

Effect of Sulfate Load on Sulfur Removal in Model Constructed Wetlands

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Abstract. Four model constructed wetlands (CWs) were designed to investigate the effects of sulfate load on sulfate and sulfide removal. The results showed that as the sulfate load increased from 1.42 to 7.01 g S m⁻³ d⁻¹, the sulfate removal rate increased from 1.42 to 3.16 g S m⁻³ d⁻¹, and the sulfide discharge rate increased from 0.08 to 1.46 g S m⁻³ d⁻¹. The total sulfur removal rate ranged between 1.29 and 1.74 g S m⁻³ d⁻¹. The sulfide in the effluent only accounted for 5.55%–46.9% of the removed sulfate. This indicated that CWs can effectively reduce sulfide discharge while removing sulfate. The conversion of dissolved sulfide into deposited sulfur by CW matrix was a main way for sulfide removal. Elemental sulfur, acid volatile sulfide (AVS), and pyrite-sulfur were the main forms of sulfur deposition in this study. The accumulations of these three sulfur compounds were 16.6–36.2, 22.3–36.0, and 49.7–63.6 mg S kg⁻¹ gravel, respectively. Sulfur balance analysis showed that 42.9%–71.1% of the removed sulfate was deposited in the matrix, and only 0.84%–2.34% was absorbed by the plant.

1. Introduction

Domestic sewage and industrial wastewater both contain sulfate. The sulfate concentration in the municipal sewage is generally 40–200 mg L⁻¹ [1]. In some coastal areas such as Hong Kong, the sulfate concentration in the municipal sewage is 500 mg L⁻¹ due to using seawater to flush the toilet. Sulfate not only has a corrosive effect on the concrete structure of buildings at high concentrations [2], but also accelerates the release of phosphorus in riverbeds and aggravates the water eutrophication [3]. In the anoxic condition, the sulfide produced from sulfate reduction would cause black odor, and damage the health of plants, animals as well as humans [4]. Therefore, the removal of sulfate in sewage has attracted more and more attention.

Anaerobic biological treatment is widely used for treating sulfate-containing wastewater at present. The main forms include anaerobic filter, anaerobic sequencing batch sludge process (ASBR), up-flow anaerobic sludge bed (UASB), and so on. Sulfate reduction is the main sulfate removal pathway in these technologies. However, sulfide will usually be produced during sulfate reduction, which accounts for about 70%–93% of the removed sulfate [5, 6]. Therefore, it is necessary to combine with the biological or chemical oxidation of sulfide to achieve sewage discharge standard [7, 8]. This greatly increases the construction and operation costs.

Constructed wetlands (CWs) are widely used for treating wastewater due to their low implementation costs and simple operation [9]. It has been found that the anoxic condition in CWs can provide favorable conditions for sulfate reduction [10]. Wiessner et al. [11] found that the sulfate removal efficiency in CWs was up to 90%. Simultaneously, the CWs can effectively control sulfide



discharge. Wiessner et al. [11] also found that sulfide in the effluent of CWs was 8%–20% of the removed sulfate. While in the study of Chen et al. [12], the ratio was only 1%–4%. Therefore, using CWs to treat sulfate-containing wastewater can make up the defects of the traditional anaerobic biological treatment and save the costs. However, the mechanism of simultaneous removal of sulfate and sulfide in CWs has not been completely elucidated to date, and further studies are still needed. Moreover, it has been shown that sulfate load could affect sulfate reduction rate, and therefore affect the sulfate removal and sulfide discharge [13]. This indicated that the sulfate load is an important parameter for the performance of CWs in treating sulfate-containing wastewater. Hence, it is necessary to explore the influence mechanism of sulfate load on sulfate and sulfide removal in CWs.

Therefore, the objective of this study were to quantitatively investigate the mechanism of sulfate and sulfide removal based on the sulfur analysis, and elucidate the effects of sulfate load on sulfate and sulfide removal in CWs.

2. Materials and Methods

2.1. Experimental design and operation

Four sequencing batch CWs microcosms (length: 0.3 m, width: 0.3 m, height: 0.5 m) with a pore volume of 12 L, were set up in this study. Each of them was filled with gravel (ϕ 8–13 mm, porosity: 0.4, height: 0.4 m), and planted with cattail (*Typha latifolia*) (density: 22 plants m^{-2}). The wetland microcosms were located in an air-conditioned greenhouse environment (25 ± 2 °C).

2.2. Batch experiment

In order to cultivate the plant shoots and microorganisms, the microcosms were operated in batches over a 30-day pre-incubation period. The batch experiment began after this pre-incubation period and lasted for 22 batches. Each batch of the pre-incubation and batch experiment lasted for 5 d.

The secondary effluent was collected from a neighboring wastewater treatment plant and its characteristics are shown in table 1. Concentrated glucose and starch (at a chemical oxygen demand (COD) ratio of 1:1), potassium nitrate, and sodium sulfate solutions were added to achieve the target COD, nitrate, and sulfate concentrations for the influent used in the pre-incubation and batch experiment (table 1).

Table 1. Characteristics of the WWTP secondary effluent and the microcosm influent^a.

Parameters	Concentration ^a (mg L ⁻¹)						
	COD	NO ₃ ⁻ -N	NO ₂ ⁻ -N	NH ₄ ⁺ -N	TN	SO ₄ ²⁻ -S	TS
WWTP secondary effluent							
	19.8 ± 2.2	9.8 ± 1.3	0.9 ± 0.3	1.7 ± 0.3	14.5 ± 2.5	20.5 ± 2.1	21.6 ± 1.5
Microcosm influent for the pre-incubation and batch experiment							
W1	421.5 ± 23.6	43.5 ± 2.9	1.2 ± 0.5	1.8 ± 0.3	14.5 ± 3.5	21.3 ± 0.7	21.1 ± 3.5
W2	430.8 ± 32.5	43.6 ± 3.0	0.9 ± 0.3	1.5 ± 0.4	15.0 ± 2.5	41.6 ± 1.5	42.4 ± 5.3
W3	423.2 ± 35.2	43.9 ± 2.6	1.0 ± 0.5	1.8 ± 0.4	14.7 ± 3.5	62.2 ± 1.4	62.9 ± 5.4
W4	419.5 ± 25.5	43.5 ± 2.6	1.0 ± 0.6	1.7 ± 0.4	14.7 ± 3.5	105.2 ± 1.8	107.8 ± 6.5

^a Values are given as mean ± standard deviation (n = 22).

2.3. Analysis of Aqueous Samples

Aqueous samples were taken with a 10 mL syringe at 0, 0.5, 1, 1.5, 2, 4, 8, 12, 22, 28, 36, 46, 52, 60, 70, 76, 84, 96, 100, 108, and 120 h. Sulfide was immediately analysed via the methylene blue method after the water sample was filtered through 0.45 μm membrane filters. Sulfate, sulfite, thiosulfate, and nitrate concentrations were determined by a DX ICS-3000 ion chromatography unit (Dionex

Corporation, Sunnyvale, CA, USA). Elemental sulfur in the pore water was determined by extracting samples with chloroform and analyzing by a HPLC (Agilent 1200, Agilent Technologies, Santa Clara, CA, USA) [14]. COD was determined by using standard method [15].

2.4. Analysis of Gaseous and Solid Samples

The volatilization rate of hydrogen sulfide was determined by a passive sampler (RAD 170, Supelco, Bellefonte, PA, USA). Before and after the batch experiment, aboveground and belowground plants were harvested and separated, followed by washing, drying, milling, and filtering by a mesh filter (200 meshes). Sulfur content in the plant was analyzed with an elemental analyzer (Vario EL III, Elementar, Hanau, Germany). 100g gravel was evenly weighed from the different depths of each microcosm (10, 20, 30, and 40 cm). After crushing, the gravel powder was used for measuring the form of deposited sulfur. AVS was extracted by cold diffusion absorption [16]. Acetone washing was used to extract residual sediment from AVS (5000 rpm centrifuge 5 min). 20 mL acetone was added to the remaining sediments. Then sealing and shaking the mixture for 24 h [17]. The precipitate of acetone centrifuge was used to determine pyrite-sulfur. The supernatant was transferred to the 500 mL wide mouth bottle, sealed, and evaporated to dry for determining the elemental sulfur. Both pyrite-sulfur and elemental sulfur were determined by Cr-reduction [18].

3. Results and discussion

3.1. Sulfate and sulfide in CWs pore water

As shown in table 2, the sulfate removal rate were 1.42, 2.24, 2.53, and 3.16 g S m⁻³ d⁻¹ in W1–W4, respectively, which was within the range reported by Moosa et al. [13]. Only W1 achieved complete sulfate removal, and the sulfate removal efficiency of W2–W4 were 80.9%, 61%, and 45.1%, respectively. As shown in figure 1(a), the sulfate concentration of W1–W4 was firstly increased from 21.3, 41.6, 62.2, and 105.2 mg S L⁻¹ to 26.9, 47.5, 71.4 and 117.6 mg S L⁻¹, and then decreased to 0, 7.93, 24.3, and 57.8 mg S L⁻¹, respectively. The 0–8 h period in this study was the nitrate-removal period (data not shown). Previous studies have shown that the nitrate can inhibit the sulfate reduction, meanwhile, it can also oxidize the reduced deposited sulfur in the gravel to sulfate [12], and this explained the reason for the increase of sulfate concentration during the initial 8 h. In this study, nitrate was completely removed at 8 h, which relieved its inhibition on sulfate removal, so the sulfate concentration decreased during the 8–120 h period.

Table 2. Sulfate removal rate and efficiency in the microcosms

Microcosm	Removal rate ^a (g S m ⁻³ d ⁻¹)	Efficiency (%)
W1	1.42	100.0
W2	2.24	80.9
W3	2.53	61.0
W4	3.16	45.1

^a The sulfate removal rate was calculated as follows: $SO_4^{2-}{}_{\text{removal}} = (C_{\text{in}} - C_{\text{out}}) V_w V^{-1} \text{HRT}^{-1}$, where $SO_4^{2-}{}_{\text{removal}}$ is sulfate removal rate (g S m⁻³ d⁻¹); C_{in} , C_{out} are the sulfate concentrations in the influent and effluent (mg S L⁻¹), respectively; V_w is the working volume (L); V is the gravel volume (m³); HRT is the retention time for every batch (d).

As the final product of sulfate reduction, sulfide is also a dominant sulfur compound in the pore water. As shown in figure 1(b), sulfide could only be detected when sulfate started removal (8 h). The sulfide concentrations in the W1–W4 firstly reached 3.94, 8.24, 10.5, and 24.7 mg S L⁻¹, at 60, 94, 94, and 94 h respectively, and then decreased slowly to 1.18, 6.37, 8.36, and 22.3 mg S L⁻¹, respectively. The decrease in sulfide concentration was due to that its transformation rate outpaced its production rate. Further analysis showed that the sulfide discharge in each microcosms accounted for 5.53%–49.8%

of the removed sulfate, which meant that the sulfide produced from sulfate reduction could be further transformed. This indicated that the CW microcosms in this study had a significant sulfide-removal capacity. The potential reasons included: (1) hydrogen sulfide emission; (2) plant uptake; and (3) the deposition of sulfur compounds, including calcium sulfate, metal sulfide, and elemental sulfur [11, 19, 20]. In this study, the amount of hydrogen sulfide gas was below the detection limit, which indicated that hydrogen sulfide emission was negligible. The plant uptake rate for sulfur ($0.03\text{--}0.04\text{ g S m}^{-3}\text{ d}^{-1}$) was two orders of magnitude lower than the sulfate removal rate, which meant that plant uptake had a marginal effect. In addition, the calcium ion content in pore water was too low ($< 10\text{ mg L}^{-1}$) to form a large amount of calcium sulfate. The gravel of this research contained high iron content ($\sim 5.5\%$), which could lead to the formation of metal sulfide and elemental sulfur [21]. Therefore, the formation and deposition of elemental sulfur and metal sulfide might be the main pathway for sulfide removal.

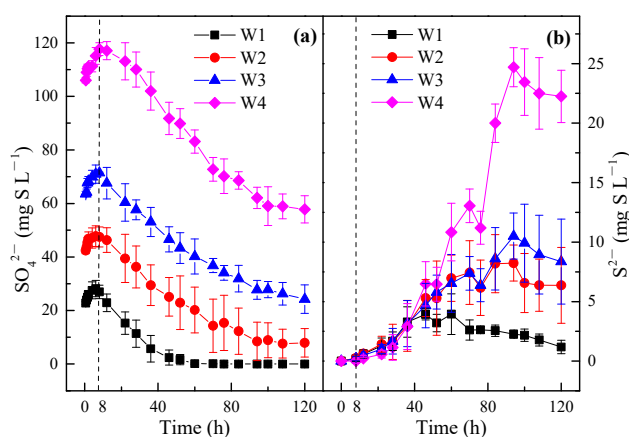


Figure 1. Concentrations of sulfate (a) and sulfide (b) in the microcosms. Error bars represent \pm standard error of the mean ($n = 22$).

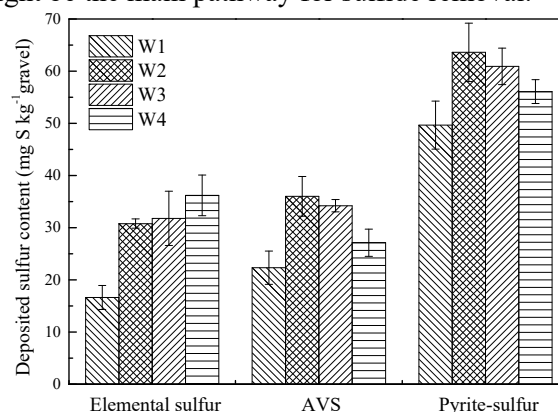
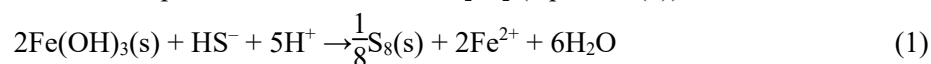


Figure 2. The deposited sulfur contents in the microcosms. Error bars represent \pm standard error of the mean ($n = 3$).

3.2. Deposited sulfur

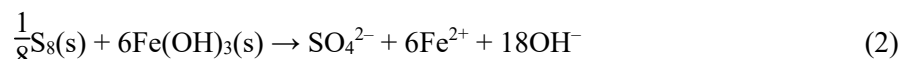
Previous studies have shown that elemental sulfur, acid volatile sulfide (AVS), and pyrite-sulfur are the main forms of deposited sulfur in marine and lacustrine sediments [22]. As shown in figure 2, all the three forms of deposited sulfur accumulated during the batch test. Among them, the accumulation of elemental sulfur was the lowest, which was $16.6\text{--}36.2\text{ mg S kg}^{-1}\text{ gravel}$, and the accumulation of AVS and pyrite were higher, which were $22.3\text{--}36.0$ and $49.7\text{--}63.6\text{ mg S kg}^{-1}\text{ gravel}$, respectively.

Elemental sulfur is an important product of sulfide oxidation [23]. The presence of elemental sulfur indicated that the occurrence of sulfide oxidation. Previous study has shown that, in natural sediments, iron(III) is a ubiquitous electron acceptor for sulfide oxidation [22] (equation (1)):



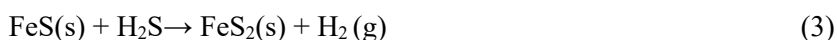
As mentioned above, the wetland matrix contained abundant iron, so it was inferred that the accumulation of elemental sulfur was the result of sulfide oxidation by iron(III). According to previous study [24], the rate of the above-mentioned sulfide oxidation was positively correlated with the sulfide concentration. Therefore, as the sulfide concentration increased (figure 1(b)), the accumulation of elemental sulfur increased from 16.6 to $36.2\text{ mg S kg}^{-1}\text{ gravel}$.

AVS is produced from the reaction between ferrous ion and sulfide [25]. The ferrous ion can be produced from the chemical iron(III) reduction by dissolved sulfide (equation (1)). Besides, the biological reduction of iron(III) by elemental sulfur with the participation of sulfur oxidizing bacteria (SOB) is also a potential process (equation (2)) [26]. The electron transfer during the latter process is three times higher than the former, and thus should be the main source of ferrous ion:



Obviously, the amounts of dissolved sulfide and elemental sulfur should possess effects on the production of ferrous ion, and thus affect the accumulation of AVS. As shown in figure 2, the AVS accumulation in W1 was the lowest (22.3 mg S kg⁻¹ gravel). This was because both the amounts of sulfide and elemental sulfur in W1 were the lowest (figures 1(b) and 2), and could reduce limited iron(III) to produce ferrous ion, which limited the accumulation of AVS. However, with the increase in the amounts of sulfide and elemental sulfur in W2–W4, the accumulation of AVS decreased from 36.0 to 27.1 mg S kg⁻¹ gravel. The cause might be that the gradual increased sulfide concentration inhibited the activity of SOB [27]. This lowered the iron(III) reduction rate by elemental sulfur, and negatively affected ferrous ion production, and therefore, the AVS accumulation was decreased.

Under anoxic condition, pyrite is mainly produced by the reaction of AVS and sulfide (equation (3)) [21]:



Burton et al. [21] found that the pyrite formation rate was positively correlated with the content of AVS and the dissolved sulfide. The accumulation of pyrite-sulfur was the lowest in W1 (49.7 mg S kg⁻¹ gravel), and that in W2–W4 showed a downtrend from 63.6 to 56.1 mg S kg⁻¹ gravel. It could be note that the relationship of pyrite accumulation among microcosms was the same as that of AVS accumulation. This indicated that the AVS content should be the primary control of pyrite accumulation in this study.

As mentioned above, the sulfide produced from sulfate reduction in the CWs could be further converted into deposited sulfur and removed from the pore water, through the following pathways in this study: (1) the oxidation to elemental sulfur by iron(III); (2) reaction with ferrous ions to produce AVS; (3) reaction with AVS to produce pyrite-sulfur.

3.3. Sulfur balance

As shown in figure 3, 5.55%–46.9%, 1.10%–4.01% and 2.48%–7.27% of the removed sulfate were discharged from the microcosms in the forms of sulfide, elemental sulfur, and thiosulfate, respectively. 13.0%–15.6%, 9.75%–18.3% and 20.2%–39.9% were converted to elemental sulfur, AVS and pyrite, and deposited in the gravel. The absorption of sulfate by plants was very limited, only accounting for 0.84%–2.34% of removed sulfate. The sulfur balance showed that the sulfide in the effluent in this study was less than 50% of the removed sulfate. It showed that the CWs could effectively control the sulfide discharge while removing sulfate. The gravel of wetland played an important role, which could convert the sulfide into the deposited sulfur like elemental sulfur, AVS, and pyrite-sulfur through physical, chemical, and biological processes (e.g. oxidation and precipitation).

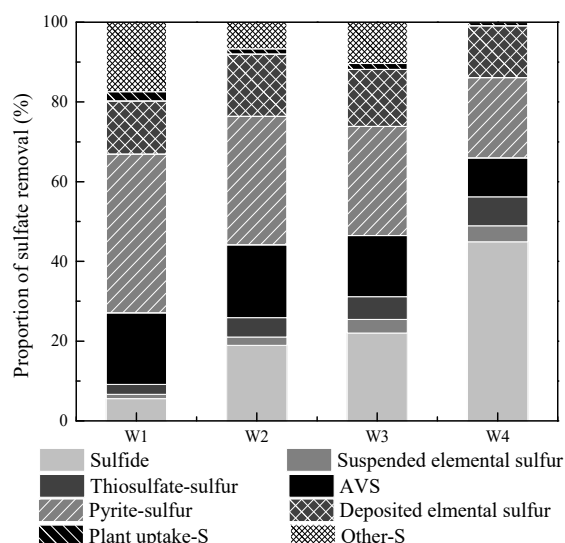


Figure 3. The proportions of various sulfate removal routes.

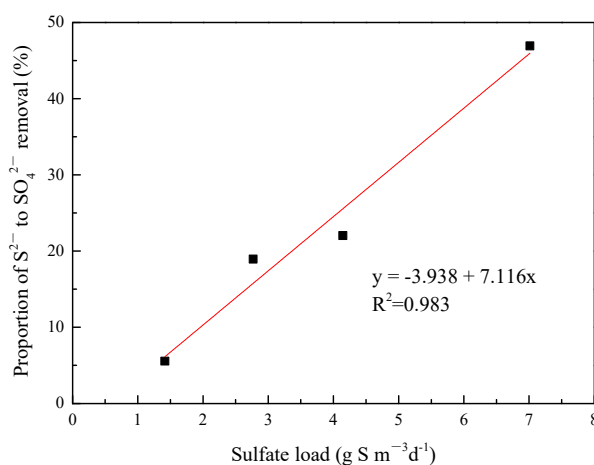


Figure 4. The relationship between the proportion of discharged sulfide to removed sulfate-sulfur and the sulfate load.

3.4. Engineering Significance

It is an urgent problem that how to efficiently and economically remove sulfate from wastewater and control sulfide discharge in engineering. The result showed that, as a sewage treatment technology with good treatment effect and low operating cost, CWs can achieve effective sulfate removal, and meanwhile reduce the sulfide discharge via the matrix. This makes up for the shortage of traditional anaerobic biological sulfate wastewater treatment. However, the study also found that as the sulfate load increased from 1.42 to 7.01 $g\ S\ m^{-3}\ d^{-1}$, the proportion of discharged sulfide in the removed sulfate increased from 5.55% to 46.9%. Figure 4 showed that there was a significant positive correlation between this proportion and sulfate load ($R^2 = 0.983$). This meant that when the sulfate load is high, the CWs will not be able to effectively remove sulfide. As mentioned above, the iron in the wetland matrix played a decisive role in controlling sulfide discharge. A reasonable iron content could promote the formation of deposited sulfur, and then achieve efficient sulfide removal. In order to provide theoretical basis and technical support for the treatment of sulfate-containing wastewater with CWs, it is necessary to further investigate the iron cycle and its interaction with carbon and sulfur cycles in CWs.

4. Conclusion

As the sulfate load increased from 1.42 to 7.01 $g\ S\ m^{-3}\ d^{-1}$, the sulfate removal rate increased from 1.42 to 3.16 $g\ S\ m^{-3}\ d^{-1}$, and the sulfide discharge rate increased from 0.08 to 1.46 $g\ S\ m^{-3}\ d^{-1}$. The produced sulfide proportion accounted for 5.55%–46.9% of the removed sulfate, indicating that CWs can effectively reduce sulfide while removing sulfate.

Wetland matrix can convert sulfide into deposited sulfur, which was a main sink for sulfide removal. Elemental sulfur, acid volatile sulfide (AVS), and pyrite-sulfur were the main forms of deposited sulfur in this study, with the accumulation of 16.6–36.2, 22.3–36.0, and 49.7–63.6 $mg\ S\ kg^{-1}$ gravel.

Sulfur balance analysis showed that 42.9%–71.1% of the sulfate removal was deposited in the gravel, and only 0.84%–2.34% was absorbed by the plant.

Acknowledgments

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