Chemosphere 141 (2015) 94–99

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effect of humic substances on phosphorus removal by struvite precipitation

Zhen Zhou *, Dalong Hu, Weichao Ren, Yuzeng Zhao, Lu-Man Jiang, Luochun Wang

College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, China
College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Changyang Rd #2588, Shanghai 200090, China

HIGHLIGHTS

- Inhibitory effect of humic substances on struvite precipitation was studied.
- Humic substances inhibited struvite precipitation at pH 8.0–9.0 and low Mg/P ratio.
- Humic substances changed structure and morphology of precipitated struvite crystals.
- Coprecipitation of humic substances compromised precipitated struvite purity.

ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form 26 May 2015
Accepted 29 June 2015

Keywords:
Struvite
Humic substances
Phosphorus
Precipitation
Wastewater

ABSTRACT

Humic substances (HS) are a major fraction of dissolved organic matters in wastewater. The effect of HS on phosphorus removal by struvite precipitation was investigated using synthetic wastewater under different initial pH values, Mg/P molar ratios and HS concentrations. The composition, morphology and thermal properties of harvested precipitates were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and thermo-gravimetric analysis (TGA), respectively. It showed that inhibition effect of HS reached its maximum value of 48.9% at pH 8.0, and decreased to below 10% at pH > 9.0. The increase of Mg/P ratio enhanced phosphorus removal efficiency, and thus reduced the influence of HS on struvite precipitation. At pH 9.0, the inhibitory effect of initial HS concentration matched the modified Monod model with half maximum inhibition concentration of 356 mg L^{-1}, and 29% HS was removed in conjunction with struvite crystallisation. XRD analysis revealed that the crystal form of struvite precipitates was changed in the presence of HS. The morphology of harvested struvite was transformed from prismatic to pyramid owing to the coprecipitation of HS on crystal surface. TGA results revealed that the presence of HS could compromise struvite purity.

1. Introduction

Phosphorus (P) is a finite resource, and it was estimated that global reserve life of phosphate rock can only be mined economically somewhere between 50 and 100 years owing to its worldwide application in both industry and agriculture (Jordaan et al., 2010; Muster et al., 2013). In addition to being diminishing resource, P in the discharged wastewater is a threat to surface water quality (Wang et al., 2010; Triger et al., 2012; Liu et al., 2013). Therefore, P recovery from wastewater has gained attention both as a way of pollutant removal and to make the recovered P available for beneficial use. One of the most efficient ways to recover P from wastewater is through simultaneous precipitation of soluble ortho-phosphate (PO_4^{3-}-P) and ammonium nitrogen (NH_4^+-N) in the formation of struvite ($MgNH_4PO_4{\cdot}6H_2O$). The struvite method has been applied to recover N and P from livestock wastewater (Song et al., 2007; Jordaan et al., 2010; Huang et al., 2011; Foletto et al., 2013; Kim et al., 2014), reject water from sludge digestion and dewatering process (Yoshino et al., 2003; Iqbal et al., 2008; Xu et al., 2011b; Kruk et al., 2014), urine (Triger et al., 2012; Liu et al., 2013), landfill leachate (Kochany and Lipczynska-Kochany, 2009), fertilizer industry (Hutnik et al., 2013), etc. Struvite is a valuable slow-release fertilizer, with higher purity and lower heavy metal content than commercial phosphate fertilizers, and could be directly used for horticulture and agriculture without traditional sludge handling process (Jordaan et al., 2010; Wang et al., 2010).

Owing to the high concentration of dissolved organic matters (DOM) in P-rich wastewater (livestock wastewater, anaerobic

* Corresponding author.
E-mail address: zhouzhen@shiep.edu.cn (Z. Zhou).

http://dx.doi.org/10.1016/j.chemosphere.2015.06.089
0045-6535/

supernatant, urine, and/or landfill leachate), simultaneous removal of DOM was observed during struvite precipitation (Kochany and Lipczynska-Kochany, 2009; Foletto et al., 2013), and the decrease of DOM was found to be in favor of struvite crystallization (Kim et al., 2014). Humic substances (HS) are a major fraction of DOM in most of P-rich wastewater (Kochany and Lipczynska-Kochany, 2009; Foletto et al., 2013). For instance, HS dominate the organic fraction of mature landfill leachate by as much as 60%, and usually ranged from tens to hundreds mg L^{-1} (Sir et al., 2012). HS contain carboxylic, phenolic, alcoholic, quinone, amino and amido groups, and the presence of these groups results in their abilities of colloid-like adsorption, ionic exchange, complex formation and oxidation/reduction (Lipczynska-Kochany and Kochany, 2008). For P recovery from wastewater, it is necessary to get information about the effect of HS on struvite precipitation. There are a limited number of studies on growth inhibition of struvite crystals by inorganic ions (e.g. Ca^{2+}, K^{+}, CO_3^{2-}) (Xu et al., 2011b; Muster et al., 2013; Kruk et al., 2014), acetate (Iqbal et al., 2008), acetohydroxamic acid (Downey et al., 1992), phosphorcitrate (Wierzbicki et al., 1997) and herbal extracts (Chauhan and Joshi, 2013). However, to date, interference effects of HS, one of the major fractions in wastewater, on struvite precipitation are scarcely reported in the literature, and it should be very useful for understanding the struvite precipitation in real wastewater rich in DOM.

The objective of this study is to investigate the inhibitory effect of HS on the struvite precipitation under different initial pH values, Mg/P molar ratios and HS concentrations. After struvite precipitates were recovered, their composition, morphology and thermal properties were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and thermo-gravimetric analysis (TGA), respectively. The results obtained in this study are expected to provide an insight for P removal by struvite precipitation in the presence of HS.

2. Materials and methods

2.1. Preparation of wastewater

Stock solutions were prepared to form artificial wastewater by dissolving an analytical reagent grade of $Na_2HPO_4{\cdot}6H_2O$ and NH_4Cl chemicals in distilled water to get an initial PO_4^{3-}-P and NH_4^+-N concentration of 95 and 272 mg L^{-1}, respectively. The initial pH was then adjusted to 7.0–12.0 using 0.45 M NaOH or 1 M HCl solutions. 6 g L^{-1} HS solution with fulvic acid $\geqslant$90% was prepared and mixed with artificial wastewater before experiment. Stock solution of 0.6 M $MgCl_2{\cdot}6H_2O$ was added to the solutions in the batch reactors immediately before the experiments were initiated.

2.2. Batch experiments

Batch experiments of struvite precipitation were implemented using a jar tester (ZR4-6, China) at 20 °C. The addition of $MgSO_4$ solution was carried out under continuous stirring at a faster speed (G = 105.0 s^{-1}, GT = 94,500) for 2 min to ensure rapid mixing. Then, the stirring rate was maintained at the consigned slow value (G = 105 s^{-1}, GT = 82,620) for 15 min. The pH was recorded using an HQ30d portable meter (Hach, USA). A mixed liquor sample of 30 ml was taken from reactors at frequent intervals, and filtered by 0.45 μm cellulose acetate membrane for dissolved compound analysis. The precipitates were washed with deionized water and dried in an oven at 303 K that didn't influence the nature of precipitates (Foletto et al., 2013).

Nine initial pH values (7.0, 8.0, 8.5, 9.0, 9.5, 10.0, 11.0, 11.5 and 12.0) were chosen to compare pH effects on struvite precipitation in the presence (40 mg L^{-1}) and absence of HS at an initial Mg/P ratio of 1.2. Six Mg/P ratios (0.2, 0.5, 0.8, 1.0, 1.5 and 2.0) were used to study the effect of Mg/P ratio on struvite precipitation. The initial pH was maintained at 9.0 in the presence (30 mg L^{-1}) and absence of HS. Ten initial HS concentrations (6, 12, 18, 24, 30, 36, 42, 48, 54 and 60 mg L^{-1}) were used to evaluate the effect of HS concentration on struvite precipitation. All the experiments were performed in duplicate. The initial pH and Mg/P ratio were maintained at 9.0 and 1.2 for the batch test, respectively.

2.3. Inhibition model

The inhibition ratio (IR) of HS on P removal efficiency (PRE) is defined as

$$IR = \frac{PRE_0 - PRE_i}{PRE_0} \times 100\% \tag{1}$$

where PRE_0 and PRE_i are the PRE in the absence and presence of HS, respectively, %.

The relation between PRE and HS concentration can be formulated by a modified Monod equation (Zhou et al., 2014).

$$PRE_i = PRE_0 \frac{K_i}{K_i + C_{HS}} \tag{2}$$

where C_{HS} is the concentration of HS, mg L^{-1}; K_i is the inhibition constant of HS, mg L^{-1}. The multiplicative inverse of PRE_i is linear with the concentration of HS.

$$\frac{1}{PRE_i} = \frac{1}{PRE_0} + \frac{C_{HS}}{K_i PRE_0} \tag{3}$$

2.4. Chemical and instrumental analyses

NH_4^+-N and PO_4^{3-}-P were measured according to Nessler's reagent and ammonium molybdate spectrophotometric methods (Chinese NEPA, 2012) using a 2802 UV/VIS Spectrometer (Unico, USA), respectively. The concentration of HS was determined using the modified Lowry method (Xu et al., 2011a). Morphology of the crystals was analyzed using XL30FEG Scanning Electron Microscope (Philips, Netherland). The precipitates were characterized by D8 Advance Powder X-ray Diffractometer (40 kV, 40 mA, step size 0.1°, Bruker Ltd., Germany). XRD diffractograms were evaluated by means of Jade 6.5. TGA was carried out on Netzsch STA 409 analyzer at a heating rate of 10 °C min^{-1} at an air flow rate of 35 ml min^{-1}.

3. Results and discussion

3.1. Effects of HS on phosphorus removal under different pH values

Fig. 1 shows the effect of HS on PRE at Mg/P ratio of 1.2 under different initial pH values. In the absence of HS, the PRE increased from 9.7% at initial pH 7.0 to 90.3% at initial pH 9.5, then remained above 90% at initial pH of 9.5–11.5, and then decreased with further increase of initial pH. When pH was below 8, no visible precipitates were observed, and the PRE was very low (<25%). The observed PRE results were in agreement with previous works concerning struvite precipitation of swine wastewater, where a wide range of the optimum pH (8.0–10.5) (Song et al., 2007; Bhuiyan et al., 2008; Fernandes et al., 2012; Foletto et al., 2013) was reported.

As shown in Fig. 1a, the PRE with the addition of 40 mg L^{-1} HS showed similar trend of PRE variation with pH as that in the absence of HS. The PRE slightly increased from 11.2% at pH 7.0 to 12.7% at pH 8.0, rapidly increased to 82.1% at pH 9.5, then