# **Optimization of SO<sub>2</sub> and NO<sub>x</sub> sequential wet absorption in a two-stage bioscrubber for elemental sulfur valorisation**

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#### Abstract

Removal of SO<sub>2</sub> and NO<sub>x</sub> from flue gases has become an important issue in air pollution control. A two-stage bioscrubber based on a sequential wet absorption of SO<sub>2</sub> and NO<sub>x</sub> followed by a two-stage biological process has been proposed in order to valorise SO<sub>2</sub> and NO<sub>x</sub> by elemental sulphur production. Biological process characterization established a maximum sulfate loading rate (5 kg S·m<sup>-3</sup>·d<sup>-1</sup>) and an optimal *COD/S* ratio (5.4 g O<sub>2</sub>·g S<sup>-1</sup>) in order to maximize elemental sulfur production and to avoid biological process limitations. Absorption of SO<sub>2</sub> and NO<sub>x</sub> 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  $CO_2$ ,  $SO_2$  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  $SO_2$  and  $NO_x$  from off-gases [2].  $SO_2$  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 NOx, 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,

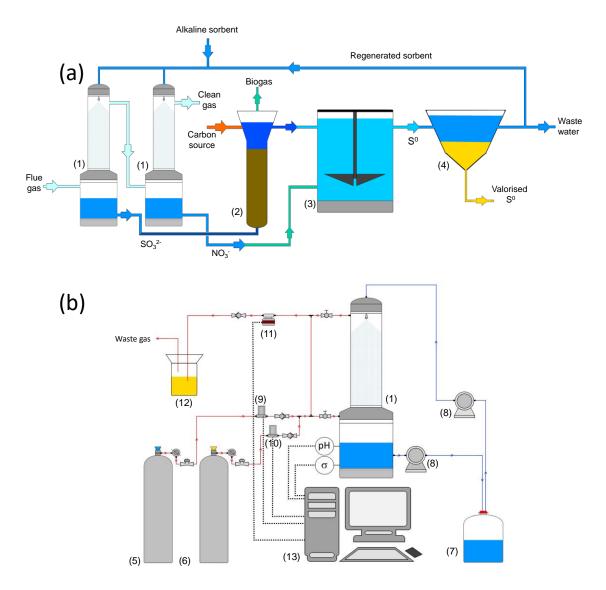
alternative flue gas treatment technologies based on biological processes are needed [3,4]. This is the case of the two-stage bioscrubber based on the biotechnological process described in [5], which can be implemented to recover elemental sulfur from SO<sub>2</sub> and NO<sub>x</sub> contained in flue gases. The process is based on a sequential absorption of SO<sub>2</sub> and NO<sub>x</sub> 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 SO<sub>2</sub> 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<sub>x</sub> to NO<sub>2</sub> 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 SO<sub>2</sub> and NO<sub>x</sub> 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 SO<sub>2</sub> and NO<sub>x</sub> 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 CO<sub>2</sub>, which is retained as dissolved CO<sub>2</sub>. 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<sub>2</sub>/NO, (7) sorbent tank, (8) sorbent pump, (9) air mass flow controller, (10) SO<sub>2</sub>/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<sub>2</sub> and limit the absorption of NO<sub>x</sub>. In the second column the conditions which NO<sub>x</sub> 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  $\mu$ m 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<sub>2</sub>/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<sub>2</sub> and NO<sub>x</sub> (as a mixture of NO and NO<sub>2</sub>) in the outlet gas phase was performed using an electrochemical SO<sub>2</sub> sensor (SO2-B4, Alphasens, UK), an electrochemical NO sensor (4NO-2000, EuroGas, UK) and an electrochemical NO<sub>2</sub> sensor (4NO2-2000, EuroGas, UK), all of them with a measuring range from 0 to 2000 ppm<sub>v</sub>. 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<sub>2</sub> and/or NO<sub>x</sub>. Synthetic flue gas for the experimental study of NO<sub>x</sub> 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  $20\pm1$  °C and atmospheric pressure. Absorption efficiency was evaluated for each pollutant by means of the following expression:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100 \tag{1}$$

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.

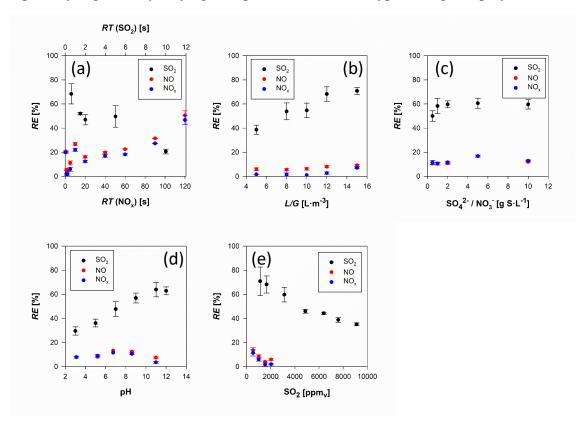
The experimental setup used in the study of biosulfur production from the sulfate-rich effluent consisted of a UASB reactor in series with a continuous stirred tank reactor (CSTR). The UASB reactor for sulfate reduction had a total volume of 2.5 L and an effective volume (Sludge bed volume) of 1 L. The 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 SO<sub>2</sub> absorption efficiency. Sorbent flowrate was assessed as L/G ratio. An inlet SO<sub>2</sub> concentration of 2000 ppm<sub>v</sub>, a flue gas retention time (*RT*) of 2s, a sorbent pH of 6, a L/G of 7.5 L·m<sup>-3</sup>, a sorbent temperature of 298±1.5 K and a sulfate concentration in fresh sorbent of 0 g·L<sup>-1</sup> 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) SO<sub>2</sub> concentration, on SO<sub>2</sub>, NO and NO<sub>x</sub> removal efficiency (*RE*).

Results shown in figure 2 depict the effect of the tested operating variables on  $SO_2$  absorption efficiency (*RE*). As expected  $SO_2$  absorption efficiency was strongly affected (in this order) by flue gas and sorbent flowrates, sorbent pH and  $SO_2$  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 gasliquid contactor increase with gas flowrate, enhancing SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> *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<sub>2</sub> *RE* raised from 29.6 to 60.8%. The capability to neutralize protons released during SO<sub>2</sub> 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<sub>x</sub> stream was generated as a mixture of pure NO and air. The NO is partially oxidized to NO<sub>2</sub> resulting in a NO, NO<sub>2</sub> and air mixture. NO inlet concentration is defined as the sum of NO and NO<sub>2</sub> concentrations. The generated NO<sub>x</sub> stream contained a 90-95% of NO and 5-10% of NO<sub>2</sub>. Spray scrubber characterization for NO<sub>x</sub> 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<sub>x</sub> (*RE*). Influence of such parameters was studied within their typical range keeping as reference value an inlet concentration of 1500 ppm<sub>v</sub>, a *RT* of 2s, a sorbent pH of 6, a *L/G* of 7.5  $L \cdot m^{-3}$ , and a nitrate concentration in sorbent of 0 g·L<sup>-1</sup>. Results are shown also in Figure 2, considering both NO and NO<sub>x</sub>.

Absorption of NO<sub>x</sub> 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 L·m<sup>-3</sup> only increased the *RE* of NO<sub>x</sub> 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<sub>x</sub> 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<sub>v</sub>. 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<sub>2</sub> in order to assess the use of biological-origin effluents as alkaline sorbent for the absorption of SO<sub>2</sub> and NO<sub>x</sub>. The

limits of the system were explored by increasing sulfate loading rate (*SLR*), from 2.9 to 8.1 kg S·m<sup>-3</sup>·d<sup>-1</sup>, and organic loading rate (*OLR*), from 12.0 to 27.1 kg O<sub>2</sub>·m<sup>-3</sup>·d<sup>-1</sup>, 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].

Period	Days	Sulfate <sub>inlet</sub>	COD/S <sub>inlet</sub>	SLR	OLR	S-EC	COD-EC	C-HCO <sub>3</sub>
		[mg S·L <sup>-1</sup> ]	$[gO_2{\cdot}g^{\text{-}1}S]$	$[kgS{\cdot}m^{\text{-3}}{\cdot}d^{\text{-1}}]$	$[kg  O_2 {\cdot} m^{\text{-}3} {\cdot} d^{\text{-}1}]$	$[kg \ S {\cdot} m^{\text{-}3} {\cdot} d^{\text{-}1}]$	$[kg \ O_2 {\cdot} m^{-3} {\cdot} d^{-1}]$	$[g C \cdot L^{-1}]$
Ι	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	$0.07 \pm 0.04$
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	$0.10{\pm}0.04$
V	238-288	859±30	3.1±0.2	$8.1 \pm 0.8$	25.4±2.6	3.4±0.5	7.2±4.2	$0.06 \pm 0.04$
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	$0.08 \pm 0.04$

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

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<sub>2</sub> concentrations, above 0.12 g C·L<sup>-1</sup>, were obtained. However, when organic matter accumulation problems appeared carbonate concentration dropped below 0.08 g  $C \cdot L^{-1}$ . Overall, C concentrations from 0.06 to 0.12 g C-HCO<sub>3</sub><sup>-</sup> L<sup>-1</sup> 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 g C-HCO<sub>3</sub><sup>-</sup> L<sup>-1</sup> at the outlet of the anaerobic stage. However, the inorganic C availability for absorption was affected by the performance of the microaerofilic 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 mg  $S \cdot L^{-1}$ . 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

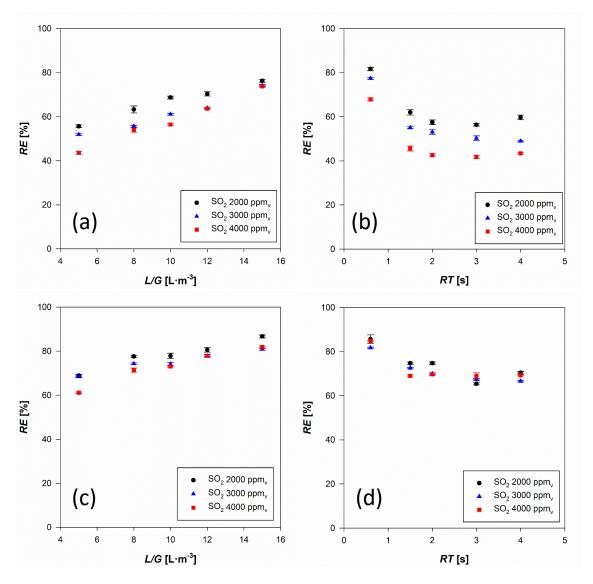
oxygen concentration did not allow heterotrophic bacteria growth avoiding competence with sulfur oxidizing bacteria. In addition, it was also observed that under the operating conditions tested neither the consumption of inorganic carbon during the partial autotrophic oxidation of sulfide nor CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> concentrations of 0.05 and 0.20 g C·L<sup>-1</sup> 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<sub>2</sub> concentration on system *RE*.



**Fig. 3** SO<sub>2</sub> removal efficiency using synthetic sorbents reproducing biological process effluent. Sorbent prepared with a dissolved CO<sub>2</sub> concentration of 0.05 g C·L<sup>-1</sup> different SO<sub>2</sub> concentration vs. (a) *L/G* ratio and (b) flue gas residence time. Sorbent prepared with a dissolved CO<sub>2</sub> concentration of 0.20 g C·L<sup>-1</sup> different SO<sub>2</sub> 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 SO<sub>2</sub> 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<sup>-1</sup> 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<sub>v</sub> of SO<sub>2</sub> were fed respectively.

Same trend was observed when a 0.20 g C·L<sup>-1</sup> sorbent was used (Fig. 3d). In this case SO<sub>2</sub> *RE* rose from 62.1 to 81.8% and from 65.4 to 85.4% when a flue gas of 2000 and 4000 ppm<sub>v</sub> of SO<sub>2</sub> was studied. On the other hand, an increase of *L/G* ratio from 5 to 15 L·m<sup>-3</sup> also improve SO<sub>2</sub> *RE*. Using a 0.05 g C·L<sup>-1</sup> sorbent, an improvement from 43.3 to 75.1% at 4000 ppm<sub>v</sub> of SO<sub>2</sub> and from 55.4 to 78.1% at 2000 ppm<sub>v</sub> of SO<sub>2</sub>. In this case,

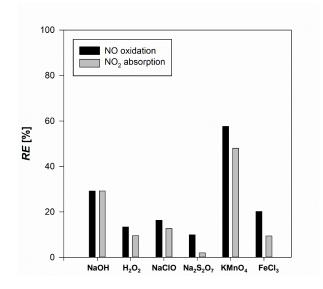
higher *RE* were also observed when a 0.20 g C·L<sup>-1</sup> sorbent was tested. Increasing *L/G* ratio from 5 to 15 L·m<sup>-3</sup>, *RE* rose from 68.1 to 82.1% and from 60.7 to 76.8% working with a 2000 and a 4000 ppm<sub>v</sub> SO<sub>2</sub> concentration.

These results showed that SO<sub>2</sub> *RE* obtained using the sorbent with the highest CO<sub>2</sub> concentration are about a 10% higher. This trend confirmed that the utilisation of dissolved CO<sub>2</sub> solutions as flue gas sorbents was not limited by CO<sub>2</sub> 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 g C·L<sup>-1</sup> sorbents exhibited a similar performance to NaOH based sorbents. Besides, it can be observed that working with a higher dissolved CO<sub>2</sub> 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<sub>x</sub> absorption

Comparing absorption of NO and NO<sub>x</sub> (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<sub>2</sub>, but the system was not able to absorb the generated NO<sub>2</sub>. According to Liu et al. (2010) this phenomenon is caused because reagent is exhausted during NO oxidation and is not available for NO<sub>2</sub> absorption. For this reason, a NO<sub>x</sub> absorption enhancement was tested by including some oxidizing reagents in the scrubbing solution. This alternative was evaluated assessing several oxidants for NO<sub>x</sub> absorption. The improvement on NO oxidation and NO<sub>2</sub> absorption was studied using KMnO<sub>4</sub> (0.3 M), NaClO (0.4 M), Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> (0.2 M), H<sub>2</sub>O<sub>2</sub> (0.15 M) and FeCl<sub>3</sub> (0.4 M). The sorbent-flue gas ratio and the flue *RT* were set at 15 L·m<sup>-3</sup> and 60 s, respectively. Results are presented in Figure 3.



**Fig. 3** RE for NO oxidation and NO<sub>x</sub> absorption using as sorbent: NaOH, H<sub>2</sub>O<sub>2</sub>, NaClO, Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub> and FeCl<sub>3</sub>

Experimental results (Figure 3) of NO<sub>x</sub> absorption using oxidizing agents showed higher *RE* for NO oxidation than for NO<sub>2</sub> absorption. Sorbents based on H<sub>2</sub>O<sub>2</sub>, NaClO, Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and FeCl<sub>3</sub> presented similar oxidation efficiencies, ranging between 12 and 18%. However, both Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and FeCl<sub>3</sub> are acid salts and therefore, presented low absorption efficiencies. Despite NO<sub>2</sub> presented a higher solubility, the alkaline character of the sorbent is key to obtain great NO<sub>x</sub> *RE*. Alkaline sorbent presented similar efficiencies both for NO oxidation and NO<sub>2</sub> absorption, close to the 30% and higher than the exhibited for most of the tested oxidants. On the other hand, the KMnO<sub>4</sub> solution stands out from the other sorbents showing oxidation and absorption efficiencies close to 50 and 60%, respectively. However, by-products generated during NO<sub>x</sub> 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<sub>x</sub> wet-scrubbing.

# 4. Conclusions

Experimental results obtained in this work enable to establish the optimal operating conditions for the sequential wet-scrubbing of SO<sub>2</sub> and NO<sub>x</sub> from flue gas. The SO<sub>2</sub> and NO<sub>x</sub> wet-absorption presented different performances caused by the difference in their solubility. While high *RE* can be obtained for the treatment of SO<sub>2</sub> working at low *RT* (below 2 s) and at moderate L/G ratios (7.5 L·m<sup>-3</sup>), mass transport limitations for NO<sub>x</sub> absorption resulted in RE below 10% under these operating conditions. The *RT* for NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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.

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