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Organic pollutants removal and recovery from animal wastewater by mesoporous struvite precipitation

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ABSTRACT

Swine wastewater containing high concentration of phosphorus (P) and nitrogen (N) was treated by struvite precipitation method. The pH showed to have strong influence on N and P removal, whereas the excess of ammonia in the reaction medium did not show influence. The precipitated crystals were identified and analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA), atomic force microscopy (AFM), and surface area (BET) revealing that there was the formation of a pure and crystalline phase mesostructured at pH 9.5 with an average crystal size in nanometric scale.

Keywords: Struvite; Swine wastewater; Nitrogen; Phosphorus

1. Introduction

Swine wastewater contains high concentration of phosphorus (P) and nitrogen (N), and the removal of these pollutants from wastewater is important to maintain water quality, because its direct disposal in the environment can cause problems as the eutrophication [1]. Ammonia in wastewater is usually removed by biological methods such as autotrophic nitrification (conversion of NH^{4+} to NO^{3-}) [2] and heterotrophic denitrification (conversion of NO^{3-} to gaseous nitrogen) [3]. Phosphorus may be removed from wastewater by biological [4] and chemical [5] treatments. However, the struvite precipitation method is interesting because it simultaneously removes and recovers P and N from wastewater [6]. Struvite is a crystalline solid with equal molar concentrations of magnesium, ammonium, and phosphorus ($MgNH_4PO_4{\cdot}6H_2O$).

Struvite has been obtained from washing wastewater [7], nylon wastewater [8], sewage sludge [9], poultry wastewater [10], swine wastewater [11,12], and municipal landfill leachate [13] and in the synthetic form [14]. Struvite is used as a slow-release fertilizer [15]. Therefore, the production of struvite is an alternative for add value to swine wastewater, besides to decrease the impact caused by its disposal into the environment. Although there are many works in literature reporting the phosphorus and nitrogen removal by struvite precipitation method from swine wastewater, there are few studies reporting/comparing the simultaneous effects of pH and excess of ammonia in the reaction medium on the formation of struvite, since the characteristic of material formed as well as the recovering efficiency can be influenced by these variables.

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In this context, the removal of phosphorus and nitrogen by struvite crystallization of swine wastewater has been investigated. The effects of pH and excess of ammonia in the reaction medium have been studied. The synthesized nanocrystals were analyzed by XRD, TGA, AFM, and BET area.

2. Materials and methods

2.1. Treatment of swine wastewater

The swine wastewater sample used in this work was collected from a farm local. The sample was stored and preserved at 4℃ until analysis. The sample was centrifuged at 3500 rpm for 10 min to separate the solids, and the supernatant was used for chemical analysis. The characteristics of the swine wastewater are summarized in Table 1.

The system consisted of a glass batch reactor (11 × 11 × 17 cm) with a total volume of 2.0 L, constituted of a paddle of diameter 7.5 cm and height of 2.5 cm. The working volume of the reactor was 1.0 L. The reactor was operated under agitation of 200 rpm, at room temperature (25℃). Analytical grade chemicals (MgO, HCl, $H_3PO_4^{3-}$, and NaOH) were used as received. The amounts of MgO powder, HCl (4M), and $H_3PO_4^{3-}$ (4M) used in tests were calculated according to the concentration of PO_4^{3-} present in the sample of swine wastewater (see Table 1). The synthesis of struvite was evaluated in two different molar ratios, 1:1:1 and 1:1.1:1 (Mg^{2+}:NH_4^+:PO_4^{3-}), and two different pH, 9.0 and 9.5. The pH of solution was adjusted by adding the NaOH 4M. The formation of struvite normally occurs in alkaline medium, and the optimal pH value for struvite crystallization was reported in the range of 8.0–11.0 [16,17]. The addition of 10% molar excess of NH_4Cl (1M) was used to result in a 1:1.1:1 (Mg^{2+}:NH_4^+:PO_4^{3-}). All the reaction runs were carried out by 10 min and then kept at rest for 30 min. Lee et al. [18] showed that phosphorus and nitrogen removal by struvite formation is fast and did not change after 10 min. The suspensions were filtered through a 0.14 μm membrane filter, and the precipitates were washed thoroughly with distilled water and dried at 50℃ for 6 h.

Table 1
Characteristics of the swine wastewater

Parameters	Values
pH	6.5
Nitrogen (mgN L^{-1})	747
Total phosphorus (mgPO_4^{3-} L^{-1})	655
Total COD (mgO_2 L^{-1})	390

The analytical tests performed in the supernatant were pH, PO_4^{3-}, NH_4^+, and chemical oxygen demand (COD). The total dissolved phosphorus concentration was determined by potassium persulfate digestion method [19]. The nitrogen was determined with Nessler reagent colorimetric method [20]. Total COD was analyzed according to the standard methods [20]. The pH value was measured with a potentiometer (W3B, Italy). All analytical tests were carried out in duplicate and only the mean values were reported. The maximum deviation observed was about ±5.5%.

2.2. Characterization of struvite

The synthesized struvite was analyzed by X-ray diffraction (XRD), infrared spectroscopy (IR), surface area (BET), thermogravimetric analysis (TGA), and atomic force microscopy (AFM). The precipitated crystals were indentified using an X-ray diffractometer (Philips, MPD 1880 model), where the X-ray source was Cu Kα radiation, powered at 40 kV and 40 mA. The average nanocrystals size was determined through X-ray diffraction (and reflection) line broadening using the Sherrer equation: $D = K \cdot \lambda / (\beta \cos\theta)$, where D is the crystallite size, K is the Sherrer constant (0.90), λ is the wavelength of the X-ray radiation (0.1542495 nm for Cu Kα), β is the peak width at half height, and finally θ corresponds to the peak position (in the current study, $2\theta = 20.84$). Thermogravimetric analysis (TGA) was carried out on Netzsch STA 409 analyzer at a heating rate of 10℃ min^{-1} at an air flow rate of 35 mL min^{-1}. The morphology of solids was examined by atomic force microscopy (Agilent Technologies 5500 equipment). The BET surface area was obtained from nitrogen adsorption isotherms at 77 K, conducted on an ASAP 2020 (Micromeritics) system, at a relative pressure (P/P_o) from 0 to 0.99.

3. Results and discussion

3.1. Removal of organic pollutants of swine wastewater

Table 1 shows the characteristics of the swine wastewater. As can be seen, the sample has high nitrogen and phosphorus content, about 750 and 650 mg L^{-1}, respectively. The sample also has high COD content, above 300 mgO_2 L^{-1}.

Table 2 shows the results concerning the removal of P and N obtained in experimental runs carried out in this work. As observed, the excess of ammonia in reaction medium did not influence the amount of P and N removed during the struvite precipitation. However, the pH showed significant results, since at pH 9.0 was verified a reduction of about 83% for both P and N, whereas at pH 9.5 the reduction was higher than 90%.

Table 2
Performance of the process

Test condition	Final P ($mg\,L^{-1}$)	P removal (%)	Final N ($mg\,L^{-1}$)	N removal (%)	Final COD ($mg\,L^{-1}$)	COD reduction (%)
1:1:1/pH: 9.0	113.2	82.7	122	83.7	323	17.2
1:1.1:1/pH: 9.0	118.4	82.0	137.4	81.6	311	20.3
1:1:1/pH: 9.5	48.2	92.6	46.1	93.8	304	22.1
1:1.1:1/pH: 9.5	50.8	92.3	54.7	92.7	317	18.7

Song et al. [11] synthesized struvite from swine wastewater and observed reductions of P and N by about 85% and 40–90%, respectively. Ichihashi and Hirooka [12] obtained reduction of P between 70 and 82% by struvite precipitation in swine wastewater. Çelen et al. [21] reported removal ranging from 55 to 98% of P and 36–50% of N, for the liquid swine manure. The results of COD obtained in this study for all the experiments were similar, with values about 20%. Li et al. [22] reported COD reduction of about 30% in treating landfill leachate effluent. They suggested that after struvite precipitation, a biological treatment process can be accomplished to remove COD by conventional process. Ryu and Lee [23] obtained reduction of about 47% in treating swine wastewater. Ozturk et al. [24] reported that COD removal of about 50% was reached in treating anaerobically pretreated raw landfill leachate effluent by struvite crystallization.

3.2. Properties of the struvite obtained

The identification of powders was examined by XRD (Fig. 1). As shown in Fig. 1(a), it was verified the formation of a completely amorphous solid at pH 9.0 for both molar ratios. However, at pH 9.5 was verified the formation of crystalline struvite. The formation of struvite is indicated by location of the peaks, corresponding to reference database lines for struvite (Fig. 1(b)). From Fig. 1(a) it is seen no significant differences on position of the peaks between the synthesized samples in different molar ratios. Some authors have reported that optimum pH range for formation of

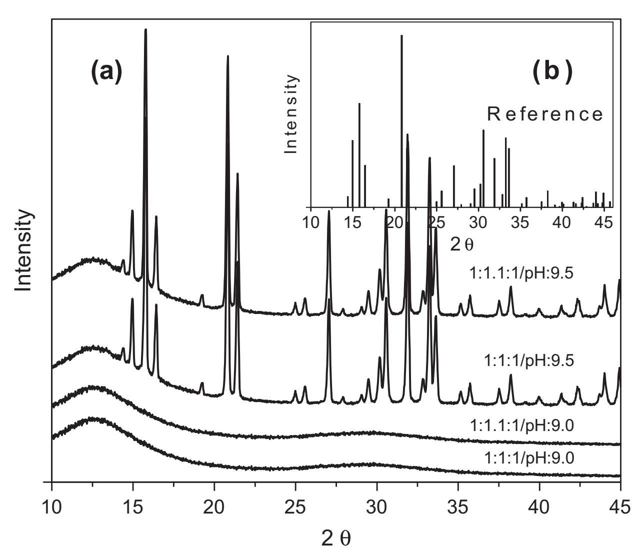

Fig. 1. XRD analysis of samples obtained at (a) different pH values and molar ratios and (b) reference struvite (JCPDS Card No. 1-077-2303).

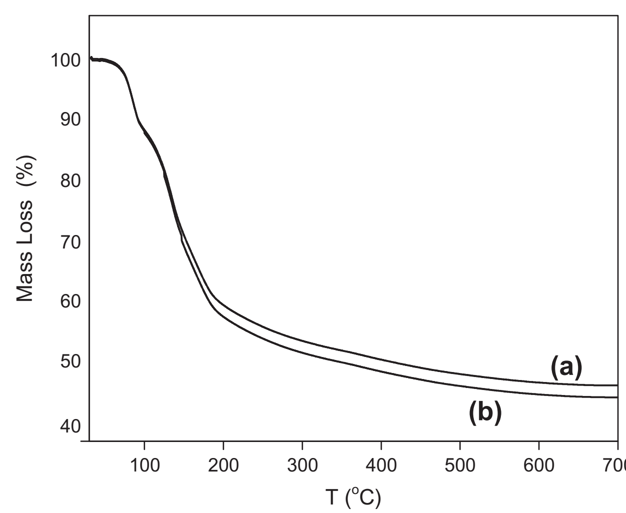

Fig. 2. TGA patterns of the struvite samples obtained at pH = 9.5, in molar ratios (Mg^{2+}:NH_4^+:PO_4^{3-}) (a) 1:1:1 and (b) 1:1.1:1.

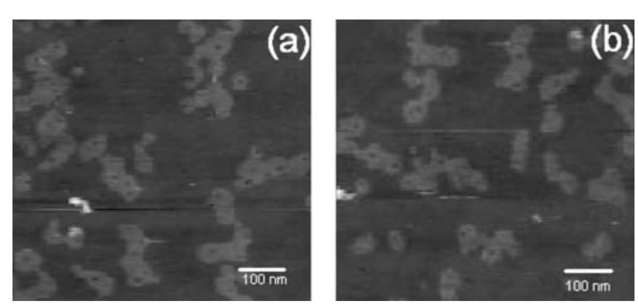

Fig. 3. AFM images of the struvite samples obtained at pH = 9.5, in molar ratios (Mg^{2+}:NH_4^+:PO_4^{3-}) (a) 1:1:1 and (b) 1:1.1:1.

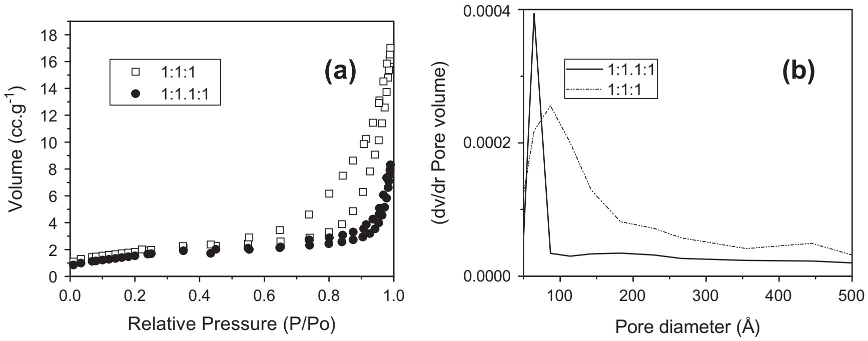

Fig. 4. (a) N_2 adsorption/desorption isotherms of the struvite samples obtained at pH 9.5 for molar ratios (Mg^{2+}:NH_4^+:PO_4^{3-}) of 1:1:1 and 1:1.1:1 and (b) pore size distribution measurement of respective samples.

struvite is very narrow and it is dependent of the quality of raw material. In previous works concerning struvite precipitation of swine wastewater, the optimum pH of 8.0–8.5 [25], 8.0–10 [26], and 9.5–10.5 [27] were reported. If the pH is maintained at values above of the optimum range the formation of $Mg_3(PO_4)_2$ occurs instead of struvite. On the other hand, if pH is maintained at values below to this range, an increase of H^+ in the solution inhibiting the struvite crystallization is observed[25]. By applying of Sherrer equation, the average nanocrystal sizes were estimated to be 51 and 53 nm, for the samples obtained at 9.5 in the molar ratios of 1:1:1 and 1:1.1:1, respectively.

The identification of single-phase struvite of the samples obtained at pH 9.5 was confirmed by thermogravimetric analysis (TGA) (Fig. 2). The theoretical mass loss for the struvite formula ($MgNH_4PO_4{\cdot}6H_2O$) upon heating was 51.42%, which is composed of mass losses of water (corresponding to 44.08%) and ammonium (corresponding to 7.34%). According to Fig. 2, the mass loss was about 50% for both samples obtained at pH 9.5, corroborating with the theoretical (51.42%) and with those reported by other researchers (52.49% [13]; 51% [28]).

The morphology of the synthesized struvite samples at pH 9.5 was determined by means of atomic force microscope (AFM). From Fig. 3, it is seen that the particles are composed of small spherical nanograins with average size of about 50 nm for both samples that are similar to the estimated from XRD analysis by Sherrer equation.

The N_2 adsorption–desorption curves were found to be of type IV (in accordance with IUPAC classification) at relative pressure > ca. 0.3, as shown in Fig. 4(a). The shape of the isotherms suggests that the sample is basically mesoporous. It was confirmed by analysis of pore size distribution (Fig. 4(b)), which is unimodal, and shows spectra of pore diameter in the mesoporous region, according to the IUPAC classification [29]. Therefore, struvite has mesopores, most likely due to the interparticles and out-of-order porosity. The results of surface area and total pore specific volume (at $P/P_o = 0.95$) were $6.70\,m^2\,g^{-1}$ and $0.0264\,cm^3\,g^{-1}$, and $5.73\,m^2\,g^{-1}$ and $0.0125\,cm^3\,g^{-1}$, for the samples obtained at pH 9.5, in molar ratios (Mg^{2+}:NH_4^+:PO_4^{3-}) of 1:1:1 and 1:1.1:1, respectively.

4. Conclusions

This study investigated the nitrogen and phosphorus removal and recovery from swine wastewater by struvite crystallization process. It was shown that the pH exerts strong influence on the efficiency of N and P removal by struvite precipitation, whereas the excess of ammonia (10 wt.%) does not exert influence. The synthesized struvite at pH 9.5 presented a crystalline phase and a mean nanocrystal size about 50 nm. The struvite obtained in this work presented a mesoporous structure, with a surface area of about $6.5\,m^2\,g^{-1}$.

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