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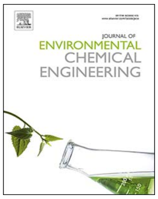

Kinetics and morphology analysis of struvite precipitated from aqueous solution under the influence of heavy metals: Cu^{2+}, Pb^{2+}, Zn^{2+}

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ABSTRACT

The present study examined the influence of metal ions (Cu^{2+}, Pb^{2+}, and Zn^{2+}) on kinetics and morphology of struvite precipitated from aqueous solutions containing equimolar ratios of struvite components: Mg^{2+}, $NH_4{}^{+}$, $PO_4{}^{-3}$. Kinetics of the struvite precipitation in the presence of metal ions [0,1, 10, 50 and 100 ppm] was evaluated through the change of pH of the precipitating solution. The kinetic evaluation demonstrated that the precipitation satisfactorily followed the first-order kinetic with respect to Mg^{2+}. It was found that for the three metal ions tested, the higher the concentrations of the metal ions: 0, 1, 10, 50, 100 ppm, the less the crystals obtained and the lower the rate constants. Depending on the concentrations of the metal ions added into the solution, the rate constants varied from 4.344 to 1.056 h^{-1} which agree with most published values. It was postulated that the metal ions were adsorbed onto the surface of the crystals and hence retarded the growth. The crystals obtained were characterized using SEM-EDX and XRPD Rietveld. The characterization revealed that the precipitates were mainly struvite of various sizes (between 10 and 60 μm) with sylvite as impurities. It is envisaged that the present study would add to the understanding of the removal of metal ions from industrial wastewater through struvite precipitation.

1. Introduction

Wastewater contains a particularly high concentration of phosphate, potassium, and ammonia which may cause eutrophication of surface waters [1]. The phosphorus concentrations in the wastewater can be reduced through mass crystallization of sparing struvite [$MgNH_4PO_4{\cdot}6H_2O$] on a mechanical mixing equipment [2,3]. In addition, the wastewater containing heavy metals namely, copper (Cu^{2+}), lead (Pb^{2+}) and zinc (Zn^{2+}), could have a negative effect on health, environment, equipment, and the aesthetic quality of the water bodies. Correspondingly, traces of heavy metals contaminated wastewater must be treated prior to its release to the environment [4,5].

Toxic heavy metals from inorganic effluent can be stabilized through conventional methods such as precipitation, cementation, sedimentation, filtration, coagulation, flotation, ion exchange and, adsorption [6–8]. However, these methods often lead to incomplete treatment, high-energy consumptions, and still produce an output of toxic sludge or waste products [9]. In this way, the conventional precipitation of heavy metals to yield hydroxides have shown the ineffectiveness in metal immobilization, especially when their concentrations are low in the solution. Alternatively, heavy metals in the wastewater can be removed simultaneously from the wastewater with a recovery of potassium, phosphate and ammonia using the precipitation agents [e.g., KOH and Mg $(OH)_2$], to produce struvite and/or struvite-K [$KMgPO_4{\cdot}6H_2O$-(KMP)] [10]. Currently, the recovery of six heavy metals [Cu, Ni, Pb, Zn, Mn, Cr (III)] from solutions can be enhanced by utilizing the self-synthesized struvite under pH variations of 6.0–10.0. Results indicated that more than 95% of those six heavy metals could be taken out from the solution by struvite precipitation [11], and the precipitating solid contains the highest quality of struvite (97%) which could be potentially utilized as fertilizer [12].

Correspondingly, several kinds of reactor systems have been developed to facilitate the wastewater treatment for not only sustainable recovery of phosphorus but also the adsorption of metals and organics into the surface of crystal struvite [5]. Consequently, the heterogeneous nucleation mechanism and crystal growth of struvite may be influenced by the presence of heavy metals. The exchange between ionized metals such as cadmium, zinc, and nickel with magnesium can occur in the crystal lattice of struvite [3]. Therefore, the interaction between metals and struvite during co-precipitation and adsorption have become a

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great concern. Knowledge of the heterogeneous nucleation in terms of the speed of nucleation and the crystal growth has received much attention for reducing the activation energy due to the catalytic effect of metal ion particles [2]. The presence of heavy metals may deteriorate the morphology of the precipitates and, in certain cases, cause the precipitation of a less stable phase instead of struvite. The advancement from the previous study [13] is shown by the findings on rate constants for the three metal ions investigated. In addition, the present study compared characterization of the precipitates with predicted precipitation using Visual Minteq. Industrialization and urbanization cause a serious problem for the environment and especially the life forms due to excessive release of heavy metals into water sources. Heavy metal ions are known to be non biodegradable and may accumulate in living tissues. Among these eco-toxic metal ions are Pb^{2+}, Cu^{2+}, and Zn^{2+}. Many industrial activities for the manufacture of batteries, ammunition, various metal products and ceramic discharge Pb^{2+} into the water bodies [14]. Copper is used extensively in various industries including refineries, paper and pulp, fertilizer, mining, and electroplating [15]. Meanwhile, industrial effluents from pulp and paper mills, organic and inorganic chemical plants, petroleum and petrochemicals, steel work foundries, and steam generation power plants may contain Zn^{2+} [16].

Microstructure and property evaluation results of selected heavy metals incorporated into the crystal lattice of struvite are required to control the quality of recovered products. The characterization methods are needed here to examine the struvite quality flushing out of the reactors. Mineralogy, morphology and final particle size are the key factors in assuring for phosphorus recovery efficiency [2].

So far there is no report on the influence of three metal ions, Pb^{2+}, Cu^{2+}, and Zn^{2+}. on struvite precipitation. Therefore, the objectives of this study were to examine the struvite precipitation under the individual influence of these metals from a kinetic and morphological point of view. This study could be useful for determining the struvite precipitation as a means of fouling prevention and mitigation in which the effluent contains heavy metal ions.

2. Materials and methods

2.1. Analytical methods and kinetic study of struvite precipitation

The crystal synthesis was performed by chemical precipitation from a synthetic waste solution, of which a mixture of 0.25 M $MgCl_2$ and 0.25 M $[(NH_4)\cdot H_2PO_4]$ solutions were prepared, and all chemicals were analytically pure grade (Merck™). In the real wastewater condition, a low magnesium content relative to ammonia and phosphates is commonly found and magnesium is added to promote the struvite crystallization process. For magnesium source, $MgCl_2$ was particularly added in the solution due to its high solubility [17].

Solutions of $MgCl_2$ and $[(NH_4)\cdot H_2PO_4]$ were filtered through 0.45 mm paper filter and reserved at least 24 h just prior to conducting experiments. The series of struvite precipitation experiments were carried out in a clean glass beaker of one-liter volume stirred at 200 rpm and equipped with temperature control unit. Adjusting pH to an initial value of 6.5 was performed by dropping wisely an aqueous solution of 0.5 M KOH during mixing of $MgCl_2$ and $[(NH_4)\cdot H_2PO_4]$ solutions, of which the molar ratio of Mg^{2+}: $NH_4{}^+$: $PO_4{}^{-3}$ (MAP) was determined as 1:1:1. The struvite precipitation can be expressed as the Eq. (1) (with n = 0, 1, and 2) [18].

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6\,H_2O \rightarrow MgNH_4PO_4\cdot 6(H_2O) + nH^+ \tag{1}$$

The concentration of $[Mg^{2+}]$ changed over time and the kinetic constants of struvite crystals were estimated according to the following Eq. (2) [13].

$$\ln(C\text{-}C_{eq}) = -k\,t + \ln(C\text{-}C_o) \tag{2}$$

Table 1
Chemical compositions of the synthetic wastewater used in the study.

Ions	$PO_4{}^{-3}$	$NH_4{}^+$	Mg^{2+}	K^+	Cl^-
(mol/kg)	0.14590	0.27290	0.16190	0.16890	0.07710

where C = $[Mg^{2+}]$ at any time t (molar)
C_{eq} = $[Mg^{2+}]$ at equilibrium (molar)
C_o = initial $[Mg^{2+}]$ at time zero (t = 0) (molar)
k = reaction rate constant (h^{-1})
t = crystallization time (min)

Furthermore, the reactions were conducted in duplicate for kinetic data. All precipitation experiments were performed at room temperature (30 °C). To control the temperature of the solution used a thermostatic controller during the kinetic experiments. Solution pH was continuously monitored using an Orion SA520 pH meter with a gel epoxy probe. The obtained precipitate was then filtered off in a paper (Schleicher&Schuell no. 604), washed with distilled water, and dried directly on the filter at room temperature. The entire time of the precipitation and filtration of struvite required 90 min.The mass scale was then measured by weighing the dried sample.

The effects of Cu^{2+}, Pb^{2+} and Zn^{2+} ions (0, 1, 10, 50 and 100 ppm) on struvite precipitation were evaluated in this work. In this experiment, each crystal of $CuCl_2$, $PbCl_2$, and $ZnCl_2$ was diluted into 500 ml volume of $MgCl_2$ solution. The ions concentration present in the synthetic solution including K^+ from KOH addition is presented in Table 1.

2.2. Chemical thermodynamic modeling

The struvite precipitation potential in the synthetic wastewater was examined using a thermodynamic chemical equilibrium model developed with the Visual Minteq software program version 3.0 [19]. Calculations were conducted using the Davies activity coefficient approximation. The program was employed to calculate the solution equilibrium model using the input data of ion concentrations in the synthetic wastewater. The Visual Minteq was selected in the study to predict the mineral speciation formed in the solution. The chemical composition of the synthetic wastewater for the input of the program is given in Table 1. The model of mineral species was subsequently calculated by the program, using pH values and temperatures of 30 °C as an input parameter. The mineral species predicted by the program were subsequently justified by the X-ray powder diffraction (XRPD) Rietveld method [20].

2.3. Materials characterization

The dried samples of precipitates were characterized through SEM coupled with an energy dispersive X-ray analysis (SEM-EDX) and XRPD method. The precipitates were ground with a pestle and mortar to obtain a powder with sizes < 75 μm. Samples with different particle sizes were embedded in epoxy on a glass slide and then sputtered with gold for SEM analysis.

Instead, the ground powder was placed in an aluminum sample holder for XRPD measurement by A Philips PW 1710 Diffractometer equipped with a Cu tube. The measured XRPD data are shown in Table 2. Identification of crystalline phases was initially performed with (Powder Diffraction File) −PDF-2 Phillips software. The candidate crystalline phases found by the search match method were then verified by the Rietveld refinement method with Program Fullprof-2k, version 3.30 [21]. The crystal structure model for the Rietveld method was obtained from the literature [AMCSD-American mineralogist of crystal structure database]. The full-width at half-maximum (FWHM) of XRPD peak profiles as a function of tan (θ) was fitted by the Fullprof program using the u-v-w formula of Caglioti et al. [22]. The cell parameters were received from the refinement, which then was used for determination of