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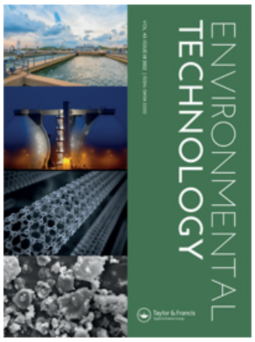

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Evaluation of the dual-process approach for *in-situ* groundwater arsenic removal

Sheng-Wei Wang [a], Shu-Yuan Pan [b], Yu-Hsuan Kao[c], Hyunook Kim[d] and Chihhao Fan [b]

[a]Department of Water Resources and Environmental Engineering, Tamkang University, New Taipei, Taiwan; [b]Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei, Taiwan; [c]Science & Technology Policy Research and Information Center, National Applied Research Laboratories, Taipei, Taiwan; [d]Department of Environmental Engineering, The University of Seoul, Seoul, South Korea

ABSTRACT

While the worldwide distribution of geogenic arsenic (As)-affected groundwater is highly overlapped with the areas with abundant groundwater, utilization of As-contained groundwater is an inevitable compromise in those areas where surface water is not enough for irrigation. Since the occurrence of As in groundwater is often accompanied by high iron (Fe) contents, the facilitation of As and Fe precipitation without adding additional oxidizers and adsorbents is considered an environmental-friendly approach to removing As in groundwater. In the present study, the oxidation/filtration dual-process with sprinkling height of 25 cm and 120 kg filter media efficiently increased the dissolved oxygen (DO) concentration (0.36–1.52 mg/L) and oxidation–reduction potential (ORP) (24–63 mV), which facilitated the formation of Fe oxides and As co-precipitation. The correlation of As removal efficiencies with their respective flow rates indicated that a decrease in groundwater Fe and an increase of Fe in sands and gravels filters as the flow rate increased evidenced the rapid oxidation of Fe to form the Fe hydroxides. In a 40-hour continuous aeration/filtration operation, As and Fe concentrations in groundwater were reduced by 79.5% and 64.88% within 40 hrs, respectively. The ease of filter replacement and cost-effectiveness in operation can be the major attractions and innovations for future field practices.

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CONTACT Chihhao Fan ✉ chfan@ntu.edu.tw Department of Bioenvironmental Systems Engineering, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei 106, Taiwan

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1. Introduction

Water deficiency has been an important issue for years. Due to precipitous slopes of river beds and limited land resources for water storage, water resource management in Taiwan is challenging. Oftentimes, the surface water supply may not be as sufficient and timely as required to meet the water demand for agriculture, resulting in the groundwater withdrawal as the additional water supply. According to the previous study [1], the average water utilization for agriculture accounts for 71.4% of the total water consumption in Taiwan, and groundwater occupies approximately 21.4% of the irrigation water in southwestern Taiwan. However, groundwater contamination by Arsenic (As) has been a concerning issue affecting its potential use for decades. Although As contamination has been proved to originate often from sedimentation processes related to subsurface biogeochemical cycles [2], previous studies indicate that the reductive dissolution of As-bearing iron (Fe) minerals is the dominant geochemical reaction for Fe reduction and As liberation into the groundwater [3]. This mechanism is driven by metal-reducing bacteria and bioavailable organic matter as an electron transformation medium [4]. To ensure the safety of agricultural production and human health, appropriate treatment of As-containing groundwater before its use for irrigation becomes critical to reduce the As accumulation in soil and crops.

For industrial wastewater treatment, numerous methods for eliminating As concentration in water have been reported, including coagulation, electrokinetics, adsorption, ion exchange, membrane techniques, filtration and oxidation [5–7]. Among these methods, coagulation, ion exchange and membrane provide high treatment efficiency (>90%) for As removal [8,9]. However, there are still limitations when applying these physio-chemical technologies to irrigation water treatment. To be specific, the co-existing anions may compete with the target As for coagulation and ion exchange and cause clogging/fouling during the treatment process [10]. Although coagulation, adsorption, and ion exchange have the advantage of cost-effectiveness [11,12], they may encounter difficulties in operation in field practices. To reduce environmental contamination, various techniques have been applied to wastewater treatment, such as electrochemical degradation [13,14] and adsorption by activated carbon [15] and nanoparticles [16]. In conventional agricultural cultivation, farmers would have doubts about adding coagulants on site. The adsorption or ion exchange shows a variety of contamination-removing capacities using different adsorbents or resins, which may not be suitable for the on-site irrigation water treatment compared to the point-of-use and point-of-entry household water purification [17]. Moreover, membrane filtration has excellent removal efficiency, but it is expensive to install, maintain, and operate [18]. In addition to the water recovery during operation, monitoring the blocking and the timing of backwashing for the filter is necessary, which imposes a technical barrier to the operations of the farmers.

Arsenate often exists in solid form with oxidized Fe minerals compared to arsenite. Generally, oxidation refers to the electron-transferring process to form insoluble Fe hydroxides by which the soluble arsenite is oxidized to arsenate. The purpose of oxidation during As removal process is the transformation of soluble arsenite to arsenate, which eventually co-precipitated with the oxidized Fe hydroxides [19]. Previous studies showed the effective arsenite oxidation by chlorine, chlorine dioxide, ozone, hydrogen peroxide, chloroamine, permanganate, and ferrate for As removal [20]. Adsorption is a popular and effective treatment for contamination removal at a low cost. For example, the reuse of coal fly ash facilitates extracting metal and amending soil. Modified coal fly ash is recently developed for polymer-flooding wastewater and coking wastewater treatment [21,22]. Fly ash was also proved as an effective permeable barrier material for removing metals [23,24]. However, the disadvantages of adding oxidants include the enhancement of potential toxicity and carcinogenicity to the ecological integrity and the requirement of sludge removal. The dissolved oxygen (DO) is often regarded as a cost-effective oxidation agent when supplied through natural surface reaeration [25]. However, only 54% of arsenite could be oxidized to arsenate in five days using natural DO. The oxygen transfer rate during the aeration process was controlled by the height of the sprinkle [26]. The results implied that aeration improvement for irrigational As-contained groundwater may be beneficial to Fe oxidation and As precipitation simultaneously. Moreover, oxidation of As-contained groundwater only transforms As into different existing forms, filtration by adsorption or precipitation is the effective process to remove the target element from the solution [5]. The Fe concentration in groundwater was crucial for As removal using a sand filter system [27]. Groundwater with a Fe/As concentration ratio greater than 50 is necessary to ensure As removal to the concentration level lower than 50 μg/L by oxidation and co-precipitation.

The lack of a sustainable approach for cost-effective As remediation is the major challenge for treating groundwater containing As [9]. Nonetheless, the removal of As from groundwater for irrigation shall consider factors of water quantity, operation cost, convenience in access, waste disposal, and farming habits. Therefore, the dual reacting mechanism, combining oxidation and filtration, could be a pragmatic solution to remove As from groundwater. Increasing oxidation rate and As-containing groundwater retention time in the filtering process are the keys to increasing the As removal efficiency. Along with the context, the purpose of this study is to evaluate the *in-situ* As removal efficiency of groundwater using the dual reacting mechanism, combining oxidation and filtration. A variety of aeration methods, filtering media, and flow rates were designed to propose an optimal operation for As removal. The willingness to accept local agriculture practitioners and the installment/maintenance costs for the system operation was also assessed. The significant advantage of the dual-process system in the present study is that the Fe in the As-affected groundwater can induce As precipitation without adding additional adsorbents.

2. Material and methods

2.1. Delineation of the experimental site

According to the periodical groundwater quality monitoring data by Taiwan EPA, the area possessing the groundwater Fe/As concentration ratio >50 covered 53.4% of the total As-contaminated area in Taiwan. The experimental site with high groundwater Fe/As ratio was selected for the study. This site has an agricultural land area of 1417.4 m^2 in central Taiwan in which groundwater pumping well may operate with a maximum withdrawing capacity of 25.2 m^3/hr. The investigated farmland has been irrigated with groundwater for rice growing for decades. The annual water requirement for rice cultivation in the area was 3.062 m^3/m^2. The annual volume of groundwater extraction was estimated to be approximately 4340 m^3.

2.2. Design of the arsenic removal system

The experimental design considered the ease and expense of system operations without causing troubles for agriculture practice, and natural aeration was used without adding oxidants or synthetic adsorbents. The removal system included a storage unit, transporting piping, and a dual-process treatment unit (Figure 1). To avoid the variation caused by unstable water flow, a raw water equalization tank (TK-001) with a volume of $\sim$1.3 m^3 was installed as the buffer and storage. A three-way joint was installed at the well outlet with a valve for flow rate control, connected to a 6-inch polyvinyl chloride pipe. A water-level metre was installed to monitor water-level variation. The transporting piping included the pipelines connecting the well, storage tank, and treatment unit. A pumping motor, flow meter, and pressure gauge were installed to monitor the stability of flow conditions. Ball valves were installed to balance the system pressure. A variable frequency centrifugal pump was used for the flow rate control for the experimental requirement. The outflow from the storage unit was adjusted to examine the As removal efficiency at different flow rates. The system adopted a treatment tank (TK-002) as the fixed-bed filter, upon which uniformly-graded gravels (with an averaged diameter of 2.0 mm) and sands (with an averaged diameter of 0.6 mm) were laid on a stainless-steel perforated plate as the granular filter for As and Fe co-precipitation. SiO_2 (99.5%) is the primary component of gravel and sand. The groundwater was sprinkled above the treatment unit to increase DO concentration when groundwater penetrated through the filtering media (i.e. sands and gravels).

2.3. Operation of the dual reacting system

The *in-situ* experiments were divided into sprinkling and granular filtering experiment (E1), flow rate evaluation experiment (E2), and overall As removal experiment (E3). The operation conditions of each experiment are shown in Table 1. E1 was conducted to evaluate the efficiency of oxidation during the aeration process using different filtering amounts while sprinkling at different heights. The sprinkler at the treatment unit inlet enhanced the surface area of the groundwater droplets, and the turbulence elevated the probability of the air–water contact, thereby increasing the DO in the water. A higher aeration efficiency may be achieved with more favourable turbulence resulting from a greater flow rate and longer water splash time or by moving the sprinkler to a higher position [26]. Three sub-experiments were conducted as follows: (a) sprinkler height of 15 cm and 60 kg of sands and gravels (E1a); (b) sprinkler height of 15 cm and 12 kg of sands and gravels (E1b); and (c) sprinkler height of 25 cm and 60 kg of sands and gravels (E1c). At a given sprinkler height, a 30 min aeration experiment with a flow rate of 2.4 m^3/hr was performed to explore the variation of DO and oxidation–reduction potential (ORP).

Subsequently, a 2 hr experiment (E2) of As removal was performed to optimize the flow rate of this dual reacting system. The experiments with different flow rates were conducted to evaluate the efficiency of As and Fe oxidation and filtration. Three sub-experiments with flow rates of 1.2 (E2a), 2.4 (E2b), and 3.2 (E2c) m^3/hr were conducted. Groundwater was introduced into the treatment system continuously for 2 hr, with a sprinkler height of 25 cm and 120 kg of sands and gravels as the filter material. Lastly, treatment of As-contained groundwater with the continuous flow (E3) was conducted according to the water demand of a full rice cultivation period. This experiment was performed continuously for 40 hr at a flow rate of 2.4 m^3/hr at the sprinkler height of 25 cm using 120 kg of sands and gravels as the filter media.

2.4. Chemical measurement of water samples and filtration grains

Water samples were collected periodically from (Figure 1) the inlet of the treatment tank (A), the filtrate after passing through the filter, (B), and the water outlet of the treatment (C) to evaluate the water quality variation. Filtering materials were vertically collected using handheld shovels and the collected samples were sieved to separate sands and gravel grains. The concentrations of concerning chemicals in groundwater at sampling point A, representing the stabilized inflow groundwater quality, were used as the initial concentrations in each experiment and were compared with the concentrations at the sampling points B and C. The DO, ORP, total As, inorganic As, Fe concentrations of water samples, and As and Fe concentrations on the surface of filter media were measured.

DO and ORP were measured using multiprobe (MiniSonde manufactured by HydroLab, U.S.A.). Cell sensors of ORP were calibrated with standard solutions (all from Merck), which has Eh = 280 mV, in the field before water sampling. The As and Fe concentrations were measured after the collected water samples were filtered with 0.45 μm glass fiber papers and acidified with HNO_3 (Merck ultrapure grade) to pH 2. The As and Fe analyses were conducted following the protocols of NIEA W434.54B and W311.53C, respectively, standard analytical protocols proposed by the EPA of Taiwan.

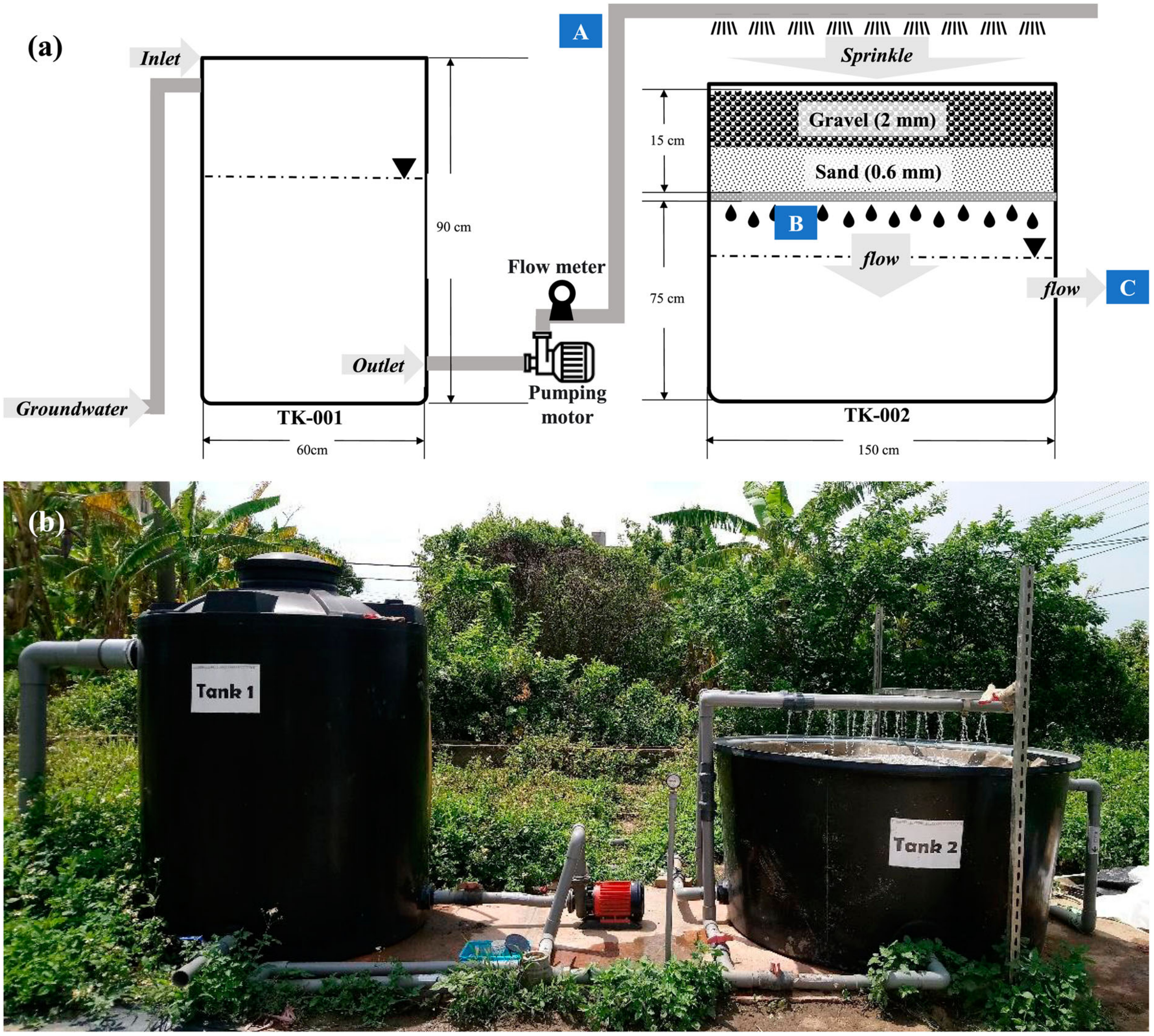

Figure 1. Design (a) and configuration (b) of the agricultural groundwater As removal system. TK-001 and TK-002 represent storage and treatment unit, respectively. A, B, C denote three water sampling locations.

Aqueous As concentrations were determined using an electro-thermal atomic absorption spectrometer (AAS, Perkin-Elmer AA100) equipped with a hydride generation (HG) system (Perkin-Elmer FIAS100). The limit of detection (LOD) and limit of quantitation (LOQ) of As are 0.03 and 1 µg/L, respectively. Aqueous Fe concentration was determined by inductively coupled plasma and atomic emission spectrometry (ICP-OES) (Varian, VISTA-MPX). The limit of detection (LOD) and limit of quantitation (LOQ) of Fe are 0.005 and 0.1 mg/L, respectively. A series of aqueous samples with blank, spike, duplicates and check samples (As a standard solution, H_3AsO_4, 1000 mg/L As; CertiPUR®, Merck Taiwan, Taipei) were measured. The variance of duplicate measurements was less than 10%; recoveries of checked and spiked samples were between 90 and 110%.

Table 1. Operation conditions of the dual reacting As removal system.

		Operation conditions		
Experiment	Hours of operation	Sprinkle height (cm)	Granular filter (kg)	Flow rate (m^3/hr)
E1 – Effect of aeration	0.5	15	60	2.4
		15	120	
		25	60	
E2 – Effect of flow rate	2	25	120	1.2
				2.4
				3.2
E3 – Overall As removal experiment	40	25	120	2.4

In the As analysis, arsenite and arsenate were separated using an anion column (Hamilton PRP-X100, 10 µm, 250 mm × 4.6 mm) connected to high-performance liquid chromatography (HPLC) (Agilent technologies 1260 infinity) that was interfaced subsequently to an inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin-Elmer SCIEX, Thornhill, Ontario, Canada). The mobile phase was a 50 mM $(NH_4)_2HPO_4$ buffer solution (pH = 5) and the flow rate was 1 mL/min. The variances of the duplicate measurements were less than 10%, and the recoveries of the check and spike samples were between 85% and 115%, respectively.

Due to the homogenous solid matrix, semi-quantitative and non-destructive analysis of field portable X-ray fluorescence (XRF), was used following the NIEA S322.60C protocol of Taiwan EPA for determining the solid phase As and Fe. In experiments E2 and E3, grain samples were air-dried over 24 hr. An Olympus Delta Premium XRF fitted with a 50 kV, 4 W Ta anode X-ray tube and a silicon drift detector was employed in the analysis. The XRF was operated following the manufacturer suggestion including measurements of (1) energy calibration check daily, (2) a silicate (SiO_2) blank, and (3) reference materials every 20–25 samples to assure the instrument performance [28].

3. Results and discussion

3.1. Effects of sprinkle height and filter material on the oxidation process

The experimental results of using various amounts of filter materials at various selected sprinkler heights are shown in Figure 2, indicating that the DO increased from 2.67–3 mg/L to 4.43–5.43 mg/L within 30 min, and an apparent increase occurred within the first 10 min of the treatment operation. The ORP of E1a (15 cm sprinkle height with 60 kg filter material) increased slightly from −111 to −89 mV, and that of E1b (15 cm sprinkle height with 120 kg filter material) was elevated the most, from −110 to −48 mV. Although the height of the sprinkler increased in E1c (25 cm sprinkle height with 60 kg filter material), the amount of the filter materials remained the same as that of E1a, causing the ORP to increase from −108 to −85 mV, which was less significant than the ORP change of E1b.

The increase in DO concentration in E1b (with 120 kg filters) with 30 min of aeration was slightly higher than that of E1a (with 60 kg filters), whereas the increase in ORP of E1b was 2.1–3.5 times higher than that of E1a. An increase in the amount of the filters might shift the redox condition from a robustly to a slightly reduced environment, facilitating the occurrence of Fe and As oxidation. In this study, sprinkler heights of 15 and 25 cm were selected to evaluate the aeration efficiency. DO concentrations and ORP of P1a and P1c increased by 6.3% and 4.6% at the 30th minute, respectively (Figure 2). This result indicated that the oxygen transfer rate increases with increasing sprinkling height. Increased sprinkling height extended the flight time of the droplets, which conduce the oxygen transfer. More atmospheric oxygen could be dissolved into the water [26]. However, excessively high sprinkling may cause the water to be susceptible to wind and spill out of the tank. Compared to the results of the E1 experiment, the E2 and E3 experiments employed the sprinkler height of 25 cm and 60 kg of sands and 60 kg of gravel for subsequent exploration.

3.2. Effect of oxidation–filtration on reducing groundwater as concentration

Figure 3 shows the results of the continuous aeration at different flow rates. An insignificant difference was observed in the equilibrated DO concentrations at location B among the three tested flow rates. The sprinkler and filtering process increased the DO by 0.92–1.73 mg/L on average. The DO at sampling point C was slightly higher than that at point B, indicating the additional contact of outflow water with atmospheric oxygen. The ORP of E2a at locations B and C increased from −102.67 mV (location A) to −1 and −6 mV, respectively, within 30 min, and remained stable until the end of the experiment (120 min). When the flow rate was raised to 2.4 m^3/hr, the ORP at location B and the outflow water (C) increased from −99.7 mV (location A) to −46.3 mV and from −99.6 mV (location A) to 1.0 at first 30 min, respectively, then slightly reduced to −73.3 mV and −41.5 mV within 90 min. The variation of ORP over time was affected by the flow rate. The low flow rate was responsible for the formation of a more oxidative environment. Taking the tank volume of ~1.3 m^3 as an example, the flow rate of E2c was 3.2 m^3/hr and the tank was nearly full in 25 min. The bottom of the tank was in an undisturbed condition after 25 min, resulting in the ORP at location C of E2c as nearly reductive as the original groundwater condition.

According to the groundwater As and Fe concentrations of each test at locations B and C (Figure 4), the As concentration at a flow rate of 1.2 m^3/hr (E2a) dropped from an average of 52.48–42.78 μg/L (B) and 42.29 μg/L (C) within 30 min, respectively and remained stable until the end of the experiment (120 min). For the experiment of E2b, the As concentration did not decrease markedly, maintaining the As concentration of around 49 μg/L at locations B and C. The effect of flow rate on the removal efficiency of groundwater As was also examined in the laboratory filtration column experiments [29]. The diminished effectiveness of As removal can be accounted for by the decrease in the

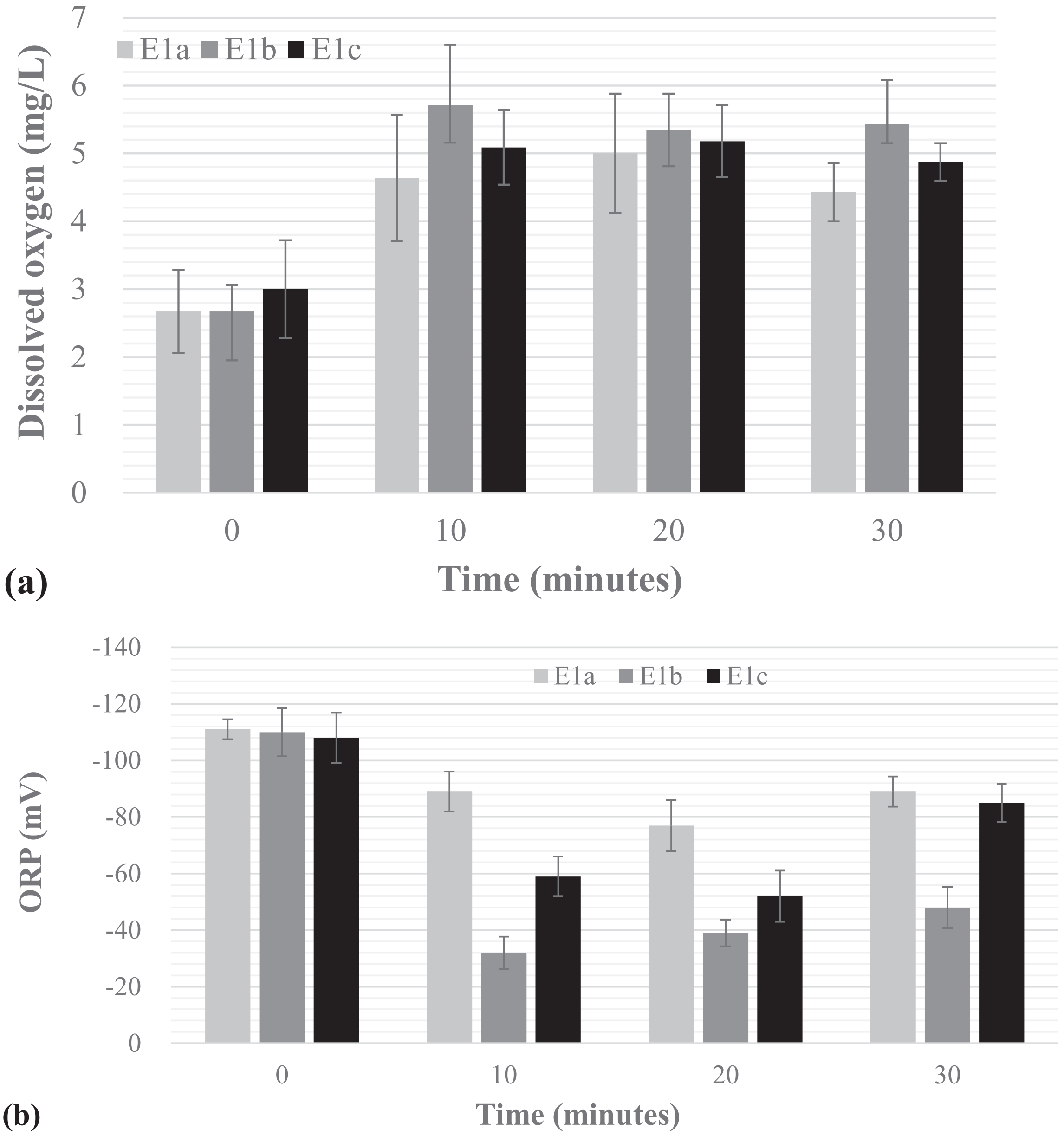

Figure 2. Variations of (a) DO concentration and (b) ORP of E1 experiment within 30 min after passing through the filter (Location B). Experiments of E1a, E1b, and E1c denoted 15 cm sprinkle height with 60 kg filter material, 15 cm sprinkle height with 120 kg filter material, and 25 cm sprinkle height with 60 kg filter material.

contact time of groundwater with filters. Although the As concentration of E2c at B and C dropped from 56.22 µg/L to 51.28 and 50.59 µg/L at the first 30 min, respectively, it increased to 73.43 µg/L (the 60th minute at B) and 68.24 µg/L (the 90th minute at C) afterwards. Groundwater As reduction is per ORP variation (as shown in Figure 3(d–f) and Figure 4(a–c)), which implies that the redox condition dominates the co-precipitation of As with Fe. Increased flow rate caused insufficient retention time of groundwater when passing through the filter layers. Moreover, even though the As concentration decrease in water was limited, the Fe concentrations in water in the three different flow rate experiments were declined, from 3.33–5 mg/L (location A) to 0.12–0.67 mg/L (location B) and 0.15–0.6 mg/L (location C).

By considering the geochemical characteristics of aqueous As and Fe species, ferrous iron may be easily oxidized under weak reductive to oxidative conditions and can be described by Equations (1) and (2) [30].

$$4Fe^{2+} + O_{2(g)} + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \qquad (1)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \qquad (2)$$

Ferrous iron can be readily precipitated in the form of amorphous $Fe(OH)_3$ with increasing ORP, which greatly

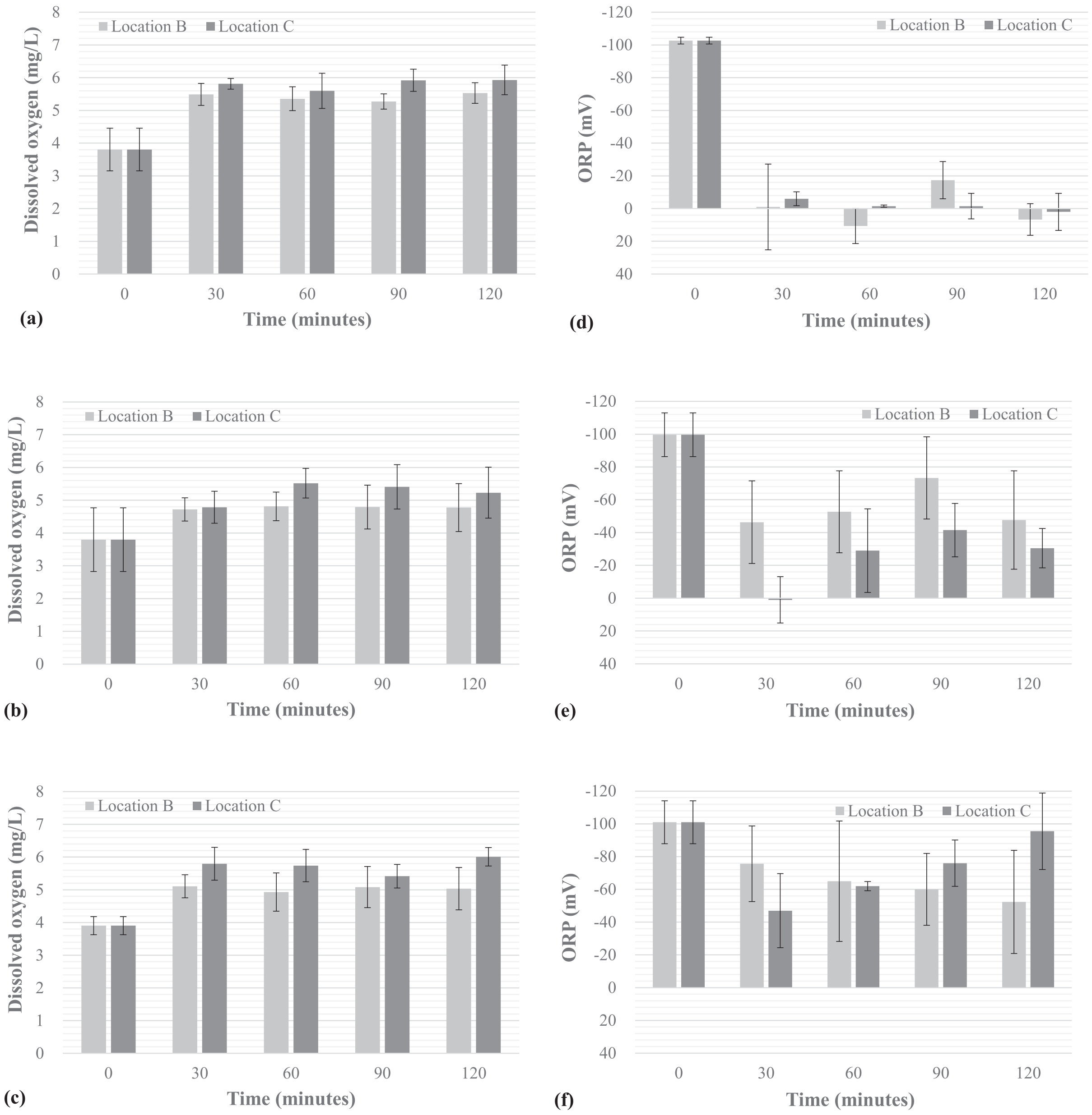

Figure 3. Variations of DO concentration (a)–(c) and ORP (d)–(f) of E2 experiment with different flow rates of 1.2, 2.4, 3.2 m^3/hr, respectively.

reduced the aqueous Fe concentration. Figure 5(a) indicates that the Fe concentrations on the surface of the sands and gravels increased with the increasing flow rate. For the gravels at the upper layer after 120 min of continuous aeration at flow rates of 1.2, 2.4, and 3.2 m^3/hr, the Fe concentrations increased by 290.44, 950.35, and 2019.61 mg/kg, respectively. Moreover, the sands at the lower layer also showed a slight increase in Fe concentrations except for the E2a experiment (1.2 m^3/hr). After 120 min of continuous aeration at flow rates of 2.4 and 3.2 m^3/hr, the Fe concentration increased by 274.67 and 936.44 mg/kg, respectively. The increase in Fe concentration on sands and gravels is not proportional to the flow rate increase, implying the occurrence of ferrous iron oxidation and Fe hydroxides precipitation on the filtering media surface.

Occurrence of As oxidation coincided with the oxidation of dissolved ferrous Fe by DO [31]. The oxidation of arsenite can be described by Equation (3) [32]. Arsenite has a low affinity to mineral surfaces, while arsenate adsorbs more easily onto solid surfaces. The adsorption affinity of arsenate to Fe hydroxides is stronger than that of arsenite [33]. Co-precipitation of As with oxidized Fe and adsorption of As onto the surface of adsorbents are two primary mechanisms of Fe-based As removal [34]. The presence of As oxyanions led to

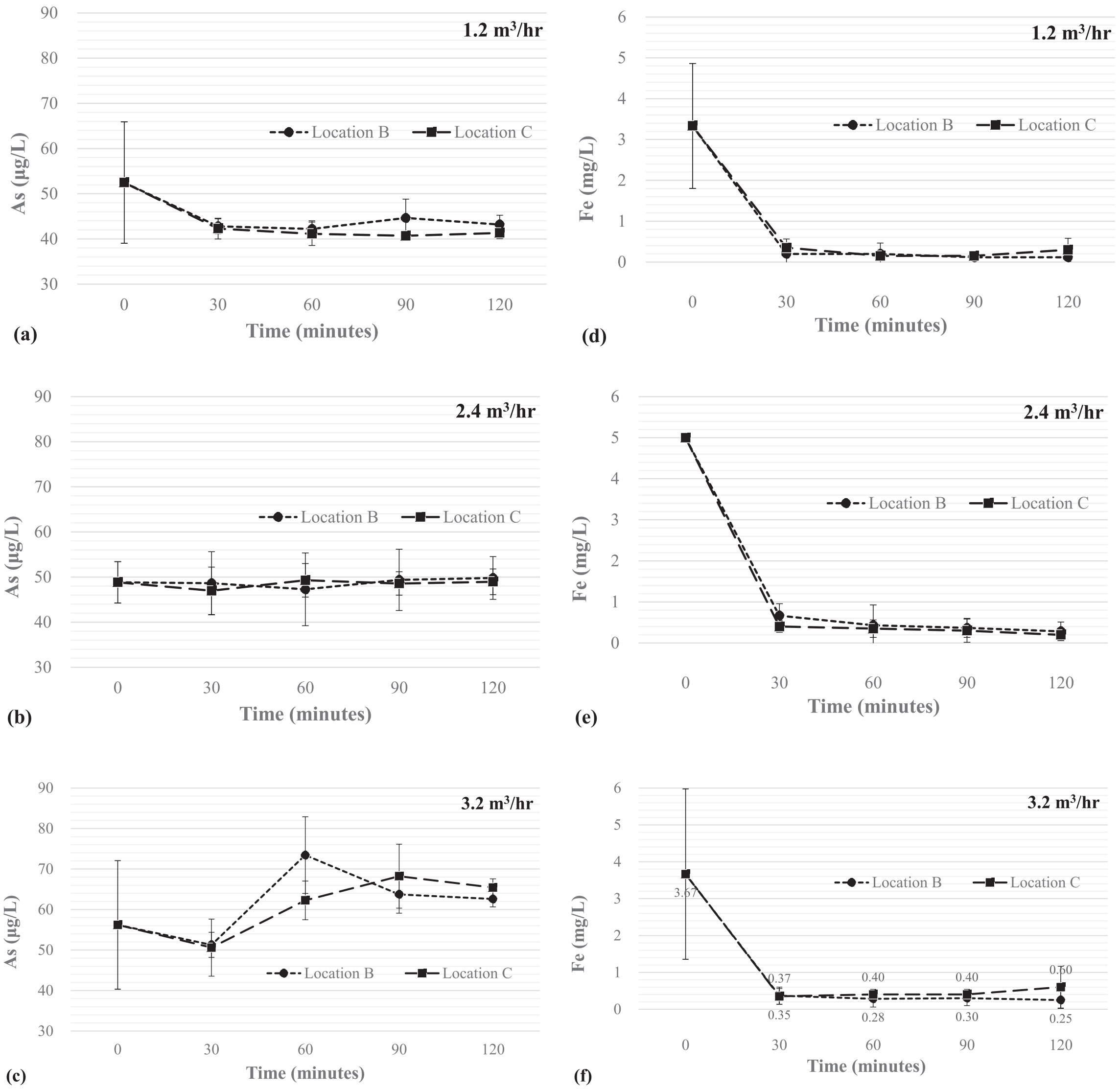

Figure 4. Variations of groundwater As (a)–(c) and Fe concentration (d)–(f) of E2 experiment with different flow rates of 1.2, 2.4, 3.2 m^3/hr, respectively.

incomplete hydrolysis of ferric Fe, such as $Fe(OH)_3$, which then complexed with As during the co-precipitation process, whereas Fe (hydr)oxides are formed before the participation of As during the adsorption process. The high groundwater Fe/As concentration ratio in this study favoured the formation of hydrolyzed ferric ions and the co-precipitation with arsenite and arsenate, which is the dominant reaction of As removal as shown in Equations (4) and (5).

$$2H_3AsO_3 + O_2 \rightarrow 2H_2AsO_4^- + 2H^+ \quad (3)$$

$$Fe(OH)_3 + H_3AsO_3 \rightarrow FeAsO_3 + 3H_2O \quad (4)$$

$$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4 + 3H_2O \quad (5)$$

Figure 5(b) shows that the As concentrations on the surface of the sands and gravels increased with the increasing flow rate. For the gravels at the upper layer after 120-min aeration at flow rates of 1.2, 2.4, and 3.2 m^3/hr, the As concentration increased by 3.5, 3.12, and 7.84 mg/kg, respectively. Moreover, the sands laid at the lower layer also showed a slight increase in the concentrations of Fe except for the 1.2 m^3/hr operation. After 120 min of continuous aeration at flow rates of 2.4 and 3.2 m^3/hr, the As concentration increased by 1.56 and 2.68 mg/kg, respectively. Previous studies indicated that filter grains with different particle sizes were able to provide sufficient sorption sites on the solid surface [35], and prevent As accumulation in the agricultural ecosystem. An increase in the As concentration on solid with increasing flow rate suggested that more precipitated ferric iron oxides on sands and gravels surface is helpful for As removal via co-precipitation. Figure 6 shows that the initial groundwater arsenate concentration at location

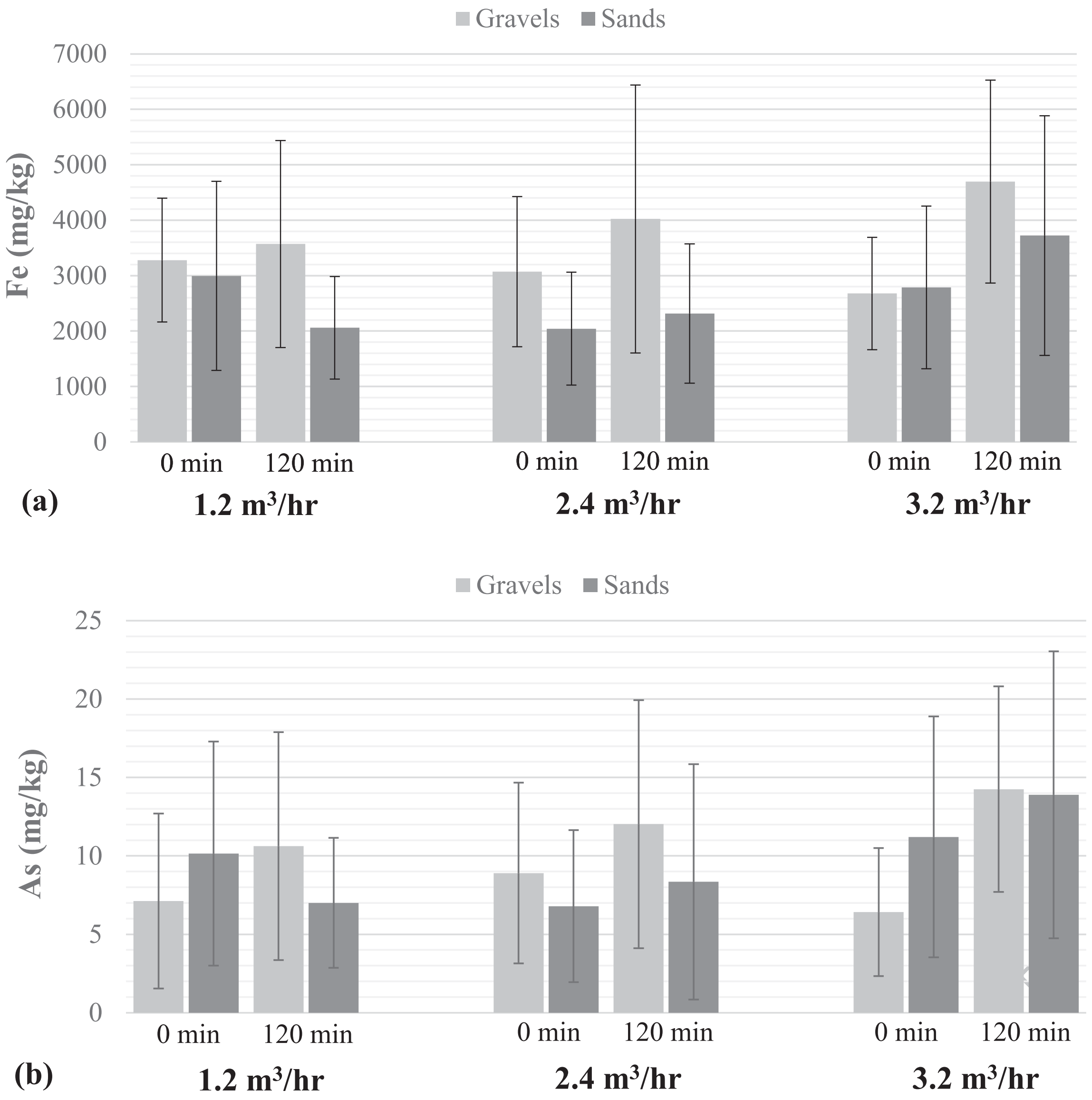

Figure 5. Initial and final (a) Fe and (b) As concentration of sands and gravels filtering granules of E2 experiment with different flow rates of 1.2, 2.4, 3.2 m^3/hr, respectively.

A in the experiments with different flow rates accounted for 2.19%–3.82% of the total As concentration removal. After 120 min of aeration, the concentrations of arsenate at location B were 29.19%, 10.15%, and 6.03%, showing a decreasing trend as the flow increased. Inorganic arsenite and arsenate are two of the most common forms in groundwater. The toxicity of arsenite is much higher than that of arsenate [36]. The sprinkle in this dual-process system facilitates not only the oxidation process but also the detoxification.

3.3. Efficiency of groundwater As removal system by the oxidation-filtration dual mechanism

The operation of groundwater pumping for rice farming usually continues for tens of hours in Taiwan. To understand if long-term pumping improves the oxidation-filtration efficiency, a 40 hr continuous aeration and filtration experiment (E3) was conducted. The flow rate was selected at 2.4 m^3/hr, which is an often-employed pumping rate in field practice. The other operating conditions remained the same as those in the E2 experiment. Figure 7(a,b) indicates that DO and ORP at location B increased in a pattern similar to that in the 2 hr experiment (Figure 3(b,e)). Aeration increased the DO and ORP by 0.36–1.52 mg/L and 24–63 mV, respectively. Because this study site is an area with many irrigation wells, the pumping of surrounding wells may have caused fluctuation of oxygen that entered the aquifer during the experiment period, causing a slight variation of DO and ORP. Anyhow, arsenic and Fe concentrations dropped by 62.76% and 61.27%, respectively, at location

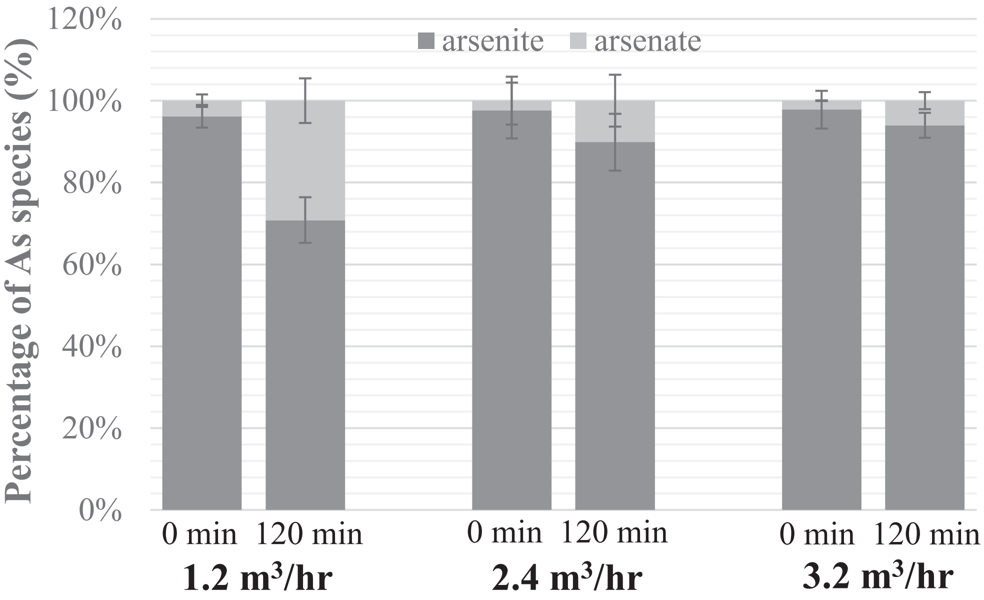

Figure 6. The converted ratio of groundwater arsenite to arsenate of E2 experiment with different flow rates of 1.2, 2.4, 3.2 m^3/hr during 120 min aeration.

B, and 60.49% and 48.41% at location C within the first 8 hr (Figure 7(c,d)). From the 8th to the 40th hour, the removal efficiency remained around 79.5% and 64.88% for As and Fe at location C, respectively. The concentrations of As and Fe at sampling point C were identical to those at sampling B, implying the chemical equilibrium of treated groundwater after the oxidation and filtration reactions in this system. Increasing the groundwater retention time in the tank helps the oxidation reactions and prevents settled particles from re-suspension. It should be noted that DO concentration at sampling point C is higher than at point A and the As and Fe concentrations at sampling point C are more stable than at point A.

Furthermore, an increase in the As and Fe concentrations in the filter materials with time indicated that immobilization of As and Fe within a 40-hr operation can meet the irrigational water demand of the cultivation period of the investigated site, and the final concentrations of As and Fe of the gravels at the upper layer were 2.60 and 2.25 times of those of the sands underneath and remained stable after 40 hr (Figure 7(e,f)). This result revealed that after aeration, the groundwater passing through the filter materials caused As and Fe to precipitate on the surface of sands and gravels, and the concentrations of As and Fe in the water presented a decreasing trend. According to the results of the E3 experiment, the groundwater As and Fe concentrations can be effectively reduced via oxidation and filtration using this dual reacting system to meet the standards of irrigational water quality (i.e. 50 µg/L and 5 mg/L for As and Fe, respectively).

3.4. Evaluation of the environmental and socioeconomic benefits of the dual-process system

To assure sufficiency in food provision, As-containing groundwater is often used for irrigation due to scarcity in surface water resources [37]. The main agricultural crop in Asian countries is rice, which is highly water-consuming cultivation. For the average water consumption of two-period rice cultivation, the maximum water consumption period was the panicle formation period (about 10 days) and the flowering period (about 18 days) with a flooding water depth of 10 cm. For the paddy field selected in this study, the maximum water consumption is 141.74 m^3, and As removal with a flow rate of 2.4 m^3/hr requires approximately 2.5 days of continuous pumping. The flow rate of the Fe-based As removal approach for agricultural irrigation (2.4 m^3/hr in this study) is different from those in household drinking water (6×10^{-3}–6×10^{-2} m^3/hr) [27] and industrial wastewater treatment (8×10^{-5}–1.6×10^{-4} m^3/hr) [29], so that the pumping flow rate must conform to the field irrigation habits, equipment operations must be simplified, and filter materials must be low-cost and easy to obtain. A low flow rate operation may be beneficial to the oxidation and co-precipitation of As and Fe, but it may not be able to meet the sufficient water demand during irrigation. An increase in flow rate merely improved the flux of arsenite through filter grains but did not improve the oxidation rate and adsorption affinity of oxidized arsenate. Besides, the proposed dual-process system was designed for simple use

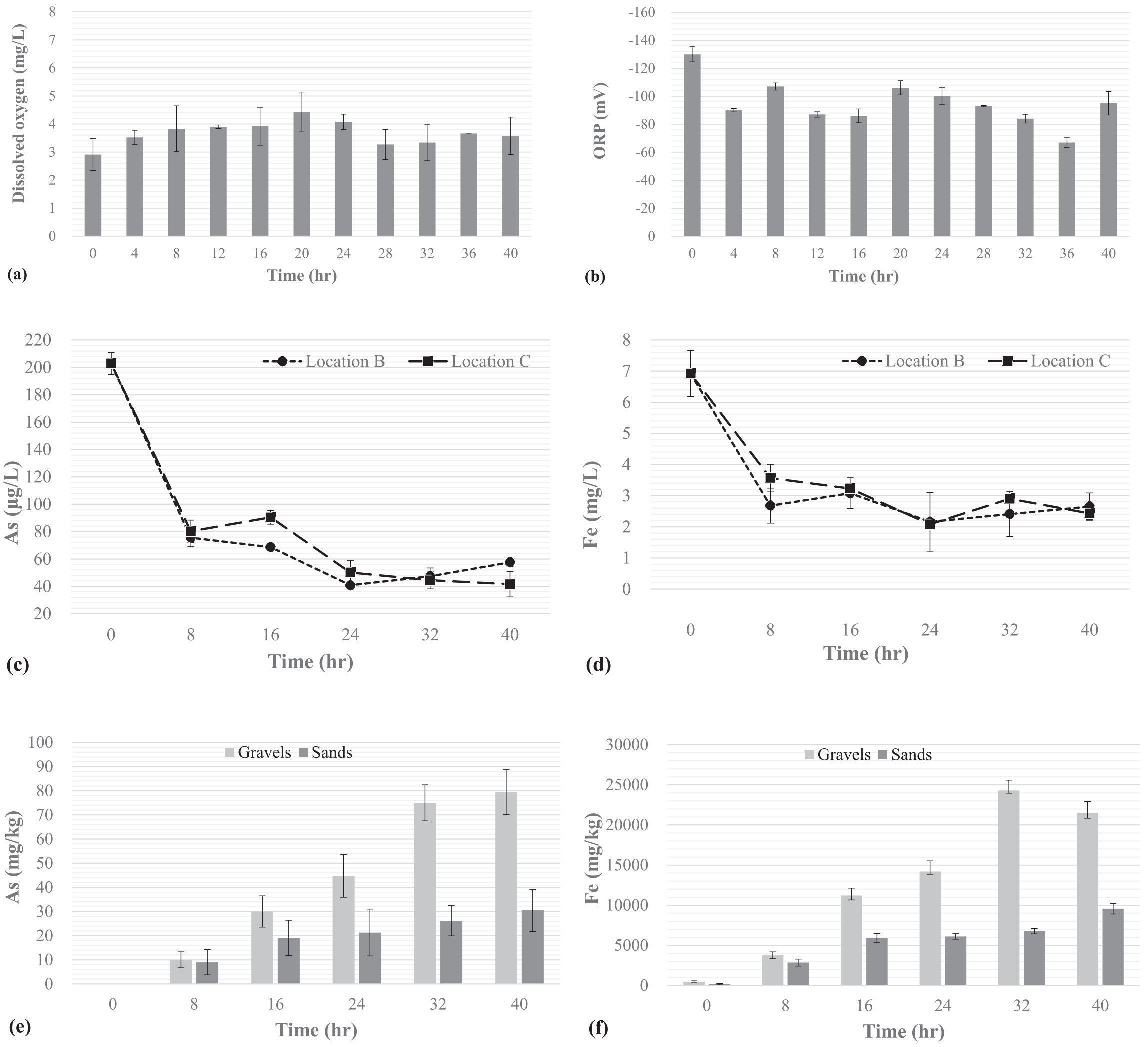

Figure 7. Performance of the agricultural groundwater As removal system with 40 hr continuous pumping. (a) and (b) represented the DO concentration and ORP variation, respectively. (c) and (d) represented the groundwater As and Fe concentrations at location B and C, respectively. (e) and (f) represented accumulated As and Fe concentrations on gravel and quartz sand, respectively.

with regular pumps, polyvinyl chloride pipes, polyethylene tanks, and easily available sands and gravels grains, under the premises of inexpensiveness and easy operation.

Urbanization has caused the fragment of agricultural land in the past few decades [38]. In Taiwan, the arable farmland area is only 1.1 ha per owner on average, and the area of the 75.2% of these owners is less than 1 ha. This resulted in the rapid increase in the installation of private pumping wells due to a limited farming scale. Southwestern Taiwan is the most important rice cultivation area that produces more than 40% of rice in Taiwan. Agricultural activities in the past decades enabled the increase of irrigation wells above 150,000. The farmers have to face the threat of As bioaccumulation in crops using groundwater for agricultural cultivation. The proposed dual-process As removal system can reduce about 60.49–79.5% of As concentration and the treatment efficiency can be improved by incorporating the recycling of the outflow, which provides a practical solution for As removal of groundwater. To meet the irrigation water demand of greater farmland area, the As removal systems developed in this study should be installed more to ensure the effective removal of As in groundwater.

In terms of the social benefits, the ease in equipment operation shall increase the acceptance of using such a treatment system for the public. The system needs to be assembled before the start of cultivation, and the sands and gravels should be replaced after harvest. Only 4–5 m^2 of space was required for the system establishment. The equalization tank may not be required if low-flow wells were used. It should also be noted that additional chemicals were not required, neither for the granular filter nor the storage tanks. Although adding more sands and gravels to the tank may improve the removal efficiency, 120 kg of sands and gravels were considered adequate based on the practical conditions, including economical affordability, the maximum load allowed of the tank, and the ease in filtering media replacement. In addition, the used filter materials can be reused for construction and landscape engineering in compliance with domestic regulations.

For the cost-effectiveness, the expense of the system included approximately 1000 USD for equipment installation and 200 USD for operation and maintenance for 10 years, including replacement of filter materials twice a year. Table 2 shows the cost of construction and operation of the As removal dual-process system. The cost for initial construction and operation for 10 years is approximately 3000 USD. In this study, the volume of treated groundwater is approximately 4340 m^3/year. Hence the cost for As removal is about 0.07 USD/m^3. The annual profit of rice cultivation in Taiwan was 4740.8 USD/ha [39], while the compensation policy for contaminated paddy soil is approximately 3100 USD/ha per year, which is still economically less favourable than using the groundwater As removal system for crop growing. The primary As removal approaches for in-situ applications are oxidation, adsorption, and coagulation (as shown in Table 3). Adding additional oxidizers and/or adsorbents increases the removal efficiencies; however, the cost-effectiveness and treatment efficiency are the major concerns for further application. According to the dual-process system proposed by this study, oxidation by sprinkling and filtration using granular filtering media can achieve the sustainable use of water resources in line with social-economic expectations. Under the circumstances that alternative irrigation water is unavailable, the proposed As removal system can greatly reduce As and Fe concentrations with reasonable construction and operation costs. Extended application of this system in the future shall effectively prevent As bioaccumulation of agro-environment and conduce sustainable utilization of arable farmlands.

Table 2. Evaluation of the main operating costs of the As removal system.

Items	Operating cost (USD)
Construction (Assuming this system can be used for 10 years)	
Tanks	400
Sprinkles	100
Piping and Motor	500
Subtotal	1000
Operation and maintenance (For two cultivation periods per year)	
Sands and gravels (120 kg)	80
Solid waste treatment	120
Subtotal	200
Total cost for 10 years	3000
Cost for As removal (per m^3)	0.07

Table 3. Efficiency and cost of *in-situ* groundwater As removal for dominant techniques (Based on Shan et al., 2018).

Technology	As removal efficiency (%)	Operating cost (USD/m^3)
Oxidation	95–98.2	Near 0–0.17
Coagulation, precipitation and filtration	82.1–99.2	Near 0–1.11
Adsorption	90.98	0.11–70.5
Membrane-based processes	Not available	Not available
Ion exchange processes	Not available	Not available
Bioremediation	Not available	Not available
Oxidation, precipitation, and filtration (This study)	79.5	0.07

4. Conclusion

In the present study, the dual-process groundwater As removal system to remove As through co-precipitation with Fe oxides was evaluated. The result of a 40-hr operation at the flow rate of 2.4 m^3/hr showed that the groundwater As and Fe concentrations dropped apparently by 62.76% and 61.27% within the first 8 hr and subsequently improved to 79.5% and 64.88% at the end of the experiment, respectively. The system operates with appropriate sprinkler height above the granular filtering media and enhanced the DO concentration and ORP of the investigated groundwater, which would further facilitate the Fe and As co-precipitation. Similar to the findings from previous studies, this study demonstrated that oxidation of As increases the ability of As to co-precipitation with Fe oxides under the geogenic condition of As and Fe coexistence in a subsurface environment. For high Fe/As-containing groundwater, abundance in Fe is sufficient for co-precipitation of arsenite and arsenate. The strengths of this treatment are to improve the oxidation rate of As and Fe by sprinkling and to immobilize As with sufficient native groundwater Fe contents. In addition to the As removal efficiency, (1) low cost of the system construction and (2) ease in operation and maintenance increase the willingness of local farms for using such a system. The dual-process groundwater As removal system provided an effective treatment of Fe and As and can be promoted to treat groundwater containing high As.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

Data are available on request from the authors.

ORCID

Sheng-Wei Wang http://orcid.org/0000-0001-5729-1978
Shu-Yuan Pan http://orcid.org/0000-0003-2082-4077
Chihhao Fan http://orcid.org/0000-0002-9840-1835

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