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Phosphorus recovery from fosfomycin pharmaceutical wastewater by wet air oxidation and phosphate crystallization

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ABSTRACT

Fosfomycin pharmaceutical wastewater contains highly concentrated and refractory antibiotic organic phosphorus (OP) compounds. Wet air oxidation (WAO)-phosphate crystallization process was developed and applied to fosfomycin pharmaceutical wastewater pretreatment and phosphorus recovery. Firstly, WAO was used to transform concentrated and refractory OP substances into inorganic phosphate (IP). At 200 °C, 1.0 MPa and pH 11.2, 99% total OP (TOP) was transformed into IP and 58% COD was reduced. Subsequently, the WAO effluent was subjected to phosphate crystallization process for phosphorus recovery. At Ca/P molar ratio 2.0:1.0 or Mg/N/P molar ratio 1.1:1.0:1.0, 99.9% phosphate removal and recovery were obtained and the recovered products were proven to be hydroxyapatite and struvite, respectively. After WAO–phosphate crystallization, the BOD/COD ratio of the wastewater increased from 0 to more than 0.5, which was suitable for biological treatment. The WAO–phosphate crystallization process was proven to be an effective method for phosphorus recovery and for fosfomycin pharmaceutical wastewater pretreatment.

1. Introduction

The occurrence of pharmaceutical and personal care product residues, especially antibiotics in environment has received considerable attention in recent years (Loganathan et al., 2009). They are considered to be emerging pollutants because they are bioactive, polar and persistent which may cause adverse effects on aquatic life and humans (Rozas et al., 2010). Additionally, antibiotics and their transformation products may result in the development of antibiotics resistant bacteria and genes (Kümmerer, 2009). Moreover, many of these pharmaceuticals are designed to be persistent and lipophilic (Loganathan et al., 2009), and are often not eliminated by wastewater treatment or biodegraded in environment (Sirtori et al., 2009). A solution to this water pollution problem has now become very urgent. Today, most drugs are manufactured through chemical synthesis. The chemical synthesis-based pharmaceutical wastewater contains a variety of organics including spent solvents, catalysts, additives, reactants, intermediates and finished products, which are refractory and microbial toxic (Oktem et al., 2007). It is estimated that approximately half of the pharmaceutical wastewaters produced worldwide are discharged without specific treatment (Chen et al., 2008). The effective disposition of these pharmaceutical residual effluents has become a challenging task.

Fosfomycin (1R-2S-epoxypropyl phosphonic acid) is a broad-spectrum antibiotic, originally isolated from fermentation broth of *Streptomyces fradiae*. Now, fosfomycin is mainly produced by chemical synthesis. Fosfomycin wastewater is the residual mother liquor effluent of the chemical synthesis-based fosfomycin pharmaceutical process. The main pollutants in the wastewater are a variety of organic phosphorus (OP) intermediates, by-products and finished products, i.e. propargyl phosphonic acid, propenyl phosphonic acid, epoxypropenyl phosphonic acid, etc., as well as some raw materials and solvents like alcohols, anilines and EDTA. Extremely high concentrations of antibiotic OP compounds in the wastewater make it recalcitrant, non-biodegradable and toxic to the biological culture. However, few related studies up to date focus on fosfomycin pharmaceutical wastewater treatment. Therefore, the development of effective methods for fosfomycin wastewater treatment becomes urgent.

Wet air oxidation (WAO) is the liquid phase oxidation of organics at elevated temperatures (125–320 °C) and pressures (0.5–20 MPa) using oxygen as oxidant (Yang et al., 2010), and it is known to have great potentials for the treatment of wastewaters containing high contents of organic matters, or toxic contaminants for which direct biological purification is unfeasible and too diluted for incineration (Oliviero et al., 2001). Till 2007, over 400 WAO

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plants had been in operation worldwide to treat preferential wastewaters from petrochemical, chemical and pharmaceutical industries as well as residual sludge from biological treatment plants (Levec and Pintar, 2007). It has been considered as one of the most promising and the simplest techniques for partial oxidation of parent pollutants into more biologically amenable intermediates (Katsoni et al., 2008), particularly for toxic organics (Suarez-Ojeda et al., 2008).

Phosphate crystallization technologies including calcium phosphate (CP) (Song et al., 2002; Bellier et al., 2006; Kim et al., 2006; Song et al., 2006) and magnesium ammonium phosphate (MAP) crystallization processes (Wang et al., 2006; Moerman et al., 2009; Saidou et al., 2009) are economically feasible, technically robust and operationally simple processes for phosphorus removal and recovery from waste streams (Shu et al., 2006). In recent years, phosphorus recovery by phosphate crystallization has become a hot topic and has been extensively studied for the treatment of a variety of phosphorus intensive wastewaters like supernatant of anaerobically digested activated sludge (Sibel and Maazuza, 2009), swine wastewater (Suzuki et al., 2007), landfill leachate (Gunay et al., 2008). Nevertheless, the application of phosphorus recovery technology to industrial wastewater treatment is still limited.

In this study, WAO–phosphate crystallization process was developed for fosfomycin pharmaceutical wastewater pretreatment and phosphorus recovery. Firstly, WAO was used to transform concentrated and refractory OP substances in the fosfomycin pharmaceutical wastewater into inorganic phosphate (IP); subsequently, the WAO effluent was subjected to CP and MAP crystallization processes for phosphorus removal and recovery. The aim of this study was to find the best way of treating harmful pollutants and recovering valuable phosphorus element from wastewaters like fosfomycin pharmaceutical wastewater containing concentrated OP compounds.

2. Materials and methods

2.1. Fosfomycin pharmaceutical wastewater

The wastewater used in this study was taken from a chemical synthesis-based fosfomycin pharmaceutical plant in Liaoning Province, the Northeastern China. The wastewater was generated from the epoxidation and chiral separation processes of fosfomycin manufacturing, which contained a variety of OP intermediates (i.e. propargyl phosphonic acid, propenyl phosphonic acid, epoxypropenyl phosphonic acid, etc.) and a little amount of finished fosfomycin products, as well as some alcohols, anilines and EDTA. The generation rate of the wastewater was 15 t d^{-1}. The wastewater possesses a COD content of 60–80 g L^{-1}, total OP (TOP) content of 8–10 g L^{-1}, PO_4^{3-}-P content of 0.8–1.2 g L^{-1}, pH value of 11.0–12.0, but the BOD of the wastewater could not be detected (lower than the detection limit).

2.2. WAO experiments

Batch experiments were carried out in an autoclave equipped with a magnetically driven stirrer and two valves for sampling (GSH-1, Dalian Tongda, China). The autoclave was made of stainless steel, with an inner volume of 2.0 L. The reaction temperature was measured by using a thermocouple and controlled by PID regulator.

Typically, 800 mL of fosfomycin pharmaceutical wastewater was introduced into the reactor. After flushing with nitrogen, the reactor was heated to the desired temperature. This procedure was used to minimize unwanted conversion during the heating-up period. Pressurization with oxygen was then completed and the reaction started at "zero time". Throughout the reaction, procedure of 180 min, the reactor contents were stirred at 800 rpm to ensure good mass transfer from the gas phase to the liquid phase (Katsoni et al., 2008). Liquid samples of approximately 2.5 mL were periodically withdrawn from the reactor through a tube inside the reactor vessel, the COD and the TOP contents were measured.

In order to investigate the effect of the reaction temperature, experiments were performed at 125–250 °C with a fixed oxygen partial pressure of 1.0 MPa (all at a reference temperature of 25 °C) and initial pH 11.2 (the original pH value of the raw wastewater). Subsequently, in order to study the influence of oxygen partial pressure, experiments were carried out from 3.0 to 6.0 MPa, with the temperature keeping constant at 200 °C and initial pH value of 11.2. Finally, the wastewater pH value was adjusted to 7.0 and 9.0 by using 6.0 M HCl, and the influence of initial pH values of the wastewater was tested at 200 °C, and 1.0 MPa. Experiments were repeated for three times to check the reproducibility of results.

2.3. Phosphate crystallization experiments

Batch experiments were performed on a magnetic stirrer with a stirring rate of 1000 rpm at room temperature of 22–25 °C (Song et al., 2007). 500 mL WAO effluent (WAO reaction parameters: temperature, 200 °C; oxygen partial pressure, 1.0 MPa; initial pH value, 11.2; reaction time, 180 min. The pH value of the WAO effluent was 6.8) was used. According to different Ca/P or Mg/N/P molar ratios designed, the $CaCl_2$ solution or both $MgCl_2$ and NH_4Cl solutions were added to the above effluent. Throughout the reaction, the pH value of the mixture was kept at 9.0 ± 0.1 for CP crystallization and 8.5 ± 0.1 for MAP crystallization by NaOH supplement. The reaction lasted for 30 min, and water samples of 1.0 mL were removed at frequent intervals and filtrated rapidly with 0.45 μm membranes. 2 μL of 6.0 M HCl was added to the filtrate rapidly to prepare samples for component analyses. The precipitate formed was dried naturally at room temperature. All the reagents were analytically pure reagents and deionized water was used in the experiments.

2.4. Analysis methods

The water samples were analyzed according to standard methods (SEPA, 2002). The concentrations of COD, PO_4^{3-}, total phosphorus (TP) were analyzed colorimetrically with a spectrophotometer (752 N, China. Specify wavelength: COD at 600 nm, PO_4^{3-} and TP at 700 nm). COD was measured with potassium dichromate digestion colorimetric method. PO_4^{3-} was measured with molybdate–ascorbic acid colorimetric method, TP was measured with persulfate digestion molybdate–ascorbic acid colorimetric method, and TOP content was determined by subtracting the PO_4^{3-}-P content from the TP value. In all the WAO experiments the TP content of the wastewater kept stable, and all TOP removed was considered to be transformed into PO_4^{3-}.

The concentrations of organic acids formed in the WAO were determined by gas chromatography (GC-7890A, Agilent, America) equipped with a capillary column (DB-FFAP 122–3232, 30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. The oven and detector temperature was 120 and 250 °C, respectively. The split–splitless ratio was 30 and helium was used as a carrier gas at the flow rate of 1.8 mL min^{-1}, and the air flow rate was set at 400 mL min^{-1}.

The morphology of the precipitates obtained was observed by using scanning electron spectroscopy (SEM, KYKY-2800, China), and the structure of the crystals was analyzed with X-ray diffraction (XRD, Rigaku DMAX-RB, Japan).