

## Article

# Chemical Removal of Cu and Zn from Swine Feces before Soil Application

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**Abstract:** Cu and Zn are known to be abundant in swine feces; hence, concentrations of these metals need to be lowered before swine feces are applied to land in order to prevent potential environmental problems. The main objective of this study was to develop an appropriate chemical process to remove Cu and Zn from swine feces using acid extractions. The removal efficiencies of Cu and Zn decreased in the order of  $H_2SO_4 > HNO_3 >$  organic acids (citric and oxalic acids). Owing to the highest removal efficiencies of Cu and Zn by using  $H_2SO_4$ , it was selected for further elimination of Cu and Zn from swine feces. By using  $H_2SO_4$ , the optimal concentration, solid-to-liquid ratio, and reaction time were 2%, 1:50, and 8 h, respectively. At the optimum conditions, Cu concentration was decreased from 198 mg/kg to 40.1 mg/kg and Zn concentration from 474 mg/kg to 80.0 mg/kg, with removal rates of 79.7% and 83.1%, respectively. The low Cu removal efficiency, resulting from the strong complexation between Cu and organic matter of swine feces, was improved by the increase in the reaction time and  $H_2SO_4$  solution concentrations. However, about half of the total nitrogen (TN) was also removed by using  $H_2SO_4$ , indicating that the swine feces treated with  $H_2SO_4$  may have poor value as fertilizer. Additional studies are required to find an optimal method to maintain TN concentrations while simultaneously removing Cu and Zn.



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**Keywords:** swine feces; metals; fertilizer; removal; sludge

## 1. Introduction

Owing to the economic profitability and low environmental pollution, swine feces have been frequently used as an alternative to chemical fertilizers [1,2]. Heavy metals, especially Cu and Zn, are abundant in swine feces as they are used in swine feed to prevent anemia and diarrhea and increase weight [3–8]. Most of Cu and Zn (up to ~95%) are excreted in swine feces, and concentrations of Cu and Zn in swine feces are greater than those in cattle and horse feces [7,9,10]. In addition, Cu and Zn concentrations in swine manure were greater than those in cattle, sheep, and poultry manure in England, Wales, and China [11,12]. Thus, compared to other metals, swine manure and feces could be a more important source for Cu and Zn in soil [6].

Land application of swine manure as a fertilizer can lead to the accumulation of heavy metals (e.g., Cu and Zn) in soil [6,11,13,14]; hence, soil and groundwater qualities possibly deteriorate, and the metals accumulated in soil can be transferred to plants in excessive amounts, which finally affect the health of animals and humans through the food chain [15]. Similarly, as swine feces can be a key source for plant nutrients Cu and Zn in soil, swine feces also can lead to too high Cu and Zn concentrations of soil. Therefore, Cu and Zn should be reduced to a moderate level swine feces before the land application of feces.

Several studies have reported the distribution and characteristics of chemical elements in swine feces and manure [1,6–8,16]. For instance, Henja et al. (2019) [6] evaluated concentrations of swine feces, manure, and feed to examine the swine rearing system. The authors concluded that the highest concentrations of Cu and Zn are observed in swine

diet and the metal concentrations of swine manure and feces are affected by feed. Svane and Karring (2019) [7] also reported that concentrations of Cu and Zn in a swine manure slurry were greater than those in cattle manure slurry; hence, cattle manure may be better as a fertilizer. Besides chemical analysis, microbiota in swine feces and manure also were analyzed. For example, the microbial community was affected by heavy metals, such as Zn and Cd [8], and swine feces and manure contained high levels of antibiotic bacteria [17].

Transformation of chemical elements (e.g., nitrogen and carbon), as well as fate of pathogens, have been examined during composting [18–20]. For instance, during the processing of composting, nitrate concentration of swine manure decreased with the depth and anoxic zone [19]. Wang et al. (2014) [14] also reported that the organic carbon content of swine manure was less than that in cow and chicken manure and that the degradability of organic matter in swine manure is faster than that in cow manure. In addition, effects of swine manure and slurry on the microbial community in soil have been examined [21–23]. For example, Suleiman et al. (2016) [23] reported that microbial diversity decreases after slurry application in soil.

However, there is lack of information regarding the appropriate process for decreasing Cu and Zn from swine feces. In contrast, several studies have been conducted to develop processes to remove heavy metals from sludge [19,24–28]. To decrease heavy metals from sludge, optimal conditions such as chemical reagent concentrations, stirring time, solid-to-liquid ratio have been reported. Furthermore, compared to inorganic acids, organic acids were reported to better extract heavy metals [29], and Cu has been one of the heavy metals with a low removal efficiency due to strong complexation with organic matter [26,30,31].

As mentioned above, concentrations of Cu and Zn needed to be decreased from swine feces before composting of swine feces. Thus, method development was conducted to suggest appropriate processes to decrease concentrations of Cu and Zn in swine feces using the reported methods for metal removal from sludge. The objective of this study was: (1) to elucidate a better chemical reagent with higher removal efficiencies of Cu and Zn from swine feces; (2) to find optimal conditions such as selected reagent concentration, reaction time, and solid-to-liquid ratio; and (3) to develop a method to increase the Cu removal efficiency.

## 2. Materials and Methods

### 2.1. Source of Swine Feces

Samples of swine feces were collected from a thickening tank of a swine fecal treatment plant in H city in Korea, which separates swine feces into solid and liquid and composts the solid. The samples were scooped into a plastic box using a plastic spoon. After collecting the swine feces from the thickening tank, the samples were transported to the lab, completely homogenized, dried at 105 °C, and maintained at room temperature until Cu and Zn removal experiments were conducted. The feces samples were taken out as needed for each experiment. Before the removal experiment, ignition loss and water content were analyzed. The ignition loss and water content were  $73.6 \pm 0.80$  (n = 4) and 58.4% (n = 1), respectively. Water content was calculated using the weight difference after drying swine feces in an oven at 105 °C, and ignition loss was analyzed by weight difference after burning swine feces at 550 °C for 3 h using dried feces.

### 2.2. Removal of Cu and Zn

#### 2.2.1. Selection of a Chemical Reagent

To investigate optimal removal conditions of Cu and Zn from swine feces, preliminary experiments were first conducted to select an appropriate chemical reagent for the removal of Cu and Zn. Owing to the lack of studies on heavy metal removal from swine feces, chemical reagents were selected from studies reported previously on the removal of heavy metals from sludge. Inorganic acid (e.g., HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) and organic acid (citric and oxalic acids) solutions were used in this study. The extracting solution concentrations were utilized from previous studies. For instance, citric and oxalic acid concentrations of 0.1 M

were prepared, as reported previously [27]. As described in a previous study [28], HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> concentrations were adjusted to 1.5 M and 1 M, respectively. The solid-to-liquid ratio was 1:50, which was the optimal ratio for the removal of heavy metals from sludge using HNO<sub>2</sub> [26]. That is, 8 g of samples were added into a beaker, and 400 mL of each reagent was added, followed by stirring the samples for 5 h in a jar tester. After stirring, the liquid was separated from feces by centrifuge (3000 rpm for 15 min), and the precipitated feces was put in an electric oven at 105 °C until dried. All removal tests were performed in duplicate in this study.

### 2.2.2. Impact of Solid-to-Liquid Ratios, Stirring Time, and Reagent Concentrations

After selecting H<sub>2</sub>SO<sub>4</sub> as the chemical reagent, the impact of solid-to-liquid ratio was investigated. For this test, various ratios (e.g., 1:10, 1:25, 1:37.5, 1:50, 1:100, and 1:200) were utilized. The samples were stirred for 5 h. After the optimal ratio was selected, the effect of H<sub>2</sub>SO<sub>4</sub> concentrations (0.5%, 1%, 2%, 5%, 7%, 10%, and 15%) on the Cu and Zn removal efficiencies was investigated. The stirring time was fixed at 5 h with a solid-to-liquid ratio of 1:50. After this test, the effect of the stirring time on the Cu and Zn removal was investigated using the optimal concentration and solid-to-liquid ratios. The feces samples were stirred for 1 h, 2 h, 3.5 h, 5 h, and 8 h. Regression analysis of Excel was used to obtain a *p* value at 95% confidence level in order to measure statistical significance between removal efficiency and the conditions. There is statistical significance if the *p* value is less than 0.05. If the *p* value is greater than 0.05, however, there is no significance.

### 2.2.3. Addition of the Ultrasound Process

Ultrasound-assisted H<sub>2</sub>SO<sub>4</sub> removal of Cu and Zn was performed to examine the application of the ultrasound process via the variation in the sonication time (1 h, 2 h, and 4 h). An ultrasonic machine (Sonictopia, STH-750S) was operated at a frequency of 20 kHz by using a cylindrical titanium probe (diameter of 10 mm and length of 125 mm) [26]. The same solid-to-liquid ratio (1:50) was utilized in this test with 1% and 10% H<sub>2</sub>SO<sub>4</sub> solutions.

### 2.3. Analyses of Cu and Zn

After stirring the swine feces, the feces were dried in an oven and digested with c-H<sub>2</sub>SO<sub>4</sub> and 60% HClO<sub>4</sub> solutions. The detailed digestion process was reported elsewhere [26]. The accuracy of this experiment was investigated using certified reference materials (CRM) (Metals in Sewage Sludge, Sigma–Aldrich, product ID: SQC001S) for the analysis of the feces samples [26]. Flame atomic absorption measurements were carried out to determine the Cu and Zn concentrations (Varian, AA240FS). Table 1 listed the recoveries and method detection limits for Cu and Zn. After removal and analysis, the removal efficiency was estimated using the following equation [26]:

$$\text{Removal efficiency (\%)} = (C_i - C) / C_i \times 100$$

where *C<sub>i</sub>* and *C* represent concentrations of Cu and Zn before and after removal experiments, respectively.

**Table 1.** Recoveries for the CRM and method detection limits for AA analysis.

	Cu	Zn
Recovery (%) (n = 2)	106	112
SD	5.06	8.03
Method detection limit (mg/kg dry solids)	0.027	0.036

#### 2.4. Analysis of Total Nitrogen

Total nitrogen (TN) was measured by Korean Standard Methods of Water Quality Test. First, dried swine feces (0.1 g) was added into a 250 mL glass bottle, followed by the addition of 50 mL of deionized water (DIW) and 50 mL of alkali  $K_2S_2O_8$ . Second, alkali  $K_2S_2O_8$  was prepared by dissolving 15 g of NaOH and 50 g of  $K_2S_2O_8$  in 1 L of DIW. Next, the 250 mL bottles containing the samples were autoclaved for 40 min, followed by cooling the bottles at room temperature. The supernatant was filtered, and HCl was added to the filtrate. After measuring the absorbance at 220 nm, TN concentrations were calculated using a calibration curve prepared in advance using a  $KNO_3$  solution. The accuracy of TN analysis was investigated by the same CRM used to examine the accuracy of Cu and Zn analysis in feces samples. The accuracy was  $99.0 \pm 4.2\%$  ( $n = 2$ ).

### 3. Results and Discussion

#### 3.1. Selection of Method

The concentrations of Cu and Zn before and after treatment are indicated in Appendix A. Before the treatment, the initial concentrations of Cu and Zn were 198 and 474 mg/kg, respectively. Based on the previous studies [1,6,7], Cu and Zn concentrations were varied. For instance, Cu concentrations (mg/kg dried) of swine feces were 650 in England, 514 in German, 784 in China, and 131 in Denmark. Zinc concentrations were 470 in England, 93~8239 in German, 1113 in China, and 232.5 in Denmark. Thus, the concentrations of Cu and Zn in the swine feces collected for this study were not generally higher than in other studies. Table 2 lists the removal efficiencies of Cu and Zn from swine feces by using several reagents. It was difficult to select the best chemical reagent due to the different concentrations for each reagent. Despite this, the removal method for Cu and Zn using 10%  $H_2SO_4$  was adopted herein as the highest removal efficiencies of Cu and Zn were observed by using 10%  $H_2SO_4$ . Copper removal efficiency decreased in the order of  $H_2SO_4 > HNO_3 > \text{oxalic acid} > \text{citric acid}$  (Table 2). Similarly, Zn removal efficiency using inorganic acids ( $H_2SO_4$  and  $HNO_3$ ) was greater than that using organic acids (citric and oxalic acids) (Table 2). Studies on the removal of heavy metals from swine feces using both inorganic and organic acids have been rare. Thus, our results were compared with those of studies reported previously on the removal of metal from sludge.

**Table 2.** Removal efficiency with chemical reagents ( $n = 2$ ).

Reagent	Cu		Zn	
	RE (%)	SD	RE (%)	SD
$HNO_3$	80.5	1.98	83.6	2.15
$H_2SO_4$	91.4	0.24	90.1	1.04
Citric acid	12.9	5.82	64.9	1.46
Oxalic acid	50.9	3.01	56.6	3.49

Contrary to the results obtained herein, some studies have a lower removal efficiency of heavy metals by using inorganic acids [29,32]. For instance, Veeken and Hamelers (1999) [29] reported that the removal efficiencies of Cu and Zn from sludge decreased in the order of citric acid (70% and 90% for Cu and Zn) > oxalic acid (60% and 70% for Cu and Zn) > nitric acid (38% and 65% for Cu and Zn). Marchioretto et al. (2002) [33] also reported that the removal efficiency using citric acid was greater than that using  $HNO_3$  and HCl at pH 3 or 4. Heavy metals in sludge are adsorbed onto organic and inorganic sludge phases, as well as inorganic precipitates as in carbonates, phosphates, sulfides, etc. [34,35]. When inorganic acids are reacted with sludge, heavy metals adsorbed on sludge are exchanged by protons, thereby releasing the heavy metals from precipitates [31,35–37].

Another mechanism for the removal of heavy metals using organic acids involves their complexation with carboxylic functional groups [19,25,29,35,37] even though organic acids

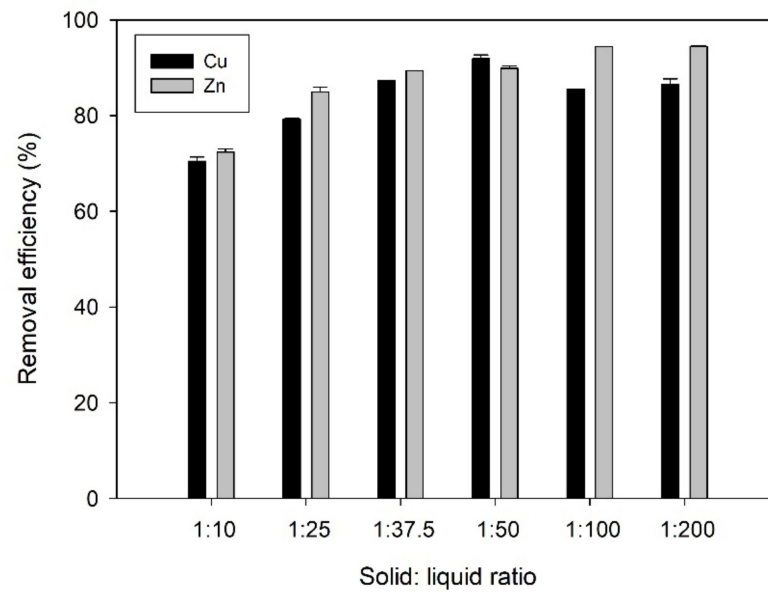
can also remove heavy metals via proton exchange [37]. Therefore, the higher removal efficiency by using organic acids is explained by their dual roles of an acid and a chelator to remove heavy metals from sludge. As a result, organic acids demonstrate promise as an alternative chemical extracting agent for the removal of metals from sludge [24,27].

The results obtained herein were different from those reported previously indicating that organic acids exhibit a higher removal efficiency for heavy metals. Our results revealed that inorganic acids are better than organic acids for the removal of heavy metals (Cu and Zn) from swine feces. Previous studies reported that the highest removal efficiencies of Cu and Zn from sludge using citric and oxalic acids are observed at pH 3–4 [29,33]. The pH of the citric and oxalic acid solutions used herein was ~1.5. Thus, the lower removal efficiencies of Cu and Zn was possibly related to the lower pH, which was not optimal to remove Cu and Zn. The removal experiment was conducted with swine feces and not sludge; therefore, the difference between sludge and swine feces may be related to the higher removal efficiency using inorganic acids. To determine the reason, additional removal experiments should be performed under the same conditions (e.g., concentrations and pH) of organic and inorganic acids.

Compared to oxalic acid, citric acid was reported to exhibit a higher removal efficiency [29,37]. As mentioned above, carboxylic functional groups serve as a chelator to complex with heavy metals. Different removal efficiencies by using citric and oxalic acids have been explained by the number of carboxylic functional groups [29,37]. A high number of carboxylic functional groups may be more advantageous for complexation with heavy metals. Citric acid has three carboxylic groups, whereas oxalic acid has two carboxylic groups. Furthermore, another mechanism can describe the lower removal efficiency by using oxalic acid. Calcium oxalate may be formed if calcium is present in the sludge, leading to the less efficient removal of heavy metals [37]. However, in this study, the use of citric acid led to a considerably lower Cu removal efficiency, a better Zn removal efficiency (Table 2). Thus, the higher Zn removal efficiency can be explained by the above-explained reason. However, additional studies are required to explain the lower Cu removal efficiency by using citric acid.

### 3.2. Optimal Solid to-Liquid Ratio

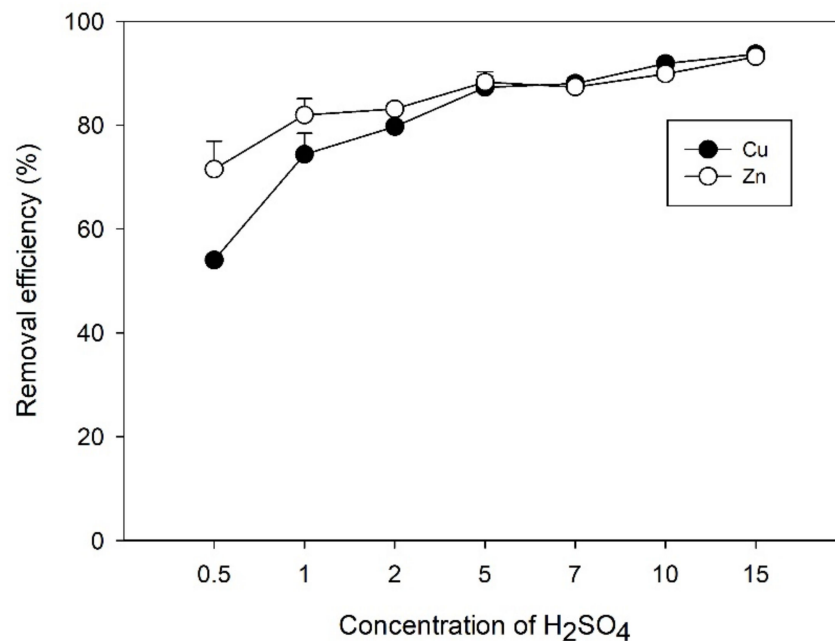
Figure 1 shows the effect of the solid-to-liquid ratio on the removal efficiencies of Cu and Zn from swine feces. The pH was not adjusted when the effect of solid-to-liquid ratios on removal efficiency of heavy metals was conducted. With the increase in the solid-to-liquid ratio, the Cu removal efficiency increased ( $p < 0.05$ ), with the maximum removal efficiency of 91.9% observed at a solid-to-liquid ratio of 1:50 (Figure 1). When the solid-to-liquid ratio was increased above 1:50, removal efficiency of Cu was lowered. This was because the correlation between solid-to-liquid ratio and removal efficiency was not significant ( $p > 0.05$ ). In contrast, Zn removal efficiency increased with solid-to-liquid ratios ( $p < 0.05$ ). The highest Zn removal efficiency (94.4%) was observed at solid-to-liquid ratios of 1:100 and 1:200. The low removal efficiency with a low solid-to-liquid ratio resulted from the incomplete mixing between the metals and  $H_2SO_4$  solution [38]. The decrease in the Cu removal efficiency with the increase in the solid-to-liquid ratio from 1:50 to 1:100 and 1:200 cannot be explained at this moment. Although the best solid-to-liquid ratios for the removal of Cu and Zn were different, the optimal solid-to-liquid ratio was selected as 1:50 due to the decrease in the Cu removal efficiency at a solid-to-liquid ratio of greater than 1:50 (Figure 1). Similarly, the same solid-to-liquid ratio of 1:50 was selected when heavy metals were extracted from sludge using  $HNO_2$  [26]. Cu and Zn removal efficiencies of 50.6% and 83.7%, respectively, were observed by stirring sludge with  $HNO_2$  for 7 h [26].



**Figure 1.** The effect of solid to liquid ratio on removal efficiency of Cu and Zn from swine feces.

### 3.3. Effect of $H_2SO_4$ Concentrations

With the increase in the  $H_2SO_4$  concentrations, the removal efficiency of Cu and Zn increased ( $p < 0.05$ ) (Figure 2). This result was similar to that reported previously, indicating that a high acid concentration leads to the high removal efficiency of heavy metals from sludge [39]. At low  $H_2SO_4$  concentrations (0.5 and 1%), the removal efficiency of Cu was less than that of Zn; however, their removal efficiencies were similar at  $H_2SO_4$  concentrations of greater than 1% (Figure 2). The use of 0.5 M  $H_2SO_4$  for heavy metal (Cd, Cu, and Pb) removal led to the lowest removal efficiency of Cu from sludge [30]. The lower Cu removal efficiency was explained by the strong organic Cu bond in sludge. Shim et al. (2020) [26] also reported that a low efficiency was observed by using  $HNO_2$  and citric acid for the removal of Cu from sludge.



**Figure 2.** The influence of concentrations of  $H_2SO_4$  (%) on removal efficiency of Cu and Zn from swine feces (reaction time: 5 h, solid to liquid ratio: 1:50).

Several studies have removal efficiencies of Cu and Zn from sludge using H<sub>2</sub>SO<sub>4</sub> as the chemical reagent [31,40–43]. However, it was difficult to directly compare the Cu and Zn removal efficiencies with previous studies because each study utilized different conditions, such as H<sub>2</sub>SO<sub>4</sub> solution concentrations, reaction time, solid-to-liquid ratio, and temperature. Table 3 lists the removal efficiencies of Cu and Zn from sludge reported previously. As mentioned above, few studies for the removal of metals from swine feces are available; hence, sludge studies have been compared. For instance, Stylianou et al. (2007) [31] conducted experiments for the removal of heavy metals from sludge using 10% H<sub>2</sub>SO<sub>4</sub> and reported Cu and Zn removal efficiencies of 38% and 72%, respectively, which were less than those observed in this study. Cu and Zn removal efficiencies of ~90% were observed by using 10% H<sub>2</sub>SO<sub>4</sub> in this study. Different removal efficiencies between two studies were possibly related to the difference in the other conditions, such as solid-to-liquid ratio and reaction time. The solid-to-liquid ratio and stirring time were 1:5 and 30 min in the previous study [31], whereas those values in this study were 1:50 and 5 h, respectively. Thus, a low solid-to-liquid ratio and reaction time could lead to the low removal efficiency.

**Table 3.** Comparison of Cu and Zn removal from sludge by H<sub>2</sub>SO<sub>4</sub> extraction.

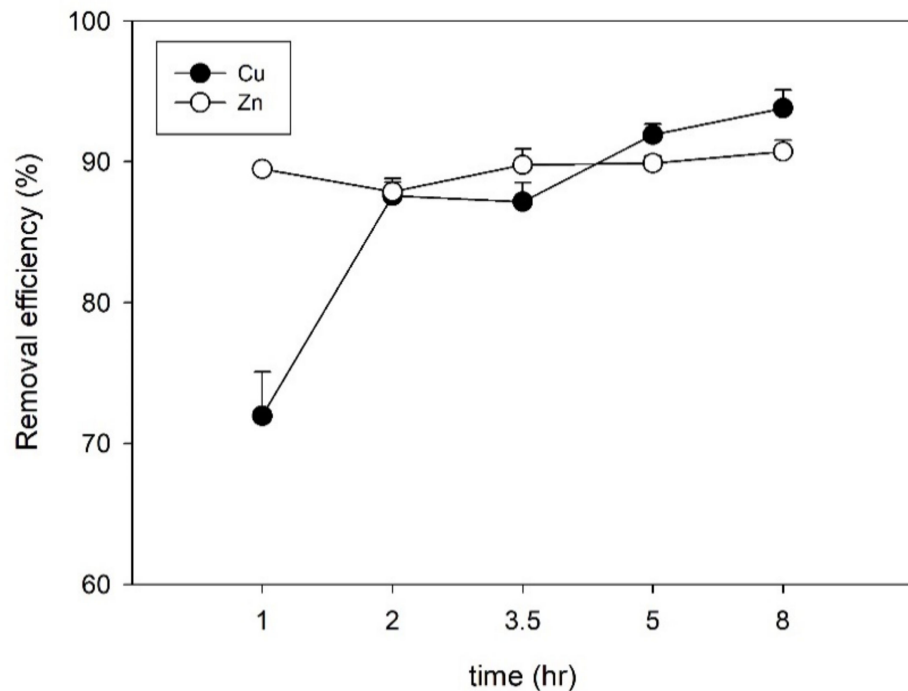
Concentration	Solid to Liquid Ratio	Reaction Time	Metal Removal Efficiency (%)		Referecnce
			Cu	Zn	
10%	1:5	30 min	54	70	Stylianou et al., 2007
20%	1:5	60 min	86	72	Stylianou et al., 2007
100 g/L	1:5	25 h	88.6	99.2	Silva et al., 2002
0.5 M		1 h	20	78	Yoshizaki and Tomida, 2000
	0.5 g/250 mL	12 h	57.8	82.3	Mingot et al., 1995
0.5 M		24 h	1	72	Jenkins and Scheybeler, 1981
10%	1:50	5 h	91.4	90.1	This study

Copper removal efficiency has increased with the increase in H<sub>2</sub>SO<sub>4</sub> concentration from 10% to 20% and prolongation of stirring time from 30 min to 60 min [31] (Table 3). However, although Stylianou et al. (2007) [31] used 20% H<sub>2</sub>SO<sub>4</sub>, the removal efficiency was still less than that observed in this study possibly due to low solid-to-liquid ratio and reaction time (Table 3). Despite different conditions, previous studies have reported that the removal efficiency of Cu has been less than that of Zn (Table 3). As mentioned above, these results have been explained by the complexation of Cu with sludge. The most important form of Cu was reported to be organic complexes in swine manure [1]. Therefore, organic Cu complexes in swine feces can also lead to a lower removal efficiency. However, at a H<sub>2</sub>SO<sub>4</sub> concentration of greater than 2%, similar Cu and Zn removal efficiencies were obtained (Figure 2). Therefore, the effect of the organic Cu complexation seems to have disappeared at H<sub>2</sub>SO<sub>4</sub> concentration of greater than 2% for the removal of Cu from swine feces.

### 3.4. Effect of Reaction Time

Figure 3 shows the effect of reaction time on the removal of Cu and Zn using 10% H<sub>2</sub>SO<sub>4</sub> and a solid-to-liquid ratio of 1:50. With the increase in the stirring time, the Zn removal efficiency did not increase noticeably ( $p > 0.05$ ) (Figure 3). The removal efficiency of Zn from swine feces reached up to ~90% in 1 h, and the removal efficiency was maintained until 8 h of reaction. In contrast, there seems to be a slight increase in Cu removal efficiency, but it was not statistically significant ( $p > 0.05$ ). The removal efficiency of Cu was 72% after 1 h of reaction, but increased to 94% in 8 h of reaction. Notably, the Cu and Zn removal efficiencies were remarkably different after a stirring time of 1 h. The removal efficiency

of Cu was considerably less than that of Zn at a stirring time of 1 h (Figure 3), suggesting that a 1 h reaction is not sufficient to break the complex between Cu and organic matter in swine feces. Our results revealed that a minimum time of 2 h is required to achieve similar removal efficiencies of Cu and Zn (Figure 3) and to break the Cu organic complex by using 10%  $H_2SO_4$  and a solid-to-liquid ratio of 1:50. In addition, the Cu removal efficiency was greater than the Zn removal efficiency when stirring was conducted for 5 h and 8 h (Figure 3). However, considering treatment cost, there was no need to extend the reaction time from 2 h to 5 h.



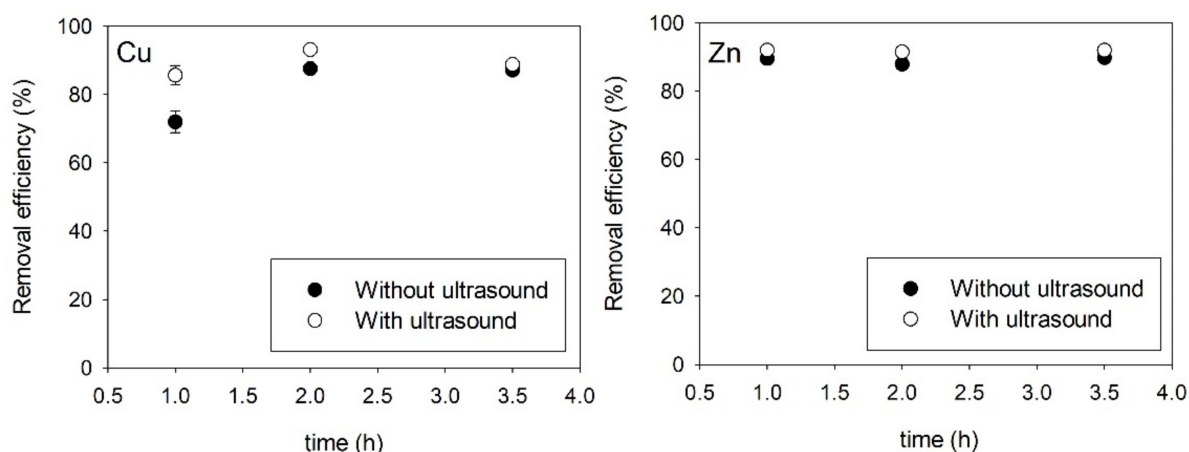
**Figure 3.** The influence of reaction time on removal efficiency of Cu and Zn from swine feces (concentration of  $H_2SO_4$ : 10%, solid to liquid ratio: 1:50).

### 3.5. Effect of the Addition of the Ultrasound Process

The addition of the ultrasound process to chemical extraction can improve the removal efficiencies of metals from sludge and decrease the reaction time [26,44,45]. Ultrasound spreads through a medium with strong energy dissipation, producing vapor bubbles that collapse and subsequently lead to acoustic cavitation [19,46]. The collapse of the bubbles instantaneously produces a local high temperature, pressure, and shear stress, which result from the disintegration of the sludge floc and cell wall; hence, heavy metals that are attached to sludge particles are released [44,47–49]. In addition, the effect of addition of the ultrasound process for the extraction of Cu and Zn from swine feces was examined.

Removal efficiencies with and without the ultrasound process by using 10%  $H_2SO_4$  were compared (Figure 4). The application of the ultrasound process led to the slight increase in the Zn removal efficiency. However, after removal was conducted by the application of the ultrasound process, the Cu removal efficiency clearly increased with stirring times of 1 h and 2 h (Figure 4). This result suggested that the ultrasound process can aid in breaking the complex between Cu and organic matter in swine feces. This result was similar to that reported previously, indicating it takes a shorter reaction time to achieve the maximum efficiency by treating the sludge with free nitrous acid and applying the ultrasound process [26].





**Figure 4.** Comparison of removal efficiencies with and without ultrasound process when 10% H<sub>2</sub>SO<sub>4</sub> was applied.

With the application of the ultrasound process the removal efficiency by using 10% H<sub>2</sub>SO<sub>4</sub> was greater than that by using 1% H<sub>2</sub>SO<sub>4</sub> (Table 4), indicating that high H<sub>2</sub>SO<sub>4</sub> concentrations were favorable for the removal of Cu and Zn from swine feces. By conducting the removal experiment for 1 h using 10% H<sub>2</sub>SO<sub>4</sub> with the application of the ultrasound process, the removal efficiency of Zn (92.0%) was greater than that of Cu (85.6%) (Table 4). However, for a 2 h reaction, the Cu and Zn removal efficiencies were not different, which was similar to the result obtained for the effect of the reaction time, suggesting that 2 h stirring was required to break the complex between Cu and the organic matter in swine feces. Meanwhile, when the removal experiment was conducted with 1% H<sub>2</sub>SO<sub>4</sub> with the application of the ultrasound process, the removal efficiency of Zn was greater than that of Cu at every interval (Table 4), indicating that 1% H<sub>2</sub>SO<sub>4</sub> was not sufficient to extract the Cu-organic complex even with the assistance of ultrasound.

**Table 4.** The influence of addition of ultrasound process on removal efficiency of Cu and Zn from swine feces.

Reaction Time (Hour)	Cu		Zn	
	1% H <sub>2</sub> SO <sub>4</sub>	10% H <sub>2</sub> SO <sub>4</sub>	1% H <sub>2</sub> SO <sub>4</sub>	10% H <sub>2</sub> SO <sub>4</sub>
1	68.3 ± 1.01	85.6 ± 2.90	83.2 ± 1.40	92.0 ± 0.21
2	75.8 ± 0.58	93.1 ± 0.29	83.4 ± 1.93	91.4 ± 0.16
4	69.8 ± 0.11	88.8 ± 1.36	79.2 ± 4.35	92.0 ± 0.13

### 3.6. Effect of H<sub>2</sub>SO<sub>4</sub> on TN Concentrations

The concentration of TN in swine feces was estimated to be 13,000 mg/kg (Table 5). According to the Korean Standards of Fertilizer, the TN concentration was equivalent to class 1 compost. As stated, the highest Cu and Zn removal efficiencies were obtained using H<sub>2</sub>SO<sub>4</sub> as the chemical reagent. However, the highest TN removal efficiency was observed by using H<sub>2</sub>SO<sub>4</sub> as the extractant in this study (Table 5). That is, the removal of TN by using H<sub>2</sub>SO<sub>4</sub> was greater than that by using citric and oxalic acids. About half of TN was removed by using 10% H<sub>2</sub>SO<sub>4</sub> at a stirring time of 5 h. In addition, the TN removal increased with the increase in the H<sub>2</sub>SO<sub>4</sub> concentrations. For example, ~70% of TN was removed during the removal process using 15% H<sub>2</sub>SO<sub>4</sub> (Table 5). These results suggested that high H<sub>2</sub>SO<sub>4</sub> concentrations to remove Cu and Zn are not always optimal to re-use swine feces as a fertilizer because the TN levels of swine feces should be maintained TN levels for recycling as a fertilizer. By using a constant concentration of 10% H<sub>2</sub>SO<sub>4</sub> to remove Cu and Zn from swine feces, the TN removal did not increase with the reaction time (Table 5). Clearly, the TN concentration increased when swine feces were treated with

10% HNO<sub>3</sub>, possibly because of the addition of nitric acid in swine feces. The addition of NO<sub>3</sub> in swine feces rendered extra good quality to the compost as per Korean standards.

**Table 5.** The removal efficiency of TN from swine feces.

		RE(%)	SD
	HNO <sub>3</sub>	–	–
	H <sub>2</sub> SO <sub>4</sub>	51.1	9.6
	Citric acid	16.8	5.5
	Oxalic acid	14.9	10.0
H <sub>2</sub> SO <sub>4</sub> concentrations (%)	0.5	–	–
	1	–	–
	2	–	–
	5	26.7	0.48
	7	41.0	1.84
	10	54.9	3.83
	15	71.7	7.47
reaction time (hour)	1	53.3	0.68
	2	51.5	0.03
	3.5	52.1	1.73
	8	56.4	1.19

–: negative efficiency.

After removal processes, we should consider disposal of H<sub>2</sub>SO<sub>4</sub> solution including Cu, Zn, nitrogen, and possibly pathogens extracted from swine feces. There is a monetary cost to discard the acid used for removal processes. In addition, the acid deposited in the swine feces can be harmful to the environment if the swine feces as fertilizer enters soil. Therefore, research should be conducted on the development of alternatives that do not require disposal costs and are harmless to the environment. Our group is working on the recycling of chemical reagents to keep the costs as low as possible. In addition, biosurfactants and bioleaching methods are also being conducted elsewhere [38,50]. However, studies on acid disposal and replacement are outside the scope of this study and should be carried out in future studies.

#### 4. Conclusions

Removal efficiencies of Cu and Zn from swine feces decreased in the order of H<sub>2</sub>SO<sub>4</sub> > HNO<sub>3</sub> > organic acids. Our results can be interpreted by sludge studies as there have been insufficient studies on the removal of Cu and Zn from swine feces. However, results of sludge studies reported previously were contrary to those obtained herein. Therefore, our results may be interpreted differently even though the removal of Cu and Zn by using organic acids was not performed with the optimal pH conditions reported in the previous study, suggesting that additional studies should be conducted to determine whether the substances containing Cu and Zn affect the removal efficiency.

Based on the removal efficiency, H<sub>2</sub>SO<sub>4</sub> was adopted to remove Cu and Zn from swine feces. The optimal concentration, solid-to-liquid ratio, and reaction time were 2%, 1:50, and 8 h, respectively, even though 10% H<sub>2</sub>SO<sub>4</sub> solutions showed the highest removal efficiency. Despite the high removal efficiency by using 10% H<sub>2</sub>SO<sub>4</sub>, a problem may arise by using 10% H<sub>2</sub>SO<sub>4</sub> as the chemical reagent because about half of the TN was also removed along with Cu and Zn, implying that swine feces treated with H<sub>2</sub>SO<sub>4</sub> may have poor value as ingredients of a fertilizer. Therefore, the 2% H<sub>2</sub>SO<sub>4</sub> concentration without a reduction in TN was determined as the optimum concentration. The application of the ultrasound

process led to the improved removal efficiency of Cu by using 10% H<sub>2</sub>SO<sub>4</sub>. The removal efficiency of Cu was less than that of Zn possibly due to the strong complexation between Cu and organic matter of swine feces. However, the removal efficiencies became similar with the increase in the reaction time and H<sub>2</sub>SO<sub>4</sub> concentrations. This result suggested that the strong organic Cu bond may have broken with the increase in H<sub>2</sub>SO<sub>4</sub> concentrations and reaction time. The addition of ultrasound process also can help break the complex between Cu and organic matter in swine feces, which can save the treatment cost.

Follow-up studies are required to elucidate influence of fertilizer made from the treated swine feces on environmental gas emissions and accumulation of metals in soil and plants. In addition, economic feasibility for the fertilizer production after metal removal should be also investigated.

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## Appendix A

Concentrations of Cu and Zn before and after Treatment (Unit: mg/kg dried). All Removal Experiments Were Conducted in Duplicate, and the Initial Concentrations Were Analyzed in Three Replicates

		Cu		Zn		
		Conc.	SD	Conc.	SD	
Before treatment		198	7.38	474	15.8	
	Reagents	HNO <sub>3</sub>	38.6	3.91	77.7	10.2
		H <sub>2</sub> SO <sub>4</sub>	17.0	0.48	46.9	4.93
		Citric acid	172	11.5	167	6.91
		Oxalic acid	97.1	5.96	206	16.6
After treatment	0.5	90.9	1.90	135	25.7	
	1	50.7	8.07	85.6	15.0	
	2	40.1	1.02	80.0	3.03	
	H <sub>2</sub> SO <sub>4</sub> concentration (%)	5	25.1	4.35	55.7	9.46
		7	23.7	0.36	59.9	8.22
		10	16.0	1.56	48.0	2.44
		15	12.5	1.63	32.3	0.57

		Cu		Zn		
		Conc.	SD	Conc.	SD	
After treatment	solid-to-liquid ratio	1:10	58.5	1.76	131	2.94
		1:25	41.2	0.31	71.4	4.83
		1:37.5	25.2	0.00	50.5	0.00
		1:50	16.0	1.56	48.0	2.44
		1:100	28.6	0.00	26.3	0.00
		1:200	26.6	2.21	26.4	0.53
	Reaction time (h)	1	55.4	6.13	50.0	1.85
		2	24.6	1.93	57.6	4.49
		3.5	25.4	2.67	48.6	5.40
		5	16.0	1.56	48.0	2.44
		8	12.3	2.59	44.1	3.87
		Ultrasound	1	62.7	2.00	79.6
1% H <sub>2</sub> SO <sub>4</sub>	2	47.9	1.15	78.9	9.16	
Reaction time (h)	4	59.8	0.23	98.6	20.6	
Ultrasound	1	28.5	5.73	38.0	1.00	
10% H <sub>2</sub> SO <sub>4</sub>	2	13.6	0.57	40.6	0.75	
Reaction time (h)	4	22.2	2.68	38.1	0.64	

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