



# Precipitation of organic arsenic compounds and their degradation products during struvite formation



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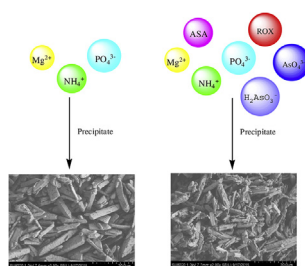
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## HIGHLIGHTS

- Organic and inorganic arsenic compounds precipitated during struvite formation.
- Precipitation of organic arsenic compounds in struvite decreased with increasing pH.
- Arsenate easily precipitate in struvite as compared to organic arsenic compounds.
- Arsenic compounds in solution affected the shape of struvite crystallization products.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Roxarsone (ROX) and arsanilic acid (ASA) have been extensively used as organoarsenic animal feed additives. Organic arsenic compounds and their degradation products, arsenate (As(V)) and arsenite (As(III)), exist in the effluent from anaerobic reactors treating animal manure contaminated by ROX or ASA with ammonium ( $\text{NH}_4^+$ -N) and phosphate ( $\text{PO}_4^{3-}$ -P) together. Therefore, arsenic species in the effluent might be involved in the struvite formation process. In this study, the involvement of organic arsenic compounds and their degradation products As(V) and As(III) in the struvite crystallization was investigated. The results demonstrated that arsenic compounds did not substantially affect the  $\text{PO}_4^{3-}$ -P recovery, but confirmed the precipitation of arsenic during struvite formation. The precipitation of arsenic compounds in struvite was considerably affected by a solution pH from 9.0 to 11.0. With an increase in pH, the content of ASA and ROX in the precipitation decreased, but the contents of As(III) and As(V) increased. In addition, the arsenic content of As(V) in the struvite was higher than that of As(III), ASA and ROX. The results indicated that the struvite could be contaminated when the solution contains arsenic species, but that could be minimized by controlling the solution pH and maintaining anaerobic conditions during struvite formation.

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## 1. Introduction

As animal feed additives, organic arsenic compounds including roxarsone (3-nitro-4-hydroxy benzene arsenic acid, ROX) and arsanilic acid (4-aminophenylarsonic acid, ASA) have been extensively used in the feed of broiler chickens and pigs to improve feed efficiency and prevent disease [1,2]. The approved dosages

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of ASA and ROX for use as animal feed additives are in a range of 50.0–100.0 mg/kg for pigs and 20.0–50.0 mg/kg for broiler chickens [1,2]. More than 1 million kilograms of ASA and ROX are consumed every year in the United States, and more was consumed in China and other developing countries [3,4]. Nevertheless, most of the organic arsenic compounds added in animal feed is excreted unchanged into manure [1]. It has been reported in a study in China that the content of arsenic in the pig manure and chicken litter were 89.3 and 21.6 mg/kg, respectively [5]. Organic arsenic compounds are transformed into inorganic arsenic compounds through both biotic and abiotic pathways [2,6,7]. Under anaerobic conditions, organic arsenic compounds were slowly degraded into inorganic arsenic compounds, including arsenite (As(III)) and arsenate (As(V)), and As(III) was the main species [2,8–10]. It was found that in the anaerobic biotransformation of ROX, more than 33% of the total arsenic existed in the form of organic arsenic compounds after 132 days of anaerobic incubation [9]. Our previous study showed that more than 40% of ASA was not degraded after 115 days of anaerobic digestion [4]. As a result, ASA and ROX and their degradation products As(V), and As(III) co-exist in the anaerobic effluent [4,9]. Organic arsenic compounds and their degradation products could be released into the environment through wastewater discharge, runoff and leaching, resulting in arsenic contamination in soils and aquatic environments [11]. Animal manure is usually treated with anaerobic digestion to reduce waste volumes and recover biogas as energy [12]. Therefore, organic arsenic compounds and their degradation products should exist in the effluent from anaerobic reactors treating animal manure and litter contaminated by organic arsenic compounds.

Anaerobic digestion has been widely used for the treatment of pig manure, municipal solid waste and agricultural residues [13]. The effluent of anaerobic reactors contains a high concentration of ammonium ( $\text{NH}_4^+\text{-N}$ ) and phosphate ( $\text{PO}_4^{3-}\text{-P}$ ), which could cause severe eutrophication in surface water after discharging into aquatic environments [14]. As a finite and non-renewable resource, phosphate has been widely used in industry and agriculture [15]. Therefore, the recovery of  $\text{PO}_4^{3-}\text{-P}$  and  $\text{NH}_4^+\text{-N}$  present in the anaerobic reactor effluent is of great significance.

Currently, the  $\text{PO}_4^{3-}\text{-P}$  removal in wastewater treatment could be accomplished via various ways, including enhanced biological  $\text{PO}_4^{3-}\text{-P}$  removal, metal precipitation and struvite crystallization [16–19]. Among them, struvite (magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$ ) crystallization is a promising process due to the simultaneous removal of  $\text{PO}_4^{3-}\text{-P}$  and  $\text{NH}_4^+\text{-N}$  to form struvite [20]. Furthermore, struvite is a valuable slow-release phosphate and nitrogen fertilizer and contains a higher content of  $\text{PO}_4^{3-}\text{-P}$  than other fertilizers. The struvite crystallization has been applied to recover  $\text{PO}_4^{3-}\text{-P}$  from the effluent of anaerobic reactors treating swine wastewater, poultry manure wastewater and sewage sludge [21].

A large number of investigations have been carried out to explore the factors affecting the struvite crystallization process, such as pH, humic substances, organic acid and heavy metal ions [22–24]. Ma and Rouff have investigated the influence of inorganic arsenic compounds on the struvite formation and found that the arsenic content in struvite increased with an increase in pH from 8.0 to 10.0 [25]. When animal feed is supplemented with organic arsenic compounds, the discharge effluent from anaerobic reactor for manure treatment may contain  $\text{PO}_4^{3-}\text{-P}$  and organic and inorganic arsenic compounds. However, so far there is no report about the impact of organic arsenic compounds on the struvite crystallization. The struvite fertilizer might be contaminated by both organic and inorganic arsenic compounds through precipitation, which will cause arsenic contamination in soils.

The main objective of this study was to investigate: (1) the influence of organic arsenic compounds and their degradation products

**Table 1**

The initial concentrations of ASA, ROX, As(III) and As(V) in the struvite crystallization experiments.

Set	ASA (mg/L)	ROX (mg/L)	As(III) (mg/L)	As(V) (mg/L)
S1	5.0			
S2	10.0			
S3	15.0			
S4	20.0			
S5		5.0		
S6		10.0		
S7		15.0		
S8		20.0		
S9			0.1	
S10			0.5	
S11			1.0	
S12			2.0	
S13				0.1
S14				0.5
S15				1.0
S16				2.0

on struvite formation, and (2) the co-precipitation of organic and inorganic arsenic compounds during the struvite crystallization process and the possible mechanism of precipitation. Two frequently used organic arsenic compounds ASA and ROX, and two main inorganic arsenic compounds As(III) and As(V), were selected as the target arsenic compounds.

## 2. Materials and methods

### 2.1. Chemicals

All of the chemicals were analytical grade and used without further purification. ROX and ASA were purchased from Sigma Co., USA. Two millimolar stock solutions of ASA and ROX were prepared in deionized water. As(III) and As(V) were purchased from the CRM/RM Information Center of China. The other stock solutions were prepared in deionized water before the experiments.

### 2.2. Experimental setup and procedure

The crystallization experiments were conducted in 500 mL beakers with a magnetic stirrer at ambient temperature. First, the calculated volume of  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4^{3-}\text{-P}$  stock solutions were added into the beaker and diluted to 250 mL with deionized water. Referring to the constituents of the actual swine wastewater [26], the molar ratio of P: N: Mg was set to 1:8:1.2 to simulate actual swine wastewater and the concentration of  $\text{PO}_4^{3-}\text{-P}$  in the initial mixture was 60.0 mg/L in all experiments. According to the initial concentrations of the four types of arsenic set in Table 1, a certain volume of arsenic stock solutions was added to the reaction system. The solution pH was adjusted to the designed value ( $\pm 0.02$ ) by adding 1.0 M NaOH or HCl. Finally, a certain volume of 1.0 M  $\text{MgCl}_2$  stock solution was added to the reaction solution. The reaction solution was stirred for 30 min and later allowed to settle for another 30 min. A 3.0-mL sample was collected from the reaction system and filtered by 0.45  $\mu\text{m}$  mixed cellulose ester membranes. In order to terminate the precipitation reaction, 8.0  $\mu\text{L}$  of HCl (10 M) was added to the sample bottle in advance. After the reaction, the crystallization product formed in the reaction was collected and dried at 40 °C for 48 h for further analysis. In addition, part of the dried precipitates was dissolved with HCl solution to analyze the content of organic or inorganic arsenic compounds.

The  $\text{PO}_4^{3-}\text{-P}$  recovery efficiency was selected to determine the influence of pH ranging from 8.0 to 12.0. To investigate the influence and precipitation of organic arsenic compounds and their degradation products on struvite crystallization, ASA, ROX, As(III) and As(V) were individually added into the reaction system at pH of 9.0, 10.0

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