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

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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 and phosphate ($\text{PO}_4^{3-}\text{-P}$) 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 $\text{PO}_4^{3-}\text{-P}$ 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.

Keywords: Anaerobic digestion, Arsanilic acid, Inorganic arsenic, Roxarsone, Struvite

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 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 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 NH_4^+ -N and PO_4^{3-} -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 PO_4^{3-} -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 (± 0.02) by adding 1.0 M NaOH or HCl. Finally, a certain volume of 1.0 M 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 μm mixed cellulose ester membranes. In order to terminate the precipitation reaction, 8.0 μL 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 PO_4^{3-} -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 and 11.0. The initial PO_4^{3-} -P concentration and N/P ratio were set to 60.0 mg/L and 8:1 for all batch assays, respectively. All experiments were carried out in duplicate.

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

2.3. Analytical methods

An UV-spectrophotometer (UV-2600, Unico, China) was used to analyze the concentrations of PO_4^{3-} -P and NH_4^+ -N according to the Standard Methods [27]. ASA and ROX were measured using high performance liquid chromatography (HPLC, 1260 Infinity, Agilent Inc., USA) equipped with a C18 column (4.6 mm×250 mm, 5 μm , GL Sciences Inc., Japan) at 264 nm. The mobile phase consisted of 0.03 M $\text{CH}_3\text{COONH}_4$, methanol and formic acid (V/V/V = 90:10:0.1) at a flow rate of 1.0 mL/min. As(III) and As(V) concentrations were determined by an atomic fluorescence spectrometry (AFS-8220, Beijing Titan Co., China) as described by Shi et al. [28]. The crystallization products were characterized by X-ray diffraction (XRD, D/MAX2500V, Rigaku, Japan) and field emission scanning electron microscope (FESEM, SU8020, Hitachi Co., Japan).

3. Results and Discussion

3.1. Effect of pH on struvite formation

Solution pH is one of the most important parameters affecting the struvite crystallization process [29]. The influence of pH on the recovery efficiency of PO_4^{3-} -P and NH_4^+ -N is shown in Fig. 1. With an increase in pH from 8.0 to 12.0, the PO_4^{3-} -P recovery efficiency increased initially, and reached a plateau at 9.0-11.0 and later decreased drastically after pH > 11.0. At pH < 8.0, the main form of phosphoric acid

in the solution is HPO_4^{2-} or H_2PO_4^- [18]. The concentration of PO_4^{3-} was too low to form struvite precipitate, and thus the PO_4^{3-} -P recovery efficiency was lower than 23%. The PO_4^{3-} -P recovery efficiency was over 90% in pH ranging from 9.0 to 11.0 and reached a maximum at pH 11.0. However, due to the increasing negative zeta-potentials, the struvite crystal size decreased with an increase in pH [30, 31]. As a result, the generated crystals had poor sedimentation performance. At $\text{pH} > 11.0$, $\text{Mg}(\text{OH})_2$ and $\text{Mg}_3(\text{PO}_4)_2$ were formed readily, but more NH_4^+ was converted to NH_3 and escaped from the solution [32]. As shown in Fig. 1, the PO_4^{3-} -P recovery efficiency rapidly decreased to 40% with an increase in pH from 11.0 to 12.0, whereas the NH_4^+ -N removal efficiency continued to increase. Consequently, the pH range of 9.0 to 11.0 was selected for the following struvite crystallization experiments. In this pH range, a higher PO_4^{3-} -P recovery efficiency could be obtained and ammonia release from solution could be prevented.

Fig. 1 Recovery efficiency of PO_4^{3-} -P and NH_4^+ -N at different initial pH values

3.2. Influences of arsenic species on struvite formation

Four types of arsenic species including ASA, ROX, As(III) and As(V) were selected to investigate their influences on the struvite crystallization process. The experiments were conducted in a pH range of 9.0 to 11.0. The influences of organic arsenic compounds and their degradation products, As(III) and As(V), on the PO_4^{3-} -P recovery efficiency are shown in Fig. 2. The PO_4^{3-} -P recovery efficiency was not obviously affected by the addition of organic arsenic compounds. As shown in Fig. 2c and d, the struvite yield was not affected by the presence of As(V) or As(III). This result is consistent with that reported in a previous study [25]. Compared with the arsenic species, pH had more significant effects on the PO_4^{3-} -P recovery efficiency.

The precipitates were collected and characterized by FESEM. The surface shapes of the precipitates obtained at pH 9.0 are illustrated in Fig. 3. The main shape of these precipitates was in the needle or rod-like forms due to the orthorhombic structure of struvite crystals. As shown in Fig. 3a, the struvite precipitate without arsenic addition had the largest diameter and a grooved surface. However, with the presence of organic or inorganic arsenic compounds, the diameter of the struvite particles became smaller and more uneven (Fig. 3b-e). The struvite crystallization process usually consisted of two stages: the rapid nucleation stage and the crystal growth stage, and the impurities could block struvite crystal growth [33]. Therefore, the changes of diameter and shape might be attributed to the co-precipitation of arsenate on struvite particles or the struvite precipitation in bulk followed by surface sorption to other arsenic compounds.

Fig. 2 Effects of (a) ASA, (b) ROX, (c) As(III), and (d) As(V) on the $\text{PO}_4^{3-}\text{-P}$ recovery efficiency as a function of pH

Fig. 3 FESEM images of struvite precipitates formed at pH 9.0 with magnification of 2000 times: (a) blank (without arsenic), (b) with 20.0 mg/L of ASA, (c) 20.0 mg/L of

ROX, (d) 2.0 mg/L of As(III), and (e) 2.0 mg/L of As(V)

3.3. Arsenic species precipitation during the struvite formation

At the beginning of the reaction, a large amount of precipitates, which could be observed with the naked eye, was formed. At a pH 9.0, the crystals obtained in the solutions containing ROX were yellowish, while the other precipitates in the existence of ASA, As(III) and As(V) were white. In the initial solutions, the color of ROX is yellow, but the solutions of other arsenic are transparent. This finding suggests that ROX might be absorbed during the struvite formation. Fig. 4 shows the concentration changing profiles of the arsenic species in the solution during struvite formation. The As(V) concentrations declined sharply and reached an equilibrium state in approximately 5 min, whereas the other arsenic species did not obviously change during the struvite precipitation (Fig. 4d), indicating that the precipitation mechanism of As(V) might be different from those for ROX, ASA, and As(III). The obvious decrease in the As(V) concentration was attributed to the similar anionic form between As(V) and PO_4^{3-} -P. As listed in Table 2, the predominant As(V) species (HAsO_4^{2-} and AsO_4^{3-}) in the aqueous solutions have similar acidity constants (pK_a) with phosphate (HPO_4^{2-} and PO_4^{3-}). This suggests that As(V) could readily occupy the same sites of PO_4^{3-} -P during struvite formation and form a magnesium ammonium arsenate hexahydrate ($\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$) precipitate [25].

The struvite precipitates were then dissolved and analyzed for the content of ASA, ROX, As(III) and As(V) by HPLC and AFS. A higher arsenic content was found

with an increasing concentration of initial organic or inorganic arsenic compounds in the solutions (Fig. 5). As(III) and As(V) were precipitated more than ASA and ROX. As shown in Fig. 5a and b, with an increase in pH, the content of ASA and ROX in the precipitate decreased, while the content of As(III) and As(V) in the struvite increased.

Table 2

Acidity constants of H_3PO_4 , H_3AsO_4 , H_3AsO_3 , ROX and ASA.

	$\text{pK}_{\text{a}1}$	$\text{pK}_{\text{a}2}$	$\text{pK}_{\text{a}3}$
H_3PO_4	2.12	7.20	12.66
H_3AsO_4	2.25	6.77	11.53
H_3AsO_3	9.29	-	-
ROX	3.43 ^a	6.38 ^b	9.67 ^c [34]
ASA	1.90 ^a	4.10 ^b	9.20 ^c [34]

Note. ^a, ^b, ^c were the functional groups associated with the pKa as shown in Fig. 6

Specifically for the assay of As(V), the arsenic content in the struvite was significantly higher than those of ASA, ROX and As(III) by several orders of magnitude. For example, the arsenic content reached 2325.0 mg/kg struvite at pH 11.0 when the As(V) concentration was 2.0 mg/L in the solution. This might be attributed to the formation and co-precipitation of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ in the aqueous solution. Over a wide range of pH values, As(III) is present mainly in a non-ionic form [35], which led to different forms of As(III) and PO_4^{3-} with differences in radius and charge. Thus, As(III) cannot form $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, and the precipitation in bulk was followed by adsorption on struvite [25].

For organic arsenic compounds, the content of ROX in the precipitates was consistently higher than that of ASA in a pH range from 9.0 to 11.0 (Fig. 5a and b). The ASA content was below the detectable limit at pH 11.0. Such a difference might be attributed to the different anionic forms and functional groups of ASA and ROX. The chemical structure of ROX consisted of nitro groups, hydroxyl groups and phenylarsenic acid, while ASA contains amino groups and phenylarsenic acid (Fig. 6). Both ASA and ROX contain arsenate acid moiety, thus, they have similar chemical properties as arsenate [36]. The arsenate acid groups in ASA and ROX may compete with phosphate for the surface sites of struvite for adsorption, but cannot form $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$. However, the negative zeta-potential of struvite increased with an increase in pH [31], and the dominant species of ASA and ROX were the tri-anionic form (i.e., $\text{AsO}_3\text{R}^{3-}$, where R is the aromatic group) at the higher pH. This led to the decrease in adsorption of the organic arsenic compounds on struvite with the increasing pH. In this study, the highest arsenic content in the struvite in the assay of ASA and ROX was 15.6 and 35.5 mg/kg, respectively. These concentrations were obtained with the addition of 20.0 mg/L of ASA or ROX at a pH 9.0 (Fig. 5).

Fig. 4 Concentration changing profiles of (a) ASA, (b) ROX, (c) As(III), and (d) As(V) in the solution during struvite precipitation at pH 9.0

Fig. 5 Arsenic content in the struvite with the presence of (a) ASA, (b) ROX, (c) As(III), and (d) As(V) in the solution at pH 9.0-11.0

Fig. 6 Chemical structural formula of (a) ASA, and (b) ROX

3.4. Crystal characteristics of precipitates

The crystallized products were characterized by XRD. The powder XRD patterns of all precipitates are shown in Fig. 7. Compared to the standard XRD spectrum, the dominant compositions of precipitates were confirmed as struvite crystals. In addition to slight variations of the intensity, the presence of organic or inorganic arsenic compounds had no obvious influences on the diffraction spectra. The intensities of (020) and (040) peaks of all precipitates, except from the ROX and As(III) solutions, tended to be stronger compared to the standard peaks of struvite. Additionally, the intensities of lattice plane (221) in all XRD patterns were weaker than those of the standard peak of struvite. The subtle change in the intensity might be caused by the difference in crystal arrangement. The reflections of precipitate obtained in the presence of As(V) was weaker than others, according to the Scherrer equation [37], suggesting the co-precipitation of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ during struvite formation.

Fig. 7 Standard XRD spectrum of struvite (a) and XRD spectra of struvite precipitates obtained in the presence of (b) blank (without arsenic), (c) 20.0 mg/L of ASA, (d) 20.0 mg/L of ROX, (e) 2.0 mg/L of As(III), and (f) 2.0 mg/L of As(V) at pH 9.0

3.5. Environmental significance

In this study, the greatest mean arsenic contents of ASA, ROX, As(III) and As(V) in the struvite were 15.6, 35.5, 25.2 and 2325.0 mg/kg, respectively when the concentrations of ASA, ROX, As(III) and As(V) were 20.0 mg/L, 20.0 mg/L, 2.0 mg/L and 2.0 mg/L, respectively. Zhang et al. have reported that the As(III) and As(V) concentrations in an anaerobic system were 41.2 mg/L and 8.7 mg/L, respectively, at an initial ROX concentration of 350.0 mg/L [2]. In the environments, the inorganic

arsenic compounds are more toxic than organoarsenicals. Therefore, the application of struvite obtained from the arsenic-contaminated wastewater as a mineral fertilizer should be paid attention. The maximum permitted concentration of arsenic is 50 mg/kg in phosphate fertilizers in China and 75 mg/kg in the United States [25, 38]. This finding means the arsenic content in struvite precipitated from arsenic contaminated wastewater effluent might exceed the maximum permitted arsenic concentrations due to the co-precipitation of As(V).

The organic arsenic content in struvite precipitates decreased with the increasing pH, but the inorganic arsenic content increased with the increasing pH. In addition, because organic arsenic compounds are mainly transformed into As(III) under anaerobic conditions, As(III) should be the dominant species in the effluent of anaerobic reactors treating organic arsenic-contaminated animal manure and wastewater. As(III) could be oxidized into As(V) under aerobic conditions [39, 40]. Since As(III) is more difficult to be precipitated during struvite formation, the arsenic content in struvite can be minimized by controlling the solution pH and maintaining anaerobic conditions during struvite formation.

4. Conclusions

In this study, the influence of ASA and ROX, and their degradation products As(III) and As(V), on struvite formation and their precipitation in struvite were investigated. It was found that the presence of ASA, ROX, As(III) and As(V) did not apparently

affect the recovery efficiency of $\text{PO}_4^{3-}\text{-P}$ in struvite precipitation, but their presence affected the particle diameter and surface shape of the precipitated struvite. The precipitation of arsenic compounds in struvite was substantially affected by the solution pH from 9.0 to 11.0. With the increasing pH, the content of ASA and ROX in the precipitates decreased, while the content of As(III) and As(V) in the struvite increased. In addition, the arsenic content of As(V) in struvite was higher than those of As(III), ASA and ROX. The As(V) was co-precipitated in struvite with the formation of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, and the other arsenic species were adsorbed onto the struvite due to surface interactions. These results suggest that the arsenic content in struvite could be minimized by controlling solution pH and maintaining anaerobic conditions during struvite formation.

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Figure Captions

Fig. 1- Recovery efficiency of $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4^+\text{-N}$ at different initial pH values

Fig. 2- Effects of (a) ASA, (b) ROX, (c) As(III), and (d) As(V) on the $\text{PO}_4^{3-}\text{-P}$ recovery efficiency as a function of pH

Fig. 3- FESEM images of struvite precipitates formed at pH 9.0 with magnification of 2000 times: (a) blank (without arsenic), (b) with 20.0 mg/L of ASA, (c) 20.0 mg/L of ROX, (d) 2.0 mg/L of As(III), and (e) 2.0 mg/L of As(V)

Fig. 4- Concentration changing profiles of (a) ASA, (b) ROX, (c) As(III), and (d) As(V) in the solution during struvite precipitation at pH 9.0

Fig. 5- Arsenic content in the struvite with the presence of (a) ASA, (b) ROX, (c) As(III), and (d) As(V) in the solution at pH 9.0-11.0

Fig. 6- Chemical structural formula of (a) ASA, and (b) ROX

Fig. 7- Standard XRD spectrum of struvite (a) and XRD spectra of struvite precipitates obtained in the presence of (b) blank (without arsenic), (c) 20.0 mg/L of ASA, (d) 20.0 mg/L of ROX, (e) 2.0 mg/L of As(III), and (f) 2.0 mg/L of As(V) at pH 9.0