completely, even in the presence of $\text{Pb}^{2+}$ (or $\text{Cd}^{2+}$) in the solution.
Figure 3. Metal removal %, $R$, in binary-metal solution ($\text{Cd}^{2+}$ and $\text{Pb}^{2+}$) for tested adsorbents with different mixing proportions (grain size = 0.105–2 mm). (a–e) x-axis is Cd:Pb ratio in binary-metal solution; (f–j) x-axis is Pb:Cd ratio in binary-metal solution. Measured pH values after the adsorption ($\text{pH}_e$) ranged 8–10 for AAC and 10–12 for SS and mixed adsorbents of SS and AAC.
In the batch adsorption tests in the binary-metal solution, the measured pH values after the adsorption (pH\text{e}) ranged from 8–10 for AAC grains (Figure 3e,j) and 10–12 for SS and mixed adsorbents of SS and AAC (Figure 3a–d,f–i). This indicated that the metals were adsorbed onto the tested adsorbents under alkaline conditions. Previous studies suggested that the metal adsorption onto cementitious and adsorbents rich in calcium metal oxides/hydroxides resulted in combined chemical processes and reactions under alkaline conditions: i.e., hydration of the adsorbent surface, hydrolysis of metal ions, physisorption, chemisorption, ion exchange, and surface complexation and precipitation [33,61,77,87–90]. For example, according to the metal speciation in pH-Eh diagram [91], Pb is presented as Pb\textsuperscript{2+} or possible to precipitate as Pb(OH)\textsubscript{2} in the range of pH = 7–12 and most probably exists as Pb(OH)\textsubscript{3}\textsuperscript{−} in the range of pH >12. On the other hand, Cd exists mainly in the forms of Cd\textsuperscript{2+} and Cd(OH)\textsuperscript{+} in the range of pH = 9–13. As shown in Table 2, the SS and AAC grains tested in this study were rich in CaO and Fe\textsubscript{2}O\textsubscript{3}. Based on the results of previous studies and the chemical compositions of tested adsorbents, the simultaneous removal of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} from the mixtures of SS and AAC grains in the binary-metal solution under alkaline conditions can be understood as shown in Figure 4. For SS grains, under the given experimental conditions, active hydroxides (-OH) on the surface of metal oxides/hydroxides (especially Fe\textsubscript{2}O\textsubscript{3}) create a negative surface charge, resulting in the formation of an inner-sphere complex (surface complexation) by replacing Ca\textsuperscript{2+} (high affinity with Cd\textsuperscript{2+}). For AAC grains, on the other hand, the ion exchange between Ca\textsuperscript{2+} and Pb\textsuperscript{2+} on the adsorbent surface becomes dominant, and the inner-sphere complex promotes the Pb\textsuperscript{2+} adsorption onto the surface with a negative charge (high affinity with Pb\textsuperscript{2+}). Because these two reactions promote the release of Ca\textsuperscript{2+} ions, the amount of Ca\textsuperscript{2+} released became higher than the amount of metal adsorbed, as shown in Figure 2. In addition, hydrated CaO releases high amounts of OH\textsuperscript{−} ions for both SS and AAC grains and promotes the precipitation of metal hydroxides (Cd(OH)\textsubscript{2} and Pb(OH)\textsubscript{2}) under the alkaline condition.

**Figure 4.** Schematics of simultaneous removal of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} by mixing grains of SS and AAC in binary-metal solution (alkaline condition).
3.3. Removal of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} in Multi-Metal Solutions and Selectivity Sequence

Simultaneous removals of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} in multi-metal solutions by the tested adsorbents were examined under different L/S ratios of 5, 10, 60, 100, and 250. The measured $R$ values of metal ions in multi-metal solutions for SS, SS+AAC [1:1], and AAC are exemplified in Figure 5, and selectivity sequences are shown in Table 6. For all tested adsorbents, the $R$ values of metals became high in low L/S conditions and decreased with increasing L/S. Especially, the $R$ values became low at L/S = 60, 100, and 250, except for the Pb\textsuperscript{2+} removal and the Cu\textsuperscript{2+} removal of SS and AAC grains at L/S = 60 (Figure 5). This suggests that control of L/S is an important factor to achieve high $R$ values in multi-metal solutions, unlike the single-metal and binary-metal solutions.

Figure 5. Metal removal %, $R$, in multi-metal solution for (a) SS, (b) SS+AAC [4:1], (c) SS+AAC [1:1], (d) SS+AAC [1:4], and (e) AAC in different L/S conditions. Measured pH values after the adsorption ($\text{pH}_e$) ranged from 8–10 for AAC and from 10–12 for SS and mixed adsorbents of SS and AAC.
As shown in Table 6, the selectivity sequences of metals in multi-metal solutions are highly dependent on the L/S for SS and AAC grains, and the Cd²⁺ and Pb²⁺ adsorptions are affected by the existence of competitive metal ions. The selectivity sequences for the mixtures of SS and AAC, on the other hand, were less dependent on the L/S compared to the results from single SS and AAC grains. For SS grains, the adsorption of Cd²⁺ (and Cu²⁺, Ni²⁺, and Zn²⁺) became much higher than that of Pb²⁺ at low L/S (=5 and 10), and the Pb²⁺ adsorption became higher than that of Cd²⁺. For AAC grains, the adsorption of Pb²⁺ (and Cu²⁺) became higher than that of Cd²⁺ at all L/S conditions in accordance with the tested results from single-metal and binary-metal solutions. For the mixtures of SS and AAC (SS+AAC [1:1]), the adsorption of Cd²⁺ became equal to the Pb²⁺ adsorption at low L/S (=5 and 10), but the sequence became the opposite at high L/S (=60, 100, and 250). Based on the test results above, therefore, the mixtures of SS and AAC grains are able to simultaneously remove Cd²⁺ and Pb²⁺ in multi-metals solution with high R values of approximately 100% at low L/S conditions (5 and 10). Again, the test results suggest the control of L/S is a key factor for the practical application of the mixtures of SS and AAC grains as adsorbents to remove Cd²⁺ and Pb²⁺ in wastewater.

In this study, SS exhibited a high capacity to adsorb Cd²⁺ from wastewater. For example, 0.105–2 mm particles of SS achieved effluent discharge standards of <0.001 mg/L for Cd²⁺ up to Ci < 1500 mg/L by the single-batch adsorption under the experimental conditions. Additionally, the SS+AAC (1:1) mixture removed 100% of Cd²⁺ and Pb²⁺ from binary and multi-metal solutions. However, the following facts should be considered in future studies and applications for the sustainable use of these low-cost adsorbents. Along with the metal adsorption process, SS and AAC grains released a relatively high concentration of Ca²⁺. Additionally, SS grains showed high alkalinity in water compared to wastewater. For wastewater, for example 0.105–2 mm particles of SS achieved effluent discharge standards of <0.001 mg/L for Cd²⁺ up to Ci < 1500 mg/L by the single-batch adsorption under the experimental conditions. Additionally, the SS+AAC (1:1) mixture removed 100% of Cd²⁺ and Pb²⁺ from binary and multi-metal solutions. However, the following facts should be considered in future studies and applications for the sustainable use of these low-cost adsorbents. Along with the metal adsorption process, SS and AAC grains released a relatively high concentration of Ca²⁺. Additionally, SS grains showed high alkalinity in water compared to wastewater.

### Table 6. Selectivity sequence of metal removal, R (%), for tested adsorbents with different liquid-to-solid ratio (L/S).

| Adsorbent | L/S | Selectivity Sequence | R (%) |
|-----------|-----|----------------------|-------|
|           |     |                      | Cd²⁺ | Pb²⁺ | Cu²⁺ | Ni²⁺ | Zn²⁺ |
| SS        | 5   | Cd²⁺ ≈ Cu²⁺ ≈ Ni²⁺ ≈ Zn²⁺ > Pb²⁺ | 100  | 86.1 | 100  | 100  | 99.8 |
|           | 10  | Cd²⁺ ≈ Cu²⁺ ≈ Ni²⁺ ≈ Zn²⁺ > Pb²⁺ | 100  | 86.9 | 100  | 100  | 99.7 |
|           | 60  | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ ≈ Ni²⁺ | 55.2 | 99.5 | 63.4 | 20.9 | 20.6 |
|           | 100 | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 51.7 | 76.2 | 63.8 | 0.9  | 8.0  |
|           | 250 | Pb²⁺ > Cd²⁺ > Cu²⁺ > Zn²⁺ > Ni²⁺ | 45.9 | 62.0 | 31.7 | 0.0  | 6.1  |
| SS+AAC [4:1] | 5   | Cd²⁺ ≈ Pb²⁺ ≈ Cu²⁺ ≈ Ni²⁺ ≈ Zn²⁺ | 100  | 100  | 100  | 100  | 100  |
|           | 10  | Cd²⁺ ≈ Cu²⁺ ≈ Ni²⁺ ≈ Zn²⁺ > Pb²⁺ | 100  | 96.4 | 100  | 100  | 44.5 |
|           | 60  | Cu²⁺ > Pb²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 46.1 | 87.8 | 99.3 | 17.9 | 23.2 |
|           | 100 | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 38.3 | 60.1 | 42.9 | 0.0  | 6.3  |
|           | 250 | Pb²⁺ > Cd²⁺ > Cu²⁺ > Zn²⁺ > Ni²⁺ | 39.1 | 37.1 | 28.4 | 0.2  | 5.3  |
| SS+AAC [1:1] | 5   | Ni²⁺ > Cu²⁺ > Zn²⁺ > Pb²⁺ > Cd²⁺ | 99.4 | 99.5 | 99.9 | 100  | 99.8 |
|           | 10  | Cu²⁺ > Pb²⁺ > Zn²⁺ > Cd²⁺ > Ni²⁺ | 97.2 | 99.2 | 100  | 23.9 | 71.4 |
|           | 60  | Cu²⁺ > Pb²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 21.9 | 97.6 | 98.5 | 0.0  | 6.5  |
|           | 100 | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 18.4 | 69.0 | 43.4 | 0.0  | 1.3  |
|           | 250 | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 17.8 | 39.6 | 18.0 | 0.0  | 0.1  |
| SS+AAC [1:4] | 5   | Pb²⁺ ≈ Cu²⁺ ≈ Zn²⁺ > Cd²⁺ > Cd²⁺ > Ni²⁺ | 41.3 | 100  | 100  | 44.7 | 71.1 |
|           | 10  | Cu²⁺ > Pb²⁺ > Ni²⁺ > Cd²⁺ > Zn²⁺ | 32.1 | 99.4 | 100  | 32.9 | 20.6 |
|           | 60  | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 19.4 | 100  | 60.1 | 17.9 | 5.3  |
|           | 100 | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 15.0 | 60.4 | 41.0 | 2.9  | 4.2  |
|           | 250 | Pb²⁺ > Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ | 14.0 | 30.7 | 25.2 | 0.0  | 2.9  |
to AAC. Therefore, those factors should be controlled before treated water is discharged into the natural environment.

4. Conclusions

The results of batch adsorption experiments of the tested adsorbents revealed that SS grains had a high affinity for Cd\(^{2+}\) (>300 mg/g) but less affinity for Pb\(^{2+}\) (<20 mg/g). In the binary-metal solution, the mixtures of SS and AAC grains, especially SS+AAC [1:1] and SS+AAC [1:4], removed 100% of Cd\(^{2+}\) and Pb\(^{2+}\) simultaneously without any effect of metal molar mixed ratios at the L/S ratio of 60. Remarkably, in the multi-metal solutions, the metal R and selectivity sequence varied depending on the mixing proportions of SS and AAC grains and L/S values. It was found that the SS+AAC [4:1] and SS+AAC [1:1] mixtures of SS and AAC grains removed 100% of Cd\(^{2+}\), Pb\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\), and Zn\(^{2+}\) simultaneously, at L/S = 10 and 60. The correlation regression showed that the ratios of released Ca\(^{2+}\) became greater than 1, meaning that approximately 2 and 6 times of Ca\(^{2+}\) were released in the one-metal adsorption process. For SS grains, active hydroxides (-OH) on the surface of metal oxides/hydroxides created a negative surface charge, resulting in the formation of an inner-sphere complex by replacing Ca\(^{2+}\). For AAC grains, the ion exchange between Ca\(^{2+}\) and Pb\(^{2+}\) on the adsorbent surface becomes dominant and the inner-sphere complex promotes the Pb\(^{2+}\) adsorption onto the surface with a negative charge. Thus, the amount of Ca\(^{2+}\) released became higher than the amount of metal adsorbed. Further studies are needed to examine the effects of other factors such as initial pH, temperature, and other competitive ions that control the heavy metal adsorption of SS and AAC grains. Additionally, the regeneration of metal-adsorbed adsorbents (i.e., collection of adsorption heavy metals from adsorbents) should be examined for practical application. The application of IBPs for the wastewater treatment, however, is essential with a high potential from the viewpoints of material efficiency and saving natural resource consumption.

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Abbreviations

AAC autoclaved aerated concrete
b Langmuir constant (g/L)
BET Brunauer–Emmett–Teller
CDW construction and demolition waste
Ce equilibrium concentration (mg/L)
Ci initial concentration (mg/L)
DI deionized water
EC electrical conductivity (mS/cm)
EDX energy-dispersive X-ray spectroscopy
Gs specific gravity (-)
IBPs industrial by-products
Kf Freundlich adsorption capacity (L/g)
LOI loss on ignition (%)

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