Biofiltration of high concentration of H2S in waste air under extreme acidic conditions

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Highlights

H_2S biofiltration was carried out under extreme acidic conditions

Expanded schist topped with a nutritional material UP20 was used as packing material

A maximum elimination capacity of 24.7 g m^{-3} h^{-1} was recorded (H_2S up to 250 ppmv)

Watering was efficient to restrict acidification and improve biofilter performance

Satisfactory H_2S removal was achieved through the combination of schist and UP20

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Biofiltration of high concentration of H_2S in waste air under extreme acidic conditions

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Abstract

Removal of high concentrations of hydrogen sulfide using a biofilter packed with expanded schist under extreme acidic conditions was performed. The impact of various parameters such as H_2S concentration, pH changes and sulfate accumulation on the performances of the process was evaluated. Elimination efficiency decreased when the pH was lower than 1 and the sulfate accumulation was more than 12 mg $S\text{-}SO_4^{2-}$/g dry media, due to a continuous overloading by high H_2S concentrations. The influence of these parameters on the degradation of H_2S was clearly underlined, showing the need for their control, performed through an increase of watering flow rate. A maximum elimination capacity (EC_{max}) of 24.7 g m^{-3} h^{-1} was recorded. As a result, expanded schist represents an interesting packing material to remove high H_2S concentration up to 360 ppmv with low pressure drops. In addition, experimental data were fitted using both Michaelis–Menten and Haldane models, showing that the Haldane model described more accurately experimental data since the inhibitory effect of H_2S was taken into account.

Key words: *Biofiltration; Hydrogen sulfide; Sulfate accumulation; pH; Gas treatment; Pressure drop.*

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1 Introduction

Hydrogen sulfide is one of the main malodorous compounds present in waste gases. It can be produced by several industrial processes such as petroleum refining, wastewater treatment, food processing and paper manufacturing [1]. Hydrogen sulfide is an extremely toxic pollutant which damage human health, corrodes equipment and form poisonous sulfur dioxide (SO2) during its oxidation. Due to its adverse effects to both humans, environment and installation, regulations to control air pollutants are becoming more and more stringent.

Processes used to remove H_2S from waste gas streams involve either physical treatment or chemical oxidation. Some methods require chemicals, large investment and operational costs (e.g. high pressures, high temperatures, substantial energy). In addition, these methods are less effective and more expensive for treating H_2S in waste gas streams. To overcome these difficulties, biological treatment processes can often serve as suitable alternatives to physico-chemical systems. Biofiltration appears to be an attractive technology owing to its high efficiency, cost effectiveness, low energy consumption and environmental acceptability. Although H_2S biofiltration has been extensively studied [2–7], only few studies devoted to the treatment of high H_2S concentrations in air under extreme acidic conditions were carried out [8,9].

Biofiltration is based on the capacity of some microorganisms to transform contaminants. In biofilm, pollutants are absorbed from a gas to an aqueous phase where microbial attack occurs. In the case of the hydrogen sulfide biodegradation, the metabolites are mainly sulfate and sulfur solid by sulfide oxidizing bacteria (SOB) namely *Thiobacillus* sp. The following overall biological reactions [9] can be expressed by Eqs (1, 2):

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad \textbf{Eq.1}$$

$$2S^0 + 3O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad \textbf{Eq.2}$$

Depending on oxygen rate, hydrogen sulfide is converted to elemental sulfur (S^0) or sulfate (SO_4^{2-}). In oxygen-limited environments, oxidation may proceed only to elemental sulfur. Consequently, the biofilter bed becomes yellow and clogged over time due to the accumulation of S^0. However, in air, oxygen is abundant, and most of the H_2S is converted

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into sulfate, which lead to media acidification. Sulfate accumulation and pH drop can inhibit the microbial activity and can lead to a decrease in the performances of the biofilter [10].

Biofilter performances can be governed by the properties and the characteristics of the packing material such as porosity, water retention capacity, surface area, density and buffer capacity. Various types of media have been used such as organic, inorganic and synthetic. Organic materials used in biofilters include pine bark, peat, compost and soil [5,11–14]. These media have been widely used owing to their low prices, their porosity and the diversity of microbial flora. However, watering the biofilter to maintain bed's humidity leads to bed compaction. As a result, pressure drops increase and the purification performances decrease. Hence, the use of inorganic materials seems be favorable because of their excellent mechanical properties which can limit these pressure drops even during a long operating period [15]. The inorganic materials used include lava rocks [16,17] and expanded schist [6,7,15]. Generally, these packing materials have to be inoculated with sludge from wastewater treatment plants containing various non-specific microbial communities which enhance the performance of the biofilter [18–20]. In addition, nutrient equilibrium play an important role in the microbial growth. Generally, in order to provide nutrients to microorganisms, biofilters are sprinkled by a nutritive solution. Synthetic nutritional materials as BIOSORBENS™ (consisting of hydrophilic mineral cores coated with hydrophobic sorption material) [21] or UP20 [4] were also manufactured. This material makes the addition of nutritive solutions unnecessary. Recent studies on laboratory-scale biofilters have highlighted that expanded schist as packing material completed with UP20 is suitable for H_2S biofiltration in terms of removal efficiency [6,15,22].

Biofiltration was widely used to remove low concentration of H_2S from air. However, only few studies focused on the efficiency of this process facing high concentration of H_2S. The accumulation of sulfuric acid generated by H_2S oxidation leads to a significant acidification of biofilter bed. The pH decreases when the system is overloaded by high H_2S input and can be considered as an issue for practical applications.

The purpose of this study was to evaluate the performances of a biofilter packed with expanded schist particles under high concentrations of hydrogen sulfide in air and extreme acidic conditions. A significant effort was developed to study the impact of pH changes and sulfate accumulation. Moreover, the kinetic aspects of biodegradation were described by fitting the experimental data with Michaelis–Menten and Haldane models.

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2 Materials and methods

2.1 Filter media

Expanded schist used as the microorganism support material is an inorganic support produced in Mayenne (France) by the thermal expansion reaction of schist (Figure 1). The composition of this media (Table 1) was determined using an Energy Dispersive X-ray Fluorescence Spectometer (EDX-800HS, shimadzu Company). Expanded schist has been chosen for its good mechanical properties (Table 2). The structural porosity and the specific surface area were measured by a mercury porosimiter Micromeritics AutoPore IV 9500. Using inorganic packing material like expanded schist, pressure drops associated to bed debasement and compaction are low. Pressure drop values reported by the literature range from 10 to 80 Pa m^{-1} for superficial velocity varying between 89 and 229 m h^{-1} [15].

Table 1

Table 2

2.2 Nutrients

Inorganic materials provide an interesting physical support for bacteria, but generally it does not ensure enough nutrient content. A cylindrical-shaped extruded material called UP20 was produced to provide nutrient equilibrium to microorganisms (Figure 1). This specific material, whose formulation has been described in previous works [4], has been successfully used in several studies for H_2S treatment [3,4,6,22]. UP20 contains urea phosphate (CH_4N_2O, H_3PO_4), calcium carbonate ($CaCO_3$) (C/N/P molar ratio: 100/10/5) and an organic binder (ELOTEX ST2400; 20% in mass) from Elotex Company. This material provides both nutrients and a buffering effect for biofilm and water hold-up.

Figure 1: Photography of UP20 (left) and expanded schist (right).

2.3 Experimental Set-up

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The laboratory-scale system used in this work is shown in Figure 2. It consisted of a PVC column with an internal diameter of 300 mm. Biofilter was packed with expanded schist (1 m height; volume 70 L) topped with UP20 (2 cm corresponding to 1.4 L). It was inoculated with 5 L of a diluted solution of activated sludge (about 50 mg DSS/L) from a domestic wastewater treatment plant (Tougas, Nantes, France).

The air flow is generated using a regulated fan (FMV frequency controller 2107, Leroy Somer Angoulême, France). It passes through a humidification High Density Polyethylene cylinder (HDPE) column packed with Hiflow rings (packing height = 1.50 m) of internal diameter of 200 mm. H_2S stream (99.7% purity), controlled by a mass flow controller (Model 5850S, Brooks Instrument, Hatfield, USA), was diluted in the atmospheric air at the outlet of the humidification column. The polluted air was then introduced at the bottom of the biofilter. Biofilter watering was implemented to maintain the humidity of the packing material.

Figure 2: Experimental pilot-scale biofilter**:**
1 Centrifugal fan**, 2** rotameter**, 3** humidification column**, 4** pump**, 5** injection point of H_2S**, 6** biofilter**, 7-13** gas sampling ports**, 14** leachate outlet**, 15** outlet gas.

2.4 Analytical methods

The H_2S concentration was measured with an Onyx 5220 device (measurement accuracy ± 1%) from the Cosma Environment SA Company (Passy, France) The analyzer was calibrated daily using a standard gas (400 ppmv). The eight points for gas sampling were located at the inlet and at the outlet of the biofilter, and at 10, 30, 50, 70, 90 and 100 cm from the biofilter bottom respectively (Figure 2). The pH of leachate was measured by a pH electrode (Consort) connected to a multi-parameter analyzer Consort C-561 (measurement accuracy 0.2% ± 1 digit).

Sulfate determination was carried out by the turbidimetric method as described in Standard methods for the examination of water and wastewater [23]. Samples for the sulfate determination were taken periodically from the leachate.

2.5 Operating conditions

The polluted air flow rate was 4 m^3 h^{-1} corresponding to an Empty Bed Retention Time (EBRT) of 63 s. Periodical watering (once a day) was used to maintain the humidity of the

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bed material and to avoid sulfate accumulation. It was provided at a constant flow of 0.8 L min^{-1} during 15 minutes corresponding to a tap water flow rate (Q_{Liq}) of 12 L day^{-1}. The operating conditions applied during this study are reported in Table 3.

Table 3: Operating conditions.

The removal efficiency (RE), the loading rate (LR) and the elimination capacity (EC) of the biofilter were calculated as follows:

$$RE\ (\%) = \frac{(C_{in} - C_{out})}{C_{in}} \times 100 \qquad \textbf{Eq.3}$$

$$LR\ (g\ m^{-3}\ h^{-1}) = \frac{Q}{V}\ C_{in} \qquad \textbf{Eq.4}$$

$$EC\ (g\ m^{-3}\ h^{-1}) = \frac{Q}{V}\ (C_{in} - C_{out}) \qquad \textbf{Eq.5}$$

Where C_{in} and C_{out} are the inlet and outlet concentrations (mg m^{-3}) respectively, Q is the gas flow rate ($m^3\ h^{-1}$) and V is the bed volume of packing material (m^3).

3 Results and discussion

3.1 Effect of increasing H_2S concentrations

The impact of increasing H_2S concentrations (from 40 to 360 ppmv) on the biofilter performances is shown in Figure 3. The acclimation period for the microbial population was quite short. H_2S was totally removed from the 3rd day (RE > 99%). Such observation can be explained by the bacterial inoculum and the presence of UP20 which can react (acid – base) with the polluted gas [24]. For H_2S concentrations up to 250 ppmv, a 100% RE was recorded proving the ability of the expanded schist to be used for biofiltration. As shown in Figure 3, the performance efficiency started decreasing from the 143th day. This decrease was significantly pronounced, from the 172th day, when H_2S concentration was very high (ranging from 250 to 360 ppmv). It can be due to a direct inhibitory effect on the metabolism of some microorganisms. Indeed, when the system is continuously overloaded by high H_2S input,

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H_2SO_4 is produced continuously as a by-product of the H_2S biological oxidation (Eq.2), which leads to biofilter acidification and sulfate accumulation. During this period, the pH dropped to 0.5 (Figure 3). The decrease of pH and the sulfate accumulation probably can lead to the deterioration of biofilter performances [10,25]. Sulfur oxidizing bacteria can live in environments with pH ranging between 1 and 8 [10]. The optimal pH is between 6 and 8 [1], but H_2S can also be oxidized by microorganisms like *Thiobacillus* and *Acidithiobacillus* at very acidic pH. Rodriguez *et al*. [26] found a H_2S removal efficiency of 95% at a pH between 4 and 7, and a removal efficiency of 87% at a pH between 2 and 3. Others authors observed a maximum H_2S removal at a pH value of 3.2 [10,16]. They mentioned that a low pH can significantly inhibit the biological activity of the microorganisms; therefore the removal efficiency decreases progressively. Soupramanien *et al.* [27], who measured a complete H_2S degradation at pH = 1, indicated that the pH value strongly influences the diversity of the bacterial community. However, only few data are available for pH lower than 1.

Figure 3: Removal efficiency of H_2S and pH changes in biofilter (H_2S concentrations from 40 to 360 ppmv; EBRT=63s).

3.2 Effect of sulfate accumulation and pH changes on H_2S removal

Due to the production of sulfuric acid, the effect of sulfate accumulation on H_2S removal was evaluated. On the 56th day, the sulfate concentration was 12.7 mg S-SO_4^{2-}/g dry media and H_2S was completely removed in the biofilter. When the sulfate concentration was less than 24 mg S-SO_4^{2-}/g dry media, the removal efficiency was above 90%. A significant decrease of the removal efficiency, to 78%, was underlined when the sulfate content was close to 49 mg S-SO_4^{2-}/g dry media (Figure 4). In the presence of large amounts of oxygen, sulfate was produced from the bio-oxidation of hydrogen sulfide by the sulfide oxidizing bacteria. Sulfate is a water soluble compound which can have a negative effect on the microbial activity. Yang and Allen [10] suggested that sulfate concentration of 25 mg S-SO_4^{2-}/g dry media was a critical level for the microbial activity. Above this level, an inhibiting effect on H_2S removal could be observed. Morgan-Sagastume and Noyola [28] suggested to work at a sulfate concentration less than 12 mg S-SO_4^{2-}/g dry media which is consequently lower than the critical level proposed by Yang and Allen [10]. To avoid SO_4^{2-} accumulation, Ramírez-Sáenz *et al*. [16] suggested periodical water cleaning of the biofilter to limit sulfate concentrations to about 8 mg S-SO_4^{2-}/g dry media. According to the present study and measurements, the

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sulfate accumulation influences significantly the degradation of H_2S for concentrations up to 12 mg S-SO_4^{2-}/g dry media (Figure 4). As a result, periodical water additions could be carried out to keep sulfate concentration lower than this critical value.

Figure 4: Effect of sulfate accumulation on H_2S degradation.

The influence of pH changes can also be clearly underlined (Figure 3). For H_2S concentrations up to 250 ppmv, the pH was 1.2 and the removal efficiency was kept constant until the 161th day (96%). It has to be noted that the layer of UP20 (2cm) located above the packing was not enough to provide a buffering effect for biofilter especially at very high H_2S concentration (above 250 ppmv). Therefore, increasing the layer thickness of UP20 to treat high concentrations of H_2S could be considered. However, a specific study should be carried out to investigate this point. Once pH dropped to values less than 1, the performance decreased significantly. Hence, the increase in the H_2S concentration (until 360 ppmv; Phase 6) led to a decrease in the pH value (around 0.5) and concomitantly a decrease in the removal efficiency (78%). From the 200th day, a decrease in H_2S concentration to 250 ppmv was applied but the pH was still less than 0.5. With the same concentration (250 ppmv) the removal efficiency decreased from 92-100% (Phase 5) to 73-80% (Phase 7; Figure 3). In order to decrease sulfate concentration and to raise the pH value in the packing material, the watering flow rate (Q_{Liq}) was increased from 12 L day^{-1} (0.007 m^3_{water} m^{-3}_{bed} h^{-1}) to 120 L day^{-1} (0.07 m^3_{water} m^{-3}_{bed} h^{-1}) from the 234th day, as pointed out by the arrow in the Phase 7 (Figure 3). The increasing of the watering flow rate allowed to maintain the pH value greater than 1, and then the removal efficiency was improved (Figure 5). For H_2S concentration of 250 ppmv, on the 224th day, the pH was 0.2 and the removal efficiency was 73%, whereas, on the 242th day, the pH was 1.8 and the removal efficiency increased to achieve 95% (Figure 3). Consequently, it clearly appeared that an efficient H_2S biofiltration required to work at a pH greater than 1. In terms of maximal elimination capacity, an improvement of around 10% was observed (EC_{max}=24.7 g m^{-3} h^{-1}).

Figure 5: Impact of the increasing of watering flow rate from 12 L day^{-1} to 120 L day^{-1} on the removal efficiency (EBRT=63s).

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3.3 Pressure drop

The pressure drop was measured daily between the ports located at 10 and 100 cm from the bottom of the biofilter. Figure 6 shows that ΔP ranged from 3 Pa m^{-1} (0.03 cm_{H2O} m^{-1}) to 94 Pa m^{-1} (0.96 cm_{H2O} m^{-1}) for gas velocities varying between 56 and 565 m h^{-1}. These values are comparable to those recorded by Dumont *et al*. [3] using pozzolan media (5 – 100 Pa m^{-1}) for gas velocities between 65 and 520 m h^{-1}, but lower than those obtained using organic packing materials in other studies. For instance, pressure drops between 500 and 1000 Pa m^{-1} were obtained in a bed consisting of compost operating at gas velocities between 72 and 1000 m h^{-1} [10]. For pine bark, ΔP varied from 15 to 388 Pa m^{-1} at gas velocities ranging between 65 and 520 m h^{-1} [3]. After 220 days of operation, ΔP increased to values between 4 and 105 Pa m^{-1} for the same velocity range. The increase of pressure drop can be related to the biofilm growth, especially when the system was overloaded by high H_2S concentrations (250 - 360 ppmv); an increase of 12% of the pressure drop was then observed. This increase can also be due to the formation of elemental sulfur (S^0) which partially clogs the packing material. This interpretation was confirmed by observing some yellow deposits in the biofilter after a long period of operation. Nonetheless, these low values showed that there was no compaction of the bed during the long operation period, which indicated that expanded schist is an interesting material for biofiltration in terms of bed mechanical stability.

Figure 6: Pressure drop measurements in the biofilter for gas velocities varying between 56 and 565 m h^{-1}.

3.4 Modeling performances by Michaelis–Menten and Haldane equations

In order to predict the performance of the biofilter, efforts were directed toward modeling. Many models are available in the literature to describe the pollutant biodegradation kinetics [29]. The elimination capacity (EC) vs pollutant concentration can be adequately described by a Michaelis–Menten model (Eq 6) [6,30,31]:

$$EC = \frac{EC_{max} C_{In}}{K_s + C_{In}} \qquad \textbf{Eq.6}$$

Where

EC_{max}: Maximal elimination capacity (g m^{-3} h^{-1})

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C_{ln}: Logarithimic average of the inlet and outlet concentrations of pollutants in the gas phase (g m^{-3})

K_s: Saturation constant (g m^{-3})

EC_{max} and K_s are calculated by rearranging Eq.6 to take the form of the Lineweaver–Burk equation below (Eq 7):

$$\frac{1}{EC} = \frac{K_s}{EC_{max} C_{ln}} + \frac{1}{EC_{max}} \quad \textbf{Eq.7}$$

In the case of biomass inhibition due to high H_2S concentrations, the Haldane model, including an inhibition term, can be used [6,32,33]. The elimination capacity is then calculated by Eq (8):

$$EC = \frac{EC^* C_{ln}}{K_s' + C_{ln} + (C_{ln}^2/K_I)} \quad \textbf{Eq.8}$$

Where

EC^*: Maximal elimination capacity in the absence of inhibition (g m^{-3} h^{-1})

K_s' : Saturation constant (g m^{-3})

K_I: Inhibition constant (g m^{-3})

Haldane's model constants (EC^*,K_s', K_I) are calculated from the regression of Eq.8, rearranged as follows (Eq 9):

$$\frac{C_{ln}}{EC} = \frac{K_s'}{EC^*} + \frac{C_{ln}}{EC^*} + \frac{C_{ln}^2}{EC^* K_I} \quad \textbf{Eq.9}$$

In this case, EC_{max} can be calculated by following the mathematical analysis reported by Sologar *et al*. [34] (Eq 10):

$$EC_{max} = \frac{EC^*}{1+2\sqrt{(K_s'/K_I)}} \quad \textbf{Eq.10}$$

Figure 7 shows EC versus C_{ln} for the biofilter at a constant EBRT of 63 s. Biodegradation kinetics values determined from the Michaelis–Menten and Haldane models are reported in Table 4.

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Table 4: Biodegradation kinetics values determined from the Michaelis–Menten and Haldane models

As observed in Figure 7, the experimental EC for H_2S was slightly better fitted by the Haldane model, certainly because of the inhibitory effect of H_2S. The experimental EC_{max} for H_2S was 22.6 g m^{-3} h^{-1}, while the EC_{max} estimated with the Michaelis–Menten model and the Haldane model were 28.6 and 22.7 g m^{-3} h^{-1} respectively. A significant inhibitory effect of H_2S on the microbial activity was therefore underlined, since the maximal elimination capacity in the absence of inhibition (EC^*) was higher than the maximal elimination capacity which takes into account inhibition effect (Table 4). The maximal elimination capacity value obtained is higher than those reported with some other packing materials. At an EBRT of 57 s, maximal removal capacities of 14 and 15 g m^{-3} h^{-1} were obtained with a pine bark and pozzolan/UP20, respectively [3]. At an EBRT of 51 s, an EC_{max} of 8 g m^{-3} h^{-1} was also achieved using pall rings as packing material [35]. Comparing biodegradation kinetics values (K_s, K'_s, K_I) with previous work data seems difficult because they depend mainly on EBRT as demonstrated by Romero Hernandez *et al*. **[6]**. Nonetheless, it can be pointed out that the K_s value obtained for expanded schist topped with UP20 was of the order of magnitude of the reported value for peat mixed with UP20, which is a classical and an efficient packing material for H_2S biofiltration (K_S = 0.089 g m^{-3} at an EBRT of 57 s) [2].

To summarize, these results demonstrated that biofilters filled with expanded schist coupled with UP20 could be suitable for industrial applications. The good mechanical behavior of the expanded schist (low pressure drop) and the ability to oxidize H_2S under extreme acidic conditions for a long period confirm the advantage of using expanded schist coupled with UP20 for long-term H_2S biofiltration. The influence of parameters as watering rate and amount of UP20 could be deeply investigated in order to determine the better biofilter performances according to the EBRT used.

Figure 7: Elimination capacity as a function of the logarithmic average of inlet and outlet concentrations in gas phase of the biofilter (C_{ln}) for H_2S (Experimental points, Michaelis–Menten and Haldane models) (EBRT=63 s; C_{ln} between 0.03 and 0.46 g m^{-3}).

4 Conclusion

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The biological removal of H_2S in waste gas was carried out under extreme acidic conditions using a biofilter packed with expanded schist and topped with a layer of a synthetic nutritional material (UP20) at a constant EBRT of 63 s. It has been shown that the combination of expanded schist and UP20 can be successfully used to remove high concentration of H_2S, up to 360 ppmv. Pressure drops were very low (around 4 Pa m^{-1} after 220 days of operation). As expected, no bed compaction was observed during the running period due to a mechanical stability of the schist material. However, if the biofilter was continuously overloaded by high H_2S concentration, the major production of the oxidation reaction was sulfuric acid. The sulfate accumulation in the biofilter bed and the significant pH decrease (pH < 1) led to a significant decrease in the performances of the process. As a result, it was required to increase the watering flow rate up to 120 L h^{-1} in order to avoid sulfate accumulation and to maintain the pH > 1. In such conditions, a removal efficiency higher than 95% was achieved for H_2S concentration up to 250 ppmv, corresponding to a maximum elimination capacity of 24.7 g m^{-3} h^{-1}.

This study shows that such double layer biofilters (nutrient provider and inorganic packing materials) give interesting performances to remove high concentrations of H_2S present in waste gas or air. However, operating conditions such as volumetric load and periodic water addition have to be controlled carefully to avoid a significant level of inhibitory by-products leading to increasing amounts of sulfate and a drastic decrease of pH.

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Figure 1: Photography of UP20 (left) and expanded schist (right).

Figure 2: Experimental pilot-scale biofilter**: 1** Centrifugal fan**, 2** rotameter**, 3** humidification column**, 4** pump**, 5** injection point of H_2S**, 6** biofilter**, 7-13** gas sampling ports**, 14** leachate outlet**, 15** outlet gas.

Figure 3: Removal efficiency of H_2S and pH changes in biofilter (H_2S concentrations from 40 to 360 ppmv; EBRT=63s).

Figure 4: Effect of sulfate accumulation on H_2S degradation.

Figure 5: *Impact of the increasing of watering flow rate from 12 L/day to 120 L/day* on the removal efficiency (EBRT=63s).

Figure 6: Pressure drop measurements in the biofilter for gas velocities varying between 56 and 565 m h^{-1}.

Figure 7: Elimination capacity as a function of the logarithmic average of inlet and outlet concentrations in gas phase of the biofilter (C_{ln}) for H_2S (Experimental points, Michaelis–Menten and Haldane models) (EBRT=63s; C_{Ln} between 0.03 and 0.46 g m^{-3}).

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Table 1: Composition of expanded schist.

Composition	%
SiO_2	55.3
Al_2O_3	20.2
Fe_2O_3	13.3
K_2O	5.1
MnO	0.1
SO_3	1.5
P_2O_5	1.9
CaO	1.2
TiO_2	1.1

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Table 2: Characteristics of expanded schist

Median pore diameter (mm)	12
Porosity (%)	47
Bulk density (kg m^{-3})	667
Apparent density (kg m^{-3})	1248
Specific surface area (m^2 m^{-3})	500

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Table 3: Operating conditions

Phase	Duration (days)	$[H_2S]$ (ppmv)	LR ($g\ m^{-3}\ h^{-1}$)	Q_{Liq} ($L\ day^{-1}$)
1	10	40	3.2	12
2	10	60	4.7	12
3	20	80	6.3	12
4	20	133	10.5	12
5	112	250	19.8	12
6	28	360	28.5	12
7	58	250	19.8	120
8	9	360	28.5	120

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Table 4: Biodegradation kinetics values determined from the Michaelis–Menten and Haldane models

Michaelis–Menten model	Haldane model
EC_{max} = 28.6 g m^{-3} h^{-1}	EC^{*} = 33.3 g m^{-3} h^{-1}
K_s = 0.070 g m^{-3}	K_s' = 0.080 g m^{-3}
	K_I = 1.53 g m^{-3}
	EC_{max} = 22.7 g m^{-3} h^{-1}

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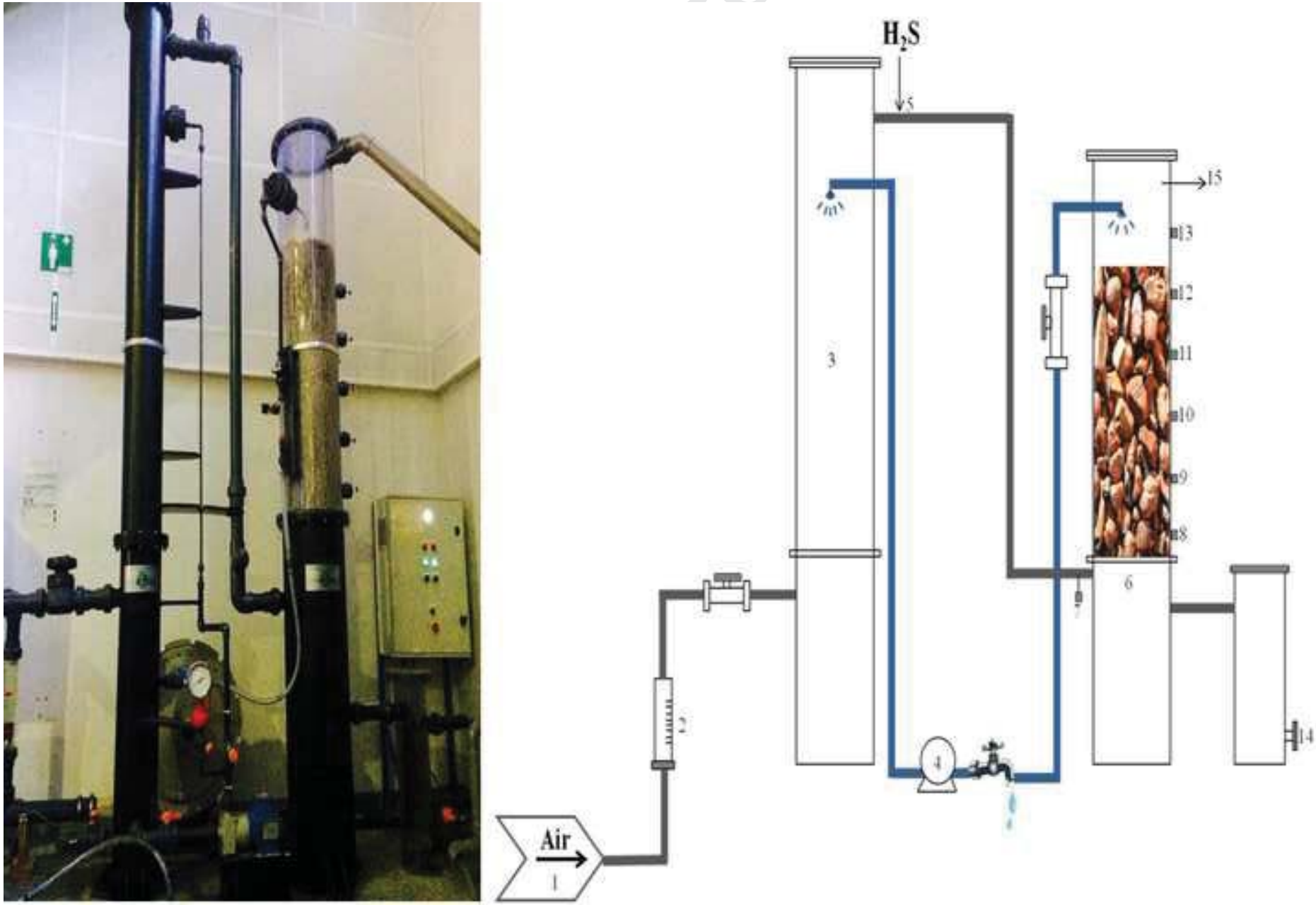
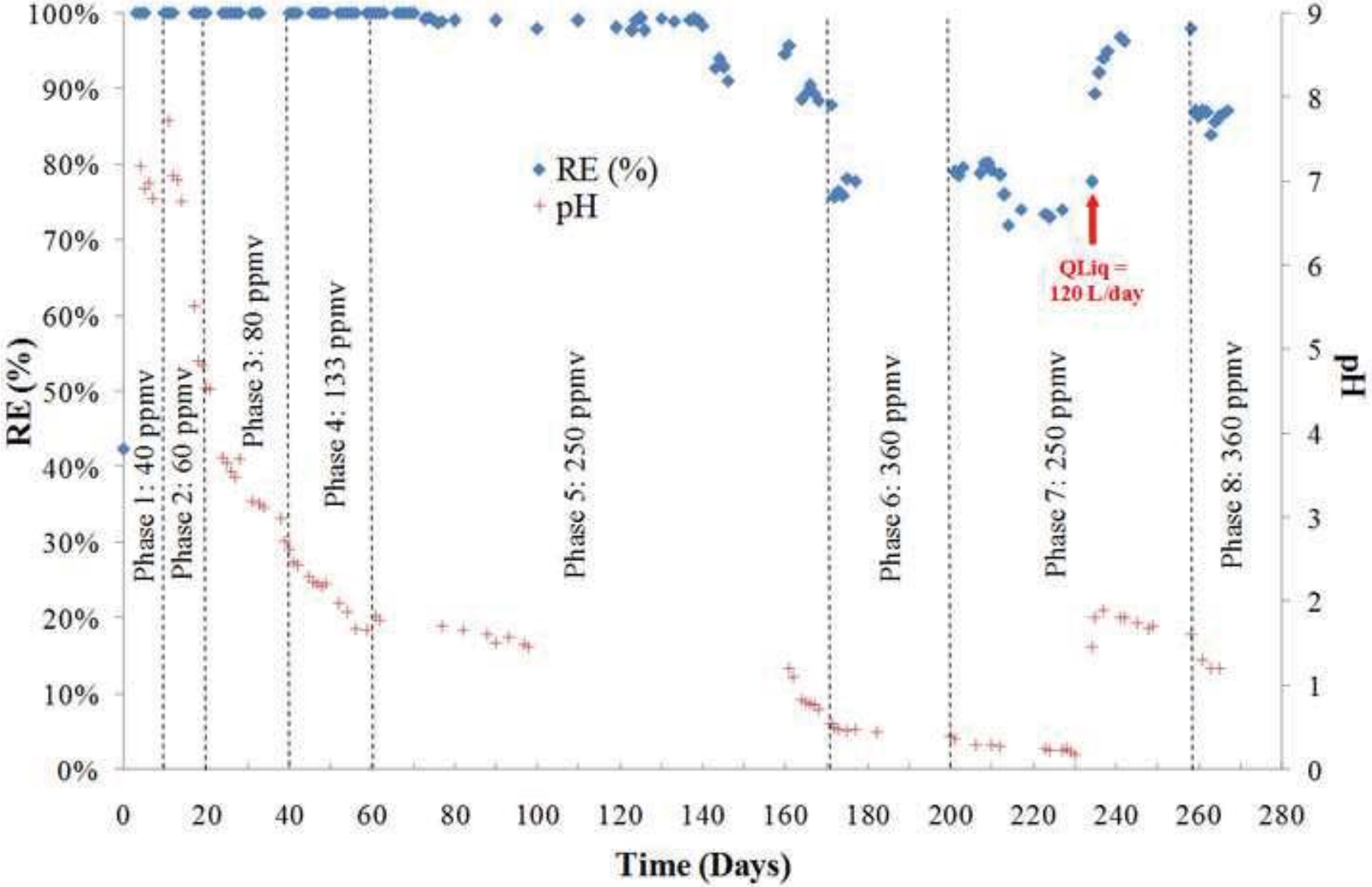
Figure

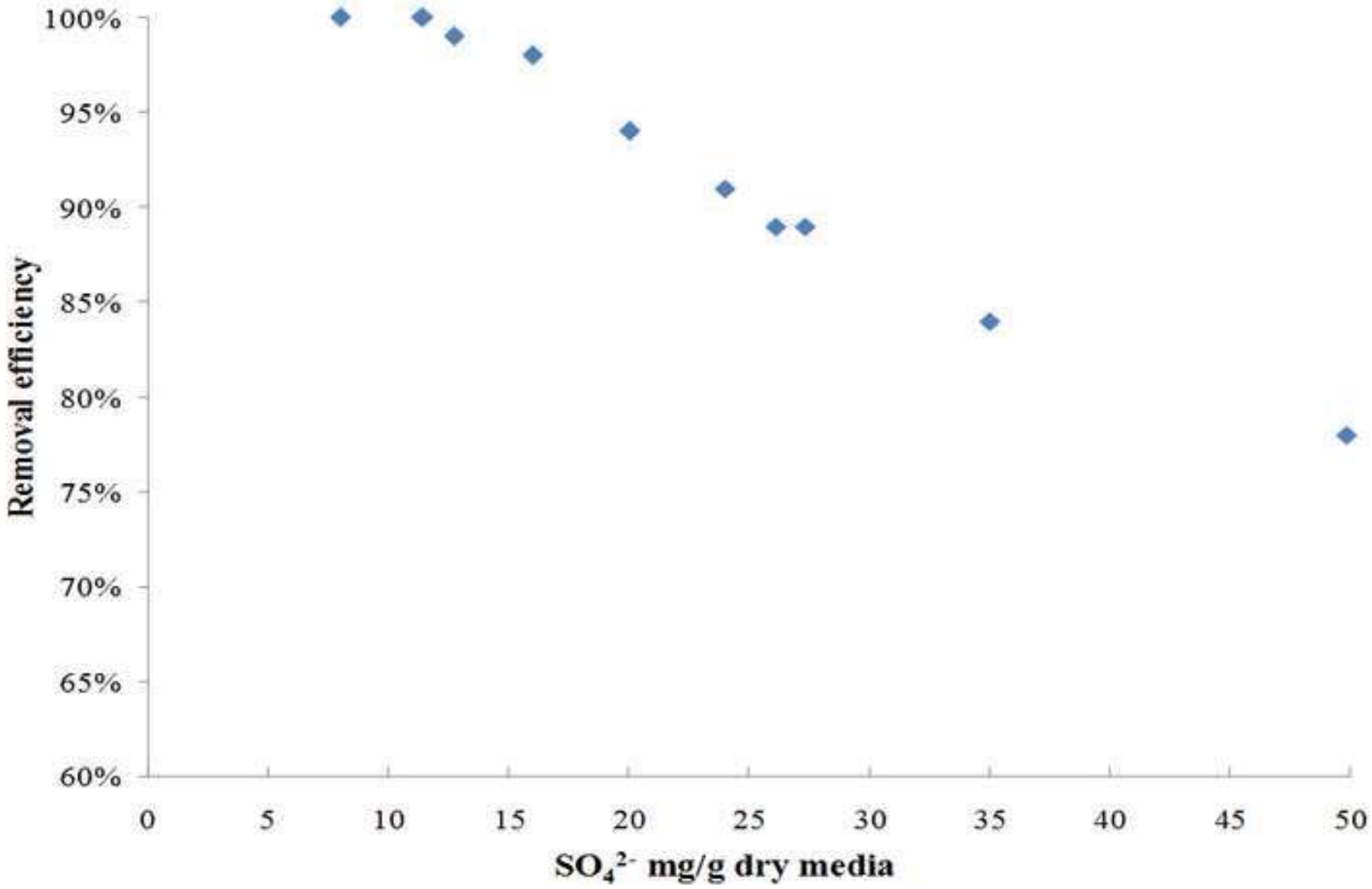
Figure



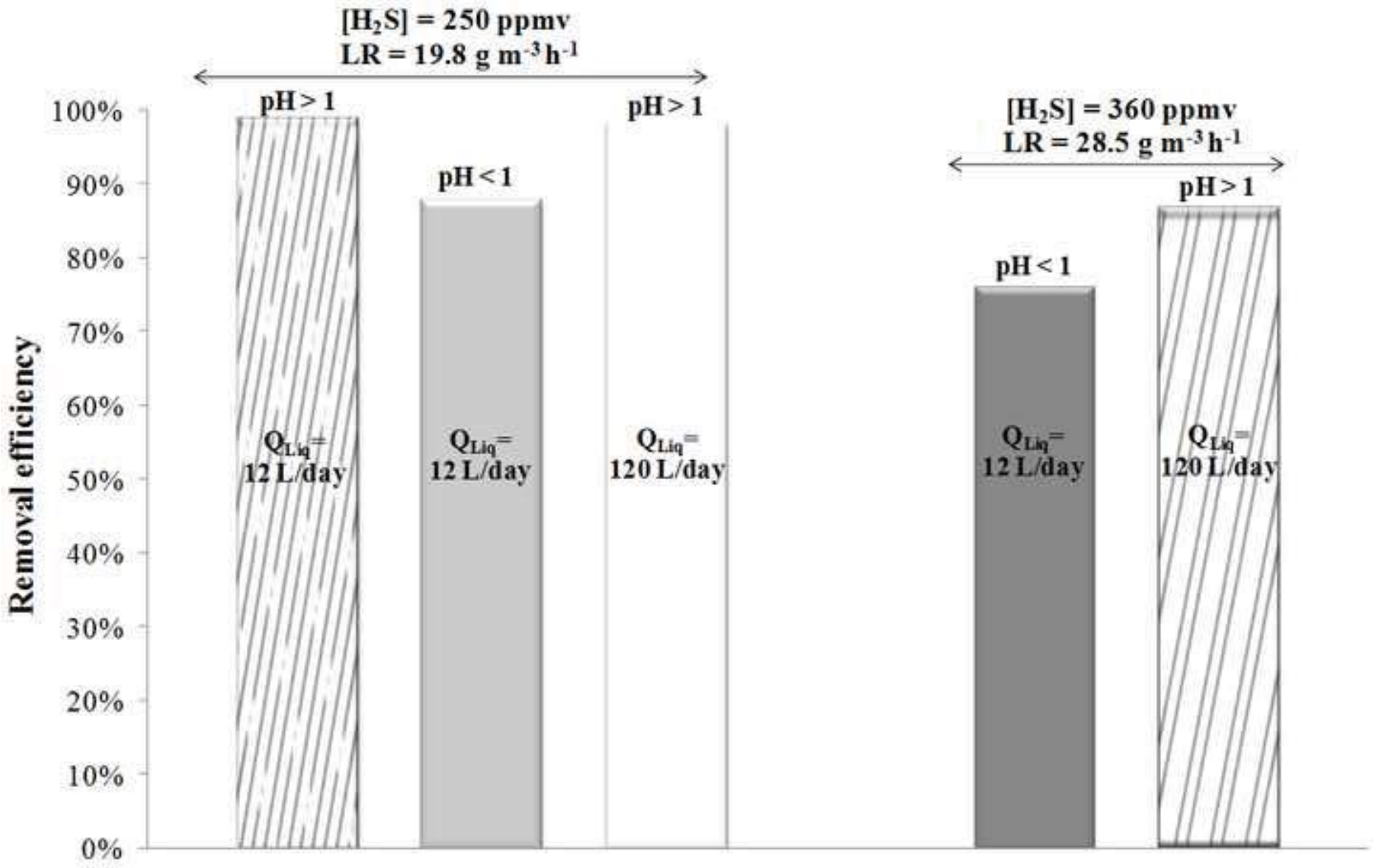
Figure


RE (%)
pH
Phase 1: 40 ppmv
Phase 2: 60 ppmv
Phase 3: 80 ppmv
Phase 4: 133 ppmv
Phase 5: 250 ppmv
Phase 6: 360 ppmv
Phase 7: 250 ppmv
Phase 8: 360 ppmv
QLiq = 120 L/day
RE (%)
pH
Time (Days)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
9
8
7
6
5
4
3
2
1
0

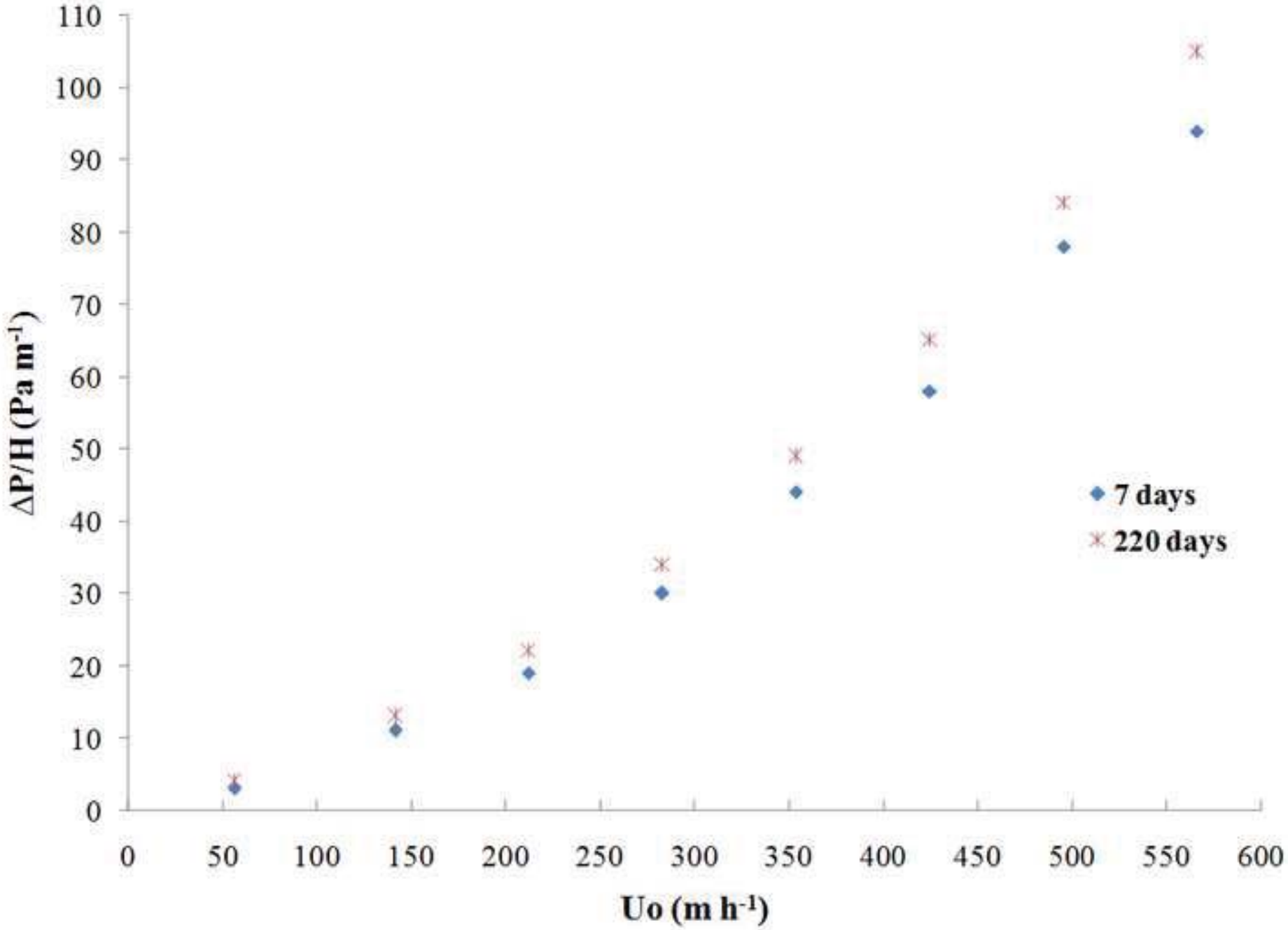
Figure


100%
95%
90%
85%
80%
75%
70%
65%
60%
Removal efficiency
0
5
10
15
20
25
30
35
40
45
50
SO4 2- mg/g dry media

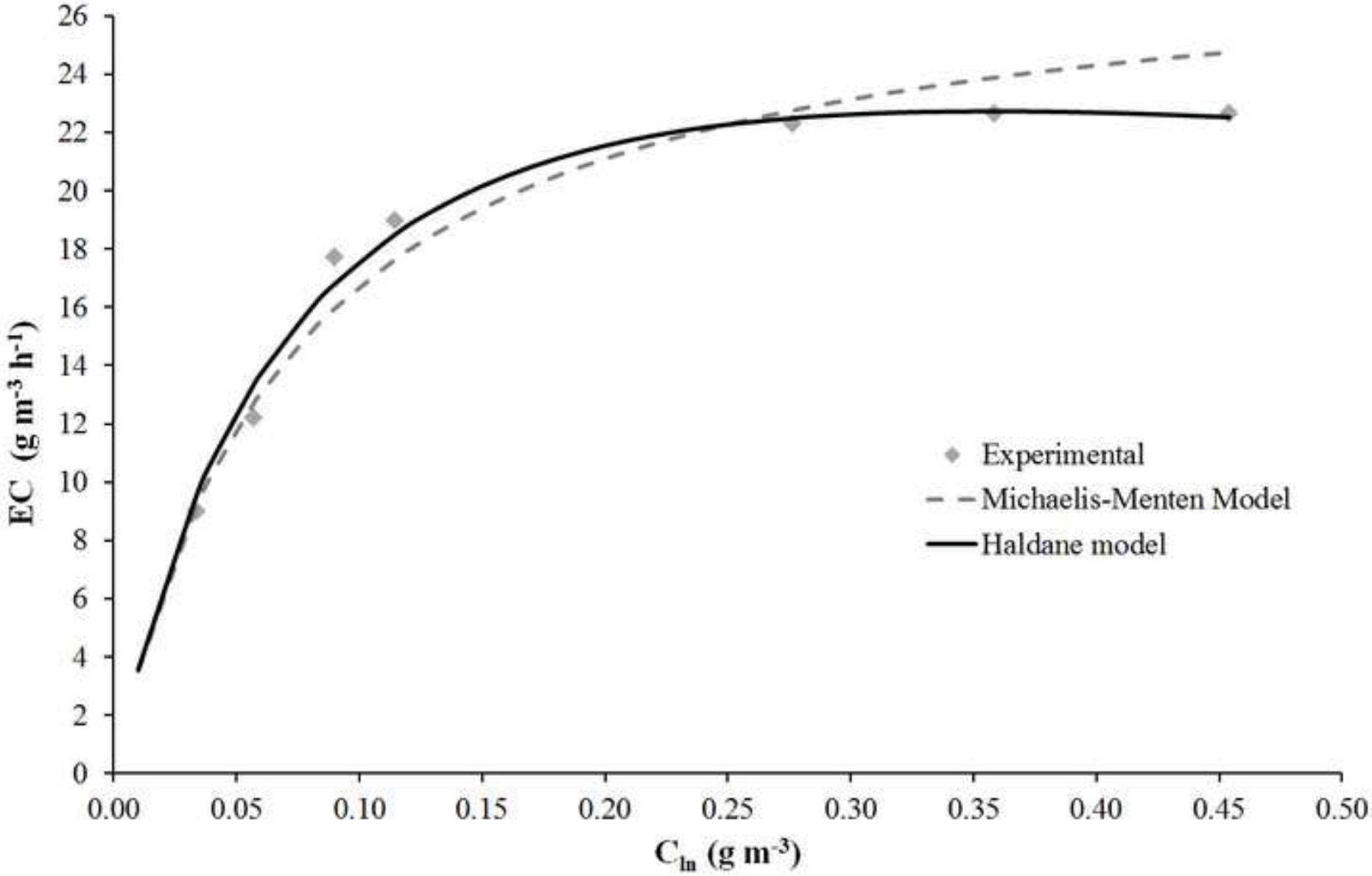
Figure


[H2S] = 250 ppmv
LR = 19.8 g m-3 h-1
[H2S] = 360 ppmv
LR = 28.5 g m-3 h-1
Removal efficiency
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
pH > 1
pH < 1
pH > 1
pH < 1
pH > 1
QLiq= 12 L/day
QLiq= 12 L/day
QLiq= 120 L/day
QLiq= 12 L/day
QLiq= 120 L/day

Figure


110
100
90
80
70
60
50
40
30
20
10
0
ΔP/H (Pa m-1)
0
50
100
150
200
250
300
350
400
450
500
550
600
Uo (m h-1)
7 days
220 days

Figure


EC (g m-3 h-1)
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
Cln (g m-3)
Experimental
Michaelis-Menten Model
Haldane model