Arsenite removal using a pilot system of ultrasound and ultraviolet followed by microfiltration

Mingcan Cui a,b, Min Jang c,e, Shaliza Ibrahim c, Beomguk Park a, Eunju Cho a, Jeehyeong Khim a,*

a School of Civil Environmental and Architecture Engineering, Korea University, 5 Anam-dong, Seoul 136-701, Republic of Korea
b Jilin Institute Chemical Technology, 5 Cheng De Jie, Jilin, China
c Department of Civil Engineering, Faculty of Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia

A R T I C L E   I N F O

Article history:
Received in revised form 2 January 2014
Accepted 6 January 2014
Available online 13 January 2014

Keywords:
Arsenite
Arsenate
Oxidation
Ultrasonics
Ultraviolet
Microfiltration

A B S T R A C T

Batch and continuous-flow pilot tests using ultrasound (US), ultraviolet (UV) and a combination of US and UV were conducted to determine the oxidation rates of arsenite [As(III)]. Compared to the single processes of US or UV, the combined US/UV system was more effective for As(III) oxidation with a synergy index of more than 1.5. A high rate constant of As(III) removal was obtained as ferrous [Fe(II)] ions existed. Like the pseudo-Fenton reaction, Fe(II) species can participate in the production of additional •OH by reacting with H2O2 produced by US, before being oxidized to Fe(III). From the results of batch tests, the optimum molar ratio of Fe(II)/As(III) and pH were found to be 83 and 6–9.5, respectively. Similarly, the continuous-flow pilot tests showed that US/UV system could remove As(III) below the regulation [10 µg L–1] of total As (As tot) at 91 of molar ratio [Fe(II)/As(III)] and 3-h HRT. The continuous-stirred-tank-reactor (CSTR) modeling showed that the scavenging effect of anionic species (Cl– and CO32–) for •OH might prevail in the single processes, whereas it is insignificant in the combined process. Without using chemicals, microfiltration (MF) was adopted to treat sludge produced in oxidation step. In terms of an engineering aspect, the operational critical flux (CF) and cycle time were also optimized through the continuous-flow tests of MF system. As an energy-utilizing oxidation technique that does not require a catalyst, the combined energy system employing US/UV followed by MF could be a promising alternative for treating As(III) and Fe(II) simultaneously.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In natural waters, especially groundwater, arsenic (As) exists as both arsenite [As(III)] and arsenate [As(V)]. Depending on the pH and redox potential, the ratio of As(V) to As(III) has been found to be in the range of 10–100 [1–3]. Hug et al. (2001) reported that total As (As tot) of groundwater in Bangladesh was detected in the range 0.061–1.24 mg L–1, of which a relatively high concentration (6–720 µg L–1) of As(III) existed. Especially, as a result of the reducing conditions in those locations, high levels of As(III) (>0.3 mg L–1) were also found in groundwater in India, Laos, Cambodia and Pakistan [4].

Many cases of arsenic contamination in groundwater are accompanied by Fe(II) contamination because of reductive releases from iron and arsenic-bearing minerals like arsenopyrite (FeAsS) [5]. Therefore, together with As, ferrous [Fe(II)] can be released and should be treated appropriately.

Owing to the high toxicity of As, the US Environmental Protection Agency published a revised arsenic standard in early 2001 of 10 µg L–1 (as total As) in drinking water. In order to meet these standards, new and innovative technologies should have not only high efficiencies, but also be economical to use, easy to operate, and sufficiently durable for long-term use.

The As species that are most often found in groundwater, As(III), is known to have toxicity of 20–60 times higher than As(V) [6]. It is also highly mobile because it exists primarily as H3AsO3 in aqueous solution at pH < 9.2 [7]. Owing to the neutral charge of As(III), it is not easy to remove As(III) directly using conventional techniques such as adsorption and co-precipitation. Accordingly, As(III) should first be oxidized to increase its treatment efficiency in water.

The oxidation of As(III) by dissolved oxygen is extremely slow. For example, only 20% of 100 µg L–1 As(III) can be oxidized after 4 months [8]. Up to now, there have been several studies of oxidation techniques, including chemical oxidation (H2O2, OCl– and S2O82–), Fenton [Fe(II)/H2O2] and ozone (O3). As(III) oxidation by ultraviolet (UV) or UV/catalyst has also been studied [9–12]. In practice, however, due to the limited UV transmittance, ultraviolet (UV) or UV/catalyst give a low efficiency in the oxidation of As(III). Particularly, the separation and reuse of TiO2 is too difficult to
apply in an actual treatment plant. Thus, it is a challenge to find an energy efficient oxidation and treatment system for As(III) using purely energy without the need for catalysts.

Until now, no attempts have been made to enhance the oxidation efficiency of As(III) by coupling ultrasound (US) to UV. Especially, sole UV has a difficulty to oxidize As(III) or organic matter in turbid water containing suspended solids. The US irradiation can also induce the cavity effect via a sequence of nucleation, growth and collapse of micro-bubbles. During this process, the sound energy can be transformed into chemical energy, producing H₂O₂ and OH radicals (·OH), which have oxidation potential of 2.8 V. When combined with UV, additional ·OH species can also be produced by the direct UV irradiation of water. Then, As(III) can be oxidized to As(V) by ·OH. To remove As(V), conventional treatment techniques such as precipitation, adsorption, and membrane techniques can be used [13–19].

Theoretically, as known in the pseudo-Fenton reaction, Fe(II) species present in arsenic-contaminated groundwater can participate in the production of additional ·OH by reacting with H₂O₂ produced by US, before being oxidized to Fe(III). Through these reactions, As(III) can be oxidized to As(V), which can be more effectively removed not only by co-precipitation with Fe(III) ions, but also by complexation with hydrous ferric oxide, Fe(OH)₃ [13,20,21].

During the removal of As(III) and Fe(II), the produced sludge usually consists of small particles. In order to remove these particles, a coagulation-flocculation step would be necessary to generate sufficiently large particles that could be easily removed in a settling basin. However, careful control in the dosing of chemicals and long settling times make the actual application difficult. As a fast separation technique without chemicals, microfiltration (MF) techniques could be employed as a simpler approach in drinking-water treatment facilities. Without a need for large space, sludge particles (0.1–1 μm) can be removed by MF using a low pressure pump [22].

The main objectives of this study are (1) to determine the oxidation kinetic constants in batch tests of US, UV and a combined system of US/UV for several parameters such as pH and power density, (2) to optimize the molar ratio of Fe(II) to As(III) for their simultaneous removal by oxidation and co-precipitation in the US/UV/Fe(II) system, (3) to determine the hydraulic retention time in the continuous-flow pilot system for meeting the effluent regulation standards of arsenic, and finally (4) to optimize the operational parameters for the treatment of suspended solids (SS) in effluent of oxidation and settling basins using the MF system.

2. Experimental materials and methods

2.1. Materials

All chemicals including sodium (meta) arsenite (NaAsO₂, purity 94%) and iron sulfate heptahydrate (FeSO₄·7H₂O, purity >99%) were analytical grade and used without further purification. Batch and continuous-flow pilot tests were conducted using solutions prepared with deionized (DI) and tap water, respectively.

A stock solution containing 200 mg L⁻¹ of As(III) was prepared and diluted using DI or tap water to the required initial concentration of As(III). The initial concentration of Fe(II) applied was also varied between 0.4 and 20 mg L⁻¹.

2.2. Reactor setup and operation of continuous-flow pilot system

Fig. 1 shows a flowchart of the treatment system, side and top views of the US/UV reactor, as well as the actual setup used for the batch and continuous-flow pilot tests. As shown in Fig. 1A, the treatment system consists of an oxidation unit (US and UV), settling basin, and MF system. To avoid the reaction between Fe(II) and As(III) prior to oxidation, Fe(II) was separately injected into the reactor. An injection system for Fe(II) was installed on the top of the oxidation reactor and a stock solution of Fe(II) (1000 mg L⁻¹ as Fe(II)) was fed with a preset flowrate in order to achieve the predetermined concentration in the US/UV reactor. The reactor was octagonal (each side and height were 100 and 256 mm, respectively), made from stainless steel and with a volume of 8 L (working volume: 6 L) (Fig. 1B). At the corners of the reactor, four ultrasonic transducers (70 × 180 mm, MEGA-100, Mirae Ultrasonic Tech Co., Korea) were installed. The frequency and maximum power of each ultrasonic transducer were 332 kHz and 240 W, respectively. Four UV lamps (254 nm, UV G12T 5/VH 4P SE, Han-sung Co., Korea) were also vertically inserted into the reactor (Fig. 1C). The maximum power and intensity of each lamp were 64 W and 1.38 W cm⁻², respectively. In one corner of the reactor, a square-pyramid-type settling tank was integrated. It was 70 × 90 mm at the top side with a slope of 30°, and had a water inlet from the bottom of US/UV reactor. The total and effective volumes of settling tank were 1.2 and 1.0 L, respectively.

A microfiltration (MF) system was built to treat the effluent in the settling basin. A hydrophobic polyvinylidene fluoride membrane (GVHP) supplied by Millipore (a nominal pore size of 0.22 μm) was employed as the material for the MF. The membrane module was prepared by encasing the MF (D × d × L = 2 × 0.8 × 265 mm) in a plastic case (D × L, 50 × 200 mm), in which the effective membrane area was 477 mm². A peristaltic pump (Master Flex model 7529-00) was used to circulate the feed and supply the operating pressure. The system was operated at a controlled flux with pumped permeate. Pressure transducers were used to measure the trans-membrane pressure (TMP). The cross flow rate was controlled by the recirculation pump while the flux was fixed by the permeate pump (FC-110/Flow controller). All pressure sensors, the permeate pump and balance were connected to a computer. Each parameter was monitored continuously.

2.3. Batch tests

Batch tests were conducted using the constructed system. During the batch tests, the kinetic rate constants of As(III) oxidation by US, UV or US/UV were measured for various values of the pH and US power density. When Fe(II) was injected, only the removal of As (as As₅0₃) was measured without speciation because the chemical speciation analysis of As was significantly affected by fine particles created by Fe(II). The US was operated with a fixed frequency (332 kHz) and power density (26.3 W L⁻¹) while UV (254 nm) was run at the maximum power intensity (1.38 W cm⁻²). The power densities for US were calculated using the calorimetric method as follows:

\[
\text{Calorimetric power (W)} = m \cdot C_p \left( \frac{dT}{dt} \right) \tag{1}
\]

where \(C_p\) is the heat capacity of the solvent (J kg⁻¹ K⁻¹), \(m\) is the mass of solvent (kg), and \(dT/dt\) is the difference between the initial and final temperatures after a time interval \(dt\) (s). The power density was calculated using the following equation:

\[
\text{Power density} = \frac{P_c}{V_L} \tag{2}
\]

Here, \(P_c\) and \(V_L\) are the calorimetric power and the liquid volume, respectively.

For the kinetic tests of As(III) oxidation or As₅0₃ removal, the rate constant \(k_1\) was obtained by applying the following pseudo-first-order kinetic model:

\[
\ln[\text{As}_3/\text{As}_5] = -k_1 t \tag{3}
\]

Here, \(\text{As}_3\) and \(\text{As}_5\) are the concentrations of As(III) or As₅0₃ at the initial and time \(t\), respectively.
2.4. Continuous-flow pilot tests

To conduct continuous-flow pilot tests, a peristaltic pump (GT-150, Green Tech, Korea) was used to inlet the As(III)-spiked tap water continuously into the constructed system. The pure As(III) oxidation efficiencies of US, UV and US/UV were observed with various hydraulic residence times (HRT) (0.5–3 h). By analyzing the removal efficiency of As(III), the optimum amount of Fe(II) and HRT were determined. The continuous-flow pilot system was operated with various amounts of Fe(II) injection (0–30 mg h$^{-1}$) at either 1.5 or 3 h HRT to determine the optimum injection rate of Fe(II).

2.5. Analysis

For all tests, water samples were taken at predetermined times. Chemical speciation between As(III) and As(V) was achieved using an anionic-exchange resin [Supelclean™ LCSAX solid phase extraction (SPE, 57017), 3 mL] for samples, to which Fe(II) had not been added. In the filtration step, As(V) is retained in the resin and only As(III) remains in the filtrate. The stability of arsenic speciation through filtration by the resin has been described elsewhere. For experiments added by Fe(II), $A_{\text{tot}}$ was directly analyzed after samples were filtered using a 0.45-μm pore filter. As(III) and $A_{\text{tot}}$ in the filtrate were measured using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, 5300DV, USA).

3. Results and discussion

3.1. Batch tests of As(III) oxidation

3.1.1. As(III) oxidation by US, UV, or US/UV systems and pH effects

The kinetics of As(III) oxidation by US, UV and US/UV under varying pH conditions are shown in Fig. 2A, B and C, respectively. The kinetic rate constants of As(III) oxidation in the US system at pH values of 6, 9.2 and 11 were $4 \times 10^{-3}$, $4.6 \times 10^{-3}$ and $5 \times 10^{-3}$ min$^{-1}$, while those by UV were $3.4 \times 10^{-3}$, $3.8 \times 10^{-3}$ and $4.3 \times 10^{-3}$ min$^{-1}$, respectively. Thus, US had kinetic constants about 1.2-times higher than UV. When US and UV were combined, the kinetic rate constants were $11.4 \times 10^{-3}$, $12.4 \times 10^{-3}$ and $14.2 \times 10^{-3}$ min$^{-1}$ at pH 6, 9.2 and 11, respectively, which were much higher than either US or UV alone. Compared to US, the oxidation of As(III) by US/UV was about 2.8-times faster under all pH conditions.

Fig. 1. Schematics of (A) treatment flowchart, (B) side and (C) top views of US/UV system, and (D) actual photo for experimental setup.

Fig. 2. At pH 6, 9.2 and 11, oxidation kinetics of As(III) (initial conc.: 0.2 mg L$^{-1}$) by (A) US operated at 332 kHz and 26.3 W L$^{-1}$, (B) UV (254 nm) operated at 1.38 W cm$^{-2}$ of power intensity, and (C) US/UV operated at the same condition with single process.
Under the same operational conditions, the synergetic effect of US and UV can be calculated as the synergy index as follows [23]:

\[
\text{Synergy index} = \frac{k_{\text{US,UV}}}{k_{\text{US}} + k_{\text{UV}}}
\]

(4)

The synergy indexes at pH values of 6, 9.2 and 11 were calculated to be 1.54, 1.48 and 1.52, respectively, with an average value of 1.51. Hence, this can infer that the combined process of US/UV has a higher efficiency in As(III) oxidation than US or UV singly applied.

The synergetic effect of the US/UV process can be explained as follows. The sonolysis by US can induce the cavitation effect via sequences of nucleation, growth and collapse of micro-bubbles, which can produce -OH (Eq. (5)). In a chain reaction, H₂O₂ is formed by -OH (Eq. (6)) and then decomposes by UV to -OH (Eq. (7)). Therefore, in terms of -OH production, the combined process of US/UV is more advantageous than US or UV.

Sonolysis by US

\[
\text{H₂O} \overset{\text{US}}{\rightarrow} \text{H} + \text{HO} \tag{5}
\]

OH + -OH \rightarrow H₂O₂ \tag{6}

Photolysis by UV

\[
\text{H₂O₂} \overset{\text{254 nm}}{\rightarrow} \text{OH} + \text{HO} \tag{7}
\]

The oxidation of As(III) by -OH are described by reactions (8) and (9).

Oxidation of As(III)

\[
\text{As(III)} + \text{OH} \rightarrow \text{As(IV)} + \text{HO}^- \tag{8}
\]

As(IV) + -OH \rightarrow As(V) + -OH \tag{9}

For all processes, the kinetic rate constants increased as pH increased. Pettine et al. (1999) addressed the relationship between pH and the kinetic rate constants of As(III) oxidation by hydrogen peroxide as follows [9]. Thermodynamically, As(III) oxidation is favored as pH increases:

\[
\text{Log } K = (-10.68 \pm 0.31) + (1.37 \pm 0.03) \text{pH} \tag{10}
\]

The oxidation reaction of As(III) species with -OH can be represented by Eqs. (11) and (12). The most dominant As(III) species in the pH ranges of 6–9.2 and 9.2–11 are H₂AsO₄⁻ and H₂AsO₅⁻, respectively:

\[
\text{H₂AsO₃} + \text{OH} \rightarrow \text{HAsO₄}²⁻ + 3\text{H}⁺ \tag{11}
\]

\[
\text{H₂AsO₅}^- + \text{OH} \rightarrow \text{HAsO₆}³^- + 2\text{H}⁺ \tag{12}
\]

The free energies of formation under standard conditions (ΔG°) for Eqs. (11) and (12) are -41.74 and -54.34 kcal mol⁻¹ [24], respectively, while the corresponding equilibrium constants are 4.30 × 10³⁰ and 7.59 × 10³⁹ for Eqs. (11) and (12). This suggests that the reaction is thermodynamically favorable in the high pH range.

3.1.2. Effect of US power density

The kinetic constants of As(III) oxidation according to the US power density were measured for the US and US/UV systems at pH 6. The US frequency and UV (254 nm) power intensity were kept fixed at 332 kHz and 1.38 W cm⁻², respectively, while pH and temperature were maintained at 6 and 22 ± 0.5 °C, respectively. The kinetic rate constants of both US and US/UV linearly increased with the US power density (Fig. 3). The slope of US/UV (0.46) was 2.9–times larger than that of US (0.16).

According to the US power density, the synergetic effect of US/UV for oxidizing As(III) can be explained as follows. As the US power density increased, the rate of -OH and H₂O₂ generation increased. As described in Section 3.1.1, the chain reaction involving the generation and decomposition of -OH and H₂O₂ induced by US/UV resulted in a higher kinetic rate constant for As(III) oxidation than that made by US alone.

3.2. Batch tests of As(III) removal

3.2.1. As(III) removal by Fe(II) and oxidation system

For this experimental section, only the removal of As(III) was measured without speciation. Therefore, the measured arsenic was dissolved total As (Astot), Fig. 4A shows Astot remained after 1 h of operation, for which various concentrations of Fe(II) were introduced into each oxidation system (US, UV or US/UV). The US frequency and power density were fixed at 332 kHz and 26.3 W L⁻¹, respectively, while the UV power intensity was 1.38 W cm⁻². All experiments were conducted at pH 6 and 22 ± 0.5 °C.
In all cases, the remained As$_{\text{tot}}$ decreased as the Fe(II) increased. Both US and US/UV completely removed As$_{\text{tot}}$ at 12.4 mg L$^{-1}$ Fe(II). For the solely UV system, about 0.06 mg L$^{-1}$ As$_{\text{tot}}$ was remained at >0.4 mg L$^{-1}$ Fe(II) applied.

Fig. 4B shows the molar ratios of As(III) removed with respect to the Fe(II) concentration injected. Although the molar ratios in all systems increased as the Fe(II) concentration decreased, they differed by the system for a given Fe(II) concentration.

As(III) species ($pK_{a1} = 9.2$) are electrostatically neutral at pH 6, whereas As(V) species are negatively charged [e.g., H$_2$AsO$_4^-$ (~90%) and H$_2$AsO$_4^-$ (~10%) at pH 6], Fe(II) can only be precipitated as Fe(OH)$_2^-$ at pH values above 8, but Fe(III) can be easily precipitated above pH 4. As(V), the oxidized form of As, can be removed by co-precipitation with Fe(III) as FeAsO$_4^-$, as well as by adsorption with amorphous Fe(OH)$_3$. Thus, as higher oxidation for As(III) and Fe(II) occurs, the molar ratio increases. When As(III) (0.2 mg L$^{-1}$, 0.0027 mmole L$^{-1}$) was completely removed at 12.4 mg L$^{-1}$ of Fe(II) in the US and US/UV systems, the molar ratio of removed As(III) to applied Fe(II) was 0.012 mol As(III)/mol Fe(II) (Fig. 4B). For the UV system, it was only 0.0056 mol As(III)/mol Fe(II) for 20 mg L$^{-1}$ Fe(II). The US system had a molar ratio below 0.08 mol As(III)/mol Fe(II) at <1 mg L$^{-1}$ Fe(II), while the UV system had much higher molar ratios than the US system [e.g., 0.34 mol As(III)/mol Fe(II) at 0.2 mg L$^{-1}$ Fe(II)]. Accordingly, the UV system had a high oxidation efficiency at <0.5 mg L$^{-1}$ Fe(II). Owing to limited UV transmittance, however, its oxidation efficiency decreased sharply as Fe(II) increased. Compared to the single-process, the combined system showed higher molar ratios for the overall concentration of Fe(II) applied. Hence, this enhanced efficiency might be due to not only the chemical aspect such as chain reaction involving the generation and decomposition of OH and H$_2$O$_2$ induced by US/UV, but also the physical aspect of US such as micro-streaming and shockwaves that could disperse suspended solids, increasing the UV transmittance.

Kinetic tests were conducted to determine the rate constants of As(III) removal by US/Fe(II) and US/UV/Fe(II), as well as the effect of pH on them. The optimum concentration (12.4 mg L$^{-1}$) of Fe(II) determined previously was used in both systems. Fig. 5A and B show the remained As over time for the US and US/UV systems, respectively.

Although the complete removal of As(III) using US and US/UV was achieved with 12.4 mg L$^{-1}$ Fe(II), the kinetic results showed that the rate in the US/UV system was about twice that of the US system for the pH values investigated. The kinetic rate constants for US and US/UV obtained from the pseudo-first-order kinetic model were 6.72 \times 10^{-2} and 14.2 \times 10^{-2} min$^{-1}$, respectively. Although it is not possible to differentiate oxidation speeds in the removal rates by co-precipitation, the US or US/UV coupled with Fe(II) had removal rate constants that were 12–16 times higher when compared to the constants obtained from pure oxidation tests. These increases could be explained by the fact that Fe(II) species can participate in the pseudo-Fenton reaction of the US oxidation process. During this process, Fe(II) species can harvest additional OH by reaction with H$_2$O$_2$ produced by US and be eventually oxidized to Fe(III). Through these reactions, As(III) can be oxidized to As(V), which can be removed by co-precipitation with Fe(III) ions, as well as by complexation with hydrous ferric oxide, Fe(OH)$_3$ [13,20,21]. As shown in Section 3.1.1, a higher pH resulted in a higher rate constant even though the effect of pH was not significant within the same system.

Fig. 6 shows the As(III) removal of US/Fe(II) and US/UV/Fe(II) according to power density of US (US frequency: 332 kHz, UV power intensity: 1.38 W cm$^{-2}$, temperature: 22 ± 0.5 °C, and Fe(II) concentration: 12.4 mg L$^{-1}$). Clearly, this result represents a synergetic effect on the combined system of US and UV. At the same US frequency, the production of OH and H$_2$O$_2$ by sonolysis increases as the US power density increases. Through the combination with UV, however, the H$_2$O$_2$ produced by US can be effectively decomposed to OH. This effect may increase the total concentration of OH, even at a low US power densities. Thus, it can infer that the operating energy of US can be reduced through combining with UV.

### 3.2.2. Effect of pH and Fe/As molar ratio on the removal of As(III) by US/UV/Fe(II)

With various molar ratios of Fe(II) to As(III), As(III) (0.2 mg/L) was treated at various pH values in the combined US/UV system. After 1 h of operation, the remained As (as As$_{\text{tot}}$) was measured. The concentration of As$_{\text{tot}}$ was found to decrease as the molar ratio of Fe to As increased (Fig. 7). In addition, the optimum pH was found to be 6.5 in all cases. When the molar ratio was either 83 or 107, the remained As$_{\text{tot}}$ was below 10 μg L$^{-1}$ in the pH range of 6–10. Thus, a molar ratio of 83 for Fe/As could be the optimum dosage for the removal of As$_{\text{tot}}$ to below the regulatory value (10 μg L$^{-1}$).
In the previous study on As(III) removal by US and Fe(II), the XRD analysis of the sludge showed two definitive phases of FeAsO4 and Fe(OH)3 [25]. Definitely, this result of XRD analysis meant that As(III) was oxidized into As(V) which can be further co-precipitated with Fe(III) or complexed with Fe(III), even though it is difficult to find out the partitioning coefficients for co-precipitation and complexation.

As shown in Section 3.1, the oxidation rate constants of As(III) increased as the pH increased. However, after a certain pH value, the remaining As(III) increased again (Fig. 7). Depending on the molar ratio of Fe(II) to As(III), the inflection points of the remaining As(III) increased different. This may be caused by the dominant species at high pH, OH−, competing with Fe(III) in the co-precipitation with Fe(III). In addition, a negatively charged surface group, FeO2−, hinders the complexation of As(V) [16,26]. As an interesting aspect, higher molar ratio of Fe(II) to As(III) had a wider range of pH for As(III) removal. This might be caused by the fact that a comparatively higher amount of Fe(II) could supply more available sites for removing arsenic via co-precipitation or complexation.

3.3. Continuous-flow pilot tests

3.3.1. Oxidation process

As(III)-spiked tap water was prepared for As(III) oxidation by US, UV and US/UV. The oxidation efficiency of each system was measured during continuous-flow tests, and continuous-stirred-tank-reactor (CSTR) modeling was also conducted for comparison with the experimental data. By assuming the oxidation reactor to be a CSTR, the mass balance can be established to determine operational parameters in the water treatment process, such as the hydraulic retention time (HRT).

\[ \frac{dC}{dt} = QC_0 - QC + Vr_c \]  

where \( V \) is the volume of the reactor (m³), and \( C \) and \( C_0 \) are the concentration (mg L⁻¹) of As(III) in the effluent and influent, respectively. \( Q \) is the flow rate and \( r_c \) is the oxidation rate (mg L⁻¹ h⁻¹) of As(III). Eq. (13) can be transformed to Eq. (14) by assuming steady-state conditions (\( dC/dt = 0 \)):

\[ \frac{C_t}{C_0} = \frac{1}{1 + k \times \text{HRT}} \]  

By using the kinetic rate constants obtained from the batch experiments, the ratio of As(III) out to As(III) in the effluent via HRT was obtained from the modeling data (dotted lines in Fig. 8). The pseudo-first-order rate constants obtained from the batch tests were 0.24, 0.204 and 0.684 h⁻¹ for US, UV and US/UV, respectively. The symbols in the figure denote the actual data measured in the continuous-flow pilot tests.

As the HRT increased, the ratios of As(III) out to As(III) in the effluent decreased for all systems. The As(III) oxidation efficiencies for a given HRT were in the order US/UV > US > UV. In particular, for a HRT of 3 h, US/UV had an oxidation efficiency of about 80%, which is about twice that of US (40%) or UV (36%). The similarities between data obtained from the actual tests and those from the modeling were investigated by running t-tests. The ratios of As(III) out to As(III) inlet obtained from the US and UV systems were lower than those from modeling over the whole HRT range. The p-values for US (0.027) and UV (0.003) were lower than 0.05 (the significance level), representing significant differences between the modeled and actual data. However, US/UV had a p-value of 0.343. As shown in the cases using US or UV, the oxidation efficiencies were lower for the actual tests conducted using tap water. This might be caused by the scavenging effect of anionic species such as chloride and carbonate for -OH and H2O2 as shown in the following reactions. Compared to -OH, the product radicals (-CO3⁻, -HO₂⁻, -HOCl⁻ and -Cl⁻) have weaker and slower oxidation potentials [27]:

\[
\begin{align*}
\text{OH} + \text{CO}_3^- & \rightarrow \text{OH}^- + \text{CO}_2 \quad (15) \\
\text{H}_2\text{O}_2 + \text{CO}_3^- & \rightarrow \text{HCO}_3^- + \text{HO}_2 \quad (16) \\
\text{OH}^- + \text{Cl}^- & \rightarrow \text{HOCl}^- \quad (17) \\
\text{HOCl}^- + \text{H}^+ & \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad (18) \\
\text{H}_2\text{O}_2 + \text{Cl}^- & \rightarrow \text{H}^+ + \text{Cl}^- + \text{HO}_2 \quad (19)
\end{align*}
\]

However, when UV is combined with US, the scavenging effect by anionic species might be not seen because H2O2 produced in the radical reaction can be effectively decomposed by UV rather than scavenged by anions.

3.3.2. As(III) removal in the continuous-flow pilot system

To determine the optimum amount of Fe(II) to inject into the US/UV system, 1.5- and 3-h HRTs were selected for the continuous-flow tests with various Fe(II) injection rates (Fig. 9). As the molar ratio of Fe(II) to As(III) increased, As(III) decreased sharply to below 50 mg L⁻¹ for the 1.5-h HRT. However, for the 3-h HRT, more As(III) was removed at the same molar ratio of Fe(II)/As(III) and ~10 mg L⁻¹ As(III) remained at a molar ratio of 91. Thus, when HRT is greater, the oxidation of Fe(II) and As(III) can be enhanced to yield a higher As(III) removal efficiency because the main mechanisms of As(III) removal are the adsorption by Fe(OH)3 and co-precipitation as FeAsO4, which are the solid forms of the oxidized species of Fe and As. However, when the molar ratio was greater than 91, As(III) did not decrease further. From this result, it can be inferred that the
oxidation efficiency can be decreased owing to the limited UV transmittance when the system contains a high concentration of Fe(II).

3.3.3. Sludge treatment using MF

As an engineering aspect, it is needed to optimize the sludge treatment using MF that was adopted as the rapid post-treatment. When the US/UV system was operated with Fe(II) injection rate of 15 mg h⁻¹ and a 3-h HRT, about 15 mg L⁻¹ of suspended solids were produced. Only 30% of SS was removed by the settling basin because the particle size (0.3–3 μm) was too small to settle in the 30-min settling time. Firstly, for effluent containing about 10 mg L⁻¹ of SS, the MF system was operated to determine CF (488 L m⁻² h⁻¹) by measuring the TMP at various fluxes (Fig. 10A). Through passing through MF, filtrate did not contain any SS and remained Asrot. Secondly, the MF system was operated at 50% of the critical flux (244 L m⁻² h⁻¹) to find the operating time cycle. As water passed through, the flux decreased to 130 L m⁻² h⁻¹ and TMP reached 135 kPa after 1200 min (20 h) (Fig. 10B). When the MF system was operated at 30%, 50% and 80% of CF, it reached a steady state of 121, 135 and 248 kPa of TMP, respectively, corresponding to 32, 20 and 12 h of operation time (Fig. 10C). The time required for back washing has a linear relationship with the flux as shown below:

\[
\text{Time (h)} = -0.079 \times \text{flux (L m}^{-2} \text{h}^{-1}) + 42. 
\]  

(20)

4. Conclusions

Several batch tests of US, UV and US/UV systems were conducted to determine the oxidation and removal of As(III) with Fe(II). Continuous-flow pilot tests were also performed to obtain operational parameters such as the molar ratio of Fe(II) to As(III) and HRT. For all tests, the US/UV system had higher efficiencies in As(III) oxidation than either of the single processes, with a synergy index of about 1.5. When Fe(II) was simultaneously added to the US/UV process, As(III) could be removed by oxidation followed by complexion and co-precipitation. As Fe(II) existed, the removal speed of Asrot was comparably higher than the oxidation speed of As(III). This might be due to the participation of Fe(III) in the pseudo-Fenton reaction by US/UV and the complexing effect of Fe(III) with As(V). The optimum molar ratio of Fe(II)/As(III) and pH were found to be 83 and 6–9.5, respectively. The continuous-flow pilot tests of As(III) oxidation by US, UV or US/UV were conducted for various HRTs. CSTR modeling was also performed using the kinetic rate constants obtained in the batch tests. The As(II) oxidation efficiencies determined from the actual tests employing US or UV were lower than those from the CSTR modeling, whereas no differences were seen for the US/UV process. The scavenging effect of anionic species (Cl⁻ and CO₃²⁻) for -OH might dominate in the single processes, whereas it is insignificant in the combined process. As found in the continuous-flow pilot tests, the optimum molar ratio of Fe/As was 91, which is similar to that from the batch tests. The results of the MF operational tests demonstrated that the MF system can treat effluents (~10 mg L⁻¹ SS) from US/UV and settling basin perfectly, and the operational critical flux (CF) and cycle time for the microfiltration (MF) system were optimized to be 244 L m⁻² h⁻¹ and 20 h, respectively. As an energy-utilizing oxidation technique that does not require a catalyst or chemicals, the combined energy of US/UV followed by MF system can effectively treat not only As(III) but also simultaneously occurring Fe(II) in groundwater. However, more studies are necessary to find out the scavenging effect of other anions such as silicate, sulfate and phosphate, as well as reduce the optimum HRT through finding out the design factors. Since US/UV has an enhanced oxidation and energy efficiencies, it has a high potential of application for remediating recalcitrant organic compounds.

Acknowledgments

This work was supported by the Basic Science Research Program through a National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (KRF-2009-0092799) and supported by a Korea University Grant.

References


