

Optimization of SO₂ and NO_x sequential wet absorption in a two-stage bioscrubber for elemental sulfur valorisation

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Abstract

Removal of SO₂ and NO_x from flue gases has become an important issue in air pollution control. A two-stage bioscrubber based on a sequential wet absorption of SO₂ and NO_x followed by a two-stage biological process has been proposed in order to valorise SO₂ and NO_x by elemental sulphur production. Biological process characterization established a maximum sulfate loading rate (5 kg S·m⁻³·d⁻¹) and an optimal *COD/S* ratio (5.4 g O₂·g S⁻¹) in order to maximize elemental sulfur production and to avoid biological process limitations. Absorption of SO₂ and NO_x species is highly dependent on the absorption effluents compositions. In this sense, the success of the two-stage bioscrubber process lies in an optimal sequential transfer of pollutants to the liquid. Differences in the solubility of pollutants enable the individual absorption of pollutants in two in-series scrubbers operated under different pH and residence time conditions. In addition, the use of secondary effluents from the reduction-oxidation biological process as absorbent was demonstrated as a key parameter to improve the efficiency and reduce operating costs.

1. Introduction

Combustion processes gives rise to one of the main air pollution sources with the release of harmful chemicals such as CO₂, SO₂ and NO_x to the atmosphere [1]. Although reduction of flue gases emissions is in the public administration and industrial sector agenda, treatment has become critical in order to avoid health or welfare problems to the ecosystems. With this aim several technologies have been developed to remove SO₂ and NO_x from off-gases [2]. SO₂ is usually removed from flue gases in wet absorption facilities by reacting with lime or limestone. Differently, selective catalytic reduction processes are mainly used in NO_x removal [2] since among NO_x, nitric oxide (which accounts for more than 90% in flue gases) shows a low solubility. Despite high removal efficiencies can be obtained for the treatment of both pollutants, some difficulties appear when both compounds are present simultaneously. In addition, technologies abovementioned involve important drawbacks such as a high reagents and energy consumption and undesirable by-products generation. These limitations are accentuated when the abatement of high pollutants concentrations is required. For this

reason, alternative flue gas treatment technologies based on biological processes are needed [3,4]. This is the case of the two-stage bioscrubber based on the biotechnological process described in [5], which can be implemented to recover elemental sulfur from SO₂ and NO_x contained in flue gases. The process is based on a sequential absorption of SO₂ and NO_x to obtain, separately, first a sulfate-rich stream and, secondly, a nitrite or nitrate-rich stream used to feed two biological reactors. In the former, a heterotrophic reduction of the absorbed SO₂ is carried out to obtain a dissolved sulfide-rich stream. In the latter, a partial oxidation of dissolved sulfide to elemental sulfur through autotrophic denitrification is performed. The two-stage bioscrubber concept may allow a reduction in the consumption of reagents and the recovery of elemental sulfur as valuable product for the industry [6,7] improving the existing flue gas treatment technologies from an economic and technical point of view.

Although the core of the process is the biological stage where flue gas wastes are converted into a valorized product, the quality and the amount of biological sulfur produced is strongly related to the bioreactors inlet streams [3]. For this reason, this study is focused on the optimization of the sequential absorption of both pollutants to ensure a high overall process efficiency. In this sense, the use of effluents from biological process as alkaline sorbent in wet flue gas spray tower together with a NO_x to NO₂ oxidation stage previous to absorption, were evaluated.

2. Experimental methods

2.1. Two-stage bioscrubber

The two stage bioscrubber integrates in a single process the removal of SO₂ and NO_x from flue gases and the treatment of the resulting liquid wastes towards elemental sulfur recovery (Figure 1a). The bioscrubber consisted of a first absorption stage with a slightly alkaline solution, where SO₂ and NO_x are sequentially absorbed, followed by a heterotrophic upflow anaerobic sludge blanket (UASB) reactor for the reduction of sulfate in series with downstream bioreactor for the partial oxidation of sulphide to elemental sulfur. In this way the waste generated in the treatment of flue gases is reduced to a low salinity wastewater stream that can be treated in a conventional wastewater treatment plant. Besides, one of the main products of the oxidation of the carbon source used in the UASB is CO₂, which is retained as dissolved CO₂. The low aeration conditions of the overall biological process enables the reuse of the effluent as alkaline sorbent in the wet-absorption stage.

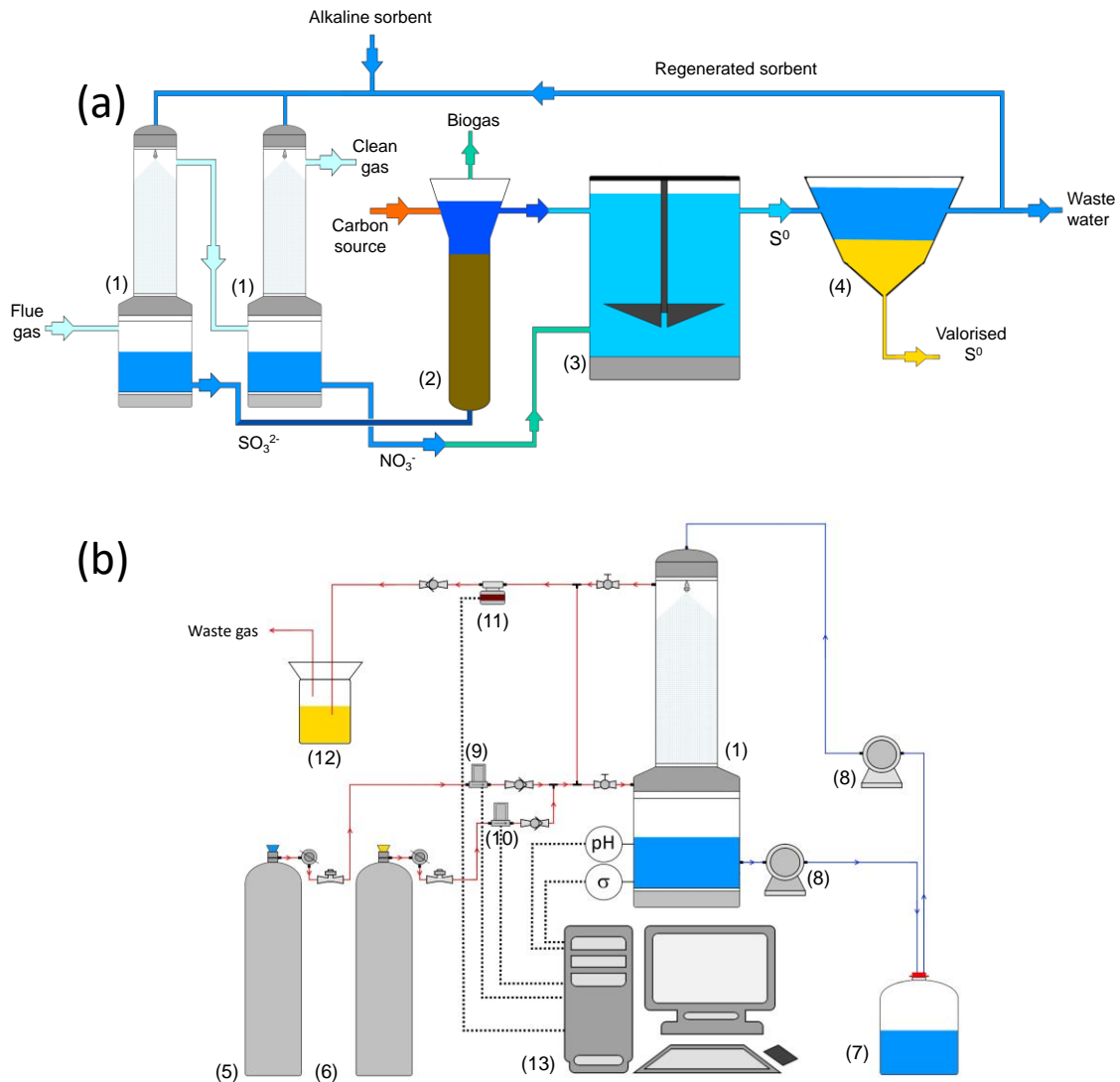


Fig. 1 (a) Schematic of the two-stage bioscrubber, (1) Spray absorber for flue gas treatment, (2) sulfate reduction bioreactor, (3) anoxic sulfide oxidation reactor and (4) elemental sulfur settler. (b) Schematic of the bench-scale spray absorber used to study flue gas absorption process: (1) spray absorber, (5) bottled air, (6) bottled SO_2/NO , (7) sorbent tank, (8) sorbent pump, (9) air mass flow controller, (10) SO_2/NO mass flow controller, (11) electrochemical sensors, (12) NaOH filter and (13) monitoring computer

Due to the low solubility of NO_x , the first spray scrubber is operated under a pH, gas contact time and sorbent-flue gas ratio (L/G) conditions that increase the solubility of SO_2 and limit the absorption of NO_x . In the second column the conditions which NO_x solubility is enhanced are established.

2.2. Experimental apparatus

A schematic diagram of the experimental lab-scale spraying-absorber used in the study of flue gas absorption is shown in Figure 1b, including the flue gas mimics and the sorbent supply systems, the bench-scale spray tower and the flue gas analysis system. The spray tower was fabricated in PVC and consists of a gas-liquid contact section (5.9 cm of internal diameter and 30 cm high) and a liquid reservoir (11 cm of

internal diameter and 20 cm height) with a working volume of 1800 mL. Sorbent is injected into the top of the column using a peristaltic pump (7554-94 L/S pump, Masterflex, USA) and is atomized in drops of 50-100 μm of diameter through a spray nozzle (490.403.1Y.CA, Lechler, Germany). The pH and the ionic conductivity were continuously measured at the reactor outlet using a multi-analyte probe (Multi 3420, WTW, Germany). The synthetic flue gas consisted of a mixture of SO_2/NO and air, prepared by mixing metered amounts of gases using mass flow controllers (EL-Flow Select, Bronkhorst, The Netherlands), is fed counter-currently from the bottom of the gas-liquid contactor. Continuous monitoring of SO_2 and NO_x (as a mixture of NO and NO_2) in the outlet gas phase was performed using an electrochemical SO_2 sensor (SO2-B4, Alphasens, UK), an electrochemical NO sensor (4NO-2000, EuroGas, UK) and an electrochemical NO_2 sensor (4NO2-2000, EuroGas, UK), all of them with a measuring range from 0 to 2000 ppm_v . Measurement of higher pollutants concentrations required flue gas dilution, performed by two flowmeters (2100, Tecfluid, Spain). Residual flue gas was bubbled through a NaOH filter before its emission to the atmosphere.

Absorption experiments were performed separately for each pollutant generating a synthetic flue gas by mixing air SO_2 and/or NO_x . Synthetic flue gas for the experimental study of NO_x absorption was generated as a mixture of pure NO and air. The selected fresh sorbent was continuously fed to ensure constant pH and composition at reactor inlet. The compounds concentration, pH and ionic conductivity at liquid outlet were continuously monitored until achieving steady state condition. Experiments were performed at constant temperature of 20 ± 1 $^\circ\text{C}$ and atmospheric pressure. Absorption efficiency was evaluated for each pollutant by means of the following expression:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100 \quad (1)$$

Where C_{in} is the inlet pollutant concentration and C_{out} is the outlet pollutant concentration in ppm. To ensure experiments accuracy, three replicate measurements were made, obtaining relative errors below 5%. In this paper only average values are shown.

The experimental setup used in the study of biosulfur production from the sulfate-rich effluent consisted of a UASB reactor in series with a continuous stirred tank reactor (CSTR). The UASB reactor for sulfate reduction had a total volume of 2.5 L and an effective volume (Sludge bed volume) of 1 L. The reactor was a glass-made jacketed reactor connected to a thermostatic bath to control the temperature at 35°C . The UASB was designed with a riser with two different diameters. Most of the riser had an internal diameter of 51 mm. Downstream of the UASB partial oxidation of sulfide was performed in a glass-made CSTR with a volume of 6 L. the CSTR was continuously fed with the effluent of the UASB. The partial oxidation was performed ensuring microaerophilic conditions. Additional information of both reactors operation, monitoring and control can be found in [5].

3. Results

3.1. Characterization of two-stage bioscrubber

3.1.1. Characterization of flue gas absorption

Absorption is mainly influenced by flue gas and sorbent flowrates, pollutant inlet concentration and sorbent pH. For this reason, the study presented herein focused firstly on the individual influence of these parameters on SO₂ absorption efficiency. Sorbent flowrate was assessed as *L/G* ratio. An inlet SO₂ concentration of 2000 ppm_v, a flue gas retention time (*RT*) of 2s, a sorbent pH of 6, a *L/G* of 7.5 L·m⁻³, a sorbent temperature of 298±1.5 K and a sulfate concentration in fresh sorbent of 0 g·L⁻¹ were defined as reference according to common conditions[2]. The individual influence of parameters was assessed separately (figure 2) by varying each parameter within its typical range in spray scrubbers.

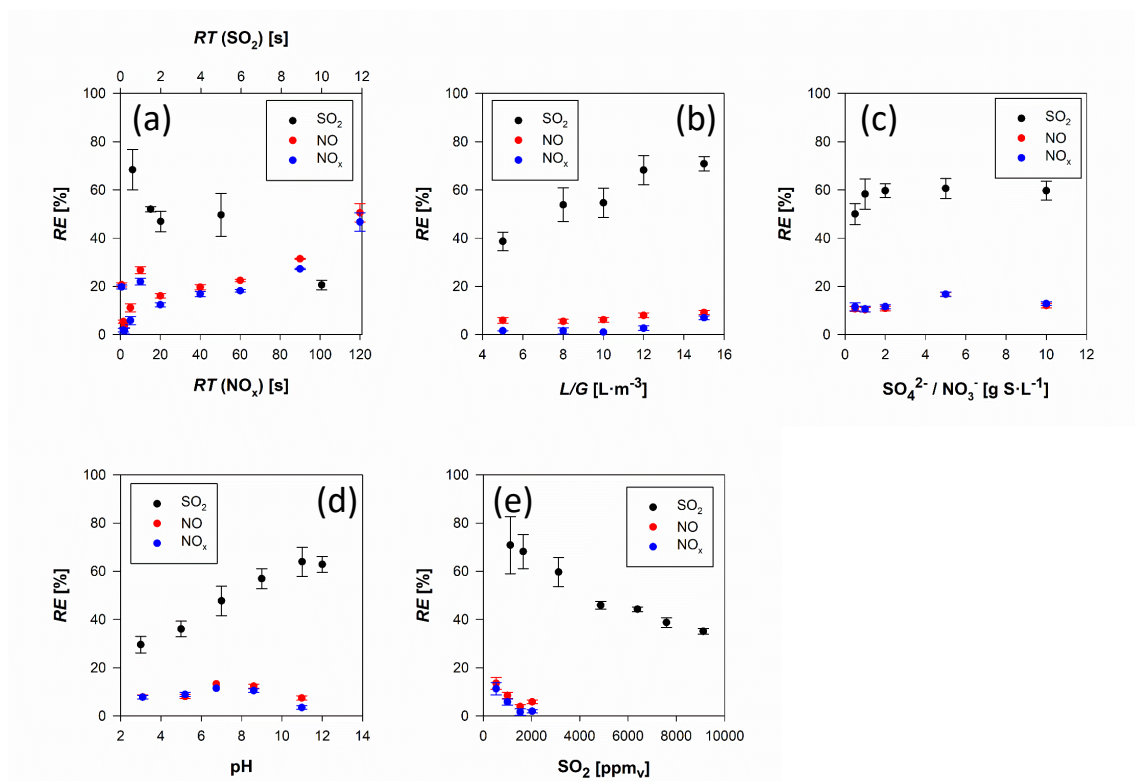


Fig. 2 Influence of (a) flue gas residence time, (b) *L/G* ratio, (c) sulfate concentration, (d) sorbent pH, and (e) SO₂ concentration, on SO₂, NO and NO_x removal efficiency (*RE*).

Results shown in figure 2 depict the effect of the tested operating variables on SO₂ absorption efficiency (*RE*). As expected SO₂ absorption efficiency was strongly affected (in this order) by flue gas and sorbent flowrates, sorbent pH and SO₂ inlet concentration, while the sulfate concentration of the sorbent and the flue gas temperature had a slight impact on *RE*, which remained practically constant over the assessed ranges. These trends were in agreement with results found in literature[2].

A *RT* decrease from 10 to 0.6 s (Figure 2a) resulted in a *RE* improvement around 50%, from 20.6 to 68.4%. This is explained because keeping the *L/G* ratio, turbulences

in gas-liquid contactor increase with gas flowrate, enhancing SO_2 mass transfer to the liquid bulk. Increasing the volumetric flow ratio increases the diameter of the droplets and thus the gas-liquid mass transfer interface, which is favourable to SO_2 removal. As can be observed in Figure 2b, an L/G increase from 5 to $15 \text{ L}\cdot\text{m}^{-3}$ led to an SO_2 RE increase from 38.7 to 70.8%. Likewise, according to Figure 2d, when sorbent pH was increased from pH 3 to pH 12 the SO_2 RE raised from 29.6 to 60.8%. The capability to neutralize protons released during SO_2 absorption at higher pH in the liquid phase improves RE . However, increasing the sulfate concentration had no effect on RE . In Figure 2c, it can be observed a slight increase in RE (from 50 to 60%) as the presence of sulfate in the sorbent increased. The influence of flue gas temperature on RE was even slighter.

The optimal conditions for SO_2 absorption can be selected from the univariate analysis of the six operating parameters shown in Figure 2. Completing the study with the characterization of NO_x absorption make possible to define those conditions so that the selective separation of both pollutants can be performed.

Synthetic NO_x stream was generated as a mixture of pure NO and air. The NO is partially oxidized to NO_2 resulting in a NO, NO_2 and air mixture. NO inlet concentration is defined as the sum of NO and NO_2 concentrations. The generated NO_x stream contained a 90-95% of NO and 5-10% of NO_2 . Spray scrubber characterization for NO_x absorption was studied assessing the influence of flue gas contact time, L/G ratio, nitrate sorbent concentration, sorbent pH and NO inlet concentration on the absorption of NO_x (RE). Influence of such parameters was studied within their typical range keeping as reference value an inlet concentration of 1500 ppm_v, a RT of 2s, a sorbent pH of 6, a L/G of $7.5 \text{ L}\cdot\text{m}^{-3}$, and a nitrate concentration in sorbent of $0 \text{ g}\cdot\text{L}^{-1}$. Results are shown also in Figure 2, considering both NO and NO_x .

Absorption of NO_x was low under the tested conditions. Figure 2b shows that operating parameters tested had only a slight influence on RE . In this sense, increasing the sorbent-flue gas ratio from 5 to $15 \text{ L}\cdot\text{m}^{-3}$ only increased the RE of NO_x from 5.9 to 9.2%. Similarly, no significant effects were observed for nitrate sorbent concentration (Figure 2c) and sorbent pH (Figure 2d). All these results are explained by mass-transfer limitations due to the low solubility of NO_x species. Mass transport limitation is accentuated when NO inlet concentration increases (Figure 2e) where RE drops from 15 to 6% when NO inlet concentration rises from 500 to 2000 ppm_v. On the other hand, in Figure 2d it is observed that increasing flue gas RT , i.e. contact time between sorbent and flue gas, it is possible to improve absorption capacities obtaining RE over 50% at RT of 120s.

3.1.2. Characterization of biological stage for elemental sulfur valorisation

The characterization of the two-stage biological process for elemental sulfur production was performed separately for each reactor. The UASB performance was evaluated during 400 days of continuous operation quantifying sulfate removal efficiency (S - RE), chemical organic demand (COD) removal efficiency (COD - RE) and

sulfate and *COD* eliminations capacities (*S-EC* and *COD-EC* respectively). The characterization of UASB operation was completed evaluating the generated CO_2 in order to assess the use of biological-origin effluents as alkaline sorbent for the absorption of SO_2 and NO_x . The limits of the system were explored by increasing sulfate loading rate (*SLR*), from 2.9 to $8.1 \text{ kg S}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, and organic loading rate (*OLR*), from 12.0 to $27.1 \text{ kg O}_2\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, at different *COD/S*-sulfate ratios. Table 1 shows the results obtained from the long-term UASB operation. Additional results of long-term UASB operation can be found in [7].

Table 1 Conditions tested and elimination capacities obtained in the UASB during long-term performance.

Period	Days	Sulfate _{inlet}	<i>COD/S</i> _{inlet}	<i>SLR</i>	<i>OLR</i>	<i>S-EC</i>	<i>COD-EC</i>	C-HCO_3
		[mg S·L ⁻¹]	[g O ₂ ·g ⁻¹ S]	[kg S·m ⁻³ ·d ⁻¹]	[kg O ₂ ·m ⁻³ ·d ⁻¹]	[kg S·m ⁻³ ·d ⁻¹]	[kg O ₂ ·m ⁻³ ·d ⁻¹]	[g C·L ⁻¹]
I	0-99	235±17	3.8±0.8	3.2±0.4	12.0±2.1	2.4±0.6	10.1±2.3	0.12±0.03
II	99-115	235±17	5.3±0.6	2.9±0.9	15.8±4.6	2.4±0.4	12.6±1.0	0.16±0.01
III	115-197	442±47	5.4±1.0	4.6±0.8	24.4±6.9	4.3±0.8	9.4±4.9	0.07±0.04
IV	197-238	442±47	5.4±0.6	5.0±0.4	27.1±2.5	3.9±0.6	9.8±4.2	0.10±0.04
V	238-288	859±30	3.1±0.2	8.1±0.8	25.4±2.6	3.4±0.5	7.2±4.2	0.06±0.04
VI	288-400	442±47	4.5±1.4	6.0±1.4	25.7±6.9	2.6±0.8	6.7±3.7	0.08±0.04

The evaluation of the effluent of the UASB reactor during all this period revealed that the carbonate concentration resulting from glycerol oxidation was strongly related with system efficiency. In this sense, when the system was operated under stable conditions high CO_2 concentrations, above $0.12 \text{ g C}\cdot\text{L}^{-1}$, were obtained. However, when organic matter accumulation problems appeared carbonate concentration dropped below $0.08 \text{ g C}\cdot\text{L}^{-1}$. Overall, C concentrations from 0.06 to $0.12 \text{ g C-HCO}_3^- \text{ L}^{-1}$ were found along the different operating conditions of the UASB reactor. According to the UASB performance in Table 1, period III provided the higher *S-EC*, corresponding to a C concentration of $0.07 \text{ g C-HCO}_3^- \text{ L}^{-1}$ at the outlet of the anaerobic stage. However, the inorganic C availability for absorption was affected by the performance of the microaerophilic stage for S recovery. Thus, the performance of the CSTR setup used for biosulfur production from the sulfide generated in the UASB was assessed for a period of 120 days. Detailed results obtained during CSTR monitoring are presented in [5]. Preliminary study of partial sulfide oxidation was performed using dissolved oxygen as electron acceptor instead of a nitrate-rich stream in order to simplify reactor control and operation. In this sense, oxygen was only supplied through reactor agitation. Nevertheless, similar behaviour should be expected working with nitrate as electron acceptor instead of dissolved oxygen. The reactor was operated maintaining an average pH of 7.5 and an average ORP of -380 mV. During this period sulfate concentration at UASB inlet ranged between 235 and 450 $\text{mg S}\cdot\text{L}^{-1}$. For this reason, sulfide concentration from the UASB effluent was not stable. Thus, it was not possible to

operate CSTR under steady-state conditions hindering an optimal partial oxidation of sulfide. It must be highlighted that an adequate electron acceptor supply by means of nitrate dosing or aeration control would give place to an optimal elemental sulfur production. The study of CSTR performance was completed monitoring *COD* concentration at the inlet and the outlet of the reactor. Results revealed that low oxygen concentration did not allow heterotrophic bacteria growth avoiding competence with sulfur oxidizing bacteria. In addition, it was also observed that under the operating conditions tested neither the consumption of inorganic carbon during the partial autotrophic oxidation of sulfide nor CO_2 stripping in the CSTR modify alkaline character of the obtained effluents.

3.2. Optimization of flue gas absorption step

3.2.1. Optimization of SO_2 absorption

The optimization of pollutants removal in the absorption stage was studied from a technical and economical point of view exploiting the alkaline character of the effluent of the biological process. Since the alkalinity released in spray scrubbers during CO_2 stripping can replace the utilisation of reagents such as NaOH or limestone, the reuse of the effluents of the biological process as sorbents in the wet-spray scrubbing was evaluated experimentally.

To this aim, the effluent of the CSTR was used as key absorber in the absorber unit. Taking into account the results presented in Table 1 this study was performed considering the two extreme cases. In Fig. 3 results obtained using effluents with dissolved CO_2 concentrations of 0.05 and 0.20 g C·L⁻¹ are presented. The pH of CSTR effluent was 7.5. The assessment of regenerated sorbents efficiency was completed quantifying the effect of *L/G* ratio, the retention time and the SO_2 concentration on system *RE*.

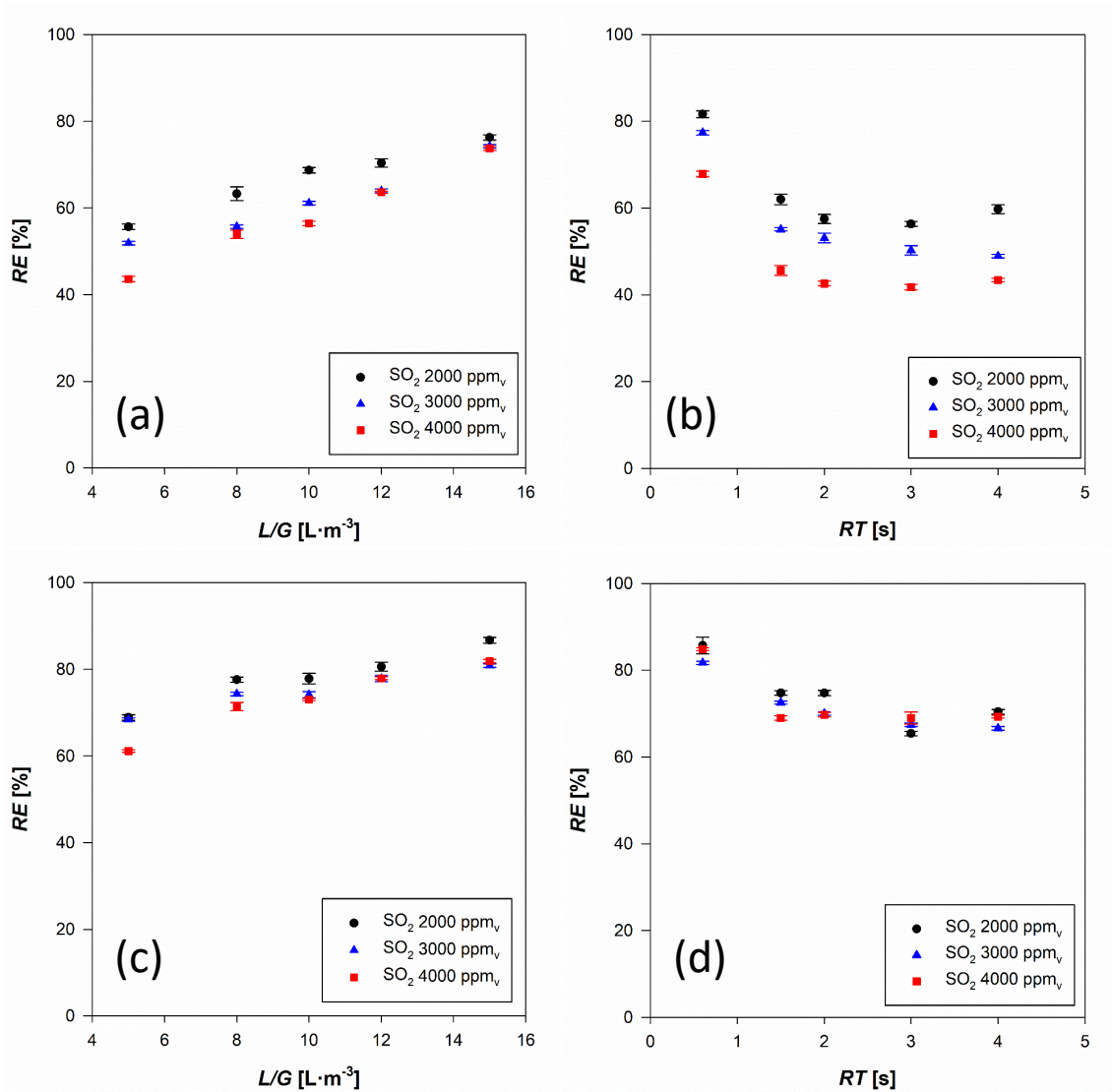


Fig. 3 SO₂ removal efficiency using synthetic sorbents reproducing biological process effluent. Sorbent prepared with a dissolved CO₂ concentration of 0.05 g C·L⁻¹ different SO₂ concentration vs. (a) L/G ratio and (b) flue gas residence time. Sorbent prepared with a dissolved CO₂ concentration of 0.20 g C·L⁻¹ different SO₂ concentration vs. (c) L/G ratio and (d) flue gas residence time

Results presented in Fig. 3 confirmed that CSTR effluent exhibited an excellent performance as SO₂ sorbents. A strong effect of flue gas flowrate, L/G ratio and pollutant flue gas concentration on absorption efficiency was also observed. In Fig. 3b, using a 0.05 g C·L⁻¹ sorbent a RT decrease from 4 to 0.6 s resulted in a RE improvement from 38.4% to 68.2% and from 55.3% to 82.7% when a flue gas of 2000 and 4000 ppm_v of SO₂ were fed respectively.

Same trend was observed when a 0.20 g C·L⁻¹ sorbent was used (Fig. 3d). In this case SO₂ RE rose from 62.1 to 81.8% and from 65.4 to 85.4% when a flue gas of 2000 and 4000 ppm_v of SO₂ was studied. On the other hand, an increase of L/G ratio from 5 to 15 L·m⁻³ also improve SO₂ RE . Using a 0.05 g C·L⁻¹ sorbent, an improvement from 43.3 to 75.1% at 4000 ppm_v of SO₂ and from 55.4 to 78.1% at 2000 ppm_v of SO₂. In

this case, higher RE were also observed when a $0.20 \text{ g C}\cdot\text{L}^{-1}$ sorbent was tested. Increasing L/G ratio from 5 to $15 \text{ L}\cdot\text{m}^{-3}$, RE rose from 68.1 to 82.1% and from 60.7 to 76.8% working with a 2000 and a 4000 ppm_v SO_2 concentration.

These results showed that SO_2 RE obtained using the sorbent with the highest CO_2 concentration are about a 10% higher. This trend confirmed that the utilisation of dissolved CO_2 solutions as flue gas sorbents was not limited by CO_2 stripping in the spray scrubber since most of the alkalinity contained in these solutions can be released during scrubbing process. Thus, these results also highlighted that wet-spray scrubber is a good alternative for flue gas treatment.

Finally, results obtained operating the bench-scale spray scrubber with conventional sorbents (Fig. 2) and reused effluents (Fig. 3) were compared. In this sense, experimental results showed that $0.05 \text{ g C}\cdot\text{L}^{-1}$ sorbents exhibited a similar performance to NaOH based sorbents. Besides, it can be observed that working with a higher dissolved CO_2 concentration RE was even improved. These results proved that biological effluents are a good alternative to replace conventional alkaline sorbents in wet flue gas absorption. Thereby, the operational improvement of the absorption stage, both from an economical and a technical point of view, obtained using reused sorbents was confirmed.

3.2.2. Optimization of NO_x absorption

Comparing absorption of NO and NO_x (Fig. 2), it is observed that NO presented always a slightly higher RE . This difference is explained because of wet-scrubbing mechanisms. Under tested conditions NO was partially oxidized to NO_2 , but the system was not able to absorb the generated NO_2 . According to Liu et al. (2010) this phenomenon is caused because reagent is exhausted during NO oxidation and is not available for NO_2 absorption. For this reason, a NO_x absorption enhancement was tested by including some oxidizing reagents in the scrubbing solution. This alternative was evaluated assessing several oxidants for NO_x absorption. The improvement on NO oxidation and NO_2 absorption was studied using KMnO_4 (0.3 M), NaClO (0.4 M), $\text{Na}_2\text{S}_2\text{O}_7$ (0.2 M), H_2O_2 (0.15 M) and FeCl_3 (0.4 M). The sorbent-flue gas ratio and the flue RT were set at $15 \text{ L}\cdot\text{m}^{-3}$ and 60 s, respectively. Results are presented in Figure 3.

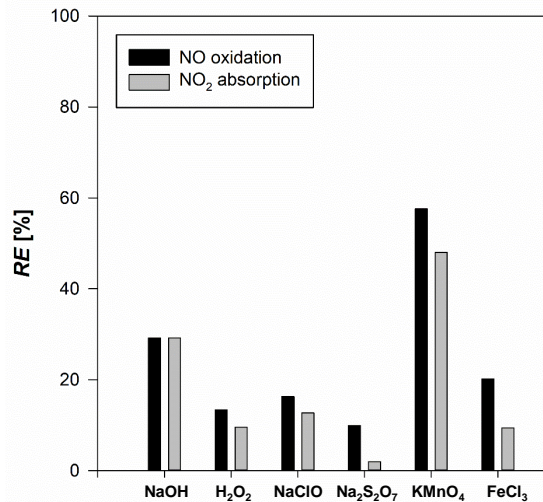


Fig. 3 RE for NO oxidation and NO_x absorption using as sorbent: NaOH, H₂O₂, NaClO, Na₂S₂O₇, KMnO₄ and FeCl₃

Experimental results (Figure 3) of NO_x absorption using oxidizing agents showed higher *RE* for NO oxidation than for NO₂ absorption. Sorbents based on H₂O₂, NaClO, Na₂S₂O₇ and FeCl₃ presented similar oxidation efficiencies, ranging between 12 and 18%. However, both Na₂S₂O₇ and FeCl₃ are acid salts and therefore, presented low absorption efficiencies. Despite NO₂ presented a higher solubility, the alkaline character of the sorbent is key to obtain great NO_x *RE*. Alkaline sorbent presented similar efficiencies both for NO oxidation and NO₂ absorption, close to the 30% and higher than the exhibited for most of the tested oxidants. On the other hand, the KMnO₄ solution stands out from the other sorbents showing oxidation and absorption efficiencies close to 50 and 60%, respectively. However, by-products generated during NO_x treatment could cause toxicity problems to biological reactors, thus hindering its application as sorbent in the two-stage bioscrubber. Taking all into consideration, using alkaline sorbents, based on NaOH solutions, can be considered a promising alternative for NO_x wet-scrubbing.

4. Conclusions

Experimental results obtained in this work enable to establish the optimal operating conditions for the sequential wet-scrubbing of SO₂ and NO_x from flue gas. The SO₂ and NO_x wet-absorption presented different performances caused by the difference in their solubility. While high *RE* can be obtained for the treatment of SO₂ working at low *RT* (below 2 s) and at moderate *L/G* ratios (7.5 L·m⁻³), mass transport limitations for NO_x absorption resulted in *RE* below 10% under these operating conditions. The *RT* for NO_x abatement must be increased above 60 s in order to obtain good *RE*. This phenomenon allows to separate selectively both pollutants in two alkaline wet-scrubbers in series designed to work under clearly differentiated *RT*. In addition, second scrubber must be operated using a NaOH based sorbent in order capture NO_x from flue gas in order to maximize both oxidation and absorption efficiency. The sequential wet-scrubbing process allows to obtain two sulfate and nitrate rich streams with appropriate

characteristics for the biological process of elemental sulfur recovery. In this sense, NO_x absorption enhancement through strong oxidizers addition is not recommended because no significant improvement was observed and some toxicity problems can be introduced in the biological process. The performance of the biological stage for flue gas wastes treatment was also characterized. Despite some limitations were found during biological stages characterization, optimal operating conditions were established and *S-RE* and *COD-RE* above 95% and 90% respectively were obtained. Therefore, two-stage bioscrubber improves flue gas treatment, by valorizing pollutants as elemental sulfur and reducing the wastes generated in the process to a wastewater stream. In addition, the high carbonate content of this effluent gives it a high alkaline character that enables its use as sorbent during wet-scrubbing stage, reducing reagents consumption and operation cost.

References

- [1] Y. Liu, T.M. Bisson, H. Yang, Z. Xu, Recent developments in novel sorbents for flue gas clean up, *Fuel Process. Technol.* 91, 1175–1197 (2010).
- [2] Y. Sun, E. Zwolińska, A.G. Chmielewski, Abatement technologies for high concentrations of NO_x and SO₂ removal from exhaust gases: A review, *Crit. Rev. Environ. Sci. Technol.* 46, 119–142 (2016).
- [3] F. Jiang, L. Zhang, G.L. Peng, S.Y. Liang, J. Qian, L. Wei, G.H. Chen, A novel approach to realize SANI process in freshwater sewage treatment - Use of wet flue gas desulfurization waste streams as sulfur source, *Water Res.* 47, 5773–5782 (2013).
- [4] J. Qian, H. Lu, F. Jiang, G.A. Ekama, G.H. Chen, Beneficial co-treatment of simple wet flue gas desulphurization wastes with freshwater sewage through development of mixed denitrification-SANI process, *Chem. Eng. J.* 262, 109–118 (2015).
- [5] M. Mora, E. Fernández-Palacios, D. Gabriel, Feasibility of S-rich streams valorization through a two-step biosulfur production process, Submitted (2019).
- [6] M. Mora, J. Lafuente, D. Gabriel, Screening of biological sulfate reduction conditions for sulfidogenesis promotion using a methanogenic granular sludge, *Chemosphere.* 210, 557–566 (2018).
- [7] E. Fernández-Palacios, F.J. Lafuente, M. Mora, D. Gabriel, Exploring the performance limits of a sulfidogenic UASB during the long-term use of crude glycerol as electron donor, Submitted (2019).