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# Effect of struvite and organic acids on immobilization of copper and zinc in contaminated bio-retention filter media

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## ABSTRACT

Few studies have been carried out to connect nutrient recovery as struvite from wastewater and sustainable utilization of the recovered struvite for copper and zinc immobilization in contaminated soil. This study revealed the effect of struvite on Cu and Zn immobilization in contaminated bio-retention soil in the presence of commonly exuded plant organic acids. The research hypothesis was that the presence of both struvite and organic acids may influence the immobilization of Cu and Zn in soil. The outcome of this research confirmed that more than 99% of Cu and Zn was immobilized in bio-retention filter media by struvite application. Water-soluble Cu and Zn concentrations of struvite treated soil were less than 1.83 and 0.86 mg/kg respectively, and these concentrations were significantly lower compared to the total Cu and Zn content of 747.05 mg/kg in the contaminated soil. Application of struvite to Cu- and Zn-contaminated soil resulted in formation of compounds similar to zinc phosphate tetrahydrate ( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) and amorphous Cu and Zn phases. Struvite was effective in heavy metal remediation in acidic soil regardless of the presence of Ca impurities in struvite and the presence of plant organic acids in soil. Overall, this study revealed that struvite recovered from wastewater treatment plants has potential for use as an amendment for heavy metal remediation in contaminated bio-retention soil.

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## Introduction

Due to global industrialization, excessive amounts of wastewater containing high levels of N and P as nutrients are discharged into the environment, causing eutrophication (Awual, 2019; Zhang et al., 2017), which has detrimental consequences for the aquatic ecological environment. Meanwhile, the accumulation of heavy metals in soils and subsequently in the food chain are potential threats to human health (Asrari, 2014; Rene et al., 2017) creating a worldwide problem, and needs greater attention. Therefore, it is beneficial to recover nutrients such as ammo-

nium and phosphate as struvite from wastewater to avoid eutrophication, and reuse them in soil heavy metal remediation.

Among the commonly encountered heavy metals of concern, Cu and Zn are hazardous (Chen et al., 2016) and have been included in the priority pollutant list by the United States Environmental Protection Agency (EPA, 2003). Many different industries, such as mining and smelting, metal recycling, plumbing and fertilizers are important sources of Cu and Zn contamination (Musilova et al., 2016; Pierzynski et al., 2005). Even though Cu and Zn are essential micronutrients and vital to living organisms, elevated concentrations in soil may cause toxic effects; therefore, remediation of contaminated soil becomes necessary. The toxicity, sources, environmental issues and specific control technologies of selected heavy metals (Cu, Zn, Ag, and Mo) were discussed comprehensively by Chen et al. (2016). Masindi and Muedi (2018) demonstrated that mine effluents in South Africa

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are dominated by elevated levels of heavy metals far above the legal limits.

Kachenko and Singh (2006) investigated the source and magnitude of heavy metal contamination in soil and vegetable samples at 46 sites across four vegetable growing regions in New South Wales, Australia, and found that Cd, Pb and Zn contamination was greatest in vegetables from Boolaroo, and Cu concentrations were greatest in vegetables sampled from Port Kembla. The topsoils sampled from Boolaroo contained the highest mean concentrations of Cd (5.5 mg/kg), Pb (363.5 mg/kg) and Zn (1061.6 mg/kg). Similarly, topsoils sampled from Port Kembla were highly contaminated with Cu (83–1032 mg/kg), Zn (192–1641 mg/kg), As (0.7–62.5 mg/kg) and Cd (0.01–7.01 mg/kg). It has also been reported that many of the topsoil samples from both regions exceeded Australian background levels of heavy metals. Previous researchers (Hashempour-Baltork et al., 2019; Zwolak et al., 2019) comprehensively reviewed heavy metal contamination in food. Several other researchers have also demonstrated a high risk of food contamination due to heavy metals (Hu et al., 2019; Muhammad et al., 2019; Pu et al., 2019). These results highlight the risk of heavy metal contamination in soil on human health through the consumption of food. Therefore, it is necessary to study suitable remediation methods to avoid ingestion of heavy metals by humans.

Several remediation techniques, such as phytoremediation (Subhashini and Swamy, 2014; Yan et al., 2017) soil washing (Park and Son, 2017), immobilization (Yun and Yu, 2015), solidification (Xia et al., 2017) and heavy metal adsorbing biosorbents (Velmurugan et al., 2010) have been investigated for heavy metal reduction. Among them, immobilization, which uses inexpensive amendments to reduce the solubility of heavy metals, has been identified as a cost-effective approach (Basta et al., 2001). The most commonly applied amendments include phosphates (Du et al., 2014), zeolite (Wang et al., 2016a), bio-solids (Basta et al., 2001), biochar (Wang et al., 2018) and organic chelating acids (Wuana et al., 2010).

Among phosphate treatments, phosphoric acid (Yang et al., 2001), hydroxyapatite (Li et al., 2017a; Mignardi et al., 2012), and rock phosphate (Seshadri et al., 2017) have been studied extensively. Hafsteinsdótti et al. (2015) extensively reviewed the effectiveness of orthophosphate fixation for various heavy metals with examples from published studies. For example, several researchers demonstrated that phosphate treatments were effective in reducing Pb bioavailability through the formation of insoluble Pb phosphate minerals (Cao et al., 2009; Seshadri et al., 2017). Recently, Yan et al. (2019) demonstrated the practicability of applying low-cost hydroxyapatite to reduce the bioavailability and environmental risks of Pb in contaminated soil.

While many researchers demonstrated the prospective influence of P compounds on the immobilization of heavy metals in soil, studies have been limited on the effect of struvite on heavy metal immobilization in contaminated soils. Recently, Wang et al. (2016b) used struvite, which was precipitated from rare-earth wastewater, to immobilize Cu, Pb and Cr in contaminated soil, and concluded that struvite and plant ash were feasible amendments for Cu, Pb and Cr immobilization. Additionally, Li et al. (2017b) studied the effect of struvite-supported diatomite on Zn remediation in contaminated soils, and found that available zinc decreased by 65.38% and acid-soluble Zn decreased by 56.9% after 56 days. Jing et al. (2019) studied the utilization of struvite/diatomite compounds (MAP@Dia) for lead immobilization and found that MAP@Dia were effective in immobilizing lead in aqueous solution, with adsorption capacity of 832.47–946.50 mg/g. The main mechanism of Pb immobilization by MAP@Dia could be contributed by surface complexation and dissolution of struvite followed by precipitation of hydroxypyromorphite ( $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) (Jing et al., 2019).

In a laboratory setting, struvite formation is achieved by mixing salts of magnesium, ammonium and phosphate under alkaline pH conditions. In contrast, in a practical situation, the pres-

ence of foreign ions needs to be considered, as they may also influence the precipitation behavior of struvite and ultimately the performance (Le Corre et al., 2005; Liu and Wang, 2019). Amongst common foreign ions, calcium, which is often present in significant concentrations in sludge liquor (Le Corre et al., 2005), had a strong effect upon struvite crystallization (Li et al., 2016; Liu and Wang, 2019). Our previous studies on the effect of Ca on struvite crystallization confirmed the negative effect of Ca (Moragaspiya et al., 2019). Therefore, in this study, two types of struvite were precipitated with and without Ca in the reaction media to study the effect of struvite type on heavy metal immobilization.

Struvite often spontaneously precipitates in wastewater treatment plants, and may cause process and maintenance issues (Lizarralde et al., 2019; Somathilake, 2009). However, in the past decade, struvite precipitation has gained interest as a promising technique for ammonia and phosphate recovery from wastewater to use as a slow-release fertilizer, (Kim et al., 2018; Zhou et al., 2017) and this area has been extensively investigated. In soil, if  $\text{PO}_4$  can be released from struvite, heavy metal immobilization can be achieved by formation of metal phosphates, and a link between wastewater treatment and soil remediation can be formed.

Low-molecular-weight organic acids such as oxalic, citric, malic and acetic acid are natural products of root exudates, microbial metabolism and decomposition of soil organic matter (Montiel-Rozas et al., 2016; Strobel, 2001). Soil pH appears to be the main soil property affecting the dissolution rate of struvite granules, and plant roots also may affect the dissolution rate by acting as a sink and by modifying the chemical conditions of the rhizosphere (Degryse et al., 2017). Therefore, the effect of plant organic acids on the immobilization of heavy metals by struvite was also considered.

Based on the literature above, it is clear that investigations on the effect of struvite on heavy metal remediation are very limited and there have been no studies carried out to investigate the effect of different types of struvite on heavy metal immobilization in the presence of commonly exuded plant organic acids. There is also a gap in the literature on heavy metal remediation of stormwaters using struvite in bio-retention systems. The research hypothesis was that the presence of both struvite and organic acids may influence the immobilization of Cu and Zn in the soil. The main aim of this study was to evaluate the effect of struvite on Cu and Zn immobilization in contaminated soil in the presence of commonly exuded plant organic acids. Specific objectives of the study were: (1) Determine the impact of struvite on the immobilization of Cu in contaminated soil; (2) Determine the impact of struvite on the immobilization of Zn in contaminated soil; (3) Evaluate the impact of organic acids exuded from plant roots on the immobilization of heavy metal in contaminated soil by struvite and (4) Determine P-induced metal transformation in soil using X-ray diffraction and micro analysis.

To achieve the aforementioned aims and objectives, several characterization techniques such as ICPOES, X-ray diffraction, FT-IR, XRF, morphological analysis by Scanning Electron Microscopy (SEM), and Particle size analysis by laser diffraction were employed. Additionally, chemical analysis of selected treated soil samples was carried out using electron probe micro-analysis.

## 1. Materials and methods

### 1.1. Chemicals

Analytical grade magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ), and calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) were used in this study to prepare two types of struvite. Cupric nitrate and zinc nitrate were used to prepare contami-

nated soil (Liu et al., 2015). Acetic acid ( $\text{CH}_3\text{COOH}$ ), oxalic acid ( $(\text{COOH})_2\text{H}_2\text{O}$ ), citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) and malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ) were used as plant organic acids in the immobilization experiments. All chemicals used were of analytical grade and all solutions were prepared with milli-Q water ( $18 \Omega/\text{cm}$ , pH 6.88).

## 1.2. Precipitation of two types of struvite

Two types of struvite (Struvite Type 1 (Str-1): Precipitated without Ca in the reactor media.

Struvite Type 2 (Str-2): Precipitated with Ca:Mg mole ratio of (1:1) used in this study were synthesized using analytical grade magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ), in stoichiometric proportion of 1:1:1 (mole ratio).

A 5-L beaker was used as the reactor, wherein an IKA RCT basic magnetic stirrer running at a constant speed of 100 r/min for 60 min was used to agitate the prepared solution. The solution pH was adjusted to 9.0 by using dropwise addition of 2 and 0.1 mol/L NaOH at the beginning of each experiment. As the optimum pH range for struvite precipitation has been reported as 8.5–10 (Huang et al., 2016), pH 9 was used in this study to provide favorable conditions for the struvite precipitation reaction. All experiments were carried out at room temperature ( $25^\circ\text{C}$ ) and then samples were left overnight for settling after a 60 min reaction period. Continuous pH measurements were obtained during the 60 min reaction period and at the end of each experiment, the precipitates were filtered and dried at room temperature overnight. Struvite powder was then analyzed using XRD, FT-IR, XRF, SEM and particle size analysis techniques. All the experiments were carried out in triplicate in this study and data were statistically elaborated by standard methods using Microsoft Excel functions.

## 1.3. Heavy metal immobilization experiment

### 1.3.1. Preparation of contaminated soil

The soil (Bio-Retention-Filter media) was air dried for 1 week, homogenized and sieved to  $< 2 \text{ mm}$  particle size (Cao et al., 2009), and stored in airtight re-sealable polythene bags prior to analysis. Physical and chemical properties of the soil are presented in Section 2.1.2 below. A known mass of air-dried soil was prepared by adding cupric nitrate and zinc nitrate to yield a concentration of 800 mg/kg of Cu and Zn. The spiked soil was mixed thoroughly to achieve homogeneity and subsequently incubated at a room temperature of  $25^\circ\text{C}$  for 2 weeks. After that, spiked soil (contaminated soil) was air-dried for 1 week and stored in plastic bags for subsequent immobilization tests.

### 1.3.2. Immobilization experiment

A batch experiment was conducted to observe the immobilization efficiency of Cu and Zn in soil in the presence of struvite and organic acids. Four common organic acids: oxalic, citric, malic and acetic, were used in this study.

In this experiment, 100 g of contaminated soil was used for each treatment and 250 mL Nalgene plastic bottles were used as batch reactors. The struvite application rate was 5 g/100 g of soil, which was identified as an effective rate for immobilization of heavy metals, and the organic acid application rate was used as 1 mmol/L per 35 mg of struvite; these rates were determined based on the research outcome of previous studies by Wang et al. (2016b) and Talboys et al. (2016). Struvite and organic acids were added to soil, and each mixture was wetted with Milli-Q water and mixed thoroughly using an end-over-end shaker for 1 hr and incubated at  $25^\circ\text{C}$  for 10 days. The 10-day incubation period was selected based on the research outcomes of previous heavy metal immobilization experiments on struvite, which had used similar struvite application rates and found significant effects during the first 7 days (Wang et al., 2016b). Then the treated soil samples were dried using the freeze-drying method (Day and

Stacey, 2007) and stored in airtight plastic bottles for subsequent analysis.

### 1.3.3. Water extraction of Cu and Zn and calculation of reduction rate

The treated and dried soil was homogenized using the cone and quartering method (Campos-M and Campos-C, 2017). 5 g of soil was put in a centrifuge tube and extracted with 50 mL of milli-Q water (pH 6.88). After being shaken on an end-over-end shaker for 1 hr, the soil mixture was centrifuged at 3500 r/min for 5 min. The supernatant was filtered using a  $0.45 \mu\text{m}$  pore size Millipore filter and acidified using 2%  $\text{HNO}_3$  to analyze Cu and Zn using ICP-OES. This procedure was a modification of the methodology reported by Cao et al. (2009) for determination of water-soluble concentrations of heavy metals. The reduction of the heavy metal concentration in the water extract after each treatment was defined as the reduction rate (R, %), which was calculated using Eq. (1) below, where  $C_i$  (mg/kg) and  $C_f$  (mg/kg) are the water-extractable heavy metal concentrations in soil without and with treatment.

$$R = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

The remaining soil mixture was vacuum-filtered and dried in an oven at  $40^\circ\text{C}$  for 24 hr. Soil residues were examined with an X-ray diffractometer to identify the soil mineral phases.

## 1.4. Analytical methods

### 1.4.1. pH and electrical conductivity

A SmartCHEM-Ion3 pH analyzer (TPS, Australia) was used for pH measurements in this study. The calibration was done using standard buffer solutions (pH 4.01, 6.86 and 10.0 at  $22^\circ\text{C}$ ) with an average error less than 0.05 pH units. The pH and electrical conductivity of the soil samples used were measured in 1:5 (soil: water, m/V) (Carter and Gregorich, 2007) suspensions using calibrated pH and electrical conductivity meters. In this experiment, the soil/water suspension was stirred using an end-over-end shaker for 1 hr and allowed to settle for 30 min before taking measurements.

### 1.4.2. X-ray diffraction

Struvite precipitates were characterized using XRD (X-Ray Diffractometer, PANalytical X'Pert Pro, The Netherlands) operating in Bragg-Brentano geometry with a cobalt source (40 kV, 40 mA) following the procedure for XRD analysis in our previous studies (Moragaspiitiya et al., 2019). The patterns were collected for 30 min in the angular range of  $4 - 90^\circ 2\theta$  at step size of  $0.016^\circ$ . Phase identification was performed using PDF4+ (04-010-2533) and ICDD databases (software; X'Pert Highscore Plus (V4.5, PANalytical) and Jade (V4.1.0, Materials Data Inc.)). Soil residues were also examined with the X-ray diffractometer to identify soil mineral phases. The Rietveld method was used for quantitative phase analysis (Lu et al., 2016). For quantitative XRD analysis, the samples were weighed and a corundum ( $\text{Al}_2\text{O}_3$ , Baikaw International) internal standard was added at 10 wt.%. Then the prepared samples were micronized in a McCrone mill for 6 min with ethanol using zirconia beads. The resultant slurry was dried in an oven at  $40^\circ\text{C}$  for 24 hr and then the dried powder was pressed into a sample holder. The Rietveld method implemented in TOPAS (V5, Bruker) was used for quantitative phase analysis. The peak shapes were modeled via an instrument function determined from the NIST SRM 660a ( $\text{LaB}_6$ ) (Moragaspiitiya et al., 2019).

### 1.4.3. Scanning electron microscopy (SEM)

The morphology of the samples was observed using a scanning electron microscope (Perwitasari et al., 2017) with integrated EDS analysis (TESCAN MIRA3 FEG-SEM, Thermo Scientific Ultra Dry



Energy Dispersive X-ray Spectroscopy, AXT, Australia). Powdered samples were mounted on standard SEM pin stubs and coated with carbon for 30 min to improve the imaging of the samples. Images were obtained at 15.00 kV voltage and 13.00 beam intensity using a secondary electron detector.

#### 1.4.4. Fourier-Transform infrared spectroscopy (FT-IR) analysis

Surface functional groups of struvite were determined using FT-IR spectroscopy (Nicolet iS50, Thermo Scientific, Australia with a diamond ATR accessory, 64 scans, 4 cm<sup>-1</sup> resolution), where the spectra were recorded from 4000 to 400 cm<sup>-1</sup> (Chauhan and Joshi, 2013).

#### 1.4.5. X-ray fluorescence (XRF) analysis

Heavy metal concentrations in soil and the chemical composition of struvite were acquired using an X-Ray Fluorescence Spectrometer (PANalytical AXIOS 1 kW Wavelength Dispersive XRF spectrometer, Malvern Panalytical, U.K.). The instrument was calibrated by firstly analyzing the international Certified Reference Materials (CRMs) prior to sample analysis. Soil organic matter content was determined using loss-on-ignition (LOI) (Rayment and Lyons, 2011) and the total C and N of soil was determined using a LECO Trumac CNS (Rayment and Lyons, 2011).

#### 1.4.6. Particle size analysis

The particle size of struvite crystals was analyzed by a Malvern Mastersizer 3000 (Malvern Panalytical, U.K.) which used a laser diffraction tool to discover the volume-based particle size distribution (Moragasipitiya et al., 2019). In this analysis, the refractive index, absorption index, and density were 1.495, 0.01, and 1.7 respectively. Deionized water at 22°C was used as the dispersant and the data was analyzed using the Mastersizer software.

#### 1.4.7. Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

Metal concentrations in solutions were analyzed using the Optima 8300 dual-view inductively coupled Plasma optical Emission spectrometer (PerkinElmer Inc, USA). All samples were diluted with 2% HNO<sub>3</sub> before the analysis (Moragasipitiya et al., 2019). A set of quality control procedures, including using selected analytical certified reference materials (CRMs) and initial check verification standards (ICVs) were applied in the ICP-OES measurements. The reproducibility of analyses was determined from repeated analysis of standard solutions and blanks.

#### 1.4.8. Microprobe analysis

Cu and Zn identification of selected residual soil samples was carried out using an electron probe microanalyzer (UL-Hamid et al., 2006) (JEOL JXA 8530F Field emission electron probe microanalyzer (FE-EPMA, JEOL Ltd., Japan) with analytical conditions of 15 kV accelerating voltage, 20 nA beam current, 5 or 10 µm defocused beam diameter). Backscattered electrons were initially used to identify particles with a high atomic number, and then energy dispersive spectroscopy (EDS) was used to determine whether the particles contain Cu and Zn.

All the experiments were carried out in triplicate to ensure the accuracy and reliability of the results obtained and data were statistically elaborated by standard methods using Microsoft excel functions.

## 2. Results and discussion

### 2.1. Struvite and soil characterization

#### 2.1.1. Characteristics of struvite

As explained in Section 1.2 above, two types of struvite were used to investigate the effect of struvite type on heavy metal immobilization in contaminated soils. Based on the XRD analysis, the

**Table 1 – Composition of struvite produced, by weight fraction.**

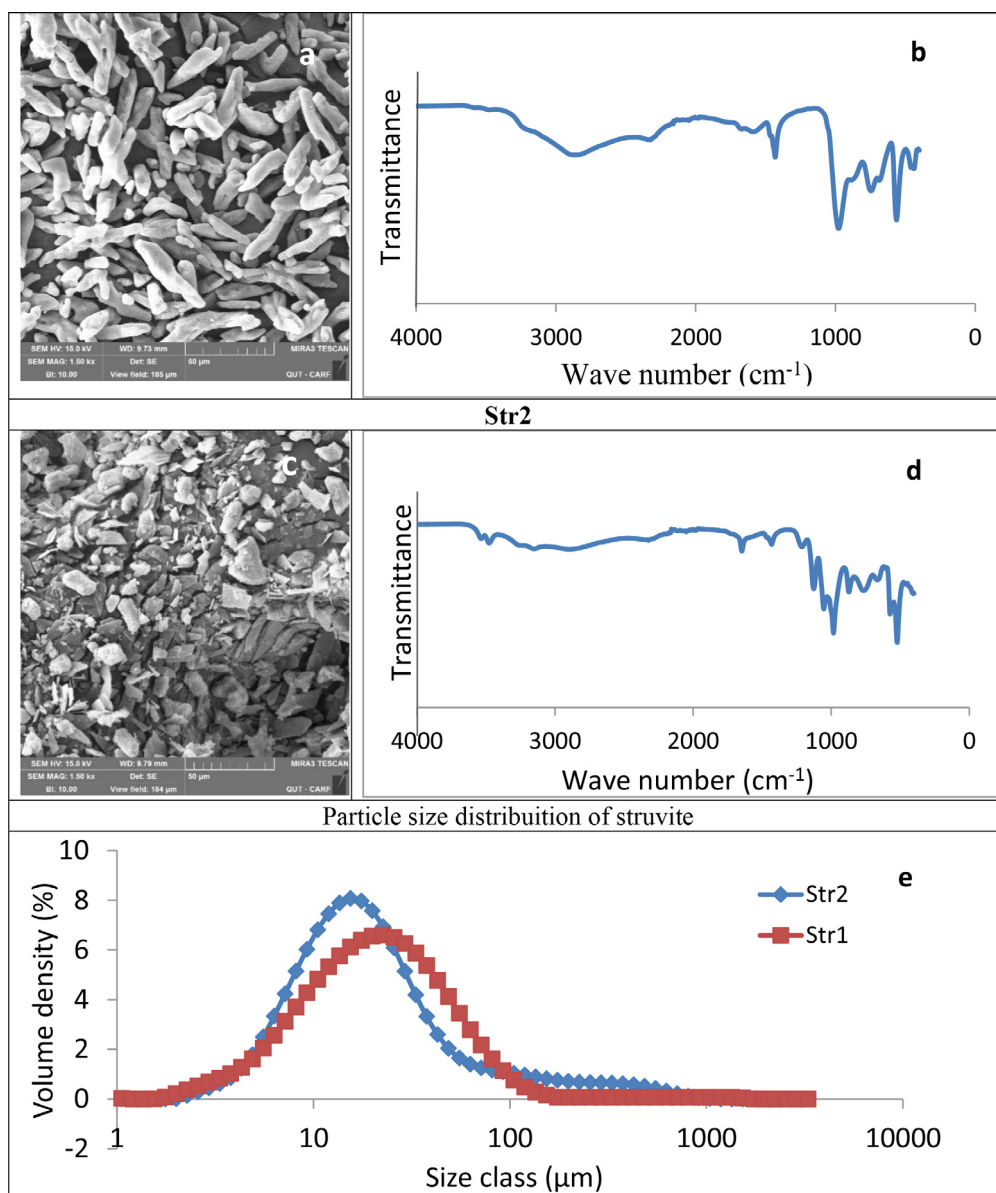
Struvite type	MgO(%)	P <sub>2</sub> O <sub>5</sub> (%)	CaO(%)	ZnO(%)	CuO(%)
Str1	16.95	28.64	ND	ND	ND
Str2	8.49	34.60	17.87	ND	ND
ND: not detected.					

dominant species was identified as struvite (Powder Diffraction File (PDF) # 04-010-2533). The composition of struvite produced was analyzed using XRF and the results are presented in Table 1 below. As shown in Table 1, the results of XRF analysis confirmed that Str2 contained Ca while Str1 was free from Ca impurities.

The SEM images, FT-IR spectra and particle size distributions of the two struvite types are presented in Fig. 1 below. As shown in Fig. 1, it can be seen that Str1 has rod-like crystals while Str2 has crystals with irregular shapes and sizes, and their surfaces were covered with small particles due to the presence of calcium ions in the initial solution. Similar rod-like struvite crystals have been observed in our previous studies (Moragasipitiya et al., 2019) with no added calcium present. These results can be further confirmed by the published results by Le Corre et al. (2005) as well. The irregular appearance of struvite crystals covered with impurities (Str2) shows the strong effect of calcium ion on the struvite crystallization process. A similar crystal morphology for struvite precipitated at a Ca:Mg mole ratio of 1:1 has been published by several other researchers (Moragasipitiya et al., 2019; Lee et al., 2013; Le Corre et al., 2005). Perwitasari et al. (2018) found that metal cations could be adsorbed onto the surface of the crystals or embedded into the crystal lattice, as revealed by EDS analysis, leading to a dramatic distortion of the shape of the crystals.

Fig. 1e below shows the mean particle size of Str1 and Str2, which was 22.6 and 17.9 µm respectively. The mean particle size of the precipitated crystals was within the range reported by other researchers (Le Corre et al., 2005). When no calcium was present, the recorded particle size was higher than that with Ca, and this data was in agreement with the SEM images presented below (Fig. 1a and c) which showed the formation of larger rod-like crystals at the expense of irregular material. Lee et al. (2013) also noted that the presence of Ca led to the creation of small particles, and this could be due to the presence of calcium phosphates or inhibited growth of struvite crystals. In agreement with these results, Perwitasari et al. (2018) confirmed that struvite crystal growth was suppressed by the presence of metal ions, even at trace amounts from 0.00 to 100 µg/L.

Fig. 1b and d show the FT-IR spectra. According to the identification of peaks, the absorption occurring between 2200 and 3400 cm<sup>-1</sup> was due to O-H and N-H stretching vibrations. Intense bands between 1590 and 1700 cm<sup>-1</sup> were attributed to O-H bending vibrations and the absorption peak at around 1435 cm<sup>-1</sup> was attributed to the N-H bending vibration in the ammonium group. The absorption peak at around 985 cm<sup>-1</sup> was due to stretching vibrations in phosphate units. Meanwhile, an intense band at around 565 cm<sup>-1</sup> was associated with metal-oxygen bonds. These observations agreed well with the FT-IR spectrum published by Arslanoglu (2019) for struvite. As illustrated in Fig. 1d, in the FT-IR spectra of Str2, additional stretching vibrations at around 553, 1059, 1133 and 1224 cm<sup>-1</sup> could be observed, and this can probably be attributed to the presence of Brushite, as Str2 was precipitated in the presence of Ca in the media. Differences in the relative intensities of peaks in different samples might be attributed to differences in the degree of crystallinity. The FT-IR spectrum proves the existence of water of hydration, PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup> and metal-oxygen bonds in the precipitated matter, and these data match with the findings of other researchers (Chauhan and Joshi, 2013). Based on the characteristics of struvite presented above, it is clear that the purity, morphology and particle size of struvite precipitated with and without Ca are different.



**Fig. 1 – SEM images, FT-IR spectra and particle size of struvite (a) SEM images of Str1; (b) FT-IR spectrum of Str1; (c) SEM image of Str2; (d) FT-IR spectrum of Str2; (e) Particle size distribution of Str1 and Str2.**

### 2.1.2. Properties of soil

Physiochemical properties of the soil used in the heavy metal immobilization study are presented in Table 2 below. It was found that the texture of the soil was sandy loam.

### 2.2. Struvite and organic acids induced metal immobilization

The mobility of metals is strongly associated with their solubility in water (Cao et al., 2009) and metals with higher water solubility show a high risk of leaching into groundwater, and are also immediately available for plants. Therefore, the water solubilities of Cu and Zn were measured using different struvite treatment combinations to identify the effect of struvite on the immobilization of heavy metals in soil. Based on the outcomes of the experiments carried out in this research work, application of struvite to the contaminated soil significantly reduced the water solubility of Cu and Zn.

This research work included two struvite types and four organic acids. Tables 3 and 4 below present the water solubility of Cu and Zn in contaminated soil respectively. As depicted in Table 3, the highest water solubility of Cu, 178.30 mg/kg of soil, was identified in the control soil sample, which did not have any treatment because lower soil pH could facilitate the increase of the dissolved fraction and the reactivity and mobility of heavy metals. The water-soluble Cu concentrations of Str1- and Str2-treated soil were 1.83 mg/kg of soil and 1.34 mg/kg of soil, respectively, and these concentrations were significantly lower compared to the total Cu content of 719.96 mg/kg in contaminated soil. The reduction rate of the water solubility of Cu in struvite-only treated soil was more than 98.90% compared to the control soil sample, as shown in Table 3 below. Supporting our results, immobilization studies carried out by Wang et al. (2016b) demonstrated that the available concentration of Cu in contaminated soil sharply reduced from 754.75 to 320.82 mg/kg in the first 7 days of immobilization. Cao et al. (2009) also demonstrated that phosphorus addition

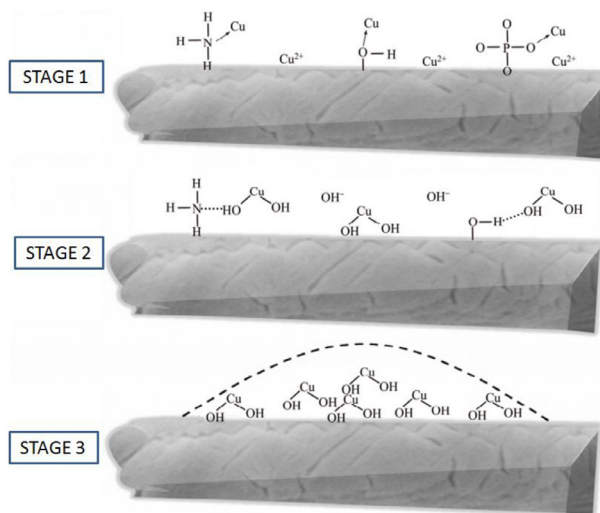
**Table 2 – Properties of soil used in this experiment.**

Property	Parent soil	Spiked soil with Cu and Zn
pH (1:5, m/V) in H <sub>2</sub> O (pH units)	5.38	5.20
Organic matter (%)	5.08%	
Total N	0.02%	
Total C	1.60%	
Total P (as P <sub>2</sub> O <sub>5</sub> )	0.04%	
Electrical conductivity (1:5, m/V) (dS/m)	0.47	
Particle size distribution (%)		
<0.05 mm (Clay and Silt)	4.51%	
0.05–2.0 mm (Sand)	94.36%	
2.0–3.0 mm (Fine Gravel)	1.15%	
Metal content (mg/kg)		
Cu	ND	719.96
Zn	ND	747.05

ND: not detected.

reduced the water solubility of Cu by 31%–80%, presumably due to their sorption on minerals such as calcite and phosphate phases.

Previous studies on heavy metal immobilization suggested different mechanisms for Cu immobilization in contaminated soil. Seshadri et al. (2017) proposed that adsorption/precipitation of metals by P compounds are the main pathways of metal immobilization by P compounds. In contrast, Sugiyama et al. (2003) proposed that dissolution/precipitation was the main mechanism for heavy metal immobilization, and they showed formation of an amorphous Cu phosphate in their studies of heavy metal immobilization. Ma et al. (1994) has also demonstrated formation of amorphous Cu phosphate on Hydroxyapatite surfaces. Consistent with previous studies, the outcomes of XRD quantification analysis confirmed the presence of higher amounts of amorphous material in struvite-treated soil (Table 5). This amorphous material may consist of Cu phosphate as well. However, Cao et al. (2009) concluded

**Fig. 2 – Sketch mechanisms of removal of Cu(II) from solution by synthesized struvite (Extracted from Peng et al., 2018).**

that 25% of Cu was removed by phosphate treatment through a dissolution/precipitation reaction, whereas Cu was mainly immobilized by surface adsorption or complexation. Similarly, Perwitasari et al. (2018) also confirmed that Cu ions could be adsorbed in the struvite structure, as revealed by EDS. Recently, Peng et al. (2018) studied the Cu(II) adsorption behavior and related mechanisms of struvite, and found that electrostatic attraction and coordination bonding supported ion sorption on the struvite surface, and the transformation of copper ion into copper hydroxide occurred on the struvite surface and within its crevices, as illustrated in Fig. 2 below.

Consistent with findings by Peng et al. (2018) and Arslanoglu (2019) clearly explained that adsorption of Cu(II) by struvite particles occurred in four stages; the first stage is a partial dissolution of the surface of the struvite particles due to the acidity of the copper solution. The second stage is the diffusion of Cu(II) ions into the struvite particles. The third stage

**Table 3 – Water solubility of Cu in contaminated soil with struvite and organic acid treatments.**

Treatment	Total Cu content (mg/kg of soil)	Water extractable Cu (mg/kg of soil) after 10 days	Reduction of water solubility (%)	Final pH
Soil (Control) (Initial pH 5.2)	719.96	178.39		5.20
Soil + oxalic acid	719.96	84.07	52.87	5.60
Soil + Str1	719.96	1.83	98.97	7.39
Soil + Str1 + oxalic	719.96	1.45	99.19	7.45
Soil + Str1 + citric	719.96	3.80	97.87	7.35
Soil + Str1 + malic	719.96	1.50	99.16	7.35
Soil + Str1 + acetic	719.96	1.94	98.90	7.36
Soil + Str2	719.96	1.34	99.25	7.41
Soil + Str2 + oxalic	719.96	0.97	99.46	7.35
Soil + Str2 + citric	719.96	1.78	99.00	7.39
Soil + Str2 + malic	719.96	1.16	99.35	7.35
Soil + Str2 + acetic	719.96	1.25	99.30	7.36
Soil + Lime (pH 6.5)	719.96	0.27	99.85	7.58
Soil + Lime + struvite	719.96	0.82	99.54	7.53
Soil + Lime + struvite + acid	719.96	0.19	99.90	7.92
Soil + Lime + acid	719.96	1.13	99.37	7.10

**Table 4 – Water solubility of Zn in contaminated soil with struvite and organic acid treatments.**

Treatment	Total Zn content (mg/kg of soil)	Water extractable Zn (mg/kg of soil)	Reduction of Water solubility (%)	Final pH
Soil (Control) (Initial pH 5.2)	747.05	417.10		5.20
Soil + acid	747.05	253.43	39.24	5.60
Soil + Str1	747.05	0.86	99.79	7.39
Soil + Str1 + oxalic	747.05	0.57	99.86	7.45
Soil + Str1 + citric	747.05	0.97	99.77	7.35
Soil + Str1 + malic	747.05	0.78	99.81	7.35
Soil + Str1 + acetic	747.05	0.80	99.80	7.36
Soil + Str2	747.05	0.42	99.90	7.41
Soil + Str2 + oxalic	747.05	0.47	99.89	7.35
Soil + Str2 + citric	747.05	0.82	99.80	7.39
Soil + Str2 + malic	747.05	0.49	99.88	7.35
Soil + Str2 + acetic	747.05	0.49	99.88	7.36
Soil + Lime (pH 6.5)	747.05	2.60	99.38	7.58
Soil + Lime + struvite	747.05	0.82	99.80	7.53
Soil + Lime + struvite+ acid	747.05	0.27	99.94	7.92
Soil + Lime + acid	747.05	0.98	99.77	7.10

**Table 5 – Mineral phases of residual soils after the water extraction.**

	Quartz (SiO <sub>2</sub> )	Plagioclase (NaAlSi <sub>3</sub> O <sub>8</sub> – CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )	K-Feldspar K (AlSi <sub>3</sub> O <sub>8</sub> )	Non-diffracting (amorphous)	Gypsum (CaSO <sub>4</sub> •2H <sub>2</sub> O)	Calcite(CaCO <sub>3</sub> )
Soil (control)	62.40	17.30	7.00	13.30	ND	ND
Soil + Oxalic acid	60.40	17.60	6.70	15.30	ND	ND
Soil + Str1	57.70	18.40	8.20	15.70	ND	ND
Soil + Str1 + oxalic	58.70	17.30	8.40	15.60	ND	ND
Soil + Str1 + citric	60.00	16.50	7.60	15.90	ND	ND
Soil + Str1 + malic	57.80	17.60	7.80	16.90	ND	ND
Soil + Str1 + acetic	58.10	15.40	7.20	19.40	ND	ND
Soil + Str2	58.30	16.50	7.90	16.20	1.20	ND
Soil + Str2 + oxalic	57.50	16.20	8.00	17.10	1.30	ND
Soil + Str2 + citric	57.30	16.40	7.80	17.20	1.30	ND
Soil + Str2 + malic	58.70	16.10	7.80	16.30	1.20	ND
Soil + Str2 + acetic	58.00	15.40	7.50	17.80	1.20	ND
Soil + lime	53.40	14.00	6.40	13.20	ND	13.10
Soil + lime + Str2	52.10	13.20	6.40	16.90	ND	11.30
Soil + lime + Str2 + Oxalic acid	51.10	13.00	6.00	17.50	ND	12.40
Soil + lime + Oxalic acid	51.60	13.90	6.60	17.00	ND	11.00

ND: not detected.

is the replacement of Mg(II) ions in the struvite particles with Cu(II) ions. In the final stage, some struvite (NH<sub>4</sub>MgPO<sub>4</sub>•6H<sub>2</sub>O) dissolves due to the acidic pH of its copper solution, facilitating the dissolution of the phosphate ions in struvite into the solution and resulting in the precipitation of some Cu(II) compounds on the surface of the struvite particles. It can be stated that a possible Cu immobilization mechanism by struvite in the current study could also be via precipitation of amorphous Cu phosphate as well as surface adsorption onto struvite surfaces.

As presented in Table 3 below, a slight increment in the reduction of water solubility of Cu with Str2 can be noticed compared to Str1, but this is not significant. As mentioned in Section 2.1.1, the key difference between the two struvite types was that Str2 contained Ca impurities, while Str1 was free from Ca impurities. Even though Str1 and Str2 were different in shape, size and purity, there was no noticeable effect between the two struvite types regarding the immobilization of heavy metals in

acidic soil, and this could be attributed to the fact that struvite dissolves rapidly under acidic conditions. This phenomenon was due to proton-promoted dissolution at lower pH in the presence of acids (Bhuiyan et al., 2008). The findings of this study highlight that struvite can be used for heavy metal immobilization in acidic soil regardless of its purity. As shown in Tables 3 and 5, it was also found that the pH of the soil increased from 5.2 to 7.4 within 10 days due to the high alkalinity of struvite, and this indicates that addition of struvite is beneficial and can be used to treat acidic soils.

It was also found that the water solubility of Cu decreased to 84.07 mg/kg with oxalic acid treatment. It is clear that oxalic acid application has a positive impact on soil, reducing the water solubility of Cu by 52% compared to the control soil sample. This could be due to the reaction of Cu with oxalic acid to form cupric oxalate, which is insoluble in water, hence reducing the water-soluble Cu content significantly. Wei et al. (2014) also noted the



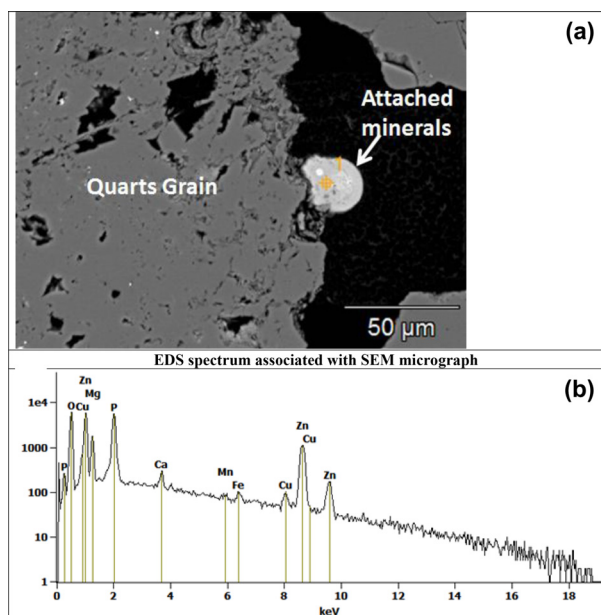
reaction of heavy metals with oxalate, and they demonstrated that oxalic acid could enhance the removal of Pb(II) from aqueous solution significantly by formation of lead oxalate.

As per Table 3 below, the reduction of the water solubility of Cu by application of Str1 and Str2 without organic acids (treatments 3 and 8) was 98.97% and 99.25% respectively, while it ranged between 97.87% and 99.46% with struvite application in the presence of organic acids (treatments 4–7 and 9–12); oxalic, citric, malic and acetic. This highlights that there is no noticeable difference among struvite treatments with and without organic acids on heavy metal immobilization. This could be because the low pH of the soil used increased the dissolution of struvite significantly, but hindered the effect of weaker organic acids. This indicates that the effect of organic acids on the dissolution of struvite was negligible in acidic soil. However, Wang et al. (2016a) revealed that both humic acid and fulvic acid accelerated Cu immobilization in contaminated soil amended by struvite and plant ash. This may be because Cu has been shown to have high association with humic and fulvic acids by forming stable complexes (Chirenje et al., 2002; Xu et al., 2016).

In this experiment, lime was added to the soil to increase the pH of the bio-retention filter media used, and initially the pH was increased from pH 5.2 to 6.5. It then increased from 6.5 to 7.9 after a 10-day incubation period with struvite and organic acid. The reduction in the water solubility of Cu in lime-treated soil was more than 99% because the rise in pH may have led to the formation of insoluble Cu hydroxides and oxides, which are then less mobile and bioavailable. These findings were consistent with Houben et al. (2013), who also stated that a rise in soil pH induces metal immobilization because it favors metal precipitation. As presented in Table 3 below, there is no noticeable difference in the reduction of water solubility of Cu, before and after struvite addition to the lime treated soil, and this can be attributed to the poor reactivity of struvite in lime-added soils. This is because the solubility of struvite is highly pH dependent, with lower solubility at higher pH (Arslanoglu, 2019; Ohlinger et al., 1998). Similarly, Valipour et al. (2016) also reported that the immobilization of metals was relatively ineffective when phosphate rock was applied to calcareous soils, which can be ascribed to the poor reactivity of apatite.

As presented in Table 4 below, the highest water solubility of Zn, 417.10 mg/kg, was found in the control soil sample, (treatment 1) which did not have any treatment because lower pH in soil may cause an increase in the dissolved fraction, and the reactivity and mobility of heavy metals. The water-soluble Zn concentrations of Str1- and Str2-treated soil (treatments 3 and 8) were 0.86 and 0.42 mg/kg respectively, and these concentrations were significantly lower compared to the total Zn content of 747.05 mg/kg in the contaminated soil. In our study, the reduction rate of the water solubility of Zn in struvite-treated soil was more than 99.9% compared to the control soil sample, as shown in Table 5 below. In agreement with previous studies (Du et al., 2014; Seshadri et al., 2017), this significant effect of struvite on the immobilization of Zn could be ascribed to the formation of zinc phosphate, which is insoluble in water, because acidic pH triggers the dissolution of struvite and releases phosphate into the soil media, facilitating reaction with available zinc. Du et al. (2014) recommended that it is suitable to apply ground and sieved phosphate as a binder to immobilize Zn in acidic soils, and this is because phosphate rock can easily dissolve and convert the phosphorus into soluble phosphate, which in turn can react with Zn to form hopeite ( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) and scholzhite ( $\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ).

Several other studies demonstrated that the immobilization of Zn was predominantly governed by the formation of zinc phosphates in the pH range 3.3–6.5 (Chen and Peurrung, 1997; Seshadri et al., 2017). A similar immobilization mechanism was presented by several other researchers as well (Corami et al., 2007; Li et al., 2017b). In particular, the fixation mechanism involves the formation of Zn phosphate on the surface of the amendment grains, followed by diffusion of Zn ions into the phosphate structure (Mignardi et al., 2012).



**Fig. 3 – (a) SEM micrograph of struvite treated soil and (b) associated EDS spectrum of mineral particles.**

However, Cao et al. (2008) reported that phosphate treatment reduced the water solubility of Zn by 40%–69%, which was probably due to sorption on minerals (e.g., calcite and phosphate phases,) and Perwitasari et al. (2018) also demonstrated that Zn ions could have been adsorbed onto the surface of the struvite crystals in their investigation. As illustrated in Fig. 3 below, microprobe analysis results confirmed the formation of zinc phosphate, a possible mechanism responsible for Zn immobilization. Similar to the case of Cu, there was no noticeable difference among struvite treatments with and without organic acid on the immobilization of Zn. This may be due to the acidic pH of the bio-retention filter media used in this study, where the lower pH hinders the effect of weaker organic acids on the dissolution of struvite as described previously.

As stated above, with the lime treatment, the pH of the soil increased from 5.2 to 7.9 within the first 10 days, and the reduction in the water solubility of Zn was more than 99%. The pH enhancement of limed soil may support the formation of insoluble Zn hydroxides and oxides, which are less mobile, and hence the water solubility of Zn was low. As per Jiang et al. (2012), one of the main mechanisms of heavy metal immobilization in high pH soil was the hydrolysis of heavy metal cations and precipitation of metal(oxy)hydroxides. In lime-applied soil, the effect of struvite treatment was not significant, as struvite dissolution was low at higher pH. This is because the solubility of struvite is highly pH dependent, with lower solubility at higher pH (Ohlinger et al., 1998).

As shown in Tables 3 and 5, the control soil samples (treatment 1), which did not have any treatment, also had the capacity for immobilizing Cu and Zn in contaminated soil, because the soil used in this experiment was bio-retention filter media, which has the ability to retain heavy metals by itself as demonstrated by other researchers (Davis et al., 2003). Soil in a bio-retention system is an important medium to adsorb trace metals from runoff, and the soil typically has a high sand content to provide rapid infiltration, but low levels of silt and clay to promote attenuation of pollutants during the infiltration (Davis et al., 2001). Davies et al. (2003) documented the effectiveness of pilot-plant laboratory bio-retention systems and two existing bio-retention facilities at removing low levels of lead, copper, and zinc from synthetic stormwater runoff. The results pre-



sented in this manuscript confirm that application of struvite to bio-retention filter media increases the capacity for heavy metal immobilization, and this can be a key point to consider when designing bio-retention systems in the future.

### 2.3. Soil residue examination

To identify the mechanism of Cu and Zn immobilization by struvite, XRD quantification by the Rietveld method and microprobe analysis of soil residues were carried out. Consistent with previous studies (Cao et al., 2009; Mignardi et al., 2012), the XRD analysis did not detect any crystalline phases of Cu and Zn in soil, and this may be due to the metal contents being lower than 1% of the sample matrix. Table 5 below depicts the quantification of mineral phases of treated and untreated soils. According to Table 5 below, it is clear that Quartz, Plagioclase, K-Feldspar and amorphous material are the main phases detected in experiments with Str1. In addition to the above minerals, soil treated with Str2 contained gypsum, and this is because Str2 was precipitated in the presence of Ca. Moreover, soil treated with lime contained calcite in addition to the minerals stated above. As shown in Table 5 below, it is clear that the amorphous content of residual soil was higher after treatment with struvite, and this indicates that extra amorphous materials were formed during the soil treatment with struvite. These amorphous materials can be oxides, hydroxides or phosphates of Cu, Zn, Mg and Ca.

Microprobe analysis of soil was carried out to identify Cu and Zn minerals in struvite-treated soil, as XRD did not detect any Cu and Zn mineral phases in residual soil. Fig. 3 below shows the morphology and EDS spectrum of a struvite-treated soil sample. As per the EDS spectrum in Fig. 3b, it is clear that Cu and Zn minerals were present and were associated with P on the surface of quartz grains. The analyses suggest that zinc phosphate tetrahydrate might be formed after the struvite treatment because calculations of element proportions, assuming zinc phosphate tetra-hydrate ( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) stoichiometry, agreed well with the obtained data. However, the Cu and Zn mineral phases formed were difficult to analyze and the analytical totals were low due to material sensitivity to the electron beam.

## 3. Conclusions

The study revealed the effect of struvite on Cu and Zn immobilization in contaminated bio-retention soil in the presence of commonly exuded plant organic acids. Based on laboratory experiments, it was concluded that more than 99% of Cu and Zn were immobilized in the bio-retention filter media by application of struvite. Struvite was effective in heavy metal remediation in acidic soil irrespective of the presence of Ca impurities in struvite and organic acids in soil.

Application of struvite to Cu- and Zn-contaminated soil resulted in formation of a compound similar to zinc phosphate tetrahydrate ( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) as well as amorphous Cu and Zn phases. Therefore, possible immobilization mechanisms involve dissolution of the struvite and precipitation of heavy-metal-containing phosphates and formation of amorphous Cu and Zn mineral phases. Additionally, surface adsorption or complexation can also be involved in immobilization of Cu and Zn in bio-retention soil.

This study concluded that struvite application increased the capacity for heavy metal immobilization in bio-retention filter media, and this can be a key point to consider when designing bio-retention systems for stormwater treatment in the future. Also, it can be stated that the findings of this research will help to fill several research gaps for researchers who are engaged in the area of bio-retention systems.

For water reuse, bio-retention filters with their natural purification processes are increasingly becoming popular in urban stormwater treatment. This study demonstrated that struvite recovered from wastewater treatment plants can potentially be

used in bio-retention filter media (soils) as an amendment for the immobilization of heavy metals such as Cu and Zn in addition to use as a fertilizer. This approach can have a remarkable impact for a sustainable environment.

## Recommendations

Additional research is warranted to investigate the effect of struvite on heavy metal immobilization in soil with different physiochemical properties.

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