

# Removal of Cd<sup>2+</sup> and Pb<sup>2+</sup> from Wastewater through Sequent Addition of KR-Slag, Ca(OH)<sub>2</sub> Derived from Eggshells and CO<sub>2</sub> Gas

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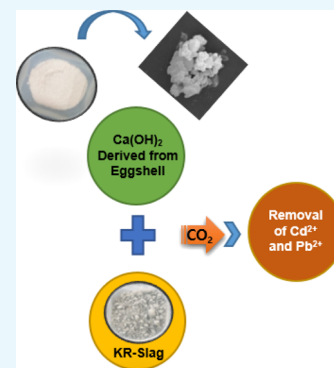
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**ABSTRACT:** The effect of heavy metals in aqueous solutions has been addressed by several methods. Precipitation using lime, slaked or quick, is one of the commonly used techniques. In this work, KR-slag was used in addition to Ca(OH)<sub>2</sub> that served as a seeding material. Furthermore, CO<sub>2</sub> has been injected into the suspensions for pH stabilization, which further increases the removal efficiency. Accordingly, results have shown a great performance regarding both removal efficiency and reduced sludge production. More than 99% of Cd<sup>2+</sup> and Pb<sup>2+</sup> was removed with 1 g/L of KR-slag, 0.5 g/L of Ca(OH)<sub>2</sub>, and CO<sub>2</sub> injection at a rate of 1 L/min. The effect of carbonation has been evaluated by examining the removal efficiency before and after carbonation. Following the injection of CO<sub>2</sub>, removal efficiency has increased from 58.7 to 99.8 and 71.2 to 99.3% for Cd<sup>2+</sup> and Pb<sup>2+</sup>, respectively. Moreover, sludge volume from this treatment method was obtained as 103 mL/L, which is much less than the sludge volume obtained from the carbonation of only Ca(OH)<sub>2</sub>, that is, 361 mL/L. Leaching of residues was also conducted to evaluate the environmental performance of the removal process. After carbonation, there was a lower concentration of metals when leached out in a wide range of pH solutions. Contrarily, it was observed that a relatively higher concentration of metals was released in acidic solutions due to the substitution of metal ions (Cd<sup>2+</sup> and Pb<sup>2+</sup>) with H<sup>+</sup> ions. Residues were then characterized by X-ray diffraction and differential thermal analysis/thermogravimetric analysis for phase identification. Both characterizations detected the presence of CaCO<sub>3</sub>, which was an indication of the transformation of Ca(OH)<sub>2</sub> to CaCO<sub>3</sub>.



## 1. INTRODUCTION

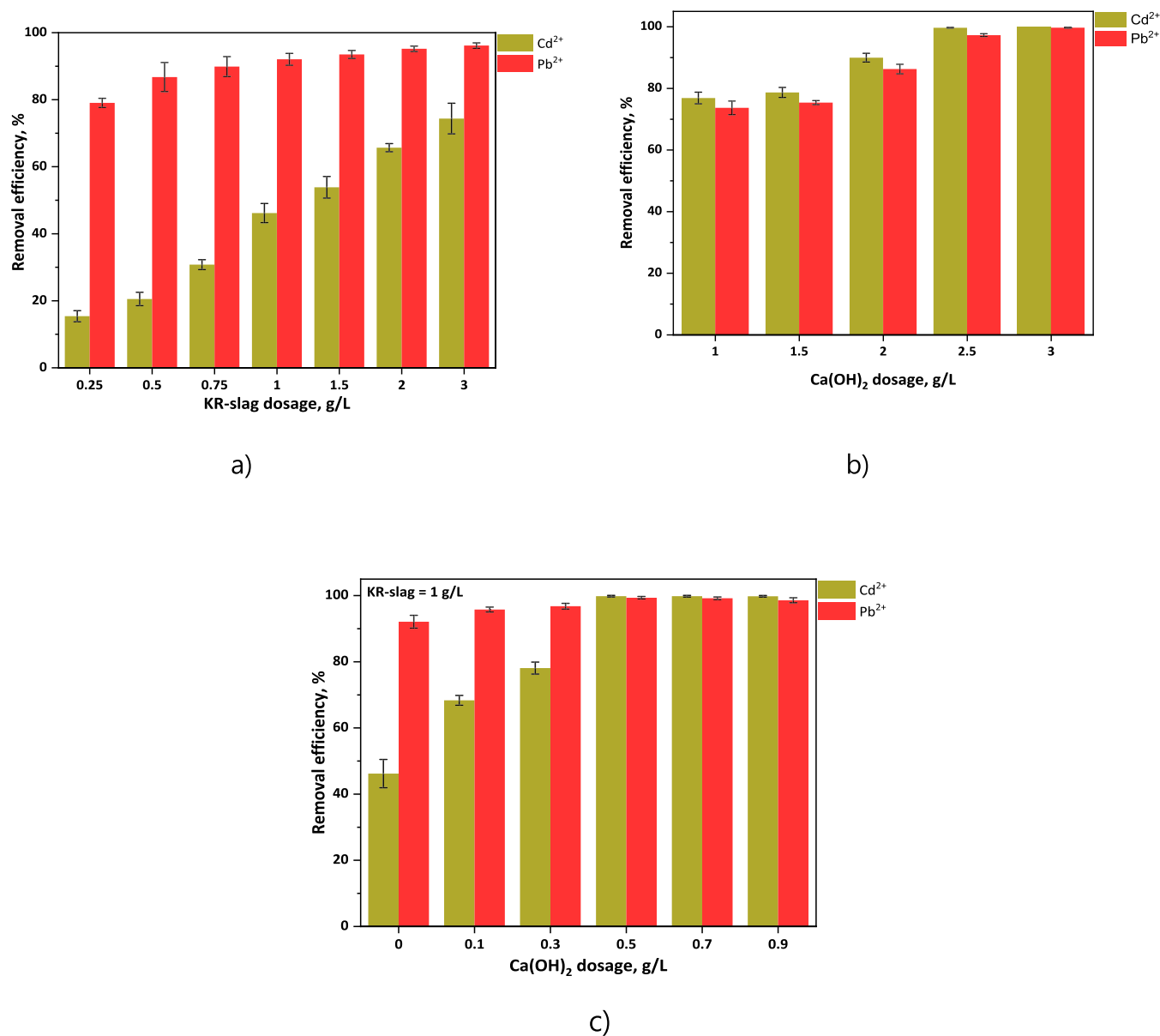
Heavy metals, for example, cadmium (Cd<sup>2+</sup>) and lead (Pb<sup>2+</sup>), are a threat to water bodies because of their harmfulness by creating intense and persistent harm to human and oceanic life.<sup>1</sup> They are ineluctable because of their wide production and applications in different industries. Currently, treatment of aqueous solutions containing toxic heavy metals has been conducted through various techniques such as Fenton-chemical precipitation,<sup>2</sup> chemical precipitation,<sup>3,4</sup> electro-coagulation,<sup>5</sup> ion flotation,<sup>6</sup> adsorption,<sup>7–14</sup> ion exchange,<sup>15</sup> layered double hydroxide precipitation,<sup>16</sup> and reverse osmosis.<sup>17</sup> However, these techniques have some limitations. For instance, adsorption is less effective for aqueous solutions containing higher concentrations of heavy metals. Membrane filtrations such as reverse osmosis have high operation costs and high energy consumption and need skilled manpower, which limit the use of this method. Ion exchange has a high cost for ion exchange materials, and some resins are not available for specific metal ions. Chemical precipitation is ordinarily applied because of its better performance and simplicity of use. It is the conversion of dissolved heavy metal ions to insoluble solid precipitates. However, chemical precipitations such as hydroxide precipitation leave alkaline solutions after treatment, redissolve back of formed metal hydroxides at lower pH, suitability problem for chelated

wastewaters and difficulty of filtration because of the gelatinous behavior of metal hydroxides.

Industrial residues such as fly ash, bottom ash, steel slags, cement waste, kiln dust, and so forth are produced as byproducts in the industries. They are composed of different metal oxides and complex minerals that can be used for further application such as for backfilling or construction. They also contain toxic heavy metals that should not be disposed of to the environment without treatment.<sup>18</sup> Industrial residues have abundant alkaline earth metals that can be used as an adsorbent for CO<sub>2</sub>.<sup>19</sup> They can also be used for the adsorption of pollutants from aqueous solutions<sup>20</sup> and also the solidification of heavy metals.<sup>21</sup> Kambara reactor slag (KR-slag) is an industrial byproduct generated from the desulfurization of molten iron in a steel factory. Lime is used as a desulfurizer from the KR mechanical stirring process that reacts with sulfur resulting in CaS. For the improvement of the desulfurization

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**Figure 1.** Removal efficiency (a) with only KR-slag, (b) with only Ca(OH)<sub>2</sub>, and (c) with Ca(OH)<sub>2</sub> and KR-slag.

process, excess lime is added, resulting in unreacted CaO.<sup>22</sup> The products CaS and unreacted CaO have a low specific gravity rising to the surface of the molten iron and then slag is formed.<sup>23</sup> The main constituents of KR-Slag are calcium oxide, iron oxide, and silicon oxide, in which calcium oxide is more than 45% depending on the amount of the desulfurizer (lime) used in the KR mechanical stirring process.<sup>24</sup> Due to the high content of calcium oxide, it has versatile applications such as a cement-free binder in concrete,<sup>23,25,26</sup> in acid mine drainage treatment,<sup>22</sup> for soil modification,<sup>27</sup> as an alkali activator of an alkali-activated system,<sup>28</sup> and backfill material. In contrast, solid wastes such as eggshells have valuable applications in versatile fields. Eggshells have been generated abundantly causing serious environmental problems. An approximate annual generation of 5.92 Mt of eggshells has been estimated.<sup>29</sup> Although the waste eggshell is composed of a valuable constituent [mainly calcium carbonate (CaCO<sub>3</sub>)], which has numerous applications,<sup>30–32</sup> most of the waste is being disposed of to the environment.

In this paper, KR-slag was used for heavy metal removal by accelerated carbonation of Ca(OH)<sub>2</sub>. This method overcomes most limitations of the current removal techniques mentioned above. It leaves the treated water at neutral pH due to the dissolution of CO<sub>2</sub> gas that also reduces the solubility of heavy metals. It is also an effective, less time-consuming, eco-friendly, and sustainable approach because it utilizes waste materials. Furthermore, it can be considered as a CO<sub>2</sub> emission mitigation approach along with heavy metal treatment. In this work, Cd<sup>2+</sup> and Pb<sup>2+</sup> removal efficiencies with carbonation of only Ca(OH)<sub>2</sub>, only KR-slag, and both Ca(OH)<sub>2</sub> and KR-slag were compared. The effect of carbonation has been studied by evaluating the removal efficiency before and after the addition of CO<sub>2</sub> gas. The performance of residues was evaluated by conducting a leaching test on the precipitates. Moreover, precipitates were analyzed further to study their removal mechanism.

## 2. RESULTS AND DISCUSSION

**2.1. Heavy Metal Removals.** Figure 1a gives the removal efficiency of heavy metals by KR-slag carbonation without the addition of  $\text{Ca}(\text{OH})_2$ . The dosage of KR-slag used was in the range of 0.25 to 3 g/L. In all the dosages,  $\text{Cd}^{2+}$  has shown a lower removal efficiency than  $\text{Pb}^{2+}$ . It was observed that the removal efficiency of  $\text{Cd}^{2+}$  increased from 15.4 to 74.4% when KR-slag dosage was increased from 0.25 to 3 g/L. Contrarily, the removal efficiency of  $\text{Pb}^{2+}$  increased from 79.0 to 96.1% when KR-slag dosage was increased from 0.25 to 3 g/L.  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were removed (74.4 and 96%, respectively) at a dosage of 3 g/L.

Figure 1b shows the removal efficiency of heavy metals by  $\text{Ca}(\text{OH})_2$  carbonation without the addition of KR-slag. Conditions of the experiment were  $\text{Ca}(\text{OH})_2$  dosage of 1–3 g/L, 100 mg/L initial metal concentration, and 1 L/min of  $\text{CO}_2$  flow rate. The removal efficiency obtained at 3 g/L of  $\text{Ca}(\text{OH})_2$  was higher for both metals (nearly 99%). The detailed results were given in a previous work.<sup>33</sup>

Although the removal efficiency with only  $\text{Ca}(\text{OH})_2$  or KR-slag as discussed above is nearly 99% at 3 g/L, the sludge produced is significant, leading to environmental pollution. The production of sludge needs to be reduced by using less dosage of precipitants taking environmental protection into account. Therefore, KR-slag was used as a seeding material in the  $\text{Ca}(\text{OH})_2$  carbonation process. Figure 1c shows the removal efficiency of heavy metals by  $\text{Ca}(\text{OH})_2$  carbonation with the addition of KR-slag. Dosage of  $\text{Ca}(\text{OH})_2$  was used in the range of 0–0.9 g/L, whereas 1 g/L of KR-slag was used in addition to  $\text{Ca}(\text{OH})_2$  for coagulation and flocculation. At 0 g/L of  $\text{Ca}(\text{OH})_2$  (only 1 g/L of KR-slag), 46 and 92% of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were removed, respectively. However, as the dosage of  $\text{Ca}(\text{OH})_2$  increased, the removal efficiency has also increased. At 0.5 g/L of  $\text{Ca}(\text{OH})_2$ , 99% of both metals was removed. Therefore, desired removal efficiency and reduced sludge production were achieved at a KR-slag dosage of 1 g/L and  $\text{Ca}(\text{OH})_2$  dosage of 0.5 g/L.

The kinetics of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  removal was conducted with an initial metal concentration of 100 mg/L using 1 g/L of KR-slag and 0.5 g/L of  $\text{Ca}(\text{OH})_2$  synthesized from eggshells. The precipitation process was completed within 10 min. Initially, both metals showed lower removal efficiencies, which increased with time and were nearly 99% at 10 min, as shown in Figure 2. Moreover, initial rapid precipitation was observed up to 6 min, followed by slower precipitation.

Suspension pH is one of the indispensable parameters in heavy metal removals. The change in pH during removal of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  is shown in Figure 3. It shows the pH change both before and after the injection of  $\text{CO}_2$ . The initial pH of the synthetic aqueous solution was  $\sim 6.0$ – $6.2$  before the addition of KR-slag and of  $\text{Ca}(\text{OH})_2$ . It increased rapidly, as both precipitants were introduced to the solution and stabilized after few minutes. The increase in pH had shown an insignificant difference in rate:  $\text{Cd}^{2+}$  has a slower rate than  $\text{Pb}^{2+}$ . This difference rate might be significant if higher concentrations of heavy metals were considered. Then,  $\text{CO}_2$  gas was then injected at 10 min, followed by a rapid decrease in solution pH and stabilized  $\sim \text{pH } 7$ .

To evaluate the effect of carbonation,  $\text{CO}_2$  with a purity of 99.9% was injected into heavy metal-containing (concentration of 100 mg/L) suspensions with 1 g/L of KR-slag and 0.5 g/L of  $\text{Ca}(\text{OH})_2$ . Initially [without the addition of KR-slag and

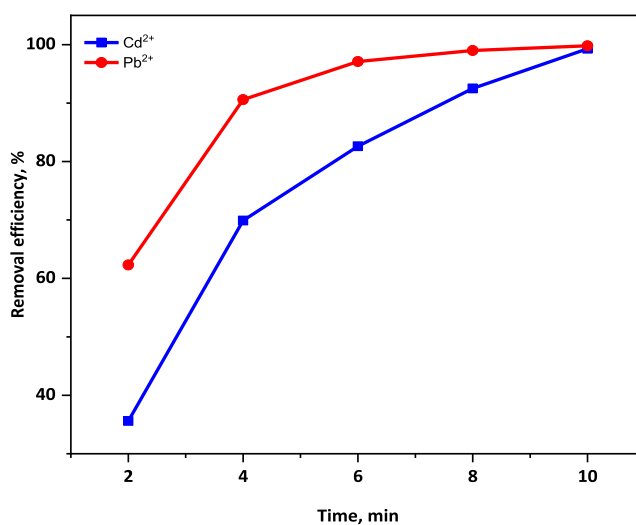


Figure 2. Kinetics of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  removal.

$\text{Ca}(\text{OH})_2$ ], the pH of all suspensions was in the range of 5.6–6.1. However, the pH immediately increased to 12 after the addition of KR-slag and  $\text{Ca}(\text{OH})_2$ . Then, it finally reduced to pH 7 after coming in contact with  $\text{CO}_2$ . Figure 4 shows that the injection of  $\text{CO}_2$  gas has increased heavy metal removal significantly. Before carbonation, both metals have shown lower removal efficiencies. This result has also been obtained in a previous study in which  $\text{Cr}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  were removed by carbonation of fly ash and lime.<sup>34</sup> For cadmium (see Figure 4a), the removal efficiency before carbonation at 0.5 g/L of  $\text{Ca}(\text{OH})_2$  was 58.7%. However, the removal efficiency increased to 99.8% after carbonation. However, for lead (see Figure 4b), the removal efficiency before and after carbonation at 0.5 g/L of  $\text{Ca}(\text{OH})_2$  was 71.2 and 99.3%, respectively. It can also be seen that the removal efficiency decreased from 71.2 to 60.3%, as the dosage increased from 0.5 to 0.9 g/L. It can be because of the thermodynamic stability of the lead– $\text{H}_2\text{O}$  system.  $\text{Pb}^{2+}$  ions will be released, as pH of the solution is low ( $< 6$ ). Additionally,  $\text{Pb}(\text{OH})_2$  will redissolve to form  $[\text{Pb}(\text{OH})_4]^{2-}$  (eq 1), as pH of the solution is high ( $> 12$ ). This elaborates on the cause of the reduction in removal efficiency at higher dosages.<sup>33</sup>



**2.2. Residue Characterization.** **2.2.1. Sludge Amount.** The main advantage of this work is the reduction of sludge production. The sludge characteristics were given in Table 1. The sludge volume was obtained as 361 mL/L for carbonation of only  $\text{Ca}(\text{OH})_2$ , whereas 103 mL/L for carbonation of both KR-slag and  $\text{Ca}(\text{OH})_2$ , indicating that more than one-third of sludge production has been reduced. Moreover, the weight of the solid after dewatering was recorded as 3.22 g/L for carbonation of only  $\text{Ca}(\text{OH})_2$ , while it was 1.52 g/L for carbonation of both KR-slag and  $\text{Ca}(\text{OH})_2$ .

**2.2.2. Leaching.** Leaching of residues obtained from the removal process was conducted in the pH range of 1 to 13. The results showed that the release of heavy metals from residues after carbonation was slower than that from the residues before carbonation, as shown in Figure 5. Generally,  $\text{Cd}^{2+}$  exhibits lower metal concentration than  $\text{Pb}^{2+}$  at all pH ranges. However, both metals have shown a higher concentration of metals at lower pH due to the presence of

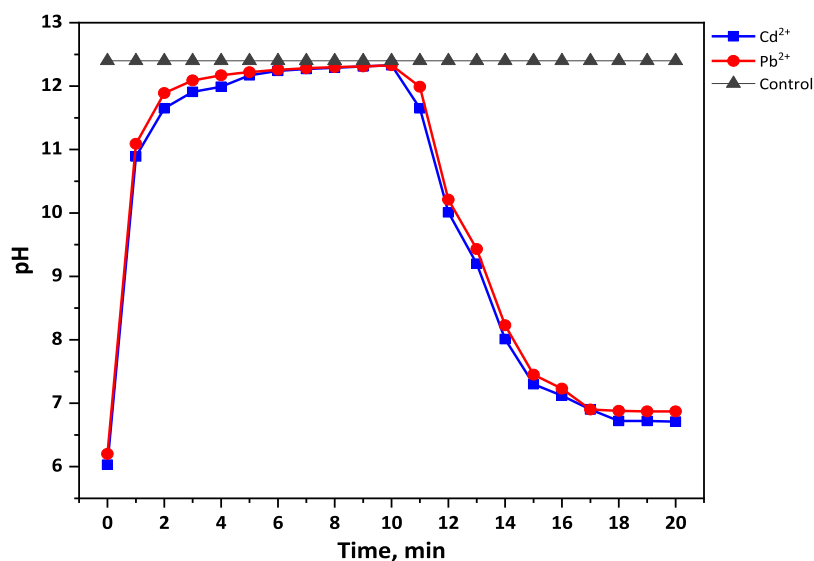


Figure 3. pH change with time.

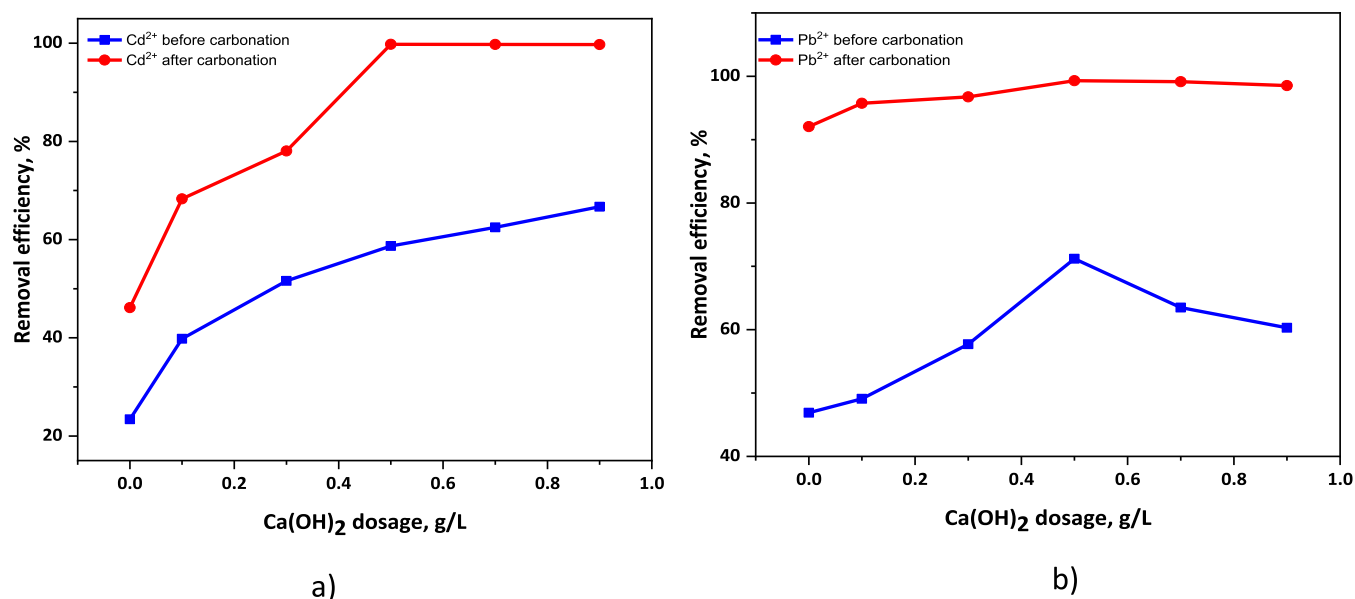
Figure 4. (a) Removal efficiency of Cd<sup>2+</sup> and (b) Pb<sup>2+</sup> before and after carbonation.

Table 1. Sludge Characteristics

sludge characteristics	carbonation of only Ca(OH) <sub>2</sub>	carbonation of both KR-slag and Ca(OH) <sub>2</sub>
sludge volume, mL/L	361	103
solid weight (after dewatering), g/L	3.22	1.52

more H<sup>+</sup> ions than the metal ions.<sup>35</sup> The leaching test shows the stabilization of heavy metals in the residue in a wide range of pH.

**2.2.3. Phase Identification.** The crystalline phase identified in KR-slag is given in Figure 6a. The main constituent of the raw material was portlandite with minor constituents of calcite, graphite, magnetite, ettringite, and free iron. Moreover, the X-ray diffraction (XRD) of Ca(OH)<sub>2</sub> synthesized from eggshells was given in a previous work,<sup>36</sup> which was mainly composed of portlandite. Figure 6b shows the crystalline phase identified in the residue after precipitation with carbonation of KR-slag and

Ca(OH)<sub>2</sub>. CaCO<sub>3</sub> was the only identified compound in the solid residue. This might be due to the difference in concentrations used of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Ca<sup>2+</sup> ions. The main peak was substituted by calcite, where portlandite was no more dominant in the precipitate. This result confirmed the total transformation of the phase during the carbonation process.

The differential thermal analysis/thermogravimetric analysis (DTA/TGA) curve of KR-slag before carbonation and the precipitate is illustrated in Figure 6. Cd<sup>2+</sup> and Pb<sup>2+</sup> precipitated from the carbonation of both KR-slag and Ca(OH)<sub>2</sub> were analogous to carbonation of only Ca(OH)<sub>2</sub>. The KR-slag showed weight losses of 12.90, 4.74, and 1.66%, corresponding to vaporization, decomposition of Ca(OH)<sub>2</sub> to CaO, and decomposition of CaCO<sub>3</sub> to CaO, respectively (see Figure 7a).<sup>37</sup> Moreover, the DTA/TGA curve of Ca(OH)<sub>2</sub> was given in a previous work.<sup>36</sup> On the other hand, the precipitate showed a total weight loss of 44.64% at 768.51 °C (see Figure 7b). This loss is mainly due to the release of CO<sub>2</sub> from CaCO<sub>3</sub>

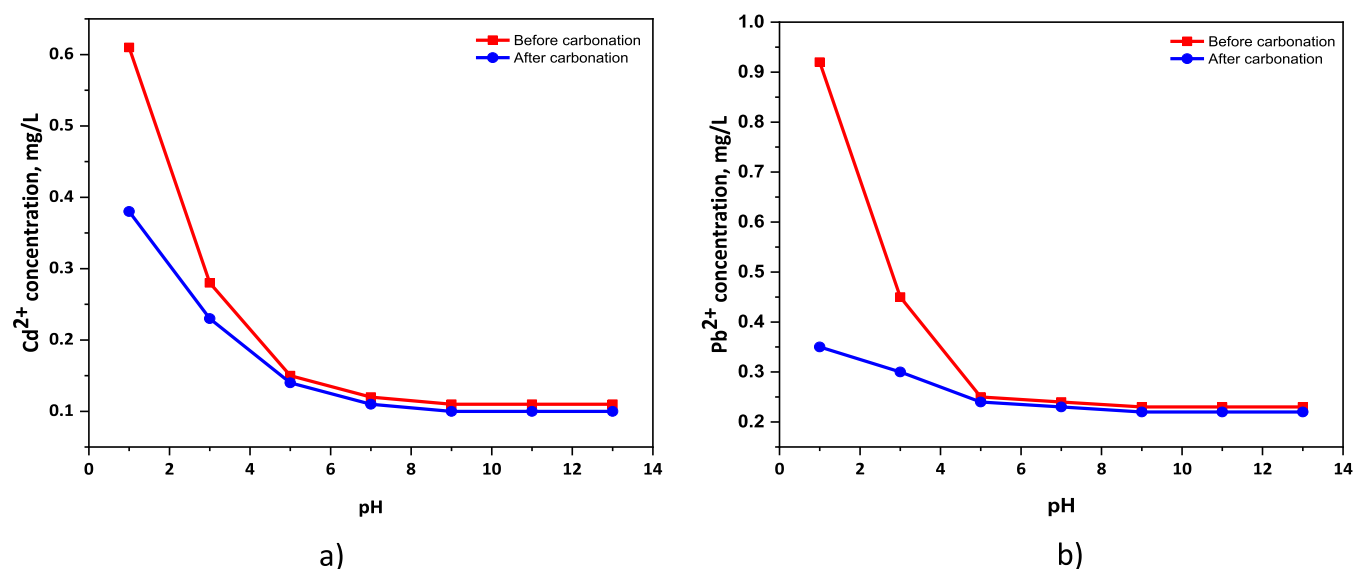


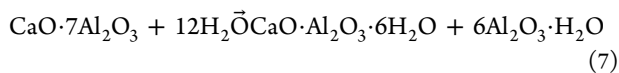
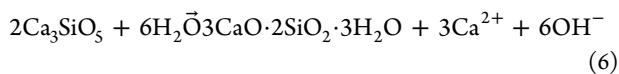
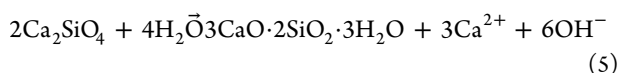
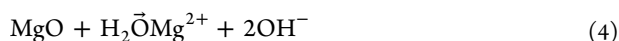
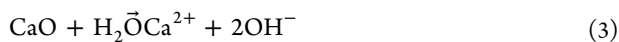
Figure 5. Leachate concentration of (a) Cd<sup>2+</sup> and (b) Pb<sup>2+</sup>.

decomposition. This result also shows a complete transformation of Ca(OH)<sub>2</sub> to CaCO<sub>3</sub>. However, the decomposition temperature of the precipitate with Cd<sup>2+</sup> and Pb<sup>2+</sup> was found to be lower than that of the precipitate without heavy metals CaCO<sub>3</sub>. A similar result has been obtained from another study.<sup>34</sup>

**2.3. Removal Mechanism.** Heavy metal removal with the addition of KR-slag and Ca(OH)<sub>2</sub> and carbonation depends on hydration and metal speciation. First, hydroxyl ions are released into the solution by hydration of KR-slag and Ca(OH)<sub>2</sub>. The hydration of Ca(OH)<sub>2</sub> is given in eq 2.



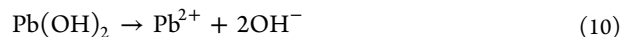
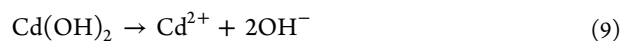
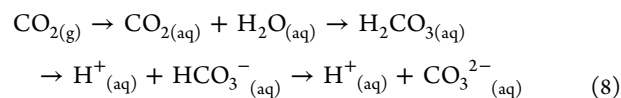
The hydration of solid phases in KR-slag such as CaO, MgO, CaO<sub>2</sub>SiO<sub>4</sub>, CaO<sub>3</sub>SiO<sub>5</sub>, and CaO·7Al<sub>2</sub>O<sub>3</sub> may occur as given in eqs 3–7.<sup>38</sup>



The abovementioned reactions resulted in the release of hydroxyl ions from the hydration of KR-slag and Ca(OH)<sub>2</sub> (before carbonation) that may result in heavy metal hydroxide precipitation. Moreover, sorption may also occur on the surface of solid phases of the KR-slag. The mechanism for treatment in the presence of Ca(OH)<sub>2</sub> is dependent on the pH of solution and metal concentrations. Therefore, it is important to observe cadmium and lead water systems. Cd<sup>2+</sup> decomposes in acidic and very alkaline solutions. In acidic and very alkaline solutions, Cd<sup>2+</sup> and HCdO<sub>2</sub><sup>-</sup> are released into the solution, respectively. Meanwhile, for solution pH in between, the stability of Cd(OH)<sub>2</sub> may prevent the mobility of Cd<sup>2+</sup>. On the

other hand, Pb<sup>2+</sup> tends to be stable thermodynamically when solutions are neutral or alkaline. In acidic and very high alkaline solutions, lead generally tends to decompose. Pb<sup>2+</sup> and HPbO<sub>2</sub><sup>-</sup> or PbO<sub>3</sub><sup>2-</sup> (depending on the oxidation) are released to the acidic and high alkaline solutions, respectively. In the meantime, PbO or Pb<sub>3</sub>O<sub>4</sub> or PbO<sub>2</sub> (depending on the oxidation) inhibits Pb<sup>2+</sup> mobility for solution pH in between acidic and alkaline solution.

Carbonic acid, bicarbonates, and carbonates obtained from the hydration of CO<sub>2</sub> gas in the presence of CO<sub>2</sub>.<sup>39</sup> Then, Cd(OH)<sub>2</sub> and Pb(OH)<sub>2</sub> will release metal ions to the solution due to low pH caused by the dissociation of CO<sub>2(aq)</sub> [eqs 9 and 10].



Lead carbonate and cadmium carbonate are the predominant species at neutral pH as predicted from the equilibrium of the Pb<sup>2+</sup>(Cd<sup>2+</sup>)–H<sub>2</sub>O–CO<sub>2</sub> system. Figure 8 gives the stability of CdCO<sub>3</sub> and PbCO<sub>3</sub> thermodynamically in the presence of CO<sub>2</sub> at a neutral pH and temperature of 25 °C. The thermodynamics calculations were carried out using Matlab R2010a software with thermodynamics parameters of all possible reactions. The concentrations of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and CO<sub>2</sub> were considered the same as the experimental condition, that is, 0.89 mM, 0.48 mM, and 0.1 M, respectively. Cd<sup>2+</sup> and Pb<sup>2+</sup> ion speciation was significantly affected by pH of the solution. At acidic and alkaline solutions, ions are released to the solution either in the form of free ions (Cd<sup>2+</sup> and Pb<sup>2+</sup>) or complex ions [Cd(OH)<sub>3</sub><sup>-</sup> and Pb(OH)<sub>3</sub><sup>-</sup>]. At neutral pH, however, CdCO<sub>3</sub> and PbCO<sub>3</sub> precipitates are produced for Cd<sup>2+</sup> and Pb<sup>2+</sup>, respectively.

Therefore, the possible reaction present in the treatment process is given in eqs 11–13. The crystal nucleation is followed by the crystal growth of CaCO<sub>3</sub>, CdCO<sub>3</sub>, and PbCO<sub>3</sub> by fast supersaturation of the abovementioned processes.

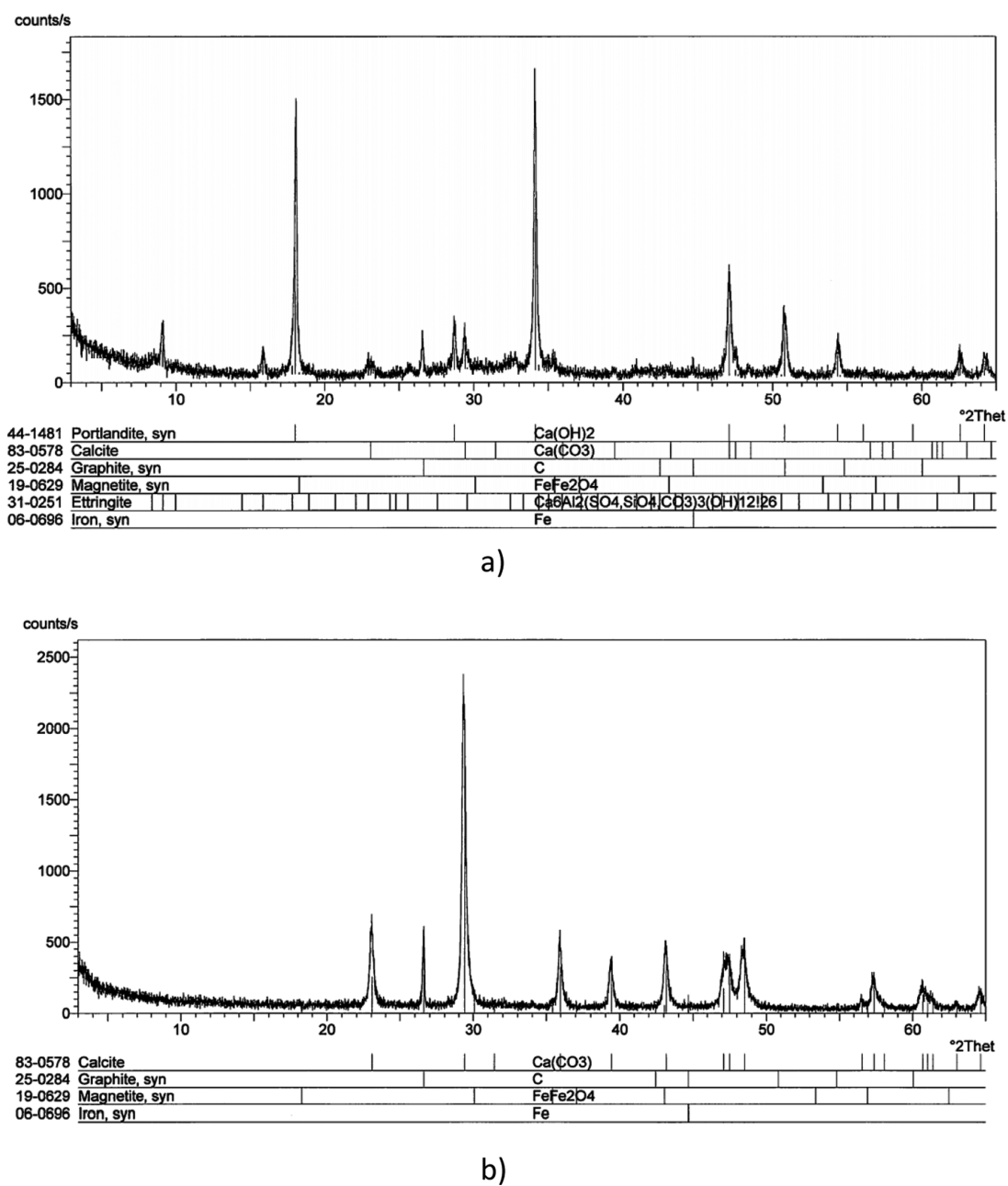


Figure 6. X-ray diffraction pattern of (a) KR-slag and (b) solid residue.

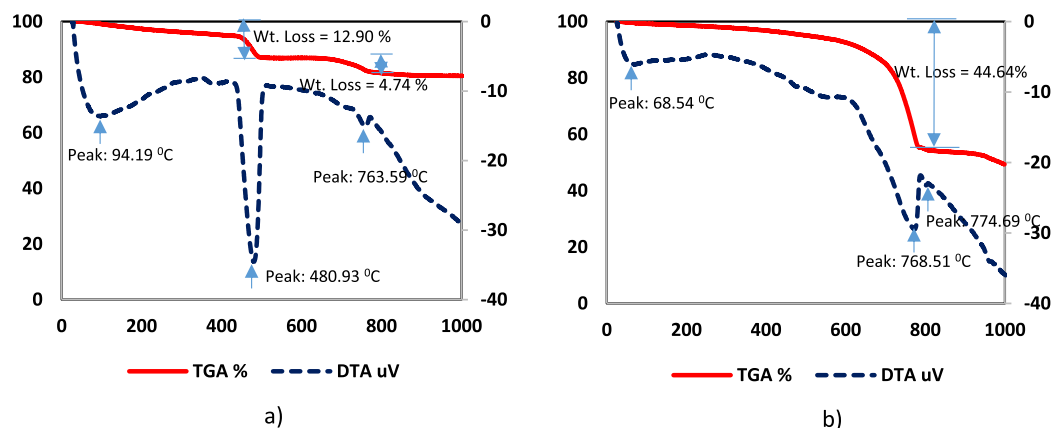
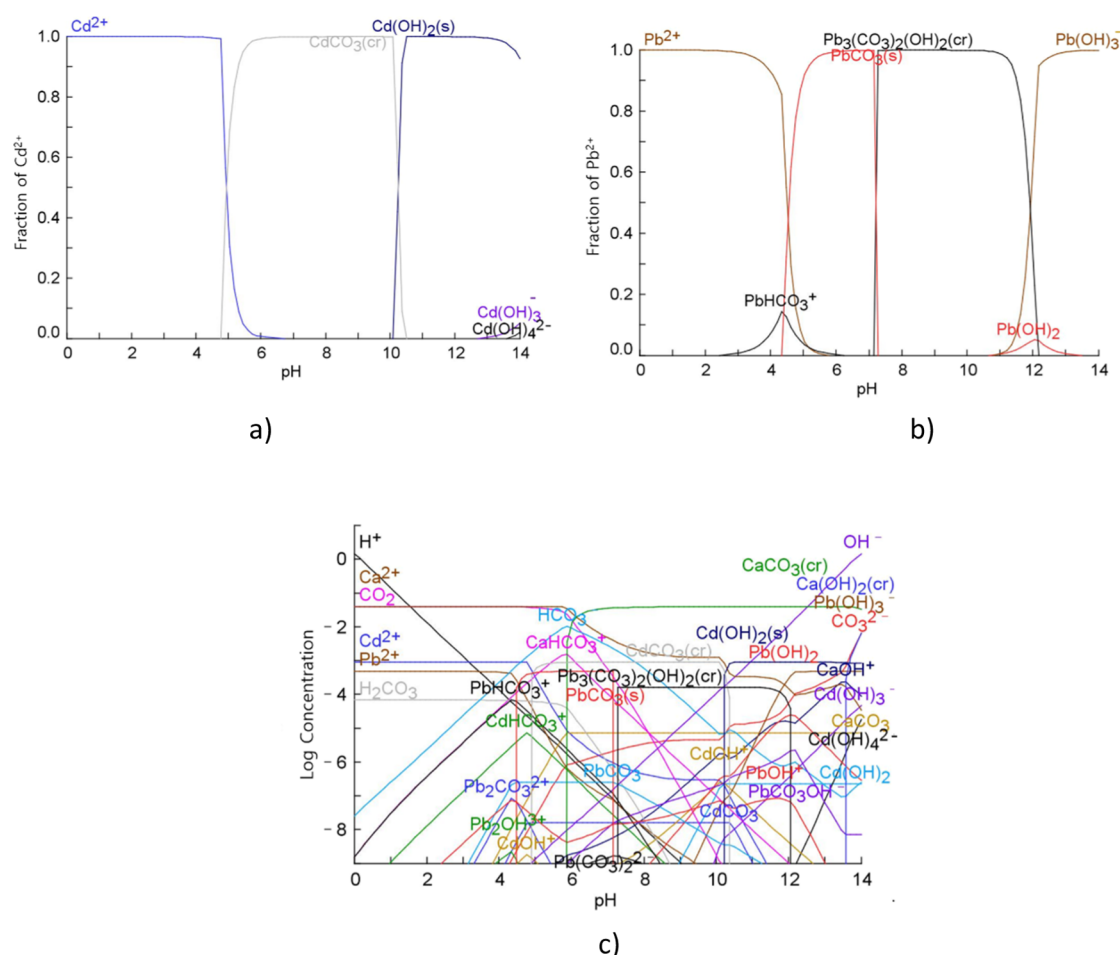


Figure 7. DTA/TGA of (a) KR-slag and (b) solid residue.



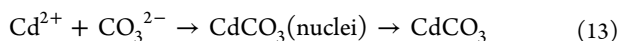
**Figure 8.** Thermodynamic stability of (a)  $\text{Cd}^{2+}$ , (b)  $\text{Pb}^{2+}$ , and (c) both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in the presence of  $\text{CO}_2$ .



11



12



### 3. CONCLUSIONS

KR-slag and  $\text{Ca}(\text{OH})_2$  with carbonation have been applied for the removal of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . High removal efficiency and reduced sludge production were obtained by the carbonation process with both  $\text{Ca}(\text{OH})_2$  and KR-slag. The  $\text{Ca}(\text{OH})_2$ –KR-slag– $\text{CO}_2$  treatment of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  achieved removal efficiencies of more than 99% with 1 g/L of KR-slag and 0.5 g/L of  $\text{Ca}(\text{OH})_2$  for both metals. Furthermore, the sludge volume was obtained as 361 mL/L for carbonation of only  $\text{Ca}(\text{OH})_2$  and 103 mL/L for carbonation of both KR-slag and  $\text{Ca}(\text{OH})_2$ . The weight of the solid after dewatering was obtained as 3.22 g/L for carbonation of only  $\text{Ca}(\text{OH})_2$  and 1.52 g/L for carbonation of both KR-slag and  $\text{Ca}(\text{OH})_2$ . This revealed that the reduction in sludge production was significant that can minimize the environmental impact. The impact of carbonation was also significant, where removal efficiency has increased from 58.7 to 99.8 and 71.2 to 99.3% for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , respectively, after the injection of  $\text{CO}_2$  gas. Leaching tests on residues were also conducted to evaluate the environmental

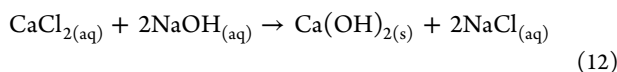
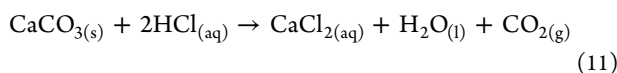
performance of the removal method. The final metal concentration after carbonation had shown a decrease in the release of heavy metals to the environment. Moreover,  $\text{Ca}(\text{OH})_2$  was completely transformed to  $\text{CaCO}_3$ , indicating the complete carbonation of the precipitants. Therefore, the inclusion of KR-slag as a seeding material in the  $\text{Ca}(\text{OH})_2$  carbonation process resulted not only in effective removal efficiency but also in a significant reduction in sludge production. Therefore, this technique of heavy metal treatment has several advantages such as  $\text{CO}_2$  sequestration, heavy metal removal, and KR-slag treatment (stabilization/solidification) prior to landfilling.

### 4. MATERIALS AND METHODS

**4.1. Materials.** Stock solutions with 1000 mg/L concentration of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in deionized water. Synthetic wastewater with 100 mg/L metal concentration was prepared by diluting the stock solution. Sodium hydroxide ( $\text{NaOH}$ ), hydrochloric acid ( $\text{HCl}$ ), and nitric acid ( $\text{HNO}_3$ ) were used for pH adjustment. Carbon dioxide gas with 99.9% purity was provided by Jeil Gas Company, Seoul, South Korea. All chemicals were provided by Junsei Chemicals Ltd., Seoul, South Korea.

The sol–gel method has been used to synthesize  $\text{Ca}(\text{OH})_2$  from waste eggshells. Powdered eggshells were first dissolved in 1 M of  $\text{HCl}$  (eq 11) to produce a homogeneous mixture of calcium chloride ( $\text{CaCl}_2$ ), followed by the dropwise addition of

1 M of NaOH to CaCl<sub>2</sub> solution (eq 12). The Ca(OH)<sub>2</sub> gel was then formed, filtered out, washed several times with distilled water, and dried in an oven at 60 °C for 24 h.



KR-slag was obtained from a company in South Korea. It is a heterogeneous material consisting largely of calcium oxide. The KR-slag was prepared for use by sieving with 100 μm sieve size and oven drying at 105 °C for 5 h.

The chemical composition of waste eggshells and sieved KR-slag is given in Table 2. Moreover, heavy metal contents in KR-slag were also analyzed, as given in Table 3, because the slag can be exposed to various heavy metals.

**Table 2. Chemical Composition of Waste Eggshells and KR-Slag**

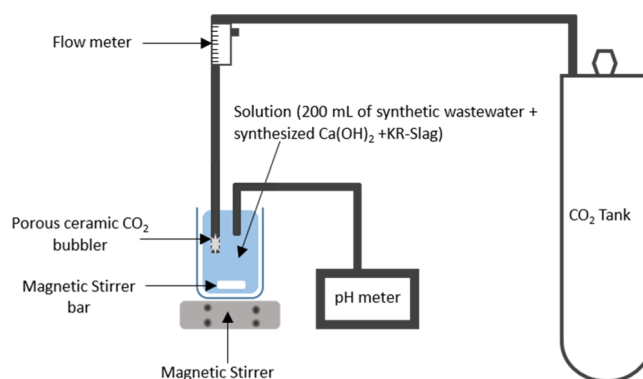
chemical composition	waste eggshells, %	KR-slag, %
SiO <sub>2</sub>	<0.01	11.2
Al <sub>2</sub> O <sub>3</sub>	<0.01	2.7
Fe <sub>2</sub> O <sub>3</sub>	<0.01	16.8
CaO	52.75	51
MgO	0.52	2.7
K <sub>2</sub> O	0.04	0.09
Na <sub>2</sub> O	0.05	0.07
TiO <sub>2</sub>	<0.01	
MnO	<0.01	1.8
SO <sub>3</sub>		4.3
P <sub>2</sub> O <sub>5</sub>	0.22	
Ig. loss	46.62	7.2

**Table 3. Heavy Metal Contents in KR-Slag<sup>a</sup>**

chemical composition	KR-slag, %
As	<0.01
Pb	N.D
Cu	N.D
Cr	N.D
Cd	N.D
Ni	N.D
Zn	N.D

<sup>a</sup>N.D = not detected.

**4.2. Methods.** **4.2.1. Precipitation.** KR-slag was used as a seeding material to enhance precipitation. Ca(OH)<sub>2</sub> was also used together with the KR-slag to elevate the pH as required. The slag was added at a rate of 0.25 g to 1 L of the heavy metal solution, and then, Ca(OH)<sub>2</sub> was added at a desired amount. To initiate coagulation and agglomeration, suspensions [synthetic wastewater with KR-slag and Ca(OH)<sub>2</sub>] were first rapidly stirred at 300 rpm for 3 min using a stirrer, followed by gentle stirring at 80 rpm for 7 min. Carbonation of suspensions was conducted simultaneously, with CO<sub>2</sub> of 99.9% purity maintained at atmospheric pressure. Figure 9 gives the schematic representation of the carbonation process. Supernatants were then allowed to settle for 30 min and then filtered by a Whatman filter (0.45 μm) before analyzing by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 8300) (ICP-OES). Triplicate measurements of metal



**Figure 9.** Schematic representation of the carbonation process.

concentrations were performed, and their average values were obtained. For further analysis, sludges were dried at 105 °C for 12 h. The pH of suspensions was constantly monitored by using a pH meter.

**4.2.2. Sludge Amount.** The sludge amount was estimated both before and after dewatering. The volumetric method has been used to determine sludge volume before dewatering that was measured by Imhoff cones after settling the treated solution for 30 min. Moreover, the solution was filtered and dried at 105 °C for 24 h to measure the weight of the solids.

**4.2.3. Leaching.** The environmental performance of sludge in a landfill was evaluated by a leaching test. It was conducted on a shaker rotated at 150 rpm with a liquid to solid ratio of 10 for 24 h at room temperature. The leaching effect was conducted in the range of pH 1–13. The supernatant liquids were then filtered through a 0.45 μm Whatman filter and analyzed by ICP-OES.

**4.3. Characterizations.** TGA/DTA and XRD were used for the characterization of solids. Decomposition temperatures of raw materials and precipitates were analyzed by thermogravimetric analysis (TGA) (Shimadzu DTG-60H) in a platinum crucible at a heating rate of 10 °C/min from ambient temperature to 1000 °C. Phase identification and structural analysis of solids were conducted by powder XRD with 2θ ranging from 10 to 90° (BD2745N, Rigaku, Tokyo, Japan). An Orion Versa Star Pro (Thermo Scientific, USA) pH meter with a glass electrode was used to constantly monitor the pH of suspensions. Pb<sup>2+</sup> and Cd<sup>2+</sup> concentrations were analyzed by ICP-OES.

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L.H.E.: Conceptualization, data curation, methodology, and writing—original draft. T.T.: Supervision. J.W.A.: Project administration, supervision, and writing—review and editing.

### Notes

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