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Arsenic accumulation and chemical fraction distribution changes in sludge in a low-sludge wastewater treatment system

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ABSTRACT

This paper investigated the accumulation of arsenic and its chemical fraction distributions in a low-sludge wastewater treatment system using "sonication-cryptic growth" method. Subsequent bio-reactors (SBR) were used; one SBR without sonication was used for control. Results showed that "sonication-cryptic growth" technique cut sludge production in SBR by 50%. The accumulation of arsenic in sludge occurred in both reactors; the accumulation was low in 0–60 days and showed a sharp increase in 60–90 days. The final sludge arsenic content in the low-sludge system was 1.23 times of that in the control system. However, the higher arsenic content in the low-sludge treatment system did not impact the COD removal and the sludge bioactivity. The low-sludge system had higher COD removal efficiency and higher sludge activity than those of the control. Further analyses of the chemical fraction distribution of arsenic showed that arsenic existed in different forms in the two systems. In the control system, the major form of arsenic in sludge was the organically bound fraction during 0–60 days, and the chemical fractions were redistributed during 60–90 days and the Fe/Mn oxide fraction and organically bound fraction were the main fractions. In the low-sludge system, the major form of arsenic in sludge was Fe/Mn oxides bound fraction during the whole operation duration.

Keywords: Sonication-cryptic growth; Bio-sludge; Arsenic; Accumulation; Chemical fractions

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1. Introduction

Wastewater treatment with activated sludge processes generates large quantities of waste sludge. The sludge, with high amount of persistent organics, pathogens, and metals, causes serious pollutions and demands enormously high treatment and disposal cost [1]. The cost of sludge treatment accounts for 30–60% of the operation cost of wastewater treatment plants [2]. Therefore, development of novel technologies for sludge minimization has been of intensive interests in the past decade, such as ozonation-cryptic growth [3], sonication-cryptic growth [4–7], chlorination [8], predation [9,10], and chemical addition [11,12]. Results showed that 30–100% of sludge reduction could be achieved in those low-sludge wastewater treatment processes [4–7,11–13].

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In many cases, municipal wastewater is mixed with industrial wastewater for treatment, and therefore contents of metals in sewage sludge are high [14]. Due to their well-known toxicity, effect of metals on biological wastewater treatment processes is of great importance [15]. Since metals in wastewater treatment systems are not degradable or vaporizable, the removal of them mainly depends on the discharge of sludge [16–18]. As less sludge is discharged during low-sludge wastewater treatment process, metals may accumulate in the system, which might damage the performance of the wastewater treatment processes. Moreover, the safe disposal of wastewater and sludge also necessitates the investigation of occurrence and fate of metals in wastewater treatment systems [16]. However, little information is available on metal accumulation in low-sludge wastewater treatment processes [19]. Therefore, it is important to analyze the potential accumulation of metals in the low-sludge wastewater treatment processes in order to facilitate the application of those processes.

Arsenic was chosen as the representative metal in the wastewater treatment sludge [15,20]. Arsenic is a typical metalloid with high toxicity and can cause severe environmental risk at low dose [21–25]. The biochemical characteristic of arsenic is a kind of protoplasm toxicity. It can affect the activity of enzyme, the respiration, division, and multiplication of cells. With the development of chemical industry, arsenic is frequently found in the wastewater and sludge. The chemical forms of arsenic were also examined. The chemical forms of metal are related to the different natures of the metal in the sludge [18–21] and determine the metal bioavailability, toxicity, and mobility [20].

The objectives of this work were to investigate the potential accumulation of arsenic in sludge during low-sludge wastewater treatment process, to examine the changes of arsenic chemical forms in the process, and to study their impact on the process. The aim was to better understand the low-sludge wastewater treatment techniques and to ensure their application in wastewater treatment.

2. Materials and methods

"Sonication-cryptic growth" method was used as the low-sludge wastewater treatment process in this study, since it was widely studied and was found effective for sludge reduction [4–7].

2.1. Materials

Artificial wastewater was used in this study and its contents were: (1) COD was 200 mg L^{-1}; (2) total nitrogen was 10 mg L^{-1}; (3) the total phosphorous was 2 mg L^{-1}; and (4) the arsenic concentration was 0.15 mg L^{-1}. The arsenic concentration in the artificial wastewater was referred to urban wastewater mixed with industrial wastewater in a local wastewater treatment plant.

The seed sludge was collected from the secondary sedimentation tank of a wastewater treatment plant in Harbin, China, which employed an anaerobic-anoxic-aerobic wastewater treatment process. The content of arsenic in the seed sludge was 1.22 mg kg^{-1}DS.

The bio-reactor used was subsequent bio-reactor (SBR), which is commonly employed in sewage treatment [26]. The SBR had a working volume of 7 L and an operational cycle of 8 h, in which 5.5 h was for aeration and 2.5 h was for settling. Excess sludge was discharged daily in order to maintain the sludge concentration in SBR around 3,000 mg L^{-1}.

2.2. Operation

Three SBR were used in this study. SBR-0 was used as blank; SBR-1 was used as control with arsenic addition but without sludge sonication, SBR-2 was used for sludge reduction with arsenic and with sonication for comparing. The SBRs were operated under room temperature.

For SBR-2, 15% sludge was taken out daily, treated in the sono-reactor and returned to the SBR. The sludge sonication was performed in a JY90-Ⅱ horn system (Ningbo Haishukesheng Ultrasonic, Ltd., China). The frequency was 25 kHz, the horn probe surface area was 2.12 cm^2, and the power range was 0–250 W. The ultrasonic intensity was 1.2 W mL^{-1} and the sonication time was 15 min, which was the most efficient energy input for sludge reduction found in the previous study [7]. After sonication, the treated sludge was returned to SBR from which it was taken out.

2.3. Analysis

The concentration of arsenic was measured by a PerkinElmer Optima 5300 DV ICP (Perkin Elmer Inc., America). The instrument operational parameters of ICP-OES were: (1) Observation mode was horizontal; (2) Temperature of ray room was 34.8 centigrade; (3) Radio-frequency power was 1.1 kW; (4) Argon gas pressure was 248 kPa; (5) Cooled gas flow was 20 L min^{-1} and Auxiliary gas flow was 2 L min^{-1}; (6) Lifting speed of pump was 1.2 mL min^{-1}; and (7) Exposure time was 25 s. The standard solution of 1.0 mg^{-1}m L arsenic was bought from Perkin Elmer Inc., which was stepwise diluted for standard curve. Standard recovery test with

6 times' parallel determination was operated for checking the accuracy of the method. The recovery was 89.8–101.2%, and the relative standard deviation was lower than 2.5%. The detection limit of ICP-OES was $0.003\,\mathrm{mg\,L^{-1}}$ for arsenic.

Wastewater sample was measured directly while sludge sample was firstly digested by a HNO_3–HF–$HClO_4$ digestion process before measurement, and the detailed procedure was shown in the Supporting information. The standard curve method was employed for element measurement. The chemical fraction of arsenic in sludge was analyzed by a five-step sequential extraction procedure [27] (detailed procedure in the Supporting information).

Wastewater was filtered before measuring COD. The sludge bioactivity was evaluated using oxygen utilization rate as reported before [7]. All other parameters were analyzed according to the standard methods [28].

All measured values of each index were average values calculated from duplicate samples.

3. Results and discussion

3.1. Performance of bioreactors

The average values of COD removal and the sludge production for SBRs were measured during 90 days' operation, as shown in Fig. 1. The sludge production for SBR was 252, 233, and $118\,\mathrm{mg\,L^{-1}\,d^{-1}}$ for SBR-0, SBR-1, and SBR-2, respectively. Clearly, arsenic addition slightly reduced the sludge production (SBR-0 vs. SBR-1); sonication reduced the sludge production by more than 50% (SBR-1 vs. SBR-2).

Changes of sludge bioactivity under different conditions are shown in Fig. 2. It was found that in the first 20 days, the bioactivity of sludge in both SBRs decreased significantly, since arsenic in the influent had adverse impact on the activated sludge. After 20 days' operation, sludge bioactivity changed slightly, showing that micro-organisms get adapt to the arsenic loaded influent and were domesticated. The initial sludge bioactivity was around $38\,\mathrm{mgO_2\,g^{-1}MLSS\,h^{-1}}$. After 90 days' operation, the sludge bioactivity in SBR-0 was stable. The sludge bioactivity in SBR-1 decreased from 38 to $18\,\mathrm{mgO_2\,g^{-1}\,MLSS\,h^{-1}}$, showing a 57% drop. In SBR-2, the sludge bioactivity dropped from 38 to $24\,\mathrm{mgO_2\,g^{-1}\,MLSS\,h^{-1}}$, showing a 39% drop. Clearly, the addition of arsenic in the influent had adverse impacts on bioreactors, which caused the decrease of bioactivity (Fig. 2) and COD removal efficiency (Fig. 1). Sonication could significantly lighten the adverse impact of arsenic on the sludge bio-activity. As a result, the COD removal in SBR-2 was higher as compared to that in SBR-1.

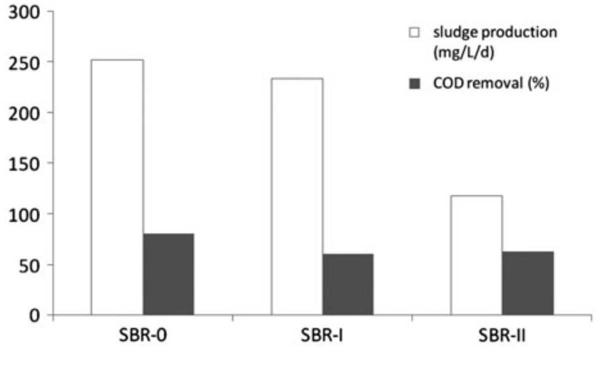

Fig. 1. Sludge production and COD removal in SBRs, average value of 90 d.

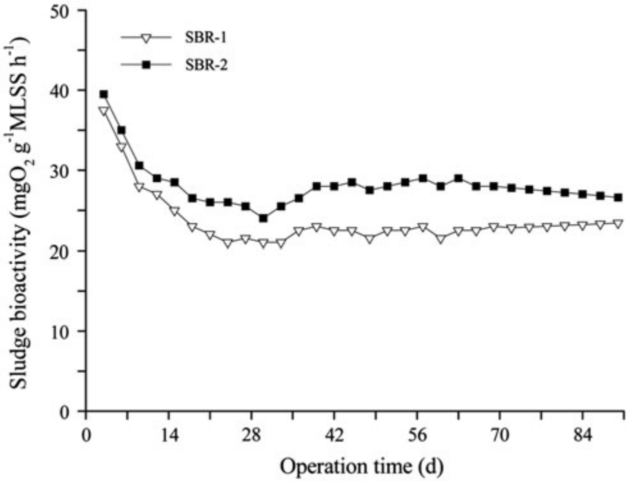

Fig. 2. Changes of sludge bio-activity during SBR operation, 90 days' operation.

3.2. Accumulation of arsenic in sludge during wastewater treatment processes

The content of arsenic in the sludge was measured per month during 90 days' operation, which was shown in Fig. 3. As a whole, the content of arsenic in the sludge of both SBRs increased after 90 days' operation. The increased content of arsenic in sludge is due to the addition of arsenic in the influent everyday. Interestingly, the content increase was nonlinear with the operational process. After operating for two months, the total contents of arsenic in the sludge of both SBR-1 and SBR-2 were low, which were 6.3 and $5.2\,\mathrm{mg\,kg^{-1}DS}$, respectively. After 90 days' operation, there was a sharp increase in the arsenic content in the sludge of SBR-1 and SBR-2 was 43.5 and $53.5\,\mathrm{mg\,kg^{-1}DS}$, respectively. The potential reason is still unclear. Sonication has very complex and dynamic effects on bacteria, which are further influenced by

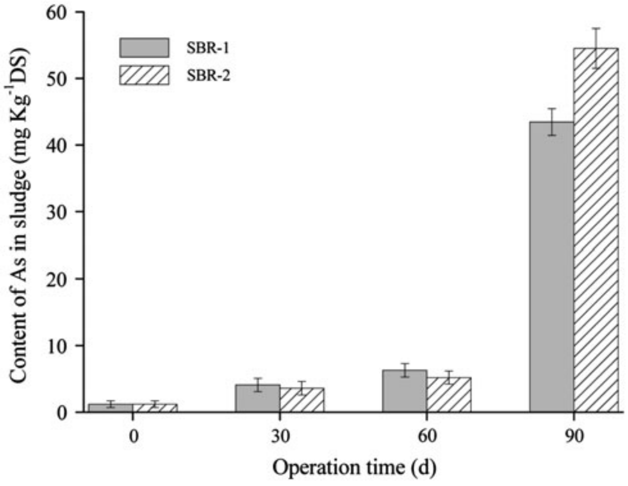

Fig. 3. Total content of arsenic in sludge during 90 days' operation.

many other factors. One effect might be that bacteria are stimulated by the ultrasound waves and excreted more extracellular enzymes, and thus enhances the bio-activity.

The initial arsenic content in the sludge was very low. The accumulation of arsenic in sludge was caused by the adsorption of arsenic from the influent onto the sludge [29]. There were three pathways that impacted the behavior of arsenic in sludge. First, physical-chemical adsorption of arsenic on the sludge surface by the actions of ion-exchange, biogenic sediment, and bio-adsorption. Second, the bio-accumulation of arsenic into the cells; partial arsenic might be transferred into the inner cell by enzymes or other carriers such as protein. Third, the discharge of arsenic in cells into water through metabolisms of micro-organisms [20,30]. The first step content change of arsenic in the sludge was the combined results of above three pathways.

From 0–20 days, the accumulated arsenic in the cells impacted the metabolisms of micro-organisms and therefore the bioactivity of sludge decreased significantly (shown in Fig. 2). After 28 days, microorganisms in sludge got adapted to arsenic in the influent and the bioactivity of sludge stabilized (Fig. 2). The domesticated micro-organisms might adsorb more arsenic, i.e. the adsorption capacity of sludge was enhanced.

On the other hand, the biochemical reaction occurred since more arsenic was transferred into the cells of micro-organisms in the sludge, and then arsenic was released by metabolisms of micro-organisms [20,29]. Therefore, the accumulation of arsenic in the sludge during 30–60 day increased a little.

During 60–90 days' operation, the metabolisms of sludge was kept stable (Fig. 2). We proposed that the micro-organisms in sludge might get used to arsenic inside the cell and no longer discharge arsenic into water, but kept all adsorbed arsenic in the sludge. Thus, the sludge adsorption of arsenic in this period was the highest and arsenic got accumulated quickly in the sludge (Fig. 3).

In order to examine above hypothesis, arsenic in the effluent was measured and the results were reported in Fig. 4. Clearly, from 0–21 days, all arsenic was adsorbed into the sludge; after 28 days, partial arsenic was discharged by micro-organisms into water and the effluent arsenic increased; finally, the micro-organisms got used to arsenic in cells and stopped discharging arsenic into water, so the effluent arsenic was zero. The final adaptation time was 49 days for SBR-2 and 72 days for SBR-1. The effluent arsenic analysis supports the above hypothesis.

The final arsenic content in SBR-2 was higher than that in SBR-1, which could be explained by two factors. Firstly, arsenic might be discharged from SBRs via discharge of sludge. Since sludge production of SBR-2 was much lower than that of SBR-1 (Fig. 1), the arsenic discharge from SBR-2 via sludge discharge was much less than that from SBR-1. Thus, more arsenic was kept in SBR-2. Secondly, micro-organisms in SBR-2 had high bio-activity than that in SBR-1, the more activate micro-organisms had higher adsorption capacity for arsenic and could endured higher arsenic content in the cells.

3.3. Chemical fractions of arsenic changes during wastewater treatment process

In Section 3.2, it was found that the micro-organism in sludge got used to arsenic in cells after certain

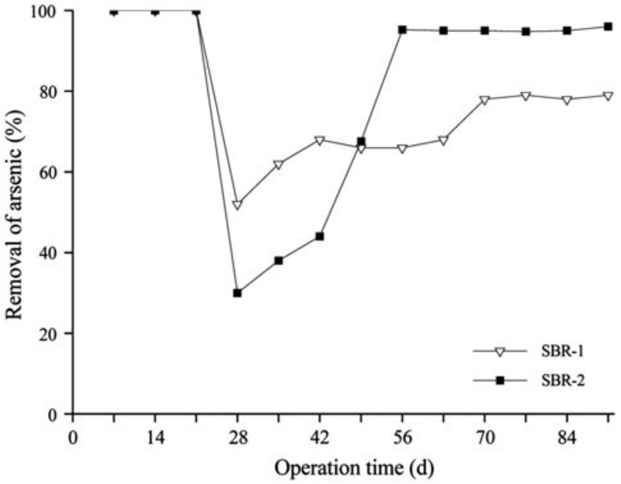

Fig. 4. Arsenic removal from the wastewater during 90 days' operation.

period. In other words, the arsenic in sludge was biologically inactivated after certain period. Generally, metal has five chemical fractions, among which exchangeable, carbonate-bound, and Fe/Mn oxides-bound fractions are considered to be mobile and bio-available; while organically bound and residual fractions are regarded as stable and non-bioavailable [20]. Therefore, we suspected that the chemical fractions of arsenic in sludge changed during the 0–90 days. The chemical fractions of arsenic in sludge were analyzed and the results were reported in Figs. 5 and 6.

Fig. 5 showed the arsenic chemical fraction distribution change in SBR-1. After 30 days' operation, the organic bound fraction increased significantly and unstable fractions (exchangeable and carbonate) were not detected; some influent arsenic was transformed to residual fraction in the sludge. Arsenic was unstable and likely to combine with the methyl radical and hydrosulfide groups [18]. Therefore, the organically bound fraction of arsenic increased sharply. During 30–60 days, the organic fraction was the major fraction, and the residual fraction formed in the first 30 days was transformed to the organically bound fractions, since the biochemical reaction occurred. During 60–90 days, chemical fraction was almost redistributed. The content of organically bound arsenic decreased and other fractions appeared. The most possible reason was that the adsorption ways of arsenic by sludge changed, and the arsenic was adhered to the sludge surface by ion-exchange precipitation. The results also could reflect the content change of arsenic in sludge after the 90 days' operation.

The changes of arsenic chemical fractions in SBR-2 were quite different during 90 days' operation, as seen in Fig. 6. After 30 days' operation, large amount of influent arsenic was transformed into Fe/Mn oxides bound fraction in the sludge. The unstable fractions (exchangeable and carbonate) reduced and the residual fraction was not detected. It might be that although arsenic was unstable and easy to combine with organic matters, sonication changed the sludge characteristics and disrupted the combination of arsenic-hydrosulfide groups or arsenic-methyl functions. During 30–60 days, Fe/Mn oxides bound fraction was the major fraction, and organic bound fraction was not detected. During 60–90 days, the chemical fraction redistribution of arsenic was found, and the organic bound fraction and the Fe/Mn oxides bound fraction were the main fractions (accounted for 37 and 27%, respectively), which might be that the adsorption of arsenic by sludge changed to passive adsorption of sludge.

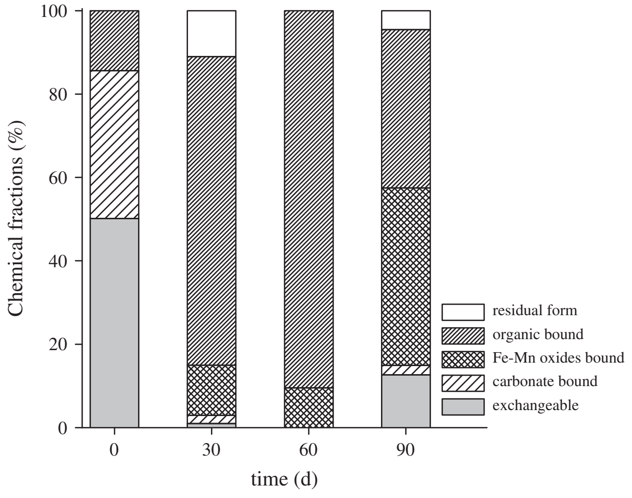

Fig. 5. Chemical fraction changes of sludge arsenic during operational duration in SBR-1 (control system).

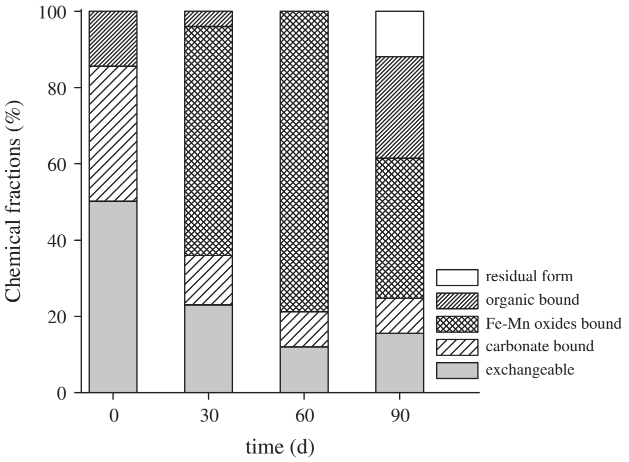

Fig. 6. Chemical fraction changes of sludge arsenic during operational duration in SBR-2 (low-sludge system).

4. Conclusions

Several conclusions were obtained as follows.

(1) Sonication-cryptic system cut about 50% of sludge production after 90 days' operation. The average COD removal after 90 days' operation in both SBR was more than 60%.
(2) Arsenic was accumulated in sludge after 90 days' sonication. In the first 60 days, the accumulation was low. During 60–90 days, arsenic had a dramatic accumulation. Possible reason for this interesting phenomenon might be the different arsenic adsorption forms by sludge during operational process.
(3) Chemical fraction distributions of arsenic changed significantly during treatment process.

During 0–60 days' operation, the organic-bound fraction was the major form in SBR-1 and Fe/Mn oxides bound fraction was the major fraction in SBR-2. After 90 days' operation, the chemical fractions of arsenic in both SBRs were redistributed. The chemical fraction distributions could reflect the arsenic adsorption forms of sludge.

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