Study on the removal and transport and migration mechanism for As with activated sludge system

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Abstract
In this paper, the removal of As and the transport and migration of As at the process of activated sludge system was studied. The results showed that the activated sludge system has high removal efficiency for As, and the removal efficiency could be nearly 100%. The initial concentration of As has effect on the removal efficiency, and within the experimental scope, the increase of initial concentration of As improved the removal efficiency for As. The distribution of As in the surface and internal in activated sludge indicates that in the process of activated sludge, the As was first transferred from water to the surface of solid and was adsorbed by the surface and then transport to the interior of microbes and take part in some metabolisms of the microorganisms. The adsorption of As by activated sludge conforms to Freundlich adsorption isotherm, and the removal of As in activated sludge system follows to the pseudo second order reaction kinetics.

Keywords: Activated sludge system, Transport mechanism, As removal, Physical and biological adsorption

Introduction
With the development of industry and agriculture, there are more and more heavy metal pollution in environment. As one kind of heavy metal, arsenic (As) has caused serious influence on water environment. By estimated, the total amount of As flow into the water environment is about 110 thousand tons per year (Bansod et al. 2017; Zheng et al. 2017; Mukherjee et al. 2017).

Arsenic and its compounds are carcinogenic to humans and other species, and are considered to be as one of environmental virulence metal together with cadmium, lead, mercury and chromium (Shen et al. 2017). Once arsenic enters into the human body, the skin, the cardiovascular systems, the nervous system, the kidney and the liver will be injured significantly. When the concentration of arsenic in the human body is 0.01–0.052 g, it will lead to arsenic poisoning; when the concentration of arsenic is 0.06–0.2 g, it will lead to death (Zeng et al. 2017; Nandre et al. 2017; Mukherjee et al. 2017; Kempahamumakkagari et al. 2017). Arsenic was considered as the priority controlled pollutants by World Health Organization (WHO) (El-Moselhy et al. 2017; Miroslav et al. 2016). In April 5, 2009, the United Nations Children’s Fund Published news bulletins in Dhaka, saying that there are 60 million people around the world are drinking water polluted by arsenic, and about 80% of them lived in Asia. With the rapid development of society, the use of arsenic is bound to expand, and the wastewater containing arsenic increases greatly. Therefore, the removal for arsenic has becoming the focus problem in water and wastewater treatment (Ding et al. 2017; Molinar and Argurio 2017; Bhowmick et al. 2015).

Biological treatment technology is developed rapidly and has been used widely in wastewater treatment (Wang et al. 2017; Erkan et al. 2017; Chen et al. 2017). Activated sludge process is one kind of biological treatment technology, and mainly focused on removing BOD or COD. Biodegradable organic matter (BOM) provides substrate for microbial re-growth in the distribution system, biological processes can effectively remove organic matter and ammonia content from raw water. In system of activated sludge technology, the microorganisms exit in form of activated sludge, which could absorb and degrade
pollution matters in sewage, and result in the decrease of many kinds of pollution (Mujtaba and Lee 2017). Because of high efficiency and strong adaptability, activated sludge technology has been seemed as the main technology in sewage and wastewater treatment. Many heavy metals have toxic on microorganisms. While in treatment system of activated sludge, some metals with low concentration are usually absorbed by activated sludge, and reduced the metals from water and wastewater.

In this paper, the effect of activated sludge system in As removal was studied, and the mechanism of As removal in activated sludge system has been explored.

Materials and methods
The main experimental materials
Inoculation sludge was obtained from the feedback sludge tank of the municipal wastewater treatment plant located in Lingshui of Dalian and pre–incubated before being put into the reactor. Synthetic wastewater fed to the reactor consisted of sucrose, NH₄Cl, K₂HPO₄, KH₂PO₄ and mineral solution (containing MgSO₄·7H₂O, CaCl₂·2H₂O, FeSO₄·2H₂O, CoCl). The experiment was carried out in a SBR reactor, and the effective volume of the reactor is 2 L. All reagents used were pure analysis grade and seemed as the As absorbed into the interior of microorganisms. Thus, the As removed from water was controlled at 0.25, 0.50, 0.75 and 1.00 mg/L respectively. The removal efficiency for As with the activated sludge system was shown in Fig. 1.

Removal for As with activated sludge system
The activated sludge system was used to treat water contaminated with As. The concentration of activated sludge was 2500 mg/L, and the initial concentration of As in water was controlled at 0.25, 0.50, 0.75 and 1.00 mg/L respectively. The removal efficiency for As with the activated sludge system was shown in Fig. 1.

From the results in Fig. 1, it could be seen that the removal for As by the activated sludge was very fast. The removal efficiency increased with the process and reached stable after a short time of the process, which indicated that the As was not only adsorbed by the surface of activated sludge, but also was transported to the interior of the microorganisms and take part in the metabolic processes of the microorganisms (Rashid et al. 2016; Kilic et al. 2008; Martínez-Alcalá et al. 2017). At the same time, the removal of As increased slightly with the increase of the initial concentration of As. Calculated results showed that when the initial concentration of As was 0.25 mg/L, the maximum removal of As by activated sludge was 0.06, 0.17, 0.28 and 0.39 mg/g, respectively.

Results
Removal for As with activated sludge system
The activated sludge system was used to treat water contaminated with As. The concentration of activated sludge was 2500 mg/L, and the initial concentration of As in water was controlled at 0.25, 0.50, 0.75 and 1.00 mg/L respectively. The removal efficiency for As with the activated sludge system was shown in Fig. 1.

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When the initial concentration of As was 0.5 mg/L, the maximum removal amount was 0.17 mg/g. When the initial concentration of As was 0.75 mg/L, the maximum removal amount was 0.28 mg/g. When the initial concentration of As was 1.00 mg/L, the maximum removal amount reached 0.39 mg/g. When the initial concentration of As is high, there is a large gradient difference in As concentration between water and the surface of sludge particles, which increases the driving force for mass transfer and enhances the removal efficiency for As.

**Kinetics and thermodynamics of removing arsenic by activated sludge system**

**The reaction kinetics study**

The initial concentration of As was controlled at 0.25, 0.50, 0.75 and 1.00 mg/L. The concentration of activated sludge was 2500 mg/L. According to formula (2), the removal amount at different time was analysis, and the results were shown in Fig. 2.

\[
q_t = \frac{V(C_{L0} - C_L)}{m}
\]  

(2)

In which, \( q_t \) is removal amount (mg/g); \( V \) is the volume of the solution (L); \( C_{L0} \) is the initial concentration of As (mg/L), and \( C_L \) is the concentration of As in water at time of \( t \); \( m \) is the mass of the activated sludge (g).

As shown in Fig. 2, the removal amount increased quickly in the first 0.5–2.0 h, and then increased slowly to stable level.

The removal kinetics data were fitted according to pseudo first order kinetics model and pseudo second order kinetics model according to the formulas (3) and (4). The fitted results were shown in Table 1.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(3)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e^2}
\]  

(4)

In which: \( q_t \) (mg/g) is the removal amount at time \( t \); \( q_e \) (mg/g) is the removal equilibrium amount; \( t \) (min) is the contact time; \( k_1 \) and \( k_2 \) is rate constant of the first and second order kinetics respectively.

From the results in Table 1, it could be seen that the \( R^2 \) of the second order kinetics model of the four conditions is nearly to 1.000 and is obviously superior to the first order kinetics model, which indicates that the removal of arsenic with the activated sludge conforms to the second order kinetics model.

**Study on thermodynamic of As removal in activated sludge system**

In activated sludge system, the removal of As may be contributed mainly to the surface adsorption of activated sludge. The adsorption isotherms were studied to explore the mechanism of surface adsorption. The concentration of activated sludge was 2500 mg/L, and the initial concentration of As was controlled at 0.2, 0.3, 0.4, 0.5, 0.6, 1.0, 1.2, 1.5, 2.0, 3.0, 5.0, 10.0, 20.0 and 50.0 mg/L respectively. The contact time was 24 h. The analysis results of Langmuir adsorption isotherm (5) and Freundlich adsorption isotherm (6) were shown in Table 2.

\[
q_e = \frac{aKLC_e}{1 + KLC_e}
\]  

(5)

\[
q_e = KFC^n_e
\]  

(6)
The fitted results showed that the surface adsorption of activated sludge for As can be described well with Freundlich adsorption isotherms very well.

**The migration and transport mechanism of arsenic in the activated sludge system**

The activated sludge reactor was conducted at continuous flow mode, and the HRT was controlled at 12 h. The initial concentration of As was 0.25 mg/L.

The concentration of As was analyzed according method described in 2.2. The distribution of As was shown in Fig. 3, and the total removal of As was shown in Fig. 4.

It could be seen from Fig. 4 that in the whole process, the removal rate for As kept at a higher level of 70–80%.

But as shown in Fig. 3, there exist some increase of As content in the third stage. Then the addition of As was stop in the experiment, and the activated sludge was cultivated without the high contamination of As for about 5 days and then to continue the experiment. But in over all, the removal of As declined gradually with the long process shown in Fig. 4.

As shown in Fig. 3, the As content in water decreased quickly at the first day of every stage, and then kept at the low level. But the As content adsorbed in surface of activated sludge was kept at a lower level all the time. While the As content in the interior of microorganisms increase at the beginning in every stage.

**Discussion**

Because of many surface functional groups and characteristics of adsorption of activated sludge, the activated sludge system has high performance for the removal of As. There are mainly the characteristic peaks in FT IR spectrum (Fig. 5) of the stretching vibration of –OH of alcohols, acids and acid-like substances on the surface of activated sludge (Lee et al. 2013). The stretching vibration peak in the range of 2930–2925 cm\(^{-1}\) (Liu et al.

### Table 1 Kinetic parameters of removal for As

| Initial concentration of As (mg/L) | \(q_e\) (Experimental results) | Pseudo first order kinetics | Pseudo second order kinetics |
|------------------------------------|-------------------------------|-----------------------------|-------------------------------|
|                                    |                               | \(q_e\) | \(k_1\) | \(R^2\) | \(q_e\) | \(k_2\) | \(R^2\) |
| 0.25                               | 0.054                         | 0.010  | 0.062  | 0.730  | 0.054  | 40.281 | 1.000  |
| 0.50                               | 0.135                         | 0.030  | 0.149  | 0.883  | 0.136  | 45.187 | 0.995  |
| 0.75                               | 0.229                         | 0.032  | 0.149  | 0.413  | 0.229  | 15.985 | 1.000  |
| 0.10                               | 0.323                         | 0.030  | 0.045  | 0.417  | 0.322  | 11.545 | 1.000  |

### Table 2 Parameters of Langmuir and Freundlich Equations

| Langmuir equation | Freundlich equation |
|-------------------|---------------------|
| \(a\)             | \(K_L\)             | \(R^2\) \(n\) | \(K_F\) | \(R^2\) |
| 27.778            | 0.120               | 0.877          | 2.767   | 0.901   | 0.968   |
The peak is the –CH peak. In the range of about 1640–1660 cm\(^{-1}\) (Song et al. 2014), the stretch-
ing vibration peaks are the peaks of –C=O and –CN on
the protein. At around 1250 cm\(^{-1}\) (Yan et al. 2010),
the peak is the –C=O deformation peak of the nucleic acid.
At 1024 cm\(^{-1}\), the peak is the stretching vibration peak
of –OH in polysaccharide. The peaks at below 1000 cm\(^{-1}\)
are the fingerprints of phosphate functional groups, sul-
fur functional groups, etc. (Aravindhan et al. 2004).
Large number of surface functional groups contribute to
the removal of As.

The As was absorbed in the surface of activated sludge
first, and then was transferred into the interior of micro-
organisms and take part in the metabolic process of
microorganisms. The mass distribution of arsenic in
solid and liquid phase in the activated sludge system
varies with time (Table 3). The distribution trend of
arsenic is that the As was gradual migrate from liquid
to solid. In the first 0.5 h, the migration rate was very
high, and then down slowly. This indicates that the As
was mainly adsorbed by the activated sludge in the first
0.5 h. The Distribution Factors (DF) increased with the
increase of the initial concentration. The reason may be
that when concentration of arsenic is low, the amount of
As absorbed by microorganisms is low, while with the
increase of concentration of As, there are more arsenic
absorbed by microorganisms.

In which, DF\(_{L/S}\) distribution factors, and C\(_L\) is the
amount of As dissolved in the liquid phase, C\(_S\) is the
amount of As adsorbed in the solid phase, C\(_T\) is the total
amount of As in the liquid and solid.

\[
DF_L = \frac{C_L}{C_T} \quad (7)
\]

\[
DF_S = \frac{C_S}{C_T} \quad (8)
\]

The DF\(_{L/S}\) increased at the first day of every stage and
then decreased in the continuous flow mode (Fig. 6).
These are because that the As was first adsorbed by
the surface of activated sludge and then transferred into
the interior of microorganisms and participate in the meta-
bolic activity, and the rate of metabolism was lower and
there exist some accumulation of As in the interior of
microorganisms. With the increase of As content accu-
mulated in the interior of the microbes, the microbial
metabolism will be inhibited to a certain extent.

The activated sludge system has high removal effi-
ciency for As in water. In scope of low initial concen-
tration of As in the study, the removal efficiency increase
with the increase of the initial concentration of As. The

\begin{table}[h]
\centering
\caption{DF of As in liquid phase and solid phase (\%)}
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
Initial concentration & 0.1 h & 0.5 h & 1 h & 2 h & 4 h & 8 h & 12 h & 24 h \\
\hline
0.25 mg/L & & & & & & & & \\
DF\(_L\) & 80.2 & 34.9 & 31.9 & 34.3 & 41.1 & 31.8 & 21.2 & 23.9 \\
DF\(_S\) & 19.8 & 65.1 & 68.1 & 65.7 & 58.9 & 68.2 & 78.8 & 76.1 \\
0.50 mg/L & & & & & & & & \\
DF\(_L\) & 74.1 & 41.1 & 38.3 & 30.8 & 18.3 & 13.2 & 19.7 & 23.4 \\
DF\(_S\) & 25.9 & 58.9 & 61.7 & 69.2 & 81.7 & 86.8 & 80.3 & 76.6 \\
0.75 mg/L & & & & & & & & \\
DF\(_L\) & 79.8 & 57.4 & 32.6 & 15.4 & 9.5 & 6.4 & 5.7 & 11.0 \\
DF\(_S\) & 20.2 & 42.6 & 67.4 & 84.6 & 90.5 & 93.6 & 94.3 & 89.0 \\
1.00 mg/L & & & & & & & & \\
DF\(_L\) & 78.6 & 54.6 & 34.2 & 22.1 & 9.9 & 8.3 & 4.3 & 7.5 \\
DF\(_S\) & 21.4 & 45.4 & 65.8 & 77.9 & 90.1 & 91.7 & 95.7 & 92.5 \\
\hline
\end{tabular}
\end{table}
As in water was first adsorbed in the surface of activated sludge, and then some was transport and migrated to the interior of microbes and take part in the metabolic activity of the microbes.

**Abbreviation**
As: arsenic.

**Authors’ contributions**
JZ conceived the project and WW contributed to the experimental design. JZ performed the experiments. SL and JL analyzed the As data. JZ acquired funding for the study. SL and QH wrote the paper. All authors read and approved the final manuscript.

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**Competing interests**
The authors declare that they have no competing interests.

**Availability of data and materials**
The datasets supporting the conclusions of this article are included within the article.

**Consent for publication**
Consent for publication has been obtained from the participants to report individual patient data.

**Ethical approval and consent to participate**
This article does not contain any studies with human participants or animals performed by any of the authors. Consent for Ethical approval was thus not required.

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**References**
Aravindhan R, Madhan B, Rao JR, Nair BLJ, Ramasami T (2004) Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. Environ Sci Technol 38(1):300–306. doi:10.1021/es034427s
Bansod BK, Kumar T, Thakur R, Rana S, Singh I (2017) A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms. Biosens Bioelectron 94(15):443–455. doi:10.1016/j.bios.2017.03.031
Bhowmick S, Kumar Kundu A, Adhikari J, Chatterjee D, Iglesias M, Nriagu J, Mazumder DNG, Shomar B, Chatterjee D (2015) Assessment of toxic metals in groundwater and saliva in an arsenic affected area of West Bengal, India: a pilot scale study. Environ Res 142(10):328–336. doi:10.1016/j.envres.2015.07.005
Chen Y, Lan S, Wang L, Dong S, Zhou H, Tan Z, Li X (2017) A review: driving factors and regulation strategies of microbial community structure and dynamics in wastewater treatment systems. Chemosphere 174(5):173–182. doi:10.1016/j.chemosphere.2017.01.129
Ding Z, Fu F, Cheng Z, Lu J, Tang B (2017) Novel mesoporous FeeAl bimetal oxides for As(III) removal: performance and mechanism. Chemosphere 169:297–307. doi:10.1016/j.chemosphere.2016.11.057
El-Moselhy MM, Ates A, Celebi A (2017) Synthesis and characterization of hybrid iron oxide silicates for selective removal of arsenic oxyanions from contaminated water. J Collid Interface Sci 488:335–347. doi:10.1016/j.jcis.2016.11.003
Erkan HS, Engin GO, Kulil B, Gunalp G (2017) Activated sludge properties in a submerged membrane bioreactor: Effect of COD/N ratio of wastewater. Int J Environ Sci Technol 14(5):933–942. doi:10.1002/s13762-016-1201-2
Kempahanumakkagari S, Deep A, Kim KH, Kailasa SK, Yoon HO (2017) Nanomaterial-based electrochemical sensors for arsenic—a review. Biosens Bioelectron 95(15):106–116. doi:10.1016/j.bios.2017.04.013
Kılıç M, Keskin ME, Mazlum S, Mazlum N (2008) Hg(II) and Pb(II) adsorption on activated sludge biomass: effective biosorption mechanism. Int J Miner Process 87(1–2):1–8. doi:10.1016/j.minpro.2008.01.001
Lee BM, Shin HS, Hur J (2013) Comparison of the characteristics of extracellular polymeric substances for two different extraction methods and sludge formation conditions. Chemosphere 90(2):237–244. doi:10.1016/j.chemosphere.2012.06.060
Liu D, Tao Y, Li K, Yu J (2012) Influence of the presence of three typical surfactants on the adsorption of nickel (II) to aerobic activated sludge. Bioresour Technol 126(7):53–63. doi:10.1016/j.biortech.2012.09.025
Martínez-Alcalá I, Guillén-Navarro JM, Fernández-López C (2017) Pharmaceutical biological degradation, sorption and mass balance determination in a conventional activated-sludge wastewater treatment plant from Murcia, Spain. Chem Eng J 316(15):332–340. doi:10.1016/j.cej.2017.01.048
Miroslov K, Nikoleta K, Mima HS (2016) Water reclamation during drinking water treatments using polyamide nanofiltration membranes on a pilot scale. Environ Sci Pollut R 23(18):17919–17927. doi:10.1007/s11356-016-6919-3
Molinari R, Argurio P (2017) Arsenic removal from water by coupling photocatalysis and complexation-ultrafiltration processes: a preliminary study. Water Res 109:327–336. doi:10.1016/j.watres.2016.11.054
Mujtaba G, Lee K (2017) Treatment of real wastewater using co-culture of immobilized Chlorella vulgaris and suspended activated sludge. Water Res 120:174–184. doi:10.1016/j.watres.2017.04.078
Mukherjee A, Kundu M, Basu B, Sinha B, Chatterjee M, Das Bairagya M, Singh UK, Sarkar S (2017) Arsenic load in rice ecosystem and its mitigation through deficit irrigation. J Environ Manage 197(5):89–95. doi:10.1016/j.jenvman.2017.03.037
Nandre VS, Bachate SP, Salunkhe RC, Bagade AV, Shouche YS, Kodam KM (2017) Enhanced detoxification of arsenic under carbon starvation: a new insight into microbial arsenic physiology. Curr Microbiol 74(5):614–622. doi:10.1007/s00284-017-1203-4
Rashid A, Bhatti HN, Iqbal M, Noreen S (2016) Fungal biomass composite with bentonite efficiency for nickel and zinc adsorption: a mechanistic study. Ecol Eng 91:459–471. doi:10.1016/j.ecoleng.2016.03.014
Shen L, Jiang X, Fu D, Li Q, Outang T, Wang Y (2017) Chemical reactive features of novel amino acids intercalated layered double hydroxides in As(III) and As(V) adsorption. Chemosphere 176:57–66. doi:10.1016/j.chemosphere.2017.02.100
Song XC, Liu DE, Zhang GW (2014) Adsorption mechanisms and the effect of oxytetracycline on activated sludge. Bioresour Technol 151(10):428–431. doi:10.1016/j.biortech.2013.10.055
Wang BB, Gu YW, Chen JM, Yao Q, Li HJ, Peng DC, He F (2017) Is polymeric substrate in influent an indirect impetus for the nitrification process in an activated sludge system? Chemosphere 177(6):128–134. doi:10.1016/j.chemosphere.2017.03.007
Yan C, Li G, Yue P (2010) Competitive effect of Cu(II) and Zn(II) on the biosorption of lead(II) by Myriophyllum spicatum. J Hazard Mater. 179(1–3):721–728. doi:10.1016/j.jhazmat.2010.03.061
Zeng C, Gonzalez-Alvarez A, Orenstein E, Field JA, Shadman F, Sierra-Alvarez R (2017) Ecotoxicity assessment of ionic As(III), As(V), In(III) and Ga(III) species potentially released from novel III–V semiconductor materials. Ecotox Environ Safe 140:30–36. doi:10.1016/j.ecoenv.2017.02.029
Zhao Y, Wang D, Xie H, Won SW, Cui L, Wu G (2015) Adsorption of Ag(I) from aqueous solution by waste yeast: kinetic, equilibrium and mechanism studies. Bioproc Biosyst Eng 38(1):69–77. doi:10.1007/s00449-014-1244-z
Zheng L, Liu Z, Yan Z, Yi X, Zhang J, Zhang Y, Zheng X, Zhu Y (2017) Deriving water quality criteria for trivalent and pentavalent arsenic. Sci Total Environ 587–588:68–74. doi:10.1016/j.scitotenv.2017.02.004

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