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Effect of power ultrasound on crystallization characteristics of magnesium ammonium phosphate

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ABSTRACT

Magnesium ammonium phosphate (MAP) crystallization could be utilized for the recovery of phosphorus from wastewater. However, the effectiveness of the recovery is largely determined by the crystallization process, which is very hard to be directly observed. As a result, a specific ultrasonic device was designed to investigate the crystallization characteristics of MAP under various ultrasonic conditions. The results demonstrated that the metastable zone width (MZW) narrowed along with the rising of the ultrasonic power. Similarly, for the 6 mM MAP solution, with the ultrasonic power gradually enhanced from 0 W to 400 W, the induction time was shortened from 340 s to 38 s. Meanwhile, the crystallization rate was accelerated till the power reached 350 W, and then remained a constant value. It can be observed from the scanning electron microscopy (SEM), the MAP crystal became bigger in size as well as the crystal size distribution (CSD) became broad and uneven, with the increase of ultrasonic power. The results indicate that the crystallization process enhanced by power ultrasound could be used as an effective method to eliminate and recover the phosphorus from wastewater.

1. Introduction

Water pollution and energy shortage have become vital problems at the global level in recent decades. It has been estimated that the water supply-to-demand gap will be approximately 40% in the next 15–20 years [1] and the phosphorus resource, which is mainly used as phosphate fertilizer is going to be run out in the next 100 years [2]. Phosphorus content in wastewater (mainly exists in the orthophosphate form), as one of the main factors for the eutrophication [3], has increased considerably in the influent of wastewater treatment plant (WWTP). However, it is still a big challenge to remove it effectively through the biological process. As a result, eliminating and recycling phosphorus from wastewater has become a hotspot in the fields of wastewater treatment and resources recycling [4,5].

By the reaction between the phosphate and other ions to form non-dissolvable compounds, such as magnesium ammonium phosphate (MAP) or hydroxyapatite [6,7], is an efficient technology to eliminate or recycling use of phosphorus from wastewater. Former studies have claimed that the phosphorus can be removed by MAP crystallization method, owing to its advantage as a slow-released fertilizer in agriculture [8–10]. Although the crystallization process has been well recognized as a promising method to eliminate the phosphorous in wastewater, how to control the crystal size distribution (CSD) of the MAP crystal produced from wastewater is still a big challenge in the water treatment area.

Ultrasonic technology functioned with cavitation effect, high temperature pyrolysis, advanced oxidation, and supercritical oxidation, has been widely applied in the fields of chemical industry, the pharmaceutical industry, food industry, etc. [11–13] Of all the properties ultrasonic cavitation is commonly recognized as the most important mechanism by which crystallization efficiency can be enhanced, and hence improves the commercial characteristics of products in yield and purity [14–16].

A previous study has shown that numerous micro-bubbles were created with the application of ultrasound, and ultrasound frequency higher than 20 kHz is actually considered as a safe, non-toxic and environmentally friendly method [17]. During the ultrasonic wave propagation process in liquid, the bubbles keep repeating the shrink and expand process till the final implosion, hence the cavitation and other related phenomena, such as micro-streaming (caused by symmetrical implosion of bubbles) and micro-jet (caused by asymmetrical implosion of bubbles), will occur [18,19]. Consequently, solid particles which are typically insoluble or slightly soluble in a solvent under ambient conditions may have very high solubility in the same solvent when exposed to

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the cavitation-caused supercritical environment [20–22]. It had also been discovered that the ions in the solution could form crystals at a low supersaturation condition with application of ultrasound, and the crystals produced were homogeneous in both size and shape. In addition, the ultrasonic process is a cost-effective and environmentally friendly method to avoid the secondary pollution, so that it has intrigued many interests to investigate the mechanisms of the crystallization process of the MAP [23–25].

This work was carried out to investigate the crystallization process (i.e. MZW, induction period and crystallization rate), crystal type, and CSD of MAP crystal under various ultrasonic conditions, aiming to promote further development of researches on the removal and recovery of phosphorus by MAP crystallization, as well as providing theoretical support for practical engineering applications.

2. Materials and methods

2.1. Materials

A self-assembled crystallizer (Fig. 1) was designed to perform this work. The ultrasonic generator (YPS17B-ZB, Hangzhou, China) contains two parts: transducer (TJS-3000, Hangzhou, China) and sonotrode (YP5020-6D, Hangzhou, China). The ultrasound (with fixed frequency of 20 kHz and various power) was stimulated by the sonotrode (the working area is a metal pole with diameter of 15 mm and height of 50 mm) submerged in approximately 400 mL solution. In order to accurately monitor the process of crystallization, a laser unit (containing a laser transmitter (JDW3-300, Beijing, China) with 5 mW power output and a laser receiver (JG2-130305, Beijing, China)), a pH value detector (PB-10, Beijing, China),and a conductivity meter (FE30, Shanghai, China) were introduced. Reacting solution in a jacketed still was stirred by the magnetic drive stirrer (85-2, Zhengzhou, China) at 400 rpm for homogeneous mixing. The temperature was controlled by a thermostatic waterbath apparatus (SLGDH-0506, Nanjing, China) to remove its slight influence on crystallization. Crystal was filtered by a vacuum pump (AP-01P, Tianjin, China) and crystal type and CSD were visualized and analyzed by a scanning electron microscope (SEM, FEI QUANTA FEG250, U.S.A.).

The raw materials used in this study were MAP ($MgNH_4PO_4 \cdot 6H_2O$, Alfa Aesa, 99.999%), ammonium dihydrogen phosphate ($NH_4H_2PO_4$, analytical grade), magnesium chloride ($MgCl_2$, analytical grade), sodium hydroxide (NaOH, analytical grade), hydrochloric acid (HCl, analytical grade) and deionized water. They were degassed in a numerical control ultrasonic cleaner (KQ-500DE, Kunshan, China) for 30 min before using). $NH_4H_2PO_4$ and $MgCl_2$ solutions with different molarities were prepared as stock solution.0.5 M NaOH and 0.5 M HCl were utilized to modulate the pH value. The main reaction between the $NH_4H_2PO_4$ and $MgCl_2$ in the solution is as follows:

$$NH_4^+ + H_2PO_4^- + Mg^{2+} + 6H_2O = MgNH_4PO_4 \cdot 6H_2O \downarrow + 2H^+ \quad (1)$$

$$NH_4^+ + HPO_4^{2-} + Mg^{2+} + 6H_2O = MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+ \quad (2)$$

$$NH_4^+ + PO_4^{3-} + Mg^{2+} + 6H_2O = MgNH_4PO_4 \cdot 6H_2O \downarrow \quad (3)$$

2.2. Determination of crystallization metastable zone width

In the metastable zone, which is the region between the saturation area and the supersaturation area, the crystallization process will not occur until additional nuclei are introduced. It was found that the crystals formed in this area were homogeneous in both size and shape, and the surface of the crystal is flat [26]. MZW is usually presented by testing parameters such as temperature, pH value, and ion concentrations etc. [27,28] In light of that MAP is sparingly soluble in water solution, so the effect of temperature on the solubility of MAP is very limited [29]. As a result, the pH value was finally chosen to represent the effect of power ultrasound on the metastable zone of MAP.

To acquire the MZW of MAP under different conditions, this experiment was divided into two stages:

(1) The first stage was to obtain the critical pH value of saturated MAP solution with or without ultrasonic conditions, defined as pH_1. Without the ultrasonic condition, certain quantity of MAP (Alfa Aesa, 99.999%) was added into 400 mL deionized water in a beaker with the consistent temperature at 20°Cwith stirring speed of 400 rpm. Then 100μL HCl was added into the solution. After the conductivity and laser power reached a steady state for 120 s, another batch of dosage was added. It could be observed that the MAP solid in the solution dissolved along with the addition of HCl. It has to be noted that 50 μL HCl should not be added before the crystals were entirely dissolved. Once the complete dissolution had been achieved and both conductivity and received laser power maintained steady for 120 s, the pH_1 without ultrasonic condition was obtained. The experiment with the ultrasonic condition was similar to that without ultrasonic condition, except that the ultrasound apparatus was turned on once the MAP had been poured into the jacketed still. The experiment was performed in triplicate for pH_1 before averaging, and the results were shown in Fig. 2a.

(2) The second stage was to obtain the critical pH value of supersaturated MAP solution with or without ultrasonic conditions, defined as pH_2. Without the ultrasonic condition, 400 mL solution mixed by the $NH_4H_2PO_4$ and $MgCl_2$ stock

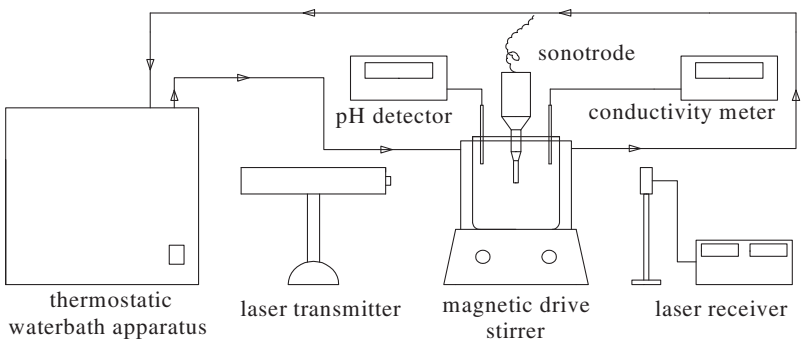

Fig. 1. Sketch of the experiment setup.