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

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ABSTRACT

Flue gases contain SO_2 and NO_x that can be treated together for elemental sulfur recovery in bioscrubbers, a technology that couples physical-chemical and biological processes for gaseous emissions treatment in a more economic manner than classical absorption. Sequential wet-absorption of SO_2 and NO_x from flue gas is thoroughly studied in this work in a two-stage bioscrubber towards elemental sulphur valorisation pursuing reuse of biological process effluents as absorbents. The optimal operating conditions required for SO_2 and NO_x absorption in two consecutive spray-absorbers were defined using NaOH-based absorbents. Overall, removal efficiencies of 98.9 and 55.9% for SO_2 and NO_x abatement were obtained in two in-series scrubbers operated under a gas contact time of 1 and 100 s, and a liquid-to-gas ratio of 7.5 and 15 $L \cdot m^{-3}$, respectively. Higher NO_x removal efficiency to clean gas emission was obtained by oxidants dosing in the absorber for NO_x absorption. High $NaHCO_3$ concentration in two-stage bioscrubber effluent was exploited as alkaline absorbent for flue gas treatment. The performance of scrubbers using an absorbent mimicking a reused effluent exhibited same removal efficiencies than those observed using NaOH solutions. In addition, the reuse of bioprocess effluent reduced reagents consumption by a 63.7%. Thus, the two-stage bioscrubber proposed herein offers an environmentally friendly and economic alternative for flue gas treatment.

KEYWORDS

32   Flue gas treatment, desulphurization, bioscrubber, SO_2 valorisation, NO_x

33

34   **1. INTRODUCTION**

35   Combustion processes give rise to one of the main air pollution sources from the
36   release of harmful chemicals such as CO_2, SO_2 and NO_x to the atmosphere (Liu et al.
37   2010; Sun et al. 2016). Depending on the fuel and the characteristics of the combustion
38   facilities, concentrations of SO_2 and NO_x in off-gases range typically between 200 and
39   4000 ppm_v, (Shen and Ayer 1975; Hu et al. 2000; Zevenhoven and Kilpinen 2001) and
40   200 and 1500 ppm_v (Chen et al. 2007; Winnes and Fridell 2010; Tian et al. 2012),
41   respectively, which significantly exceeds the levels required by the global regulations.
42   Hence, reduction of flue gas emissions is in the public administration and industrial sector
43   agenda and their treatment has become critical to avoid health and welfare problems both
44   for living organisms and ecosystems (Ağar et al. 2000; Bai and Meng 2005; Kan et al.
45   2010; Altuğ et al. 2013; Mathieu et al. 2013).

46   Several technologies have been developed to remove SO_2 and NO_x from off-gases in
47   combustion processes. Wet and dry absorption processes are the traditional physical-
48   chemical desulphurization processes (Majeed et al. 1995; Wang et al. 2012), since SO_2
49   presents a high solubility in aqueous solutions (11.29 g $SO_2 \cdot 100$ g^{-1} H_2O (Perry and Green
50   1997)). On the other hand, NO_x removal by scrubbing mechanisms is quite challenging
51   because NO, which is the major component of NO_x comprising the 90-95% of the entire
52   emission (Adewuyi and Sakyi 2013), is sparingly soluble in aqueous solutions (0.00618
53   g $NO \cdot 100$ g^{-1} H_2O (Perry and Green 1997)). For this reason, advanced treatment
54   technologies, such as selective catalytic reduction were developed for flue gas
55   denitrification (Zhu et al. 2004; Jin et al. 2005; Liu et al. 2010; Ding et al. 2014; Sun et
56   al. 2016). High removal efficiencies can be obtained for flue gas desulfurization and
57   denitrification combining these technologies (Adewuyi and Sakyi 2013; Ding et al. 2014;
58   Hao et al. 2017). However, the treatment of both acid gases through absorption and
59   catalytic technologies requires a high consumption of alkalis (Karatepe 2000) and
60   catalysts (Sun et al. 2016), which increases recurring operating costs and generates large
61   amounts of waste. Therefore, the development of novel low-cost, sustainable
62   technologies is essential. For this reason, flue gas treatment has been recently addressed
63   using biological techniques such as bioscrubbers (Lens et al. 2003; Lin et al. 2015; Sun

64　et al. 2018) and biotrickling filters (Philip and Deshusses 2003). Compared to physical-

65　chemical technologies, biological alternatives for flue gas treatment (bio-FGD) allowed

66　the recovery of pollutants as an innocuous or even a valuable product (Ottengraf and Diks

67　1992; An et al. 2010).

68　　　To this aim, a promising bioscrubbing process is presented herein to valorise pollutants

69　such as SO_2 contained in flue gases as elemental sulfur. This novel bio-FGD alternative

70　is based on the sequential absorption of SO_2 and NO_x from flue gas in two consecutive

71　scrubbers, coupled to the biological treatment of sulphate/sulphite and nitrate/nitrite

72　contained in scrubbing liquors (Philip and Deshusses 2003; Wang et al. 2013; Sun et al.

73　2018). Biological treatment of the resulting sulphate/sulphite rich-streams is performed

74　through a two-steps bioprocess consisting of sulphate/sulphite biological reduction to H_2S

75　followed by its partial oxidation to elemental sulphur under anoxic conditions using

76　nitrate/nitrite rich-stream as electron acceptor. The biological reduction of sulphate,

77　which is catalysed by sulphate reducing bacteria, has been studied over the past two

78　decades and have been developed using a different organics as carbon source (Rao et al.

79　2007; Mora et al. 2018) or an electron donor such as H_2 (Van Houten et al. 1997; Lens et

80　al. 2003), and under a wide range of operating conditions. In addition, some alternatives

81　have coupled SO_2 and NO_x abatement from flue gases using absorbed NO_x as electron

82　acceptor for autotrophic sulphide oxidation (Lee and Sublette 1991; Qian et al. 2015).

83　However, bio-FGD technologies still presents important limitations, mainly the large

84　consumption of alkali for SO_2 absorption (Lens et al. 2003), but also the use of expensive

85　carbon sources for sulphate reduction (glucose, VFA or alcohols), low NO_x removal due

86　to low NO solubility in water solutions (Adewuyi and Sakyi 2013) and reduced removal

87　efficiencies when treating SO_2 loads above 0.6 kg $S \cdot m^{-3} \cdot d^{-1}$ (Wang et al. 2013; Lin et al.

88　2015).

89　　　Recently, crude glycerol has been proposed as a competitive substrate to reduce high

90　loads of sulphate to H_2S (Mora et al. 2018). Crude glycerol is an organic waste produced

91　during biodiesel production, having the potential to improve the biological treatment of

92　flue gas scrubbing effluents. Fernández-Palacios et al. (2019) demonstrated that glycerol

93　can be successfully used for the long-term operation of a sulphidogenic, uplow anaerobic

94　sludge blanket (UASB) reactor, treating high sulphate loads (4.3 kg $S \cdot m^{-3} \cdot d^{-1}$). The

95　operation of this reactor was included in a potential alternative process to recover

96　elemental sulphur from flue gases called two-stage bioscrubber and consisting on a three

97 stages process: (1) SO_2 and NO_x sequential absorption, (2) sulphate reduction in the

98 UASB and (3) aerobic or anoxic sulphide oxidation in a continuous stirred tank reactor

99 (CSTR).

100 The sequential absorption of SO_2 and NO_x in two-stage bioscrubber is essential to

101 ensure optimal characteristics of bioreactor influents. To this aim, optimal conditions

102 required for the selective absorption of SO_2 and NOx in two consecutive spray-absorbers

103 have been studied in this work. In addition, the reduction of reagents consumption in the

104 absorption unit has been assessed studying the alkaline character of the effluent of a

105 biological process for biosulfur recovery and its performance as specific absorbent for

106 flue gas treatment. The optimization of flue gas depuration was completed studying

107 oxidative reagents dosing in absorbents to increase NO oxidation and thus, overall NOx
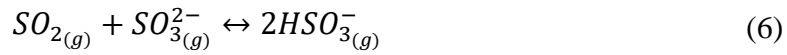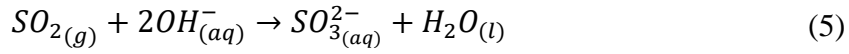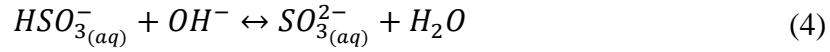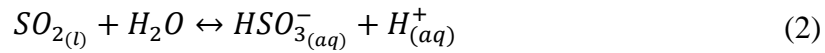
108 removal efficiency.

109

110 **2. EXPERIMENTAL METHODS**

111 ***2.1.Process chemistry***

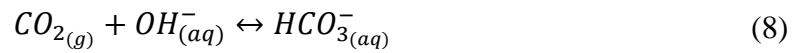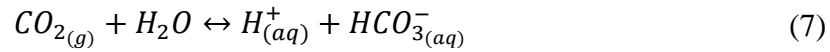112   *2.1.1. Mechanisms of SO_2 and NO_x absorption*

113 Based on the sulphur dioxide absorption mechanism (Eq. 1 to 6), flue gas

114 desulphurization through wet processes is generally performed using an alkaline solution

115 as absorbent for chemical absorption.

116 Sulphur dioxide diffuses from the gas phase to the gas-liquid interphase and it is

117 dissolved according to Henry's law (Eq. 1). In addition, a small amount of SO_2 can be

118 dissociated following Eq. 2, a first order reaction with a reaction rate of $3.4 \cdot 10^6$ s$^-$1 at

119 20ºC (Chang and Rochelle 1981). The dissolved SO_2 reacts in the presence of hydroxide

120 ions through the second order reaction presented in Eq. 3 with a rate constant exceeding

121 10^9 L·mol^{-1}·s^{-1} at 25ºC, while the generated hydrogen sulphite reacts instantaneously to

122 sulphite with additional hydroxide through proton transfer reaction defined in Eq. 4.

123 Caustic soda is usually used as absorbent since is a strong alkaline and thus a big a source

124 of hydroxide ions. In this sense, caustic soda will provide a surplus of hydroxide ions in

125 the aqueous phase and the overall reaction in the scrubber can be described according to

126 Eq. 5. On the other hand, under low pH conditions, the reaction of sulphite with dissolved

127 sulphur dioxide (Eq. 6) should be also considered.

$$SO_{2(g)} \leftrightarrow SO_{2(l)} \tag{1}$$

$$SO_{2(l)} + H_2O \leftrightarrow HSO_{3(aq)}^- + H_{(aq)}^+ \tag{2}$$

$$SO_{2(l)} + OH^- \leftrightarrow HSO_{3(aq)}^- \tag{3}$$

$$HSO_{3(aq)}^- + OH^- \leftrightarrow SO_{3(aq)}^{2-} + H_2O \tag{4}$$

$$SO_{2(g)} + 2OH_{(aq)}^- \rightarrow SO_{3(aq)}^{2-} + H_2O_{(l)} \tag{5}$$

$$SO_{2(g)} + SO_{3(g)}^{2-} \leftrightarrow 2HSO_{3(g)}^- \tag{6}$$

128

129   The wet-type processes can be implemented using other alkaline reagents such as
130 calcium compounds (Sakai et al. 2002) or $NaHCO_3/Na_2CO_3$ solutions (Ebrahimi et al.
131 2003). The absorption of SO_2 into HCO_3^-/CO_3^{2-} solutions and concomitant CO_2
132 desorption is presented in Eq. 9. For this reason, it is important to also consider CO_2
133 hydrolysis both at pH below 8 (Eq. 7) and at pH above 10 (Eq. 8).

$$CO_{2(g)} + H_2O \leftrightarrow H_{(aq)}^+ + HCO_{3(aq)}^- \tag{7}$$

$$CO_{2(g)} + OH_{(aq)}^- \leftrightarrow HCO_{3(aq)}^- \tag{8}$$

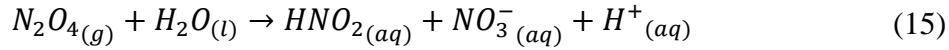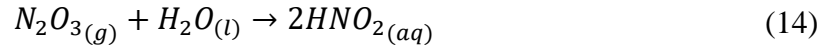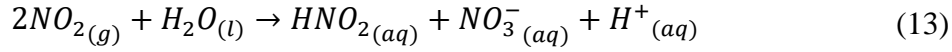$$SO_{2(l)} + HCO_{3(aq)}^- \rightarrow CO_{2(g)} + HSO_{3(aq)}^- \tag{9}$$

134

135   Gaseous NO_x is a complex mixture of nitrogen species of different oxidation states.
136 Several reactions in gas phase can be considered in a NO_x mixture (Newman and Carta
137 1988; Suchak et al. 1990; Thomas and Vanderschuren 1997). Reactions of NO and NO_2
138 in presence of oxygen are shown in Eq. 10-12, and include NO oxidation to NO_2 and the
139 instantaneous production of nitrogen species such as N_2O_3 and N_2O_4.

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \tag{10}$$

$$NO_{(g)} + NO_{2(g)} \rightarrow N_2O_{3(g)} \tag{11}$$

$$2NO_{2(g)} \rightarrow N_2O_{4(g)} \tag{12}$$

140

141   Absorption of NO_x into liquid phase takes place both from dissolution and reaction of
142 the different species present in gas phase. The NO_2, N_2O_3 and N_2O_4 are soluble gases
143 (Joshi et al. 1985) that are transferred to the liquid phase through instantaneous and
144 irreversible reaction with water to form nitrous and nitric acids as follows:

$$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{2(aq)} + NO_3^-{}_{(aq)} + H^+{}_{(aq)} \tag{13}$$

$$N_2O_{3(g)} + H_2O_{(l)} \rightarrow 2HNO_{2(aq)} \tag{14}$$

$$N_2O_{4(g)} + H_2O_{(l)} \rightarrow HNO_{2(aq)} + NO_3^-{}_{(aq)} + H^+{}_{(aq)} \tag{15}$$
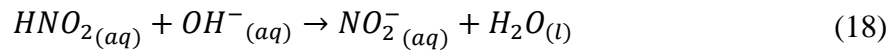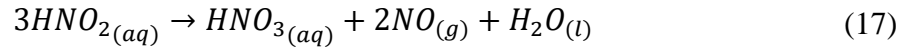
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146   Nitrous oxide can also be generated from NO. Despite NO is sparingly insoluble and
147   non-reactive with water, under low concentrations reacts with NO_2 (Joshi et al. 1985)
148   forming nitrous acid (Eq. 16).

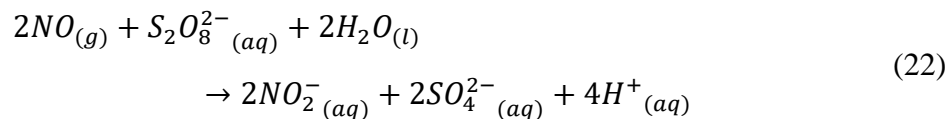$$NO_{(g)} + NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{2(aq)} \tag{16}$$
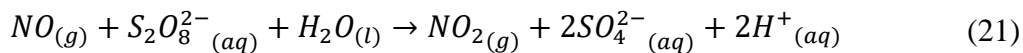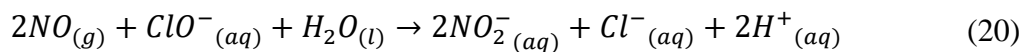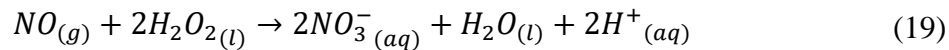
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150   In aqueous solution and especially under high nitric acid concentrations, nitrous acid
151   is very unstable and can be discomposed to NO (Eq. 17) that can be desorbed. In strong
152   alkaline solutions HNO_2 decomposes through an instantaneous proton transfer reaction
153   (Eq. 18) preventing NO release.

$$3HNO_{2(aq)} \rightarrow HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(l)} \tag{17}$$

$$HNO_{2(aq)} + OH^-{}_{(aq)} \rightarrow NO_2^-{}_{(aq)} + H_2O_{(l)} \tag{18}$$

154

155   *2.1.2. Chemistry of NO oxidation*

156   NO oxidation using oxidative reagents in the liquid phase takes place through
157   heterogeneous reactions between gaseous NO and aqueous species. Although several
158   reagents have been used for NO oxidation and absorption (Sun et al. 2016), the current
159   study is only focused on few of them. In the present work, the NO oxidation through
160   H_2O_2, NaClO, $Na_2S_2O_7$ and $KMnO_4$ solutions has been explored. Such oxidation
161   reactions are presented in Eq. 19-24.

$$NO_{(g)} + 2H_2O_{2(l)} \rightarrow 2NO_3^-{}_{(aq)} + H_2O_{(l)} + 2H^+{}_{(aq)} \tag{19}$$

$$2NO_{(g)} + ClO^-{}_{(aq)} + H_2O_{(l)} \rightarrow 2NO_2^-{}_{(aq)} + Cl^-{}_{(aq)} + 2H^+{}_{(aq)} \tag{20}$$

$$NO_{(g)} + S_2O_8^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow NO_{2(g)} + 2SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \tag{21}$$

$$2NO_{(g)} + S_2O_8^{2-}{}_{(aq)} + 2H_2O_{(l)}$$
$$\rightarrow 2NO_2^-{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} \tag{22}$$

$$2NO_{(g)} + 3S_2O_8^{2-}{}_{(aq)} + 4H_2O_{(l)}$$
$$\rightarrow 2NO_3^-{}_{(aq)} + 6SO_4^{2-}{}_{(aq)} + 8H^+{}_{(aq)} \tag{23}$$

$$3NO_{(g)} + MnO_4^-{}_{(aq)} + H_2O_{(l)} \rightarrow 3NO_2^-{}_{(aq)} + MnO_{2(s)} + 2H^+{}_{(aq)} \tag{24}$$
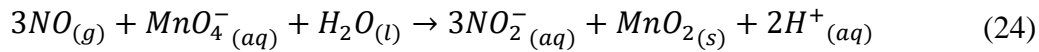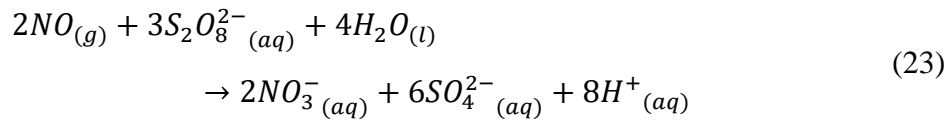
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163   ### 2.2. Two-stage bioscrubber concept

164   #### 2.2.1. Integrated flue gas bioscrubbing process

165   The two-stage bioscrubber integrates in a single process the removal of SO_2 and NO_x
166   from flue gases towards elemental sulphur valorisation. The conceptual process diagram
167   of the two-stage bioscrubber is detailed in Figure 1a and consisted of an absorption unit,
168   where sequential SO_2 and NO_x absorption is performed, and two biological reactors in
169   series for the treatment of resulting scrubbing liquors. To this aim, two consecutive spray-
170   scrubbers were designed and operated specifically for the absorption of SO_2 and NO_x,
171   respectively, obtaining separately two streams rich in sulphate/sulphite and nitrite/nitrate.
172   The first scrubber liquor is biologically treated in a heterotrophic UASB using crude
173   glycerol as carbon source. The sulphite and sulphate fed to the reactor are reduced to
174   sulphide, which is, in turn, oxidized to elemental sulphur in a consecutive CSTR operated
175   under anoxic conditions using nitrite and nitrate from the second scrubber effluent. The
176   biological sulphate reduction and the anoxic sulphide oxidation have been widely studied
177   (Jiang et al. 2013; Qian et al. 2015) and optimal conditions are described in detail in
178   Fernández-Palacios et al. (2019).

179   The absorption efficiency obtained for NO_x treatment is generally low due to the scarce
180   solubility of NO in water. Nevertheless, the biological production of elemental sulphur is
181   performed using nitrite or nitrate as electron acceptor. For this reason, spray scrubbing
182   was also selected for NO_x abatement in order to obtain a nitrogen laden aqueous stream.
183   The absorption stage was experimentally assessed herein through a lab-scale absorber.

184   #### 2.2.2. Biosulphur recuperation

185   The technological feasibility of the biological process for biosulphur production
186   consisting of the sequential UASB-CSTR experimental setup was demonstrated in Mora
187   et al. (2020). The operation of the UASB reactor resulted in a sulphate removal efficiency
188   of 68.1% treating high sulphate concentrations (1000 mg S L^{-1}) corresponding to a
189   maximum elimination capacity of 9.3 kg S m^{-3} d^{-1}. The production of intermediate

190   compounds, such as organosulfur compounds, caused a decrease of elemental sulfur
191   productivity. These results showed that the compertitiviness of the process can be
192   improved enhancing the yield of sulphate reduction to sulfide.

193   Sulfide was not detected in CSTR effluent during elemental sulphur production.
194   Besides, sulfate concentration in the effluent of the CSTR was similar than sulfate
195   concentration in the influent which indicated the full capacity of the culture to oxidize
196   partially sulfide to sulfur. These results confirmed the proper design of the CSTR aeration
197   and fed. The implementation of a aeration/stirring control system based on redox potential
198   measurement ensured sulfide limiting conditions and avoided the accumulation of
199   dissolved sulfide in the CSTR and the consequent H_2S release. The operation of CSTR
200   resulted in a sulfur productivitiy up to or 2.3 kg S m^{-3} d^{-1}. Results also showed that residual
201   COD from the UASB outlet was partially adsorbed on on biosiulfur surface affecting its
202   structure and composition.

203   Elemental sulphur recovery from the CSTR effluent still requires to be optimized.
204   Nevertheless, a first approach showed that centrifugation is an effective biosulfur
205   recovery. The centrifugation allowed the separation of biomass layer deposited on
206   elemental sulfur. The obtained product exhibited a high purity (between 87.5% and 95%)
207   and a humidity content of 46%. However, costs associated to this specific separation
208   process are considerably high. For this reason, raw biosulphur sedimentation through the
209   addition of chemical agents (coagulants and flocculants) was assessed as an economical
210   alternative to centrifugation. Sedimentation was settled up through the addition of a
211   commercial cationic coagulant (FL4820) obtaining a product with a sulfur purity of
212   74.3% and 64.4% of sedimented solids. Further optimization through tailor-made
213   surfactants in to obtain higher biosulphur purity and solids recovery capacity.

214   Finally, dried biosulfur was obtained through a thermal treatment. From the
215   thermogravimetric results drying conditions biosulphur oxidation and melting were
216   established. Then the appropriate process to recover biosulfur from the CSTR was defined
217   as a sequence of settling after coagulant addition and air drying at 100ºC.

218   *2.2.3. Experimental setup for flue gas absorption characterization*

219   The schematic diagram of the spray-absorber used for the characterization of flue gas
220   treatment is detailed in Figure 1b. Absorption was characterized separately for each
221   pollutant generating synthetic gas by mixing metered amounts of SO_2/NO and air. The

222   spray tower was fabricated in polyvinyl chloride (PVC) and consisted of a gas-liquid

223   contact section (5.9 cm of internal diameter and 30 cm high) and a liquid reservoir (11

224   cm of internal diameter and 20 cm height) with a working volume of 1800 mL. The

225   absorbent is injected into the top of the column using a peristaltic pump (7554-94 L/S

226   pump, Masterflex, USA) and is atomized in drops of 50-100 μm of diameter through a

227   spray nozzle (490.403.1Y.CA, Lechler, Germany). The pH and the ionic conductivity

228   were continuously measured at the reactor outlet using a multi-analyte probe (Multi 3420,

229   WTW, Germany). The synthetic flue gas was prepared using mass flow controllers (EL-

230   Flow Select, Bronkhorst, The Netherlands), and was fed counter-currently from the

231   bottom of the gas-liquid contactor. Continuous monitoring of SO_2 or NO_x (as a mixture

232   of NO and NO_2) in the outlet gas phase was performed using an electrochemical SO_2

233   sensor (SO2-B4, Alphasens, UK), an electrochemical NO sensor (4NO-2000, EuroGas,

234   UK) and an electrochemical NO_2 sensor (4NO2-2000, EuroGas, UK), all of them with a

235   measuring range from 0 to 2000 ppm_v. Measurement of higher pollutants concentrations

236   required flue gas dilution performed by two flowmeters (2100, Tecfluid, Spain). Residual

237   flue gas was bubbled through a NaOH filter before its emission to the atmosphere. The

238   selected fresh absorbent was continuously fed to ensure constant pH and composition at

239   reactor inlet. The compounds concentration, pH and ionic conductivity at liquid outlet

240   were continuously monitored until steady-state conditions were achieved. Experiments

241   were performed at constant temperature of 20±1 ºC and atmospheric pressure. Absorption

242   efficiency was evaluated for each pollutant by means of the following expression:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100 \qquad (25)$$

243

244   Where C_{in} is the inlet pollutant (SO_2, NO or NO_2) concentration and C_{out} is the outlet

245   pollutant (SO_2, NO or NO_2) concentration, both in ppm_v. To ensure experiments accuracy,

246   three replicate measurements were made, obtaining relative errors below 5%. In this paper

247   only average values are shown.

248   *2.3.Experimental design*

249   The characterization of wet-absorption of SO_2 and NO_x was performed assessing the

250   influence of relevant operational parameters on process removal efficiency (RE). The

251   selected parameters presented in Table 1 were the gas contact time, the liquid-to-gas

252 flowrate (L/G) ratio, the sulphate and nitrate concentration in the phase, the absorbent pH
253 (adjusted using HCl 1M and NaOH 1M), SO_2 and NO_x concentration and the gas
254 temperature. The integrated process include the recovery of energy contained in flue gases
255 for elemental sulfur drying. For this reason, it was considered that flue gases temperature
256 at scrubber inlet would be always below 80ºC. The value of listed parameters in the
257 characterization assays is detailed in Table 1.

258   According to NO_x reactions in gas phase presented in Eq. 10-12, NO contained in
259 synthetic flue gas stream was partially oxidized to NO_2. For this reason, NO_x absorption
260 was performed considering NO_x concentration as the sum of NO and NO_2 concentration
261 and assessing NO_x RE considering both NO RE and NO_2 RE.

262   The reuse of the alkalinity generated during sulphate reduction in the biological stage,
263 as absorbent in the flue gas scrubbing stage was evaluated by using different $NaHCO_3$
264 concentrations. According to Fernández-Palacios et al. (2019) during the biological
265 sulphate reduction in an UASB using crude glycerol as electron donor, the dissolved CO_2
266 concentration in the biological process effluent ranged between 0.05 and 0.20 g C-
267 $HCO_3 \cdot L^{-1}$. The suitability of reusing the biological process effluent for flue gas spray
268 scrubbing was assessed quantifying the SO_2 RE using $NaHCO_3$-based absorbents of 0.05
269 and 0.2 g C-$HCO_3^- \cdot L^{-1}$. The UASB HCO_3^- concentration range was selected for the study
270 because no carbonate lost was detected during elemental sulphur production in CSTR.
271 Both $NaHCO_3$-based were prepared by dissolving $NaHCO_3$ in distillate water and
272 adjusting pH at the CSTR outlet pH (pH 7.5). The spray scrubbing using $NaHCO_3$
273 solutions was studied considering the effect on RE of gas contact time (between 0.6 and
274 4 s), the L/G ratio (between 5 and 15 $L \cdot m^{-3}$) and SO_2 concentration in flue gas (between
275 2000 and 4000 ppm_v).

276   Finally, optimization of NO_x absorption using specific absorbents was assessed
277 including different additives in alkaline absorbent prepared with NaOH solutions at pH
278 8. The additives were selected from their oxidative character (Thomas and Vanderschuren
279 1998; Zhao et al. 2011; Li et al. 2014; Han et al. 2015; Hao et al. 2017). To this aim,
280 alkaline absorbent including $KMnO_4$ (0.3 M), NaClO (0.4 M), $Na_2S_2O_7$ (0.2 M), H_2O_2
281 (0.15 M) were prepared and tested for NO_x absorption. The potential of additives dosing
282 for NO_x abatement was evaluated maintaining the same stoichiometric ratio between NO
283 and the different oxidative reagents was maintained for the preparation of absorbents. The
284 RE of prepared absorbent for NO_x absorption was experimentally evaluated in a lab-scale

285   spray-scrubber fed with a gas stream of 500 ppm$_v$ of NO at a gas contact time of 10 s and

286   under a L/G ratio of 15 L$\cdot$m^{-3}.

287

288   **3. RESULTS**

289   ***3.1.Flue gas wet-absorption***

290   *3.1.1. Characterization of SO$_2$ wet-absorption*

291   Several sets of experiments were performed to characterize SO$_2$ wet absorption.

292   Results shown in Figure 2 depict the effect of the tested operating variables on SO$_2$

293   absorption efficiency.

294   Flue gas inlet velocity was increased resulting in a gas-liquid contact time decrease

295   from 10 to 0.6 s (Figure 2a) while the L/G ratio was maintained at 7.5 L$\cdot$m^{-3}. Results

296   showed a RE improvement of the 50%, from 20.6 to 68.4%. Keeping a constant L/G

297   within the scrubber ensures a constant gas-liquid contact-area. On the other hand, Wang

298   et al. (2015) showed that the resistance of the gas film declines due to the intensification

299   of the turbulences when the flues gas flowrate increases, enhancing SO$_2$ mass transfer to

300   the liquid bulk. According to these results, SO$_2$ absorption RE was not limited by the

301   shorter reaction times resulting from the decrease of the gas-liquid contact time

302   highlighting that absorption takes place through instantaneous irreversible reaction (Eq.

303   5), as is proposed in several studies (Hikita et al. 1977; Wang et al. 2012, 2015).

304   The L/G ratio refers to the volumetric ratio between absorbent and flue gas flowrates.

305   It is an important parameter for scrubbing performance since a higher L/G ratio results in

306   a higher SO$_2$ RE but a higher energy consumption and operating costs. The L/G ratio in

307   spray absorbers for the removal of SO$_2$ is typically set between 8 L$\cdot$m^{-3} and 25 L$\cdot$m^{-3}.

308   Considering the high performance of NaOH solutions, the desulphurization efficiency

309   was evaluated between 5 L$\cdot$m^{-3} and 15 L$\cdot$m^{-3}. To maintain the absorption characteristics,

310   experiments were performed at a gas-liquid contact time of 2 s. As showed in Figure 2b,

311   RE increased from 38.7% to 58.7% when L/G ratio rose from 5 L$\cdot$m^{-3} to 12 L$\cdot$m^{-3}, and

312   from 68.7% to 79.8% when L/G ratio rose from 12 L$\cdot$m^{-3} to 15 L$\cdot$m^{-3} (until 70.8%). This

313   trend was in agreement with results found in literature (Gao et al. 2011; Wang et al. 2012,

314   2015). Increasing the L/G ratio at a constant value of flue gas flowrate rises absorbent

315   flowrate within the scrubber. Raising absorbent flowrate in the spray absorber means

316 increasing the interface area between droplets and gas, and more SO_2 is absorbed (Zhao
317 et al. 2007). However, when the ratio was increased above 10 L·m^{-3}, the droplets area
318 was large enough, and the increase in the ratio became negligible (Wang et al. 2015).

319 In Figure 2c, it can be observed an increase in RE from 50 to 60% when ionic sulphur
320 species concentration in absorbent increased to 10 g S·L^{-1}. This results are in agreement
321 with Wang et al. (2012) that found stronger absorption capacities when Na_2SO_3
322 concentration in the absorbent exceeded 0.3 M.

323 The influence of NaOH concentration on scrubbing performance was evaluated
324 assessing the influence of absorbent pH on SO_2 RE. The pH was ranged between 3 and
325 15. The operation at pH below 7 was also evaluated to study scrubbing performance under
326 NaOH depletion conditions. Results presented in Figure 2d show two different trends
327 along the studied pH range. In this sense, at pH below 12 RE decreased linearly from
328 60.8% to 29.6% while at pH above 12 a constant RE ranging between 59.5% and 60.8%
329 was observed. At low pH, SO_2 absorption takes place through Eq. 2 which is much slower
330 than Eq. 3 and Eq. 4 (Hikita et al. 1977). This phenomenon indicated that mass transfer
331 of SO_2 to the liquid phase is governed both by gas film and liquid film resistance (Wang
332 et al. 2015), leading to low efficiencies. Nevertheless, absorption took place through Eq.3
333 and Eq.4 when pH raised due to a higher hydroxide ions concentration, and liquid film
334 resistance fell quickly (Wang et al. 2012). Under this conditions, process is governed by
335 gas mass transfer and a higher and constant overall RE was obtained.

336 The SO_2 concentration in flue gas is a parameter highly unstable depending on the fuel
337 composition or combustion facilities operation. For this reason, it is important to establish
338 the influence of SO_2 inlet concentration on sulphur removal efficiency. Results presented
339 in Figure 2e showed that the SO_2 inlet concentration increase from 1000 to 9000 ppm$_v$
340 promoted mass transfer limitations. Since the L/G ratio was kept constant at 7.5 L·m^{-3},
341 the exhaustion of the absorbent took place at higher SO_2 concentration. Under these
342 conditions, mass transfer limitations described above for low pH absorbents become
343 important resulting in a RE decrease from 70.9 to 35.1%. This results are in agreement
344 with results in literature (Gao et al. 2011; Wang et al. 2012, 2015; Rahmani et al. 2014),
345 and suggests that some actions (such as increasing L/G ratio or absorbent pH) should be
346 taken to increase RE at higher SO_2 inlet concentrations.

347   The effect of temperature on SO_2 absorption process is complex. Temperature rise can

348   reduce the solubility of SO_2 but improve mass transfer coefficient and also accelerate

349   chemical reactions rates (Wang et al. 2012). For this reason, the flue gas influence on SO_2

350   RE was evaluated. The liquid temperature at the beginning of the experiments was kept

351   at 25ºC. A flue gas temperature effect on RE was not observed within the tested range

352   (Figure 2f), since liquid phase temperature and thus SO_2 solubility, kept steady during

353   absorption.

3.1.2.   Characterization of NOx wet-absorption

355   The experimental results obtained during the characterization of NO_x absorption are

356   presented in Figure 3. Results obtained during NO_x wet-absorption characterization

357   showed RE below 50% both for NO and NO_x abatement. These results highlighted strong

358   mass transfer limitations during NO_x removal through absorption technologies due to low

359   solubility of NO in water (0.00618 g NO·100 g^{-1} H_2O). Also, small differences were

360   observed between NO and NO_x RE, since nitrogen species generated due to NO removal

361   presented a high and fast reactivity in water.

362   As observed in Figure 3a, an increase on gas retention time from 0.6 to 120 s resulted

363   in an improvement on NO_x RE from 5.4 to 50.5% because the larger gas contact time

364   increased the time available for NO oxidation through Eq. 10-12. Higher solubility of

365   oxidized nitrogen species reduced gas side mass transfer limitations, and higher overall

366   NO_x RE were obtained. Thus, the scrubbing performance for NOx abatement can be

367   enhanced by increasing retention time of flue gas in the scrubber.

368   However, the rise of L/G ratio from 5 to 15 $L·m^{-3}$ (Figure 3b) only improved NO_x RE

369   from 5.9 to 9.2%. These results evidenced that at the low contact time (2 s) maintained

370   during these assays, NO was not oxidized. Therefore, mass transfer rate of gaseous

371   species to the bulk liquid is controlled by gas film resistance. In this sense, the increase

372   of mass transfer interface at higher absorbent flowrate does not improve NO_x transfer rate

373   resulting in low RE (below 10%).

374   Results presented in Figure 3c-d showed again that at a short contact time low NO

375   oxidation took place within the scrubber. NO is still the main component of NO_x mixture

376   and under these conditions absorption is limited by Eq. 10 and gas film mass transfer

377   resistance. For this reason, an enhancement of NOx removal was not obtained increasing

378   reaction rate of aqueous species (Eq. 13-15). In this sense, no significant effects on NO_x

379   RE were observed when liquid side mass transfer and bulk liquid kinetic characteristics

380   were modified both increasing nitrate absorbent concentration (Figure 3c) and absorbent

381   pH (Figure 3d).

382   The same phenomenon was observed when NO inlet concentration was increased. In

383   Figure 3e, a RE drop from 13.9% to 5.8% is observed when inlet NO concentration raised

384   from 500 to 2000 ppm$_v$. These results highlighted the necessity of sharply reduce NO

385   mass transfer limitations, both increasing mass transfer rate or Eq. 10 reaction rate, in

386   order to obtain higher RE and to accomplish environmental requirements.

387   Similar to that observed in Figure 2, gas temperature had a no effect on NO$_x$

388   absorption. The absorbent was not warmed by the hotter flue gas stream and no changes

389   on liquid temperature were observed during experimental assays. For this reason, a

390   constant RE between 6.8% and 7.3% was obtained when inlet gas temperature ranged

391   between 298 and 333 K.

392   *3.1.3. Sequential SO$_2$ and NO$_x$ wet-absorption*

393   The segregation of sulphur and nitrogen ionic species in two separated liquid effluents

394   required for optimal performance of biological reactors was obtained through the

395   sequential absorption of SO$_2$ and NO$_x$ from flue gas. To this aim, flue gas treatment unit

396   was designed as two scrubbers in series and selective absorption of both pollutants was

397   achieved exploiting different chemical properties of both pollutants. The first scrubber

398   was designed for SO$_2$ absorption while the second one was designed for NO$_x$ absorption.

399   The operating conditions of scrubbers were defined from the experimental data obtained

400   in the characterization of flue gas absorption. The operating conditions of both scrubbers

401   established for sequential absorption of both pollutants in two consecutive units are

402   presented in Table 2. The removal efficiencies of both scrubbers for SO$_2$ and NO$_x$

403   abatement treating a gas stream with 2000 ppm$_v$ of SO$_2$ and 1500 ppm$_v$ of NO$_x$ are

404   included in Table 2.

405   The difference in water solubility of both gaseous pollutants allowed sequential

406   absorption in two consecutive scrubbers. The gas contact time was set at 1 s in the first

407   scrubber. Under these operating conditions SO$_2$ absorption was enhanced but NO$_x$

408   absorption capacity was strongly limited. Removal efficiencies obtained in the first

409   scrubber for SO$_2$ and NO$_x$ absorption are presented in Table 2. Higher SO$_2$ solubility

410   resulted in a RE of 72.9% while RE for NO$_x$ absorption was kept at 5.4%. This spray-

411   scrubber was also operated under moderate L/G ratio and absorbent pH in order to

412   increase NO_x gas-liquid mass transfer limitations and to reduce operating costs.

413   The second spray-absorber was operated at higher gas contact time to increase time

414   available for NO oxidation (Eq.10-12) and thus NO_x absorption. The L/G ratio was also

415   increased to 15 $L \cdot m^{-3}$ to intensify NO oxidation products absorption from the gas to the

416   liquid phase. Under these operating conditions NO oxidation was increased and the NO_x

417   generated were successfully absorbed, obtaining a RE for NOx removal of 50.5%. Results

418   showed that most of SO_2 still remaining in flue gas was also absorbed.

419   Although overall removal efficiencies of 98.9% and 55.9% were obtained in two

420   consecutive spray-absorbers for SO_2 and NO_x, respectively, complete flue gas treatment

421   unit should be optimized to improve overall two-stage bioscrubber performance. In this

422   sense, it is necessary to explore the reduction of operating costs, to raise SO_2 RE in the

423   first scrubber to increase sulphur recovery capacity of the process and to raise NO_x RE to

424   ensure clean gas release.

425   ***3.2. Optimization of flue gas treatment***

426   *3.2.1. SO_2 absorption using recovered $NaHCO_3/Na_2CO_3$*

427   Flue gas treatment through wet-absorption technology implies a high consumption in

428   alkali reagents and thus high recurring operating costs. To this aim, the two-stage

429   bioscrubber was designed including bioprocess effluent recirculation to the absorption

430   unit (Figure 1a) in order to recover the $NaHCO_3/Na_2CO_3$ generated during heterotrophic

431   sulphate reduction due to glycerol oxidation. The optimization of flue gas absorption from

432   an economic point of view was performed evaluating the suitability of aqueous $NaHCO_3$

433   solutions as absorbent for SO_2 removal within the concentration range in biological

434   process effluent (Fernández-Palacios et al. 2019) in order to simulate the closed-loop

435   process. This study was performed quantifying the effect of the L/G ratio, the gas contact

436   time and the SO_2 concentration on system RE.

437   Results obtained in the characterization of SO_2 absorption using mimicking absorbents

438   of biological origin are presented in Fig. 4. $NaHCO_3$ absorbent, both with low and with

439   high concentration, showed a RE for SO_2 absorption above 80% and 40% in the most and

440   less favourable case, respectively. A strong effect of L/G ratio, gas contact time and SO_2

441   concentration on absorption capacity was also observed. Experimental results obtained

442 working with an absorbent of 0.05 g C·L^{-1} concentration showed that a L/G ratio increase

443 from 5 to 15 L·m^{-3} produced an increase on SO$_2$ RE from 55.6 to 76.3% and from 43.6

444 to 73.7% feeding a SO$_2$ concentration of 2000 ppm$_v$ and 4000 ppm$_v$, respectively.

445 Conversely, increasing gas contact time from 0.6 to 4 s, the RE for SO$_2$ absorption

446 decreased from 81.6 to 59.7% and from 67.9 to 43.4% when lab-scale spray-scrubber was

447 fed with a 2000 ppm$_v$ and a 4000 ppm$_v$ SO$_2$ concentration, respectively.

448 The comparison of NaOH-based and NaHCO$_3$ absorbent performance for SO$_2$

449 treatment is presented in Table 3. Experimental results presented in Figure 2a-b and

450 Figure 4 have been summarized in Table 3, and no differences were observed between

451 both absorbent. These results demonstrate that the use of a regenerated absorbent does

452 not introduce technical limitations in the absorption stage. In addition, according to results

453 obtained working with NaOH absorbent (in Figure 2a), higher RE were also observed at

454 a low flue gas contact time. These results proved that alkalinity release due to dissolved

455 CO$_2$ stripping in spray-scrubber (Eq. 9) was more efficient when operating at high gas

456 flow rates. This is explained by turbulences in reactor under these operating conditions

457 that enhanced mass transfer of dissolved CO$_2$.

458 Results obtained using NaHCO$_3$ absorbent with higher concentration (Figure 4c-d)

459 showed the same trend. In this case, RE for SO$_2$ removal, when L/G ratio increased from

460 5 to 15 L·m^{-3}, rose from 62.1 to 81.8% and from 65.4 to 85.4% when a flue gas of 2000

461 and 4000 ppm$_v$ of SO$_2$ was studied. On the other hand, an increase of gas contact time

462 from 0.6 s to 4 s also reduced RE for SO$_2$ abatement. In this sense, RE decreased from

463 85.7% to 70.4% and from 84.8% to 69.3% was observed working at 2000 ppm$_v$ and 4000

464 ppm$_v$, respectively.

465 These results showed that RE for SO$_2$ absorption obtained using the absorbent with

466 the highest CO$_2$ concentration are about a 10% higher. This trend confirmed that the

467 utilisation of NaHCO$_3$/Na$_2$CO$_3$ solutions as flue gas absorbents was not limited by CO$_2$

468 stripping in the spray scrubber since most of the alkalinity contained in these solutions

469 can be released during scrubbing process. These results also confirmed spray-scrubber as

470 a good alternative for flue gas treatment.

471 Therefore, it can be concluded that biological effluents can be a good alternative to

472 replace conventional NaOH-based absorbent in wet flue gas absorption Thereby, the

473 reduction of reagents consumption in absorption stage showed that two stage bioscrubber

474 reduced recurring operating costs related to NaOH consumption.

475   *3.2.2. NO_x oxidation*

476   The reduction of mass transfer limitations for NO_x absorption were evaluated dosing

477 oxidative reagents in the spray-scrubber in order to reduce the release of pollutants to the

478 atmosphere. NO oxidation enriches NO_x composition in NO_2 as well as in N_2O_3 and N_2O_4

479 (according to Eq. 10-12), which react irreversibly with water forming aqueous nitrogen

480 species. This alternative was evaluated assessing several oxidants for NO_x absorption.

481 Results are presented in Figure 5, considering RE for NO oxidation and RE for the

482 absorption of oxidation products (RE-NO_x).

483   Experimental results of NO_x abatement including oxidizing agents in the scrubbing

484 solution showed higher RE for NO oxidation than for NO_x absorption. Absorbents based

485 on H_2O_2, NaClO and $Na_2S_2O_7$ presented similar oxidation efficiencies, ranging from 12

486 to 18%. However, $Na_2S_2O_7$ is an acid salt and, therefore, presented low absorption

487 efficiencies. As can be seen in Eq. 13-15, despite NO oxidation products presented a

488 higher solubility, the alkaline character of the absorbent is key for NO_x absorption.

489 Absorption based on NaOH solutions presented similar efficiencies both for NO

490 oxidation and NO_2 absorption, close to the 30% and higher than the exhibited for most of

491 the tested oxidants. On the other hand, the $KMnO_4$ solution stands out from the other

492 absorbents showing oxidation and absorption efficiencies close to 50 and 60%,

493 respectively. According to experimental results, the dosing of oxidative reagents in the

494 absorbent can be considered as a suitable alternative to increase RE for NO_x scrubbing

495 and to ensure clean gas emissions.

496   *3.3.Economic viability assessment*

497   The improvement of the treatment of combustion gases through the two-stage

498 bioscrubber was quantified from an economic point of view by calculating the savings in

499 operating costs introduced by the proposed alternative. To this aim, the treatment of a flue

500 gas stream of 20000 $Nm^3 \cdot h^{-1}$ with a SO_2 concentration of 3000 ppm_v and a NO_x

501 concentration of 500 ppm_v in a spray-scrubber was defined as case study. In addition, a

502 RE of 90% was considered for both alternatives and a stripping efficiency of the 55% of

503 dissolved CO_2 in the regenerated absorbent was supposed for the two-stage bioscrubber.

504 These conditions were selected according to typical emissions in combustion facilities

505 (Moore 1987; Karatepe 2000; Srivastava and Jozewicz 2001). According to process
506 chemistry defined in Eq. 1-18, operating costs for the treatment of the target emission in
507 a wet-absorption facility using NaOH-based absorbent and in the two-stage bioscrubber
508 considering costs-savings introduced by $NaHCO_3$ rich stream reuse in absorption were
509 calculated (Table 4).

510   The treatment of flue gas stream of the case study through a conventional spray
511 scrubber using NaOH-based absorbents implies a reagents consumption of 1685 Tn
512 $NaOH \cdot year^{-1}$. On the other hand, the biological treatment of the 76.94 kg $SO_2 \cdot h^{-1}$ resulting
513 from flue gas treatment was assessed using experimental results presented in Fernández-
514 Palacios (Fernández-Palacios et al. 2019) for the characterization of biological reactors
515 performance. According to the authors, treatment of the scrubber effluent under optimal
516 operating conditions must be performed using crude glycerol as carbon source fed at a
517 carbon/sulphur ratio of 5 g $O_2 \cdot g^{-1}$ S. The operation of both biological reactors under these
518 conditions gives rise to a process effluent with an average dissolved CO_2 concentration
519 of 0.10 g $C \cdot L^{-1}$, equivalent to an annual amount of 2558 Tn. The reuse of the $NaHCO_3$
520 produced during the bioprocess allows annual NaOH savings of 1074 Tn, reducing the
521 operating costs of wet-absorption by a 63.7%. These results demonstrate the economic
522 competitiveness of the bio-FGD alternative proposed herein.

523

524 **4. CONCLUSIONS**

525   Experimental results obtained in this work enable to establish the optimal operating
526 conditions for the sequential wet-scrubbing of SO_2 and NO_x from flue gas. The SO_2 and
527 NO_x wet-absorption presented different performances caused by the difference in their
528 solubility. While high RE can be obtained for the treatment of SO_2 working at low RT
529 (below 2 s) and at moderate L/G ratios (7.5 $L \cdot m^{-3}$), mass transport limitations for NO_x
530 absorption resulted in RE below 10% under these operating conditions. The RT for NO_x
531 abatement must be increased above 60 s in order to enable enough time for NO partial
532 oxidation and increase NO_x absorption efficiency. Thus selective absorption of both
533 pollutants can be performed in two spray-scrubbers in series designed to work under
534 clearly differentiated RT. In addition, second scrubber can include the dosing of oxidative
535 reagents in order increase NO oxidation and capture NO_x from flue gas. Thus, sequential
536 wet-scrubbing process allows to ensure clean gas emissions. The reuse of the two-stage

537 bioscrubber effluent as absorbent in the scrubbing unit showed the same RE than using a
538 NaOH-based absorbent. Economic comparison of proposed bio-FGD alternative against
539 spray-scrubber operated using NaOH-bases absorbents showed 63.74% savings on
540 operational costs due to the reduction in reagents consumption.

541

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545

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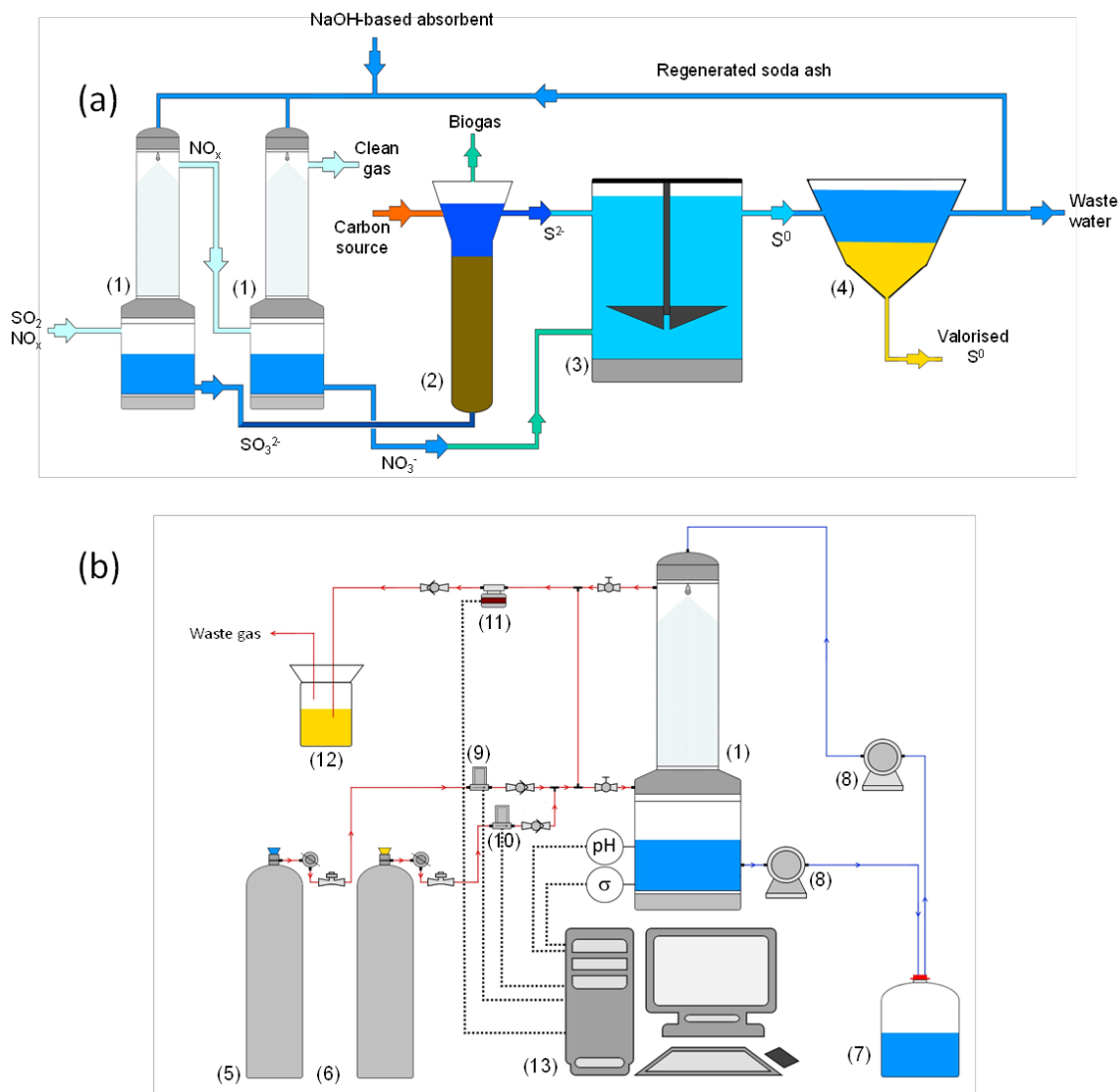
Fig. 1 (a) Schematic of the two-stage bioscrubber, (1) Spray absorber for flue gas treatment, (2) sulfate reduction bioreactor, (3) anoxic sulfide oxidation reactor and (4) elemental sulfur settler. **(b)** Schematic of the bench-scale spray absorber used to study flue gas absorption process: (1) spray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

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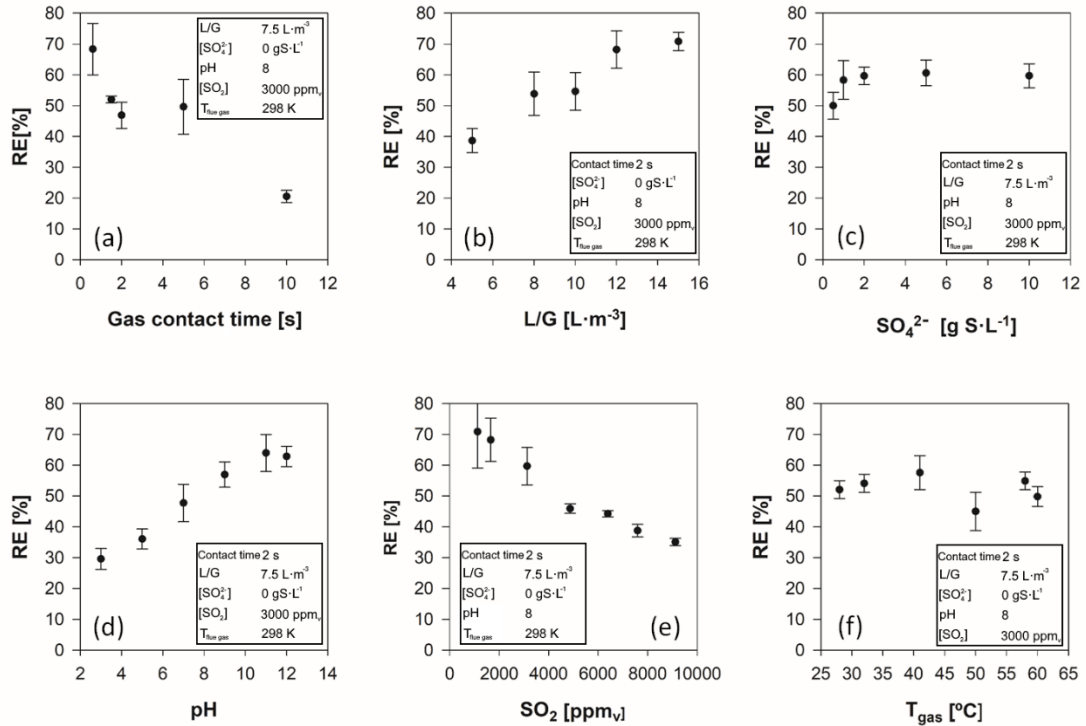
Fig. 2 Characterization of SO₂ wet-absorption in lab-scale spray-scrubber. Influence of (a) gas contact time, (b) L/G ratio, (c) sulphate absorbent concentration, (d) absorbent pH, (e) SO₂ gas concentration and (f) gas temperature
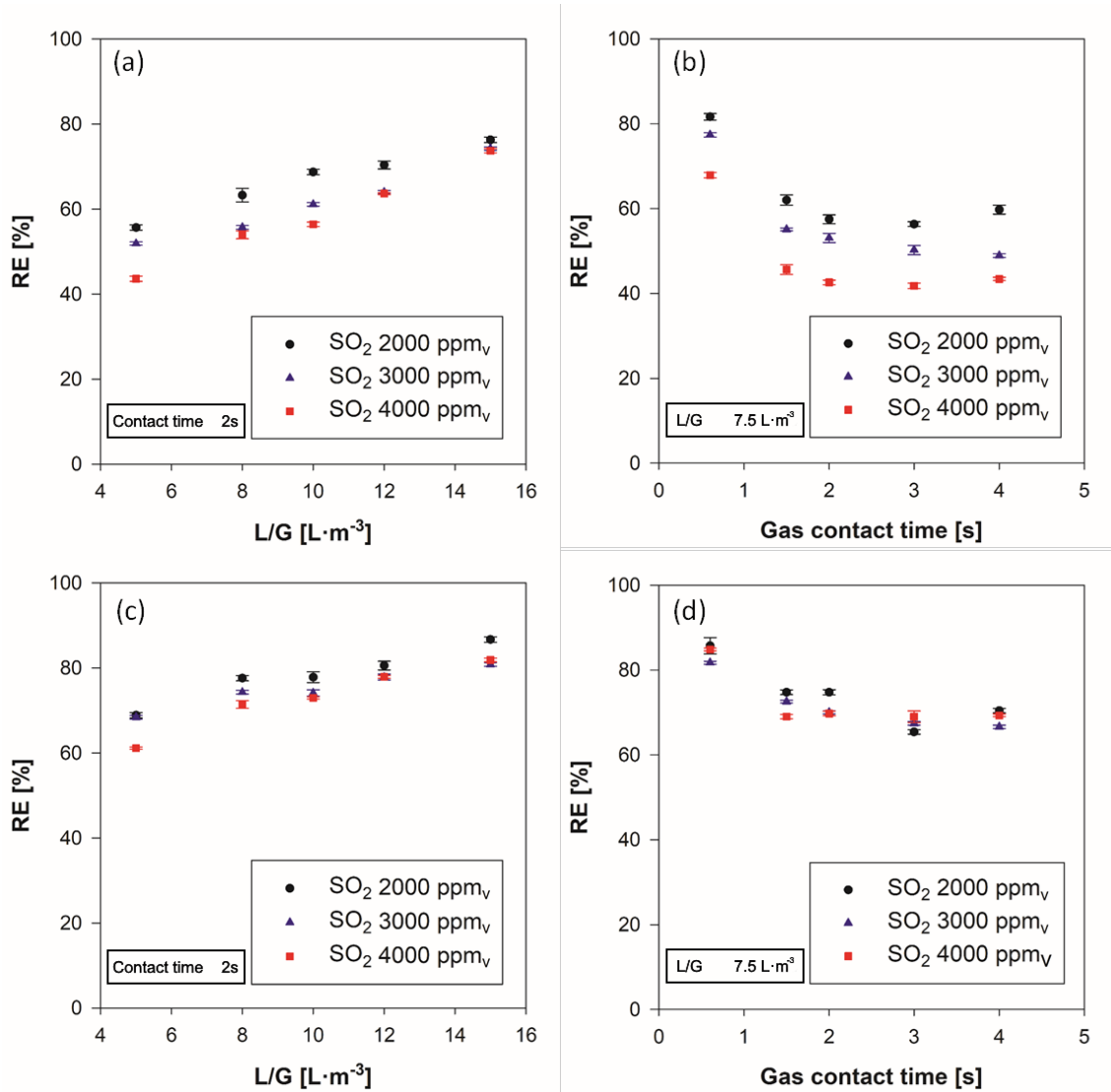
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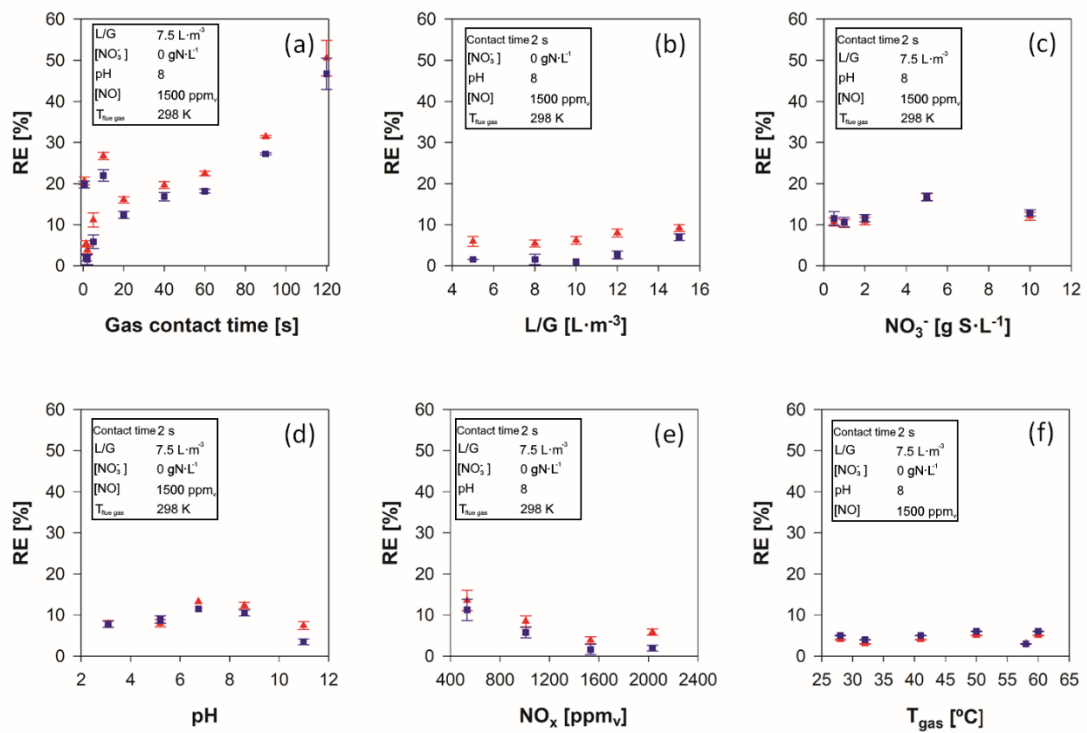
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734 **Fig. 3** Characterization of NO$_x$ wet-absorption in lab-scale spray-scrubber. RE of NO (●)
735 and NO$_x$ (■) abatement. Influence of (a) gas contact time, (b) L/G ratio, (c) nitrate
736 absorbent concentration, (d) absorbent pH, (e) NO gas concentration and (f) gas
737 temperature

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740 **Fig. 4** Results of SO$_2$ wet-absorption using a NaHCO$_3$ absorbent of 0.05 g C·L^{-1} in
741 function of (a) L/G ratio and (b) gas contact time, and using a NaHCO$_3$ absorbent of 0.20
742 g C·L^{-1} also in function of (c) L/G ratio and (d) gas contact time.

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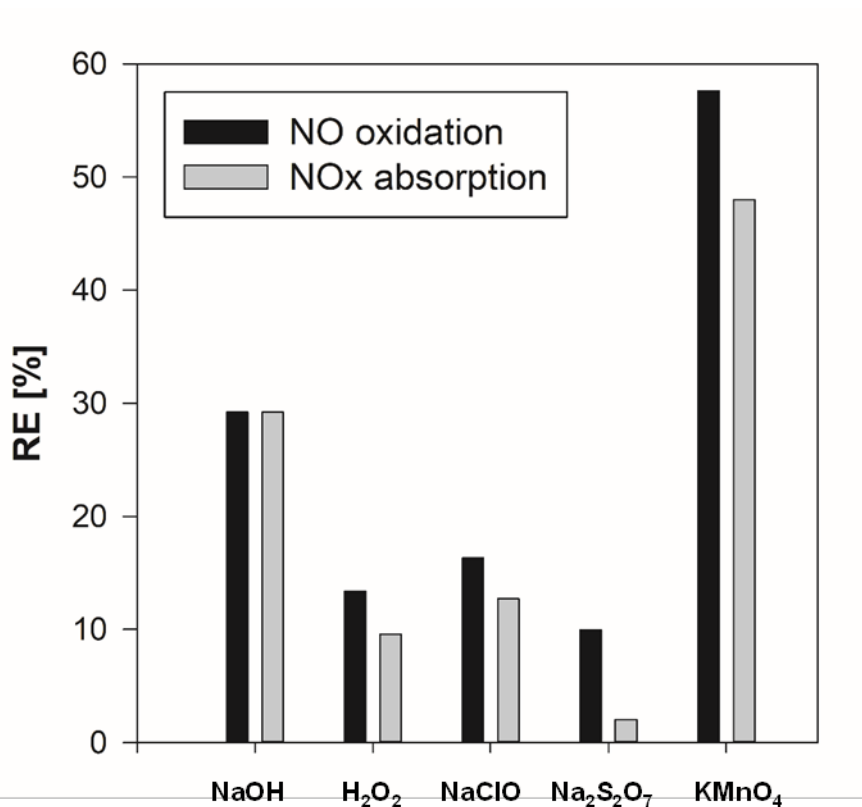
Fig. 5 RE for NO oxidation and NO_x absorption using several oxidative agents.

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Table 1 Experimental conditions used in the characterization of SO_2 and NO_x absorption.

Gas contact time [s]	L/G [L·m⁻³]	SO₄²⁻ [g S·L⁻¹]	NO₃⁻ [g N·L⁻¹]	pH	SO₂ [ppm_v]	NO [ppm_v]	T flue gas [K]
0.6-10	7.5	0	0	8	3000	0	298
2	5-15	0	0	8	3000	0	298
2	7.5	0-10	0	8	3000	0	298
2	7.5	0	0	3-12	3000	0	298
2	7.5	0	0	8	1000-9000	0	298
2	7.5	0	0	8	3000	0	298-333
0.6-120	7.5	0	0	8	0	1500	298
2	5-15	0	0	8	0	1500	298
2	7.5	0	0.1-10	8	0	1500	298
2	7.5	0	0	3-11	0	1500	298

2	7.5	0	0	8	0	1000-3000	298
2	7.5	0	0	8	0	1500	298-333

748

749 **Table 2** Operating conditions of two consecutive scrubbers established for sequential
750 wet-absorption of 2000 ppm$_v$ of SO$_2$ and 1500 ppm$_v$ of NO$_x$. RE are referred to inlet
751 pollutants concentration

	SO$_2$ scrubber	NO$_x$ scrubber
Gas contact time [s]	1	100
Absorbent pH	8	8
L/G ratio [L·m^{-3}]	7.5	15
RE-SO$_2$	72.9	25.9
RE-NO$_x$	5.4	50.5

752

753 **Table 3** Comparison of experimental SO$_2$ RE obtained working both with a NaOH-based
754 and a NaHCO$_3$ absorbent.

Gas contact time [s]	L/G ratio [L·m^{-3}]	RE [%]	
		NaOH	*NaHCO$_3$*
2	5	38.7	43.0
	15	70.9	73.0
0.6	7.5	68.4	67.9
4		49.6	49.2

755

756 **Table 4** Operational costs of the treatment of 20000 m^3 h^{-1} of flue gas with SO$_2$ and NO$_x$
757 concentration of 3000 ppm$_v$ and 500 ppm$_v$, in a spray-scrubber operated with NaOH-
758 based absorbent and with an absorbent of biological origin.

Treatment technology	Concept	Annual consumption	Annual savings	Amount [USD·year^{-1}]
Spray-scrubber	NaOH	1685 Tn (530 USD·Tn^{-1})	-	893050
Two-stage bioscrubber	NaOH	611 Tn (530 USD·Tn^{-1})	1074 Tn	323830
	NaHCO$_3$	2588 Tn	-	

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