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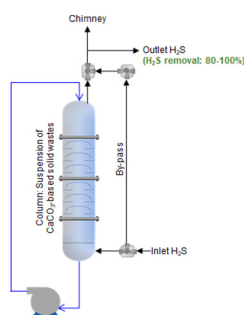
Valorization of calcium carbonate-based solid wastes for the treatment of hydrogen sulfide in a semi-continuous reactor: Part II – Slurry bubble column pilot

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- H₂S removal from the gas phase using calcium carbonate based solid wastes.
- Validation of a triphasic gas/liquid/solid process at the pilot scale.
- Validation of the process with a real gaseous effluent.



Keywords:

H₂S removal
Calcium carbonate
Solid waste
Triphasic process
Slurry bubble column pilot

This work is devoted to the removal of H₂S from the gas phase using a suspension of calcium carbonate-based residues, recovered from the production of sodium bicarbonate. A 145 L (1.6 m height and 0.34 m internal diameter) slurry bubble column (SBC) reactor was used. The gaseous effluent was fed from the bottom and got out from the top of the column. The suspension (2–20 wt%) was recirculated from the bottom to the top by a pump. This created a counter-current regime between the gas phase (from the bottom to the top) and the liquid phase (from the top to the bottom) which favors the gas/liquid exchange inside the reactor. The influence of different parameters including solid concentration in the suspension (w_s), recirculating rate of the suspension (Q_R), inlet gas flow rate (Q_G), and volume of the suspension, was investigated. The results obtained with this confirmed those at the lab scale, for both synthetic gaseous effluent (H₂S diluted in compressed air) and real gaseous effluent emitted by the buffer tank of a wastewater treatment plant. This allows validating the technology before its deployment at the large industrial scale for H₂S removal from the gas phase.

1. Introduction

Hydrogen sulfide (H₂S) is an acid gas and can be found in different environments: air, surface water, underground water, soil, sediments and fossil reserves (e.g. charcoal, natural gas, petrol) [1–3]. H₂S

emission is mostly due to natural processes but also to anthropogenic sources such as wastewater treatment plants (WWTP), food industry, paper mills, tanneries, petroleum refineries, wastes' incinerators, power plants, landfill sites etc. [4–8]. At low emission concentration (0.2 ppbv to 0.2 ppmv), H₂S starts to cause an odor [9]. At higher concentration

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Abbreviation

a	gas–liquid interfacial area (m^2/m^3)
APC	artificially-precipitated carbonate
C_i	inlet H_2S concentration (ppmv)
C_V	volume solid concentration (%)
D_A	gas diffusion coefficient in the liquid
d_b	bubble diameter (m)
D_C	column diameter (m)
d_s	Sauter mean bubble diameter (m)
k_L	coefficient of gas/liquid mass transfer from the liquid-side (m/s)
Eff	efficiency of H_2S removal (%)
m	slope of the curves
NPC	naturally-precipitated carbonate
P_s	water vapor pressure (MPa)

P_T	total pressure (MPa)
Q_G	inlet gas flow rate (m^3/h)
Q_R	liquid recirculating rate (L/h)
SBC	slurry bubble column
T	temperature (K)
U_g	superficial gas velocity (m/s)
w_s	solid content
WWTP	wastewater treatment plant
ε_G	gas retention yield
ρ_G	gas density (kg/m^3)
ρ_L	liquid density (kg/m^3)
ρ_S	solid density (kg/m^3)
σ_L	surface tension of the liquid (N/m)
μ_L	dynamic viscosity of the liquid (Pa s)
Γ	gas sparger type

(up to around 5 ppmv), this odor becomes stronger, likely the odor of rotten eggs [9]. On the other hand, the odor perception progressively decreases when H_2S concentration raises to dozens of ppmv, while the effect on the human health increases (e.g. loss of smell, eye irritation, serious respiratory irritation, loss of consciousness) [9].

Methods for H_2S removal from the gas phase have been developed for years and can be classified into three main categories: adsorption [10–16], absorption [17–22] and biological treatment [23–28]. These methods have been deployed at large industrial scale [29,30], but they still need improvement to reduce cost and to increase performance. For example, adsorption using activated carbon modified with iron oxide is efficient but the cost of this adsorbent is high (around 4000 € per ton). Biological treatment has low cost compared to adsorption and absorption, but it is sensible to the environment (temperature, humidity, gas matrix) [31]. The valorization of selected industrial byproducts of low

cost, which could match the criteria of a good sorbent, appears as pertinent route. From this point of view, our research team has studied the reactivity of calcium carbonate-based wastes rejected by the industry of sodium bicarbonate production. This later is an important chemical for the gas emission control of wastes' incinerators and its annual production reached around 53 million tons in the world in 2015 [32]. Most of them are produced by the Solvay process [33], which is accompanied by large amounts of brines containing calcium-rich minerals. Before discharging in the environment (river, sea and ocean), these brines must be neutralized by a natural carbonation process (CO_2 from the atmosphere) or an accelerated carbonation process (injection of CO_2 into brines), resulting respectively to NPC (naturally-precipitated carbonate) and APC (artificially-precipitated carbonate) – two kinds of calcium carbonate-based wastes.

Our previous work showed that both NPC and APC had very good

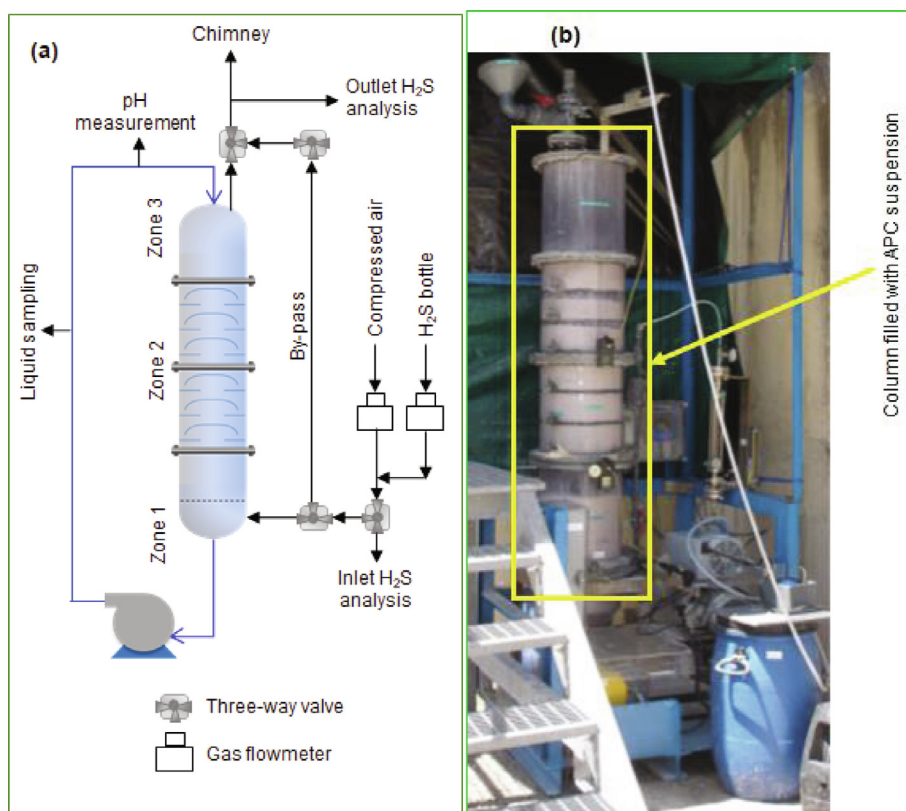


Fig. 1. Scheme (a) and photo (b) of the triphasic slurry bubble column (SBC) reactor used for the removal of H_2S from the gas phase.

Table 1

Operational limits of the triphasic bubble column reactor.

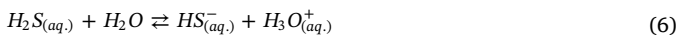
Parameter	Minimum	Maximum
Suspension volume (L)	40	70
Solid content w_s (wt.%)	0	20
Liquid circulating flow rate Q_R (L/h)	150	350

performance in the removal of H_2S from the gas phase at the lab scale [34]. Calcium carbonate solid particles and soluble mineral species, which are initially present in NPC and APC, favored the H_2S removal from the gas phase according to the following steps [34]:

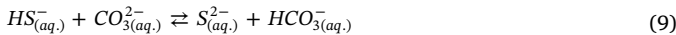
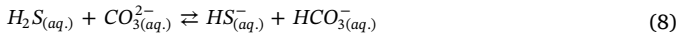
- Dissolution of calcium carbonate and other impurities (M_xA_y) leading to the release of cations and anions in solution:



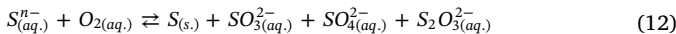
- Dissolution of O_2 and dissolution and dissociation of H_2S :



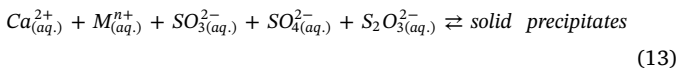
- Neutralization of soluble sulfide species:



- Oxidation of sulfide species ($S_{(aq)}^{2-}$, equivalent to the sum of $H_{2S(aq)}$, $HS_{(aq)}^{-}$ and $S_{(aq)}^{2-}$):



- Possible precipitation of soluble S-containing compounds with metallic cations:



For a possible technology transfer to a large industrial scale, pilot test must be performed to validate the concept. This is the main objective of the present work. H_2S removal from the gas phase was studied at the pilot scale using both synthetic gas emission and real gas emission from the buffer tank of a WWTP.

2. Materials and methods

Both calcium carbonate-based wastes, NPC and APC, were provided by our industrial partner (the world leader in sodium bicarbonate production). Both NPC and APC are under fine power form and could be directly used after a simple pretreatment by drying. Details on the chemical composition and physico-chemical properties of these materials are available in [34].

The reactor used in this work is a slurry bubble column (SBC). The scheme of this reactor is presented in Fig. 1. The choice of this reactor is

based on the “know-how” of our industrial partner, the world leader in sodium bicarbonate production. The reactor is composed of a column of 1.60 m height (four removable sub-columns of 0.4 m height each) and 0.34 m diameter made by PVC (nominal volume of 145 L). The column is divided into three zones. Zone 1, called bubble zone, is found at the bottom of the column where the aqueous suspension of NPC or APC particles is accumulated by gravity and where the gaseous effluent is fed to the reactor. At the bottom of the reactor, the suspension which get out the column is pumped to the head of the column with controlled liquid circulating flow rate (Q_R , m³/h). Zone 2 is composed of 6 trays which allow increasing gas/liquid exchange surface. Zone 3 is found at the top of the column where the suspension is injected to the column by pumping. With this reactor, the suspension is circulated from the bottom to the top of the reactor by a pump, and from the top to the bottom by gravity. The gaseous stream is injected at the bottom of the reactor and goes up to the top before leaving the reactor. The counter-current regime of gaseous and liquid fluids enhances the gas/liquid contact. Table 1 shows the operational limits of the column.

H_2S removal experiments were carried out with both synthetic and real gaseous effluents. Synthetic gaseous effluent was obtained by mixing compressed air with pure H_2S from a gas bottle. The concentration of H_2S was set at 150–200 ppmv, which is typical concentration of H_2S emitted from buffer tanks of WWTP. Real gaseous effluent was recovered from the buffer tank of the WWTP (capacity of wastewater treatment: 7500 m³/day) in Graulhet city (France). In fact, the buffer tank of this WWTP is covered to send emitted gases to a biological gas treatment system. This latter had usually technical problems related to weather conditions, which requires new technical solutions. In this work, a part of the gas emitted by the buffer tank has been extracted and injected to the SBC, installed on-site, for the evaluation of the performance of this pilot. The concentration of H_2S in the real gaseous effluent was found in the range of 5–200 ppmv, depending on the day and the weather conditions.

In order to start an experiment, an aqueous suspension of NPC and APC was firstly prepared using demineralized water. The solid content varied from 2 to 20 wt%. This suspension was kept homogeneous under stirring and pumped to the column. At the same time, compressed air was fed to the reactor from the bottom to keep particles under suspension. The total volume of the suspension fed to the reactor was between 40 and 70 L. Then, the experiment of H_2S removal started by switching compressed air to gaseous effluent containing H_2S . For the blank test, only demineralized water was pumped to the column instead of a suspension. During the experiment, both the inlet and outlet concentrations of H_2S as well as the pH of the suspension was continuously monitored. Details on these analyses could be found in [34]. Liquid samples were periodically withdrawn and filtered with a 0.45 μ m filtration-paper to separate sorbent particles, and the filtrate was analyzed by ICP-OES (for the determination of soluble metals) and ionic chromatography (for the determination of S^{2-} , SO_3^{-} , SO_4^{-} , $S_2O_3^{2-}$) [34]. Experiments were repeated at least twice and in all cases, the ratio of standard deviation to mean value of the H_2S removal efficiency was smaller than 3%. This confirmed the good repeatability of the tests.

The efficiency of H_2S removal is defined by Eq. (14):

$$Eff. (\%) = \frac{[H_2S]_{G,I} - [H_2S]_{G,O}}{[H_2S]_{G,I}} \times 100 \quad (14)$$

where $[H_2S]_{G,I}$ and $[H_2S]_{G,O}$ were respectively the inlet and outlet concentration of gaseous H_2S measured during the experiments.

3. Results

3.1. Blank test

Blank test was carried out with demineralized water and synthetic gaseous effluent in order to determinate the effect of water on the

removal of H_2S . The results are presented in Fig. 2. Inlet H_2S concentration varied in the range of 150–170 ppmv. At the beginning of the test, the H_2S removal efficiency reached around 50% due to the dissolution of H_2S in water. Then, it progressively decreased to around 2–10% within 60 first min of time-on-stream. After 60 min, the H_2S removal efficiency seemed to be stabilized around 2–10%. It should be reminded that with this reactor, gaseous effluent was continuously fed to the reactor while the volume of water was fixed at 40 L and was not renewed. The stabilization of the H_2S removal efficiency above 60 min could be explained by the oxidation of dissolved sulfide species ($\text{H}_2\text{S}_{(\text{aq})}$, $\text{HS}_{(\text{aq})}^-$, $\text{S}_{(\text{aq})}^{2-}$) into elemental sulfur and other products of higher oxidation degrees, e.g. SO_3^- , SO_4^- , and $\text{S}_2\text{O}_3^{2-}$ [34]. During the reaction, the pH of the solution slightly decreased, due to the dissolution of H_2S as acid gas as well as the formation of soluble sulfide species.

3.2. Comparison of NPC and APC

Previous study with a reactor at lab scale [34] showed that APC was systematically more reactive than NPC explained by the composition and structure of each material. In fact, as mentioned in our previous work [34], APC generally contains more impurities (Na, Mg, S) than NPC. In particular, aqueous suspension of APC (10 wt%) contains much more soluble species (Na, Mg, Ca, Cl, S) than that prepared from NPC. About the physical aspect, APC and NPC have comparable particle size distribution, varying from ca. 0.4 up to 300–400 μm . About the structural aspect, NPC principally contains calcite while APC contains both calcite and vaterite as highlighted by XRD and FTIR analysis [34]. In order to confirm the result obtained at the lab scale, APC and NPC suspensions were tested under the same conditions at large pilot scale. Fig. 3 shows the H_2S removal efficiency obtained with these two materials when the removal of H_2S stabilized. Once again, APC was found to be more reactive than NPC, which confirms the results obtained at lab scale. In fact, APC was formed by an artificial carbonation and was more soluble in water than NPC which was obtained by a long natural carbonation. Thus, the suspension of APC contains more soluble anions of CO_3^{2-} and OH^- than those in the suspension of NPC. These anions could neutralize soluble species of $\text{H}_2\text{S}_{(\text{aq})}$ and $\text{HS}_{(\text{aq})}^-$ (Eqs. (8) to (11)). Also, the suspension of APC contains more species such as Ca^{2+} and Mg^{2+} than that of NPC; these species being able to catalyze the oxidation of sulfide species (Eq. (12)) [34].

3.3. Influence of the solid content

The higher reactivity of APC compared to NPC has been confirmed at the pilot scale. Thus, this solid waste was selected for the next steps. Fig. 4 shows the impact of APC concentration on the H_2S removal

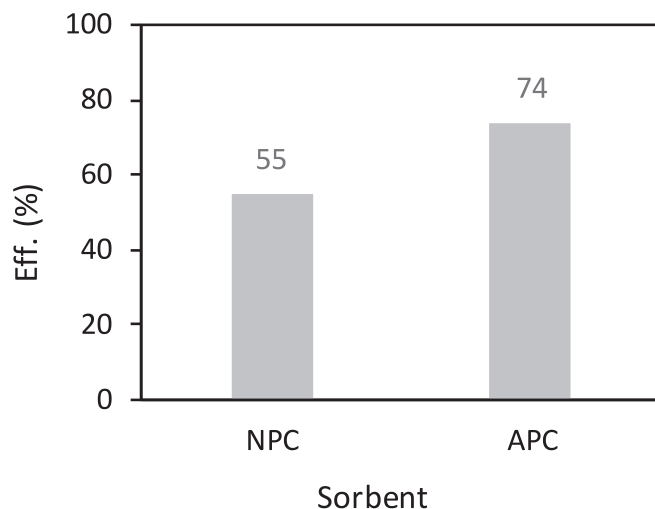


Fig. 3. Comparison of the reactivity of NPC and APC. Conditions: 40 L of suspension containing 10 wt% of NPC or APC; $Q_G = 3 \text{ m}^3/\text{h}$; $Q_R = 350 \text{ L/h}$; $C_i = 150\text{--}200 \text{ ppmv}$ of H_2S .

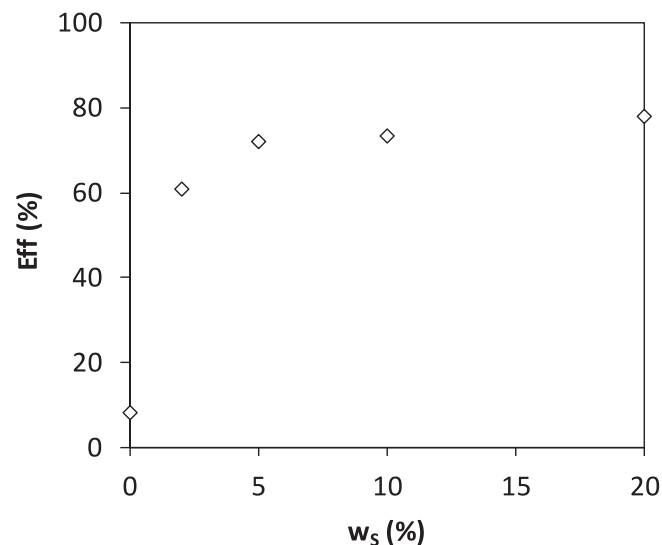


Fig. 4. Influence of the solid concentration (APC) on the efficiency of H_2S removal. Conditions: 40 L de suspension; $Q_G = 3 \text{ m}^3/\text{h}$; $Q_R = 350 \text{ L/h}$; $C_i = 150\text{--}200 \text{ ppmv}$ of H_2S .

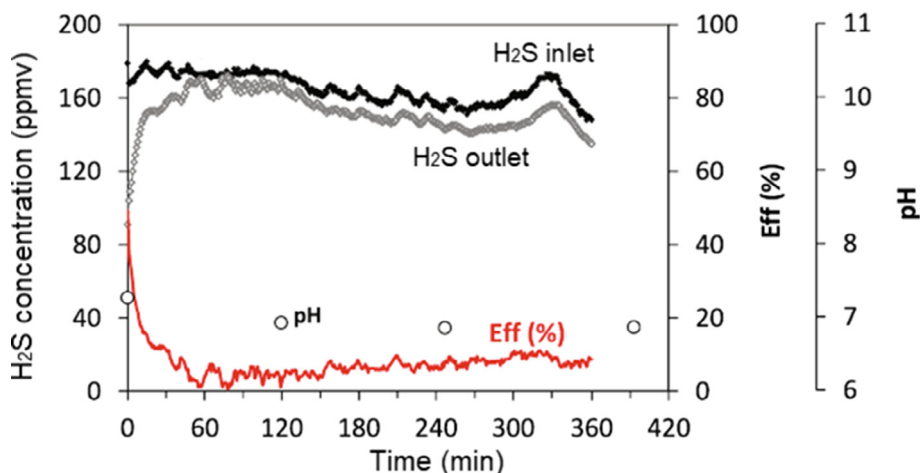


Fig. 2. Blank test: H_2S removal with demineralized water ($V_L = 40 \text{ L}$, $Q_R = 350 \text{ L/h}$, $Q_G = 3 \text{ m}^3/\text{h}$).

efficiency. As expected, increasing the APC concentration led to an increase of the H_2S removal efficiency. Adding only 2 wt% of APC allowed increasing the H_2S removal efficiency from around 8% (blank test, Fig. 2) to around 61%. At 5 wt% of APC, the H_2S removal efficiency reached around 72%. Above 5 wt% of APC, the H_2S removal efficiency only slightly increased to 74 and 78% at 10 and 20 wt% of APC, respectively. This behavior was already observed at the lab scale [34]. Taking into account the fact that energy consumed for the recirculation of the suspension by pumping increases with the solid content, a compromise needs to be established between the solid content, the gain in the H_2S removal efficiency and the energy consumed by the pump.

3.4. Influence of the contact time

The contact time could be controlled by changing the volume of the suspension, the recirculation rate of the suspension, and the inlet gas flow rate. Fig. 5 shows the influence of the recirculating rate of the suspension on the H_2S removal efficiency. Compared to a stirring reactor, the recirculating rate of the suspension plays a similar role as the stirring rotation to keep solid particles in suspension and guarantee the gas-to-liquid transfer. The impact of the recirculating rate of the suspension was investigated at different suspension volumes (40 or 60 L) and different solid contents (2 and 20 wt% of APC). In all cases, the H_2S removal efficiency was practically unchanged with the recirculating rate. So the process was not limited by gas-to-liquid transfer under the conditions used.

Fig. 6 shows the impact of the suspension volume on the H_2S removal efficiency for two values of the solid content of 2 and 20 wt%. Increasing the suspension volume allowed increasing the contact time

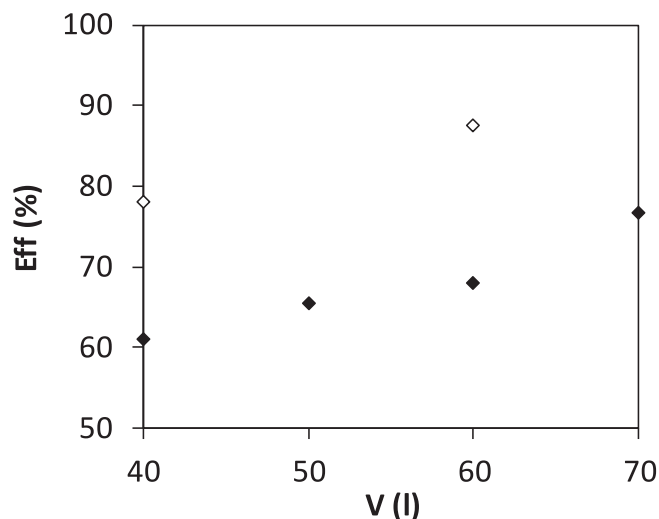


Fig. 6. Influence of suspension volume on the efficiency of H_2S removal. Conditions: Suspension of APC; $Q_G = 3 \text{ m}^3/\text{h}$; $Q_R = 350 \text{ L/h}$; $C_I = 150\text{--}200$ ppmv of H_2S .

of H_2S with the suspension, which improve the H_2S removal efficiency. For the suspension containing 2 wt% of APC, a linear increase of the H_2S removal efficiency as a function of the increase of the suspension volume was observed. For the suspension containing 20 wt% of APC, even with only two experiments at 40 and 60 L of suspension, the evolution of H_2S removal efficiency seemed to linearly increase with the suspension volume. Once again, these results confirmed those obtained at lab scale [34].

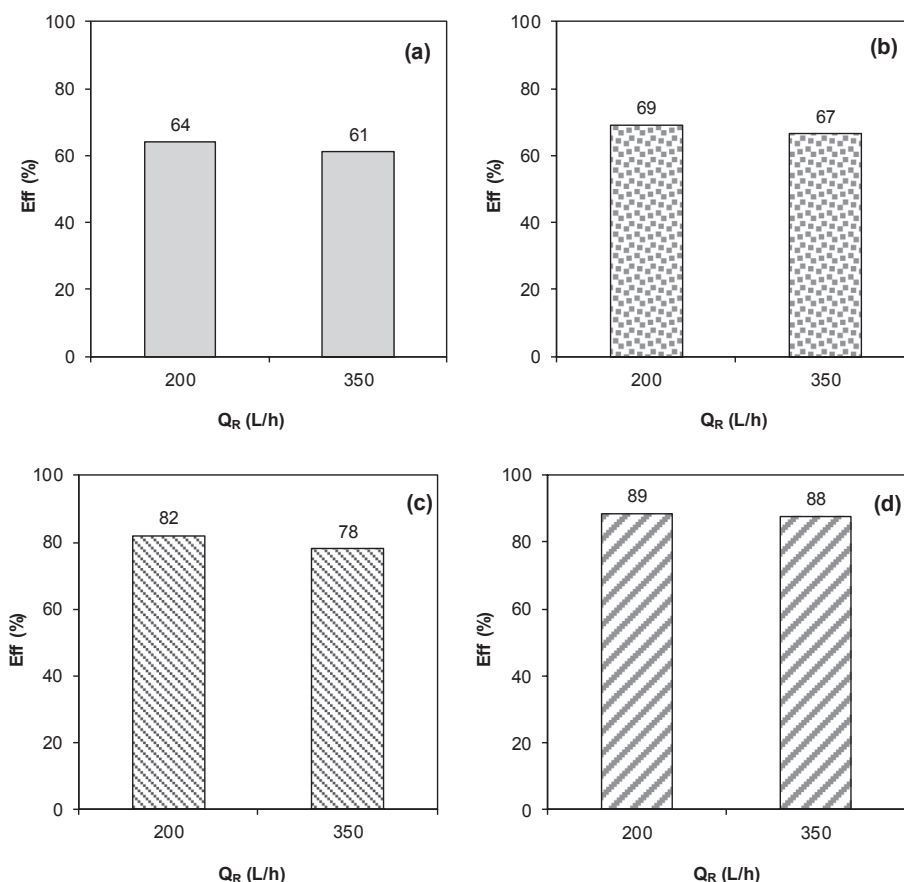


Fig. 5. Influence of the liquid recirculation rate (Q_R) on the efficiency of H_2S removal. Conditions: $Q_G = 3 \text{ m}^3/\text{h}$; $C_I = 150\text{--}200$ ppmv of H_2S . (a): 40 L of 2 wt%; (b) 60 L of 2 wt%; (c) 40 L of 20 wt%; (d) 60 L of 20 wt%.

The impact of the inlet gas flow rate (Q_G) on the H_2S removal efficiency was performed at different suspension volumes (40 and 60 L) and different solid contents (2 and 20 wt% of APC). The result is presented in Fig. 7. At low solid content of 2 wt% (Fig. 7 a and b), the H_2S removal efficiency strongly decreased when Q_G increased from 2 to 3 m^3/h . As shown in Eqs. (1) to (13), the H_2S removal starts by the dissolution of H_2S into the liquid phase. Thus, increasing Q_G reduces gas-liquid contact time and limits the dissolution of H_2S to the liquid phase.

At high solid content of 20 wt% (Fig. 7 c and d), the H_2S removal efficiency also decreased when Q_G increased from 2 to 3 m^3/h , but with a smaller extend. High solid content led to high availability of metallic cations, e.g. Ca^{2+} , Mg^{2+} , and high pH of suspension, which favor the dissolution of H_2S and the oxidation of sulfide species [34]. So, the H_2S removal efficiency was less impacted by Q_G .

3.5. Evolution of the suspension: pH

The pH of the suspension was periodically monitored and similar behavior was observed for all the tests performed with APC and NPC at the pilot scale. As example, Fig. 8 shows the pH evolution obtained with 40 L of suspension containing 2 wt% of APC. The pH seemed to follow the evolution of H_2S removal efficiency. The initial pH of the suspension reached around 8.8 as a result of the dissolution of calcium carbonate (Eqs. (1) and (2)). When the gaseous effluent passed through the suspension, H_2S from the gas phase was dissolved in the liquid phase to form soluble $H_2S_{(aq)}$ which neutralized the basicity of the suspension (Eq. (8)–(11)). This neutralization decreased the initial pH within the zone 1 in Fig. 8. Then, the pH became stable around 8 within the zone 2 in Fig. 8. In fact, the consumption of calcium carbonate by H_2S was very small compared to the initial quantity of calcium carbonate introduced

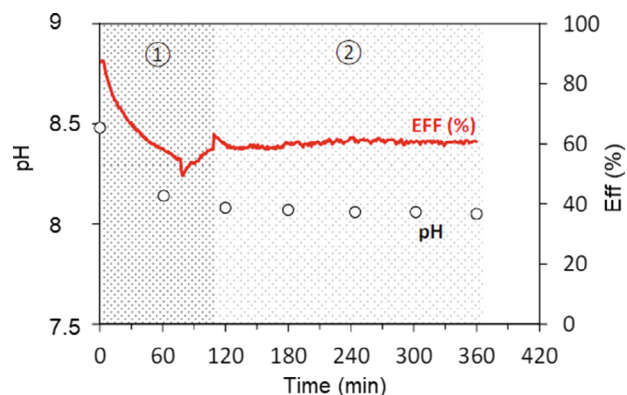


Fig. 8. Evolution of the pH of the suspension. Conditions: 40 L of suspension containing 2 wt% of APC; $Q_G = 3 m^3/h$; $Q_R = 350 L/h$; $C_I = 150\text{--}200$ ppmv of H_2S .

into the reactor. Thus, the pH was stable and conditioned by the equilibrium of calcium carbonate dissolution in water.

3.6. Evolution of the suspension: soluble species

Fig. 9 shows the concentration evolution of the main species in the liquid phase during the reaction. The term “S” means the sum of all S-containing species in the liquid phase. Fig. 9(a) and (b) report the results obtained with a suspension of APC containing 10 and 2 wt% of solid particles, respectively. Generally, the evolution of Na, Mg, Ca and S in the liquid phase was similar to each other. But their concentration changed with the solid content of the suspensions.

It is reminded that the initial APC already contained sulfur

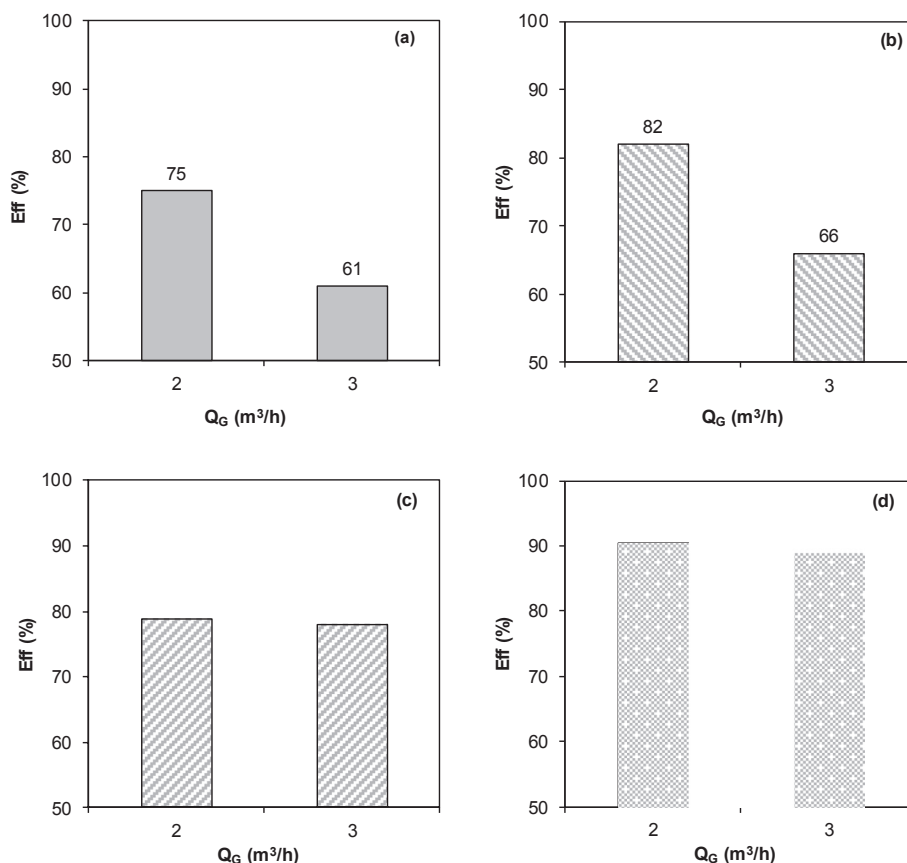


Fig. 7. Influence of the inlet gas flow rate on the efficiency of H_2S removal using APC. Conditions: $Q_R = 350 m^3/h$; $C_I = 150\text{--}200$ ppmv of H_2S . (a): 40 L of 2 wt%; (b): 60 L of 2 wt%; (c): 40 L of 20 wt%; (d) 60 L of 20 wt%.

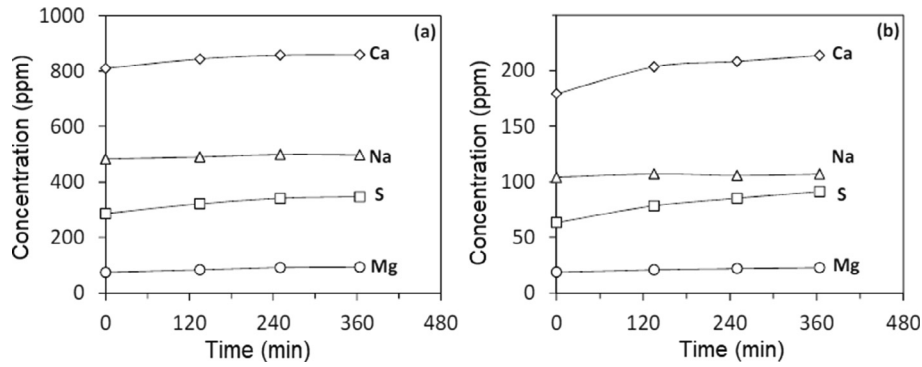


Fig. 9. Evolution of the concentration of Ca, Mg, Na and S in the liquid phase. Conditions: a) 40 L of suspension containing 10 wt% of APC, $Q_R = 350$ L/h, $Q_G = 3$ m³/h; b) 60 L of suspension containing 2 wt% of APC, $Q_R = 350$ L/h, $Q_G = 3$ m³/h.

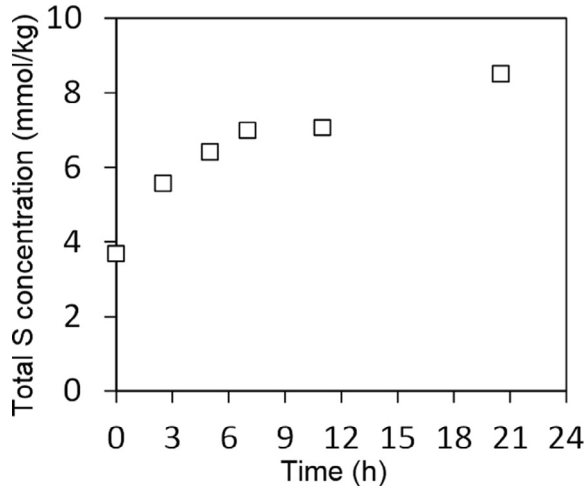


Fig. 10. Evolution of the total S concentration in the solid phase. Conditions: 40 L of suspension containing 10 wt% of APC, $Q_R = 150$ L/h, $Q_G = 3$ m³/h.

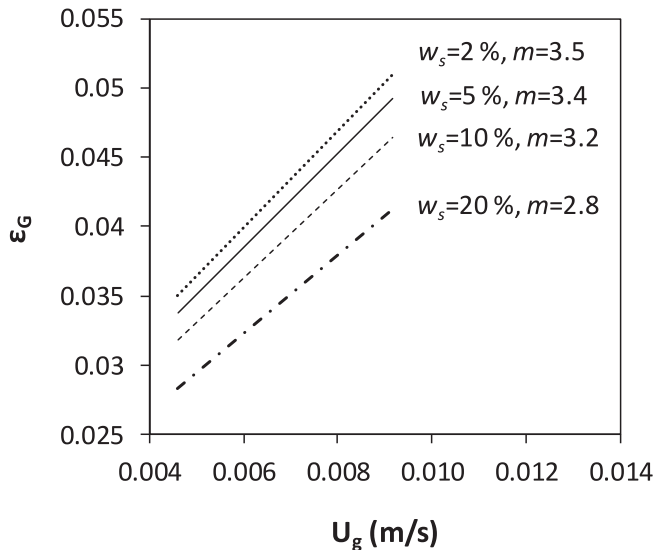


Fig. 11. Influence of the solid content and the superficial gas velocity on the gas retention yield; w_s : solid content, m : slope of the curves.

compounds [34]. When APC was dispersed in water to prepared the suspension, these sulfur compounds were dissolved in water which explains the initial concentration of S-containing compounds at the zero time in Fig. 9. Also, the partial dissolution of calcium carbonate, magnesium carbonate and sodium carbonate in water explains the

initial concentration of calcium, magnesium and sodium of the suspensions. For both suspensions, the concentration of soluble sodium and magnesium only slightly increased. On the other hand, the concentration of soluble calcium and S-containing compounds remarkably increased with the reaction time, according to the dissolution of calcium carbonate (Eqs. (1) and (2)) and hydrogen sulfide (Eqs. (4)–(12)).

3.7. Evolution of total concentration of sulfur in the solid phase

During the reaction, the total concentration of sulfur in the solid phase was also analyzed. As an example, Fig. 10 shows the results obtained with a suspension of 10 wt% APC. The total S concentration increased with the reaction time, which could be explained by the formation of elemental sulfur (Eq. (12)) and of the insoluble S-containing compounds (Eq. (13)). This again confirmed the observations at the lab scale [34]. H₂S from the gas phase was accumulated in both soluble and solid forms.

3.8. Hydrodynamic of the column

In order to explain the effect of operational parameters on the efficiency of the column, the algorithm developed by Lemoine et al. [35] has been used. This algorithm was built from more than 3000 experimental works, and consider the following factors: i) the geometry of the reactor; ii) the properties of the environment (gas, liquid, solid); and iii) the operational conditions. For the column used in this work, the following equations could be established [35,36]:

$$\epsilon_G = 4.94 \cdot 10^{-3} \left(\frac{\rho_L^{0.42} \rho_G^{0.18}}{\mu_L^{0.17} \sigma_L^{0.27}} \right) U_G^{0.55} \left(\frac{P_T}{P_T - P_S} \right)^{0.20} \left(\frac{D_C}{D_C + 1} \right)^{-0.12} \Gamma^{0.05} \exp(-2.23 C_V - 0.16 \rho_S d_{S-0.24}) \quad (15)$$

$$a = \frac{6\epsilon_G}{(1 - \epsilon_G) d_b} \quad (16)$$

$$k_L a = 6.14 \cdot 10^4 \left(\frac{\rho_L^{0.26} \mu_L^{0.12}}{\rho_G^{0.06} \sigma_L^{0.52}} \right) \left(\frac{\epsilon_G^{1.21}}{U_g^{0.12} d_b^{0.05}} \right) \left(\frac{D_A^{0.50}}{T^{0.68}} \right) \left(\frac{D_C}{D_C + 1} \right)^{0.04} \Gamma^{0.11} \quad (17)$$

where: ϵ_G gas retention yield; ρ_L liquid density (kg/m³); ρ_G gas density (kg/m³); μ_L dynamic viscosity of the liquid (Pa s); σ_L surface tension of the liquid (N/m); U_g superficial gas velocity (m/s); P_T total pressure (MPa); P_S water vapor pressure (MPa); D_C column diameter (m); Γ gas sparger type; C_V volume solid concentration (%); ρ_S solid density (kg/m³); d_S Sauter mean bubble diameter (m); a gas-liquid interfacial area (m²/m³); d_b bubble diameter (m); k_L coefficient of gas/liquid mass transfer from the liquid-side (m/s); D_A gas diffusion coefficient in the liquid; T temperature (K);

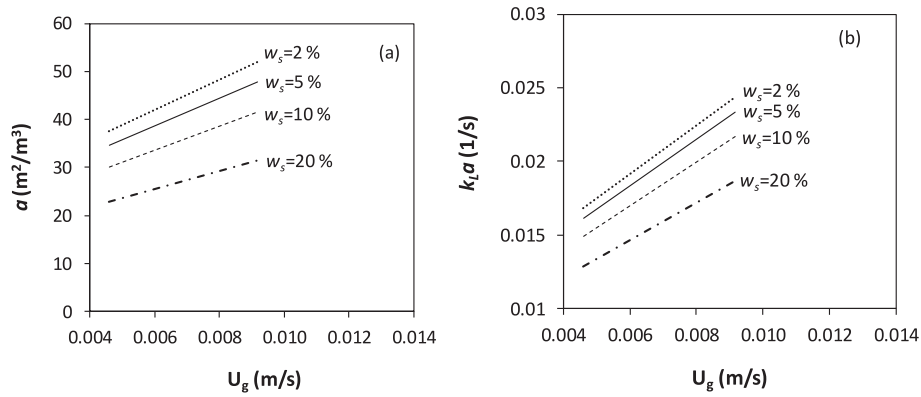


Fig. 12. Influence of the solid content and the superficial gas velocity on the surface of G/L transfer (a) and on the volume coefficient of mass transfer ($k_L a$).

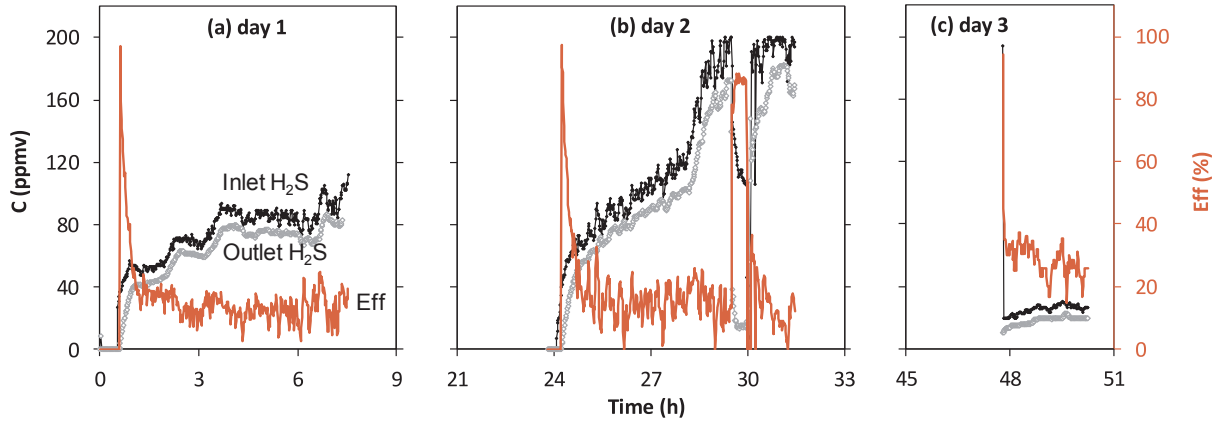


Fig. 13. H_2S removal from gas emission by a WWTP's buffer tank using only water without sorbent. Conditions: 70 L of water, $Q_R = 250$ L/h, $Q_G = 2$ m³/h.

3.8.1. Gas retention yield (ε_G)

The Eq. (15) allows estimating the value of the gas retention yield (ε_G) as function of the operational conditions. Fig. 11 shows that at a given superficial gas velocity (U_g), the gas retention yield (ε_G) decreases with the increase of the solid content of the suspensions. In fact, fine solid particles could increase of the dynamic viscosity and the density of the suspension, and so cause the coalescence of gas bubbles. At a given solid content, the gas retention yield increases with the superficial gas velocity because the latter favors the formation of turbulences which enhance the accumulation of gas bubbles in the suspension [37].

From the values estimated for the slope (m) of the gas retention yield in Fig. 11, the flow regime of the gas phase could be predicted. In fact, in the literature, it has been reported that the flow regime is homogeneous when $m \geq 1$, and is heterogeneous when $m < 1$ [38,39]. Thus, for the suspension studied in this work, the homogeneous regime is predominant.

3.8.2. Mass transfer

The value of k_L was estimated at around $5 \cdot 10^{-4}$ m/s. This value is close to the values reported in the literature for bubble column reactors [37,40,41]. As shown in Fig. 12, the gas-liquid interfacial area (a) is highly reduced by increasing the solid content at a given superficial gas velocity. This is the direct consequence of the decrease of the gas retention yield when the solid content increases. On the other hand, at a given solid content, the gas-liquid interfacial area increases with the superficial gas velocity. As explained before, the increase of the superficial gas velocity favors the formation of turbulences which allows increasing the accumulation of gas bubbles in the suspension. Similar impact of the solid content and the superficial gas velocity on the evolution of $k_L a$ is observed.

The increase of the superficial gas velocity (U_g) allows increasing the

gas-liquid interfacial area (a), but this decreases the H_2S removal efficiency. In fact, H_2S has low solubility in water and the suspension could be quickly saturated with soluble $H_2S_{(aq)}$. By definition in Eq. (14), the H_2S removal efficiency depends on inlet and outlet H_2S concentration; this latter is limited by H_2S elimination rate (Eqs. (4)–(13)). Increasing more inlet H_2S than H_2S elimination rate leads to the decrease of H_2S removal yield, despite the increase of the gas-liquid interfacial area (a).

3.9. Removal of H_2S from the gas phase emitted by a wastewater treatment plant

Before deploying the technology of H_2S removal from the gas phase using NPC or APC suspension, experiments with gases emitted by the buffer tank of a WWTP were performed. It is reminded that the initial concentration of H_2S emitted by a WWTP's buffer tank strongly depends in the weather conditions. Particularly, when it rains, H_2S concentration is practically zero.

The first experiment was done with water without sorbent. The gaseous effluent continuously passed through the column for 51 h. However, the inlet and outlet H_2S concentration could only be measured during the day (mostly between 8 a.m. and 5 p.m.), and no data was obtained during the night and the week-end because of the restriction to the access to the site. Fig. 13 shows the results obtained with this blank test. At the beginning of each day where H_2S concentration was monitored, the first points of H_2S inlet concentration was zero due to the response delay. For these points, the H_2S removal efficiency is automatically set at 0%. As expected, the inlet H_2S concentration varied as a function of the weather conditions and was found in the range of around 20–200 ppmv. The outlet H_2S concentration seemed to follow the inlet H_2S concentration. In the absence of solid particles of NPC or

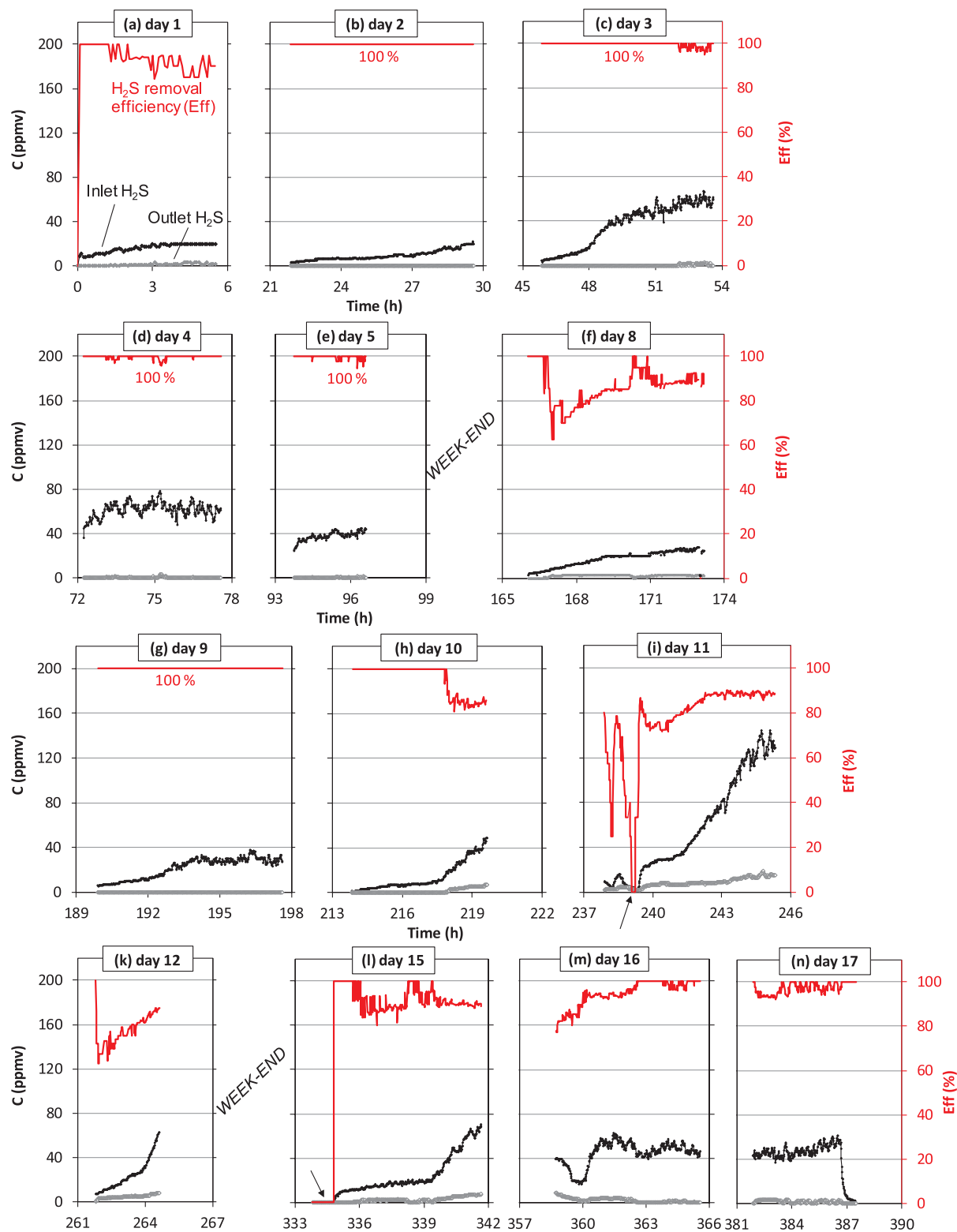


Fig. 14. H₂S removal from gas emission by a WWTP's buffer tank using APC suspension. Conditions: 70 L of water containing 5 wt% of APC, $Q_R = 250$ L/h, $Q_G = 2$ m³/h. Arrows: zone of zero inlet H₂S concentration. ■ Inlet H₂S concentration; ▬ Outlet H₂S concentration; — H₂S removal efficiency (Eff).

APC, the H₂S removal efficiency was smaller than 20%. These results again confirms those obtained with a synthetic gaseous effluent presented in Fig. 2. Without APC or NPC, water was not efficient for H₂S removal.

Fig. 14 shows the results obtained with 70 L of the suspension

containing 5 wt% of APC at the recirculation rate of 250 L/h and the inlet gas flow rate of 2 m³/h. This experiment was continuously kept for 17 days. Once again, the inlet H₂S concentration strongly varied as a function of the weather conditions. It generally increased from the morning to the afternoon because of the higher humidity and lower

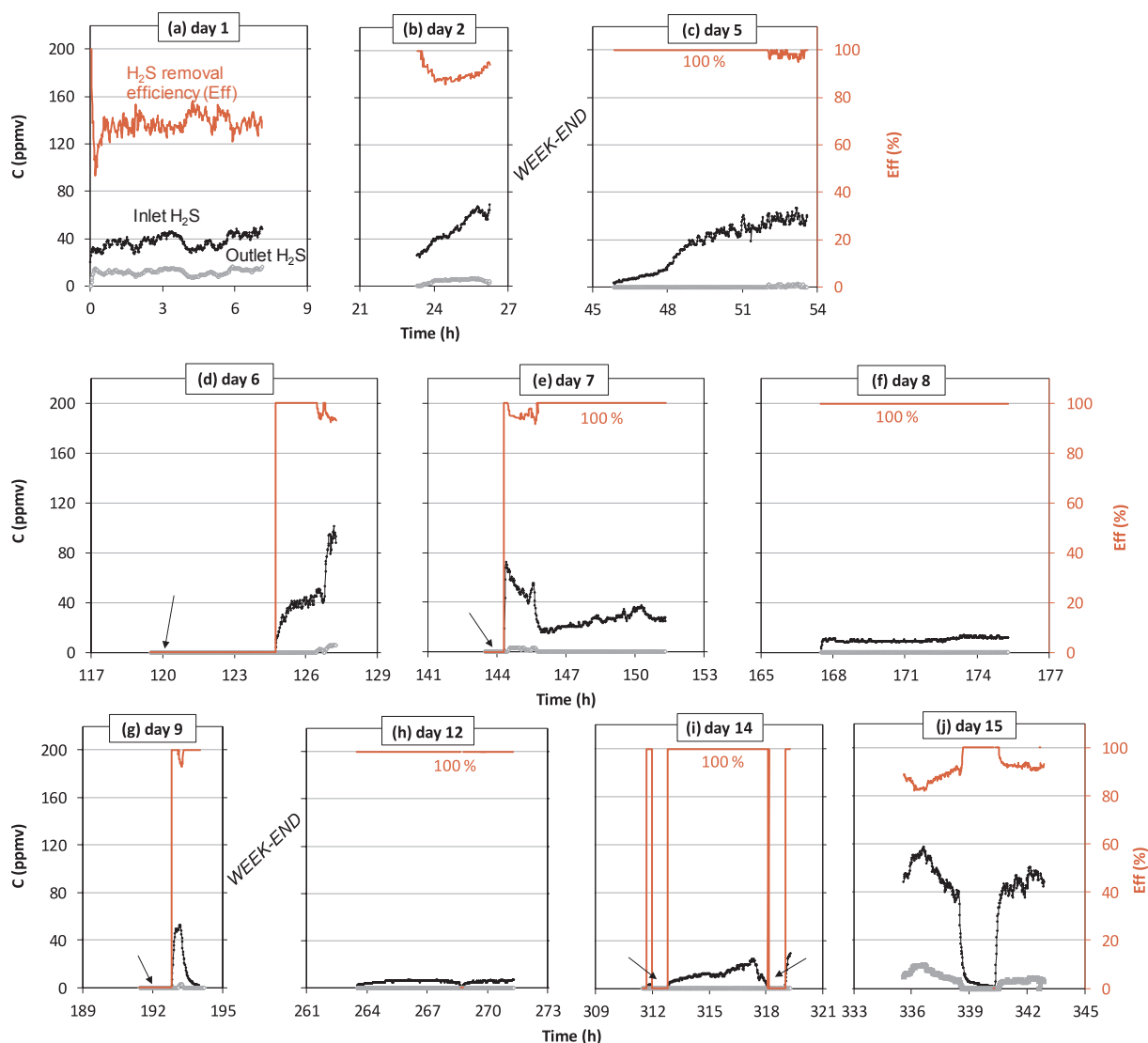


Fig. 15. H₂S removal from gas emission by a WWTP's buffer tank using APC suspension. Conditions: 70 L of water containing 5 wt% of APC, $Q_R = 250$ L/h, $Q_G = 3$ m³/h. Arrows: zone of zero inlet H₂S concentration. ■ Inlet H₂S concentration; — Outlet H₂S concentration; — H₂S removal efficiency (Eff).

temperature in the morning compared to the afternoon. In some cases, when it rained (days 11 and 15), the inlet H₂S concentration fell to zero. In all cases and regardless the inlet H₂S concentration, the H₂S removal efficiency was always higher than 60%, mostly close to 100%. For example, during the 17th day, the H₂S removal efficiency was always above 95%.

Fig. 15 shows the results obtained under the same conditions compared to those in Fig. 14, except for the inlet gas flow rate of 3 m³/h instead of 2 m³/h. This experiment was continuously kept for 15 days. During this experiment, it rained more frequently (days 6, 9, 14 and 15) where the inlet H₂S concentration fell to zero several times. The results obtained were similar to those in Fig. 14. The H₂S removal efficiency was mostly found within 80–100%.

These results demonstrated the potential application of APC as a low cost and efficient sorbent for H₂S removal from the gas phase, using the concept of the triphasic gas/liquid/solid reactor.

4. Conclusions

The reactivity of calcium carbonate-based sorbents (APC: artificially-precipitated calcium carbonate, and NPC: naturally-precipitated calcium carbonate), by-products recovered from the production of

sodium bicarbonate, was investigated in the removal of H₂S from the gas phase, using a 145 L slurry bubble column (SBC). This reactor allows performing a semi-continuous process: the gaseous effluent containing H₂S is continuously fed to the reactor while the volume of the suspension containing APC or NPC was unchanged. The experiments carried out with a synthetic gaseous effluent (H₂S diluted in compressed air) at this pilot scale confirmed the results obtained at the lab scale in our previous work [34]. The experiments performed with the gaseous effluent emitted from the buffer tank of a WWTP were also conclusive. This constitute the basis for the future deployment of this technology at large industrial scale for the treatment of H₂S from the gas phase.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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