Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Biotransformation of arsenic species by activated sludge and removal of bio-oxidised arsenate from wastewater by coagulation with ferric chloride

Harinaivo Anderson Andrianisa[a], *Ayumi Ito*[b,*], *Atsushi Sasaki*[c], *Jiro Aizawa*[a], *Teruyuki Umita*[a]

[a]*Department of Civil and Environmental Engineering, Iwate University, Ueda 4-3-5, Morioka 020-8551, Japan*
[b]*Department of Frontier Materials and Functional Engineering, Iwate University, Ueda 4-3-5, Morioka 020-8551, Japan*
[c]*Technical Division of Instrumental Analysis, Faculty of Engineering, Yamagata University, Jounan 4-3-16, Yonezawa 992-8520, Japan*

ARTICLE INFO

Article history:
Received 25 April 2008
Received in revised form
7 August 2008
Accepted 26 August 2008
Published online 6 September 2008

Keywords:
Arsenic removal
Arsenite oxidation
Arsenate reduction
Activated sludge
Chemoautotrophic arsenite oxidising bacteria
Coagulation

ABSTRACT

The potential of activated sludge to catalyse bio-oxidation of arsenite [As(III)] to arsenate [As(V)] and bio-reduction of As(V) to As(III) was investigated. In batch experiments (pH 7, 25 °C) using activated sludge taken from a treatment plant receiving municipal wastewater non-contaminated with As, As(III) and As(V) were rapidly biotransformed to As(V) under aerobic condition and As(III) under anaerobic one without acclimatisation, respectively. Sub-culture of the activated sludge using a minimal liquid medium containing 100 mg As(III)/L and no organic carbon source showed that aerobic arsenic-resistant bacteria were present in the activated sludge and one of the isolated bacteria was able to chemo-autotrophically oxidise As(III) to As(V). Analysis of arsenic species in a full-scale oxidation ditch plant receiving As-contaminated wastewater revealed that both As(III) and As(V) were present in the influent, As(III) was almost completely oxidised to As(V) after supply of oxygen by the aerator in the oxidation ditch, As(V) oxidised was reduced to As(III) in the anaerobic zone in the ditch and in the return sludge pipe, and As(V) was the dominant species in the effluent. Furthermore, co-precipitation of As(V) bio-oxidised by activated sludge in the plant with ferric hydroxide was assessed by jar tests. It was shown that the addition of ferric chloride to mixed liquor as well as effluent achieved high removal efficiencies (>95%) of As and could decrease the residual total As concentrations in the supernatant from about 200 μg/L to less than 5 μg/L.

It was concluded that a treatment process combining bio-oxidation with activated sludge and coagulation with ferric chloride could be applied as an alternative technology to treat As-contaminated wastewater.

1. Introduction

Arsenic (As) is a highly toxic element that exists in various species and the toxicity of arsenic depends on its species. The pH, redox conditions, surrounding mineral composition and microbial activities affect the form (inorganic or organic) and the oxidation state (−3, 0, +3, +5) of As. It is generally accepted that the inorganic species, arsenite [As(III)] and arsenate

* *Corresponding author*. Tel./fax: +81 19 621 6449.
E-mail address: aitou@iwate-u.ac.jp (A. Ito).
0043-1354/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2008.08.027

[As(V)], are the predominant species in most environments, although the organic ones might also be present when inorganic species undergo methylation by microorganisms (Duker et al., 2005). Because of the behavioural differences between the species, it is of importance to monitor not only the As content but also the chemical species in environmental or biological samples.

Arsenic is usually contained in geothermal water discharges and mining drainages. Agricultural and municipal effluents might also contain a significant amount of As because of As use in herbicides, pesticides, pigments, glass manufacturing, livestock feed or wood preservatives (Battacharya et al., 2007). Large-scale As contamination around the world is adversely affecting the health of millions of people (Hopenhayn, 2006). Thus, the removal of As from contaminated sites including water and wastewater has become the subject of numerous studies. However, Goldstone et al. (1990) have found that only 34% was removed by activated sludge process in a full-scale treatment plant receiving wastewater containing 15 μg As/L as daily average. Watanabe et al. (2002) have also reported that the removal of As by an oxidation ditch activated sludge process was very low (14%). Furthermore, most water quality regulations on the permissible level of As in drinking and effluent waters at national and international levels have been strengthened recently. The new regulations imply that performance of existing processes should be improved or new ones should be developed in order to meet the standards.

Coagulation process with ferric chloride ($FeCl_3$) has been investigated deeply in laboratory, pilot- and full-scale experiments and found to be efficient to remove As from various drinking water sources (Hering et al., 1996; Zouboulis and Katsoyiannis, 2002; Chwirka et al., 2004) and soil washing effluents (Jang et al., 2005). For different As-contaminated water and wastewaters, As(V) could be more efficiently removed by coagulation than As(III). Thus, when As(III) is present, it should be pre-oxidised to As(V). Processes applied to achieve this step include ozonation (Kim and Nriagu, 2000), photo-oxidation (Zhang and Itoh, 2006), or the addition of oxidising chemicals such as chlorine (Ghurye and Clifford, 2004), potassium permanganate (Li et al., 2007) or hydrogen peroxide (Pettine et al., 1999). Currently, there is a growing interest in the application of biological oxidation process as a new alternative to the use of chemical oxidants. Some microorganisms isolated from various environments, such as aquatic environments (Weeger et al., 1999), soils (Macur et al., 2004), sewage (Philips and Taylor, 1976), mine sites (Santini et al., 2000), geothermal areas (Gihring and Banfield, 2001) or water treatment filters (Lytle et al., 2007), have shown a high resistance to As and the ability to catalyse the oxidation of As(III) to As(V).

The objective of this research was to investigate the biological oxidation and reduction of inorganic As species in activated sludge process in order to develop an activated sludge-based treatment system to remove As from As-contaminated wastewater. Both laboratory experiments and field investigations in a full-scale oxidation ditch plant were carried out to clarify the ability of activated sludge to oxidise or reduce As. To our knowledge, coagulation of As in biologically treated wastewater with $FeCl_3$ has not been reported in the literature. Then, a jar test was conducted to evaluate the removal efficiency of bio-oxidised arsenate by activated sludge.

2. Materials and methods

2.1. Stock solutions and culture medium

Stock solutions of arsenite [$NaAsO_2$, 1 g As/L], arsenate [$Na_2HAsO_4 \cdot 7H_2O$, 1 g As/L], ferric chloride [$FeCl_3$, 10 g Fe/L] from Kanto Chemicals (Japan), MMA(V) [$Na_2CH_3AsO_3 \cdot 6H_2O$] and DMA(V) [$Na(CH_3)_2AsO_2$] from Trichemical Limited (Japan) were prepared with ultra pure water (Millipore, Japan). The stock solutions of arsenic species were stored at 4 °C and that of $FeCl_3$ was stored at room temperature in a dark glass container.

A culture medium (CM) proposed by Weeger et al. (1999) was used without addition of sodium lactate as an organic carbon source to isolate chemoautotrophic arsenite oxidising bacteria from activated sludge. The CM consisted of (i) solution A (1 L): 20 g of $MgSO_4 \cdot 7H_2O$; 10 g of NH_4Cl; 10 g of Na_2SO_4; 100 mg of K_2HPO_4; and 672 mg of $CaCl_2 \cdot 2H_2O$ (Kanto Chemicals, Japan), (ii) solution B (100 mL): 160 mg of $FeSO_4 \cdot 7H_2O$ (Kanto Chemicals, Japan), (iii) solution C (50 mL): 4 g of $NaHCO_3$ from (Kanto Chemicals, Japan) and (iv) solution D (100 mL): 1.733 g of $NaAsO_2$ (Wako Inc., Japan). Solution A was sterilised by autoclaving (121 °C, 15 min), and solutions B–D by filtration through a 0.2 μm pore size syringe filter (Whatman Inc., USA). A 1-L CM was made up of 100 mL of solution A, 2.5 mL of solution B, 10 mL of solution C, 10 mL of solution D, and autoclaved (121 °C, 15 min) deionised water.

2.2. Batch experiments for biotransformation of inorganic arsenic species by activated sludge

Fresh activated sludge was collected in acid-washed plastic bottles from the aeration tank in the Tonan Wastewater Treatment Plant (TWTP) located in Morioka, Japan, which receives domestic sewage not contaminated with arsenic and is operated under the conventional activated sludge process. The concentrations of As in the influent and effluent were less than 1 μg/L and the pH of the sludge was around 7 (Iwate Prefectural Sewage Public Corporation, 2005). Upon arrival to the laboratory, a desired volume of the sludge was washed three times with deionised water to remove soluble components. After settling, the supernatant was decanted and only the settled sludge was kept for the experiments. A part of the washed sludge was autoclaved (121 °C, 15 min) and again washed three times. Then, the settled sludge was kept for the experiments.

Single-metal solutions containing 100 μg As/L as As(III) or As(V) were prepared by diluting the stock solutions with deionised water. The pH (pH meter F-12, Horiba, Japan) of each solution was adjusted to 7 with NaOH or HCl solutions, and then samples were collected to determine the initial concentrations of As. Then, the washed activated sludge was suspended into the solutions containing As in 2-L shaking flasks, giving a concentration of about 0.5 g SS/L. The mixtures were thoroughly agitated on a shaker table at 120 rpm for 9 or 12 h. The experiments were carried out at 25 °C under aerobic