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1 Optimization of SO₂ and NO_x sequential wet absorption in a two-stage 2 bioscrubber for elemental sulphur valorisation

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12 ABSTRACT

13 Flue gases contain SO₂ and NO_x that can be treated together for elemental sulfur
14 recovery in bioscrubbers, a technology that couples physical-chemical and biological
15 processes for gaseous emissions treatment in a more economic manner than classical
16 absorption. Sequential wet-absorption of SO₂ and NO_x from flue gas is thoroughly studied
17 in this work in a two-stage bioscrubber towards elemental sulphur valorisation pursuing
18 reuse of biological process effluents as absorbents. The optimal operating conditions
19 required for SO₂ and NO_x absorption in two consecutive spray-absorbers were defined
20 using NaOH-based absorbents. Overall, removal efficiencies of 98.9 and 55.9% for SO₂
21 and NO_x abatement were obtained in two in-series scrubbers operated under a gas contact
22 time of 1 and 100 s, and a liquid-to-gas ratio of 7.5 and 15 L·m⁻³, respectively. Higher
23 NO_x removal efficiency to clean gas emission was obtained by oxidants dosing in the
24 absorber for NO_x absorption. High NaHCO₃ concentration in two-stage bioscrubber
25 effluent was exploited as alkaline absorbent for flue gas treatment. The performance of
26 scrubbers using an absorbent mimicking a reused effluent exhibited same removal
27 efficiencies than those observed using NaOH solutions. In addition, the reuse of
28 bioprocess effluent reduced reagents consumption by a 63.7%. Thus, the two-stage
29 bioscrubber proposed herein offers an environmentally friendly and economic alternative
30 for flue gas treatment.

31 KEYWORDS

32 Flue gas treatment, desulphurization, bioscrubber, SO₂ 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 CO₂, SO₂ 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 SO₂ 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 SO₂ 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 SO₂
49 presents a high solubility in aqueous solutions (11.29 g SO₂·100 g⁻¹ H₂O (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·100 g⁻¹ H₂O (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 SO₂ contained in flue gases as elemental sulfur. This novel bio-FGD alternative
70 is based on the sequential absorption of SO₂ 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 H₂S
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 H₂ (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 SO₂ 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 SO₂ 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 SO₂ loads above 0.6 kg S·m⁻³·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 H₂S (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, upflow anaerobic
94 sludge blanket (UASB) reactor, treating high sulphate loads (4.3 kg S·m⁻³·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) SO₂ 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 SO₂ 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 SO₂ and NO_x 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 NO_x
108 removal efficiency.

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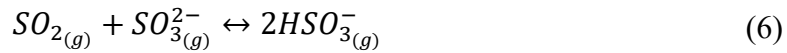
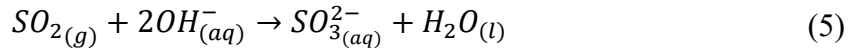
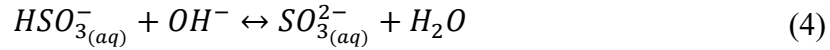
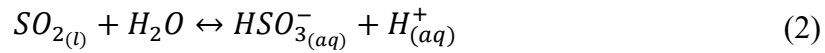
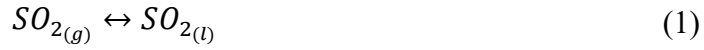
110 **2. EXPERIMENTAL METHODS**

111 ***2.1.Process chemistry***

112 *2.1.1. Mechanisms of SO₂ and NO_x absorption*

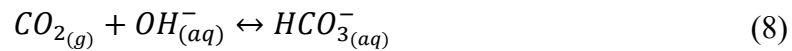
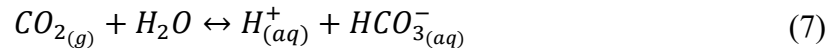
113 Based on the sulphur dioxide absorption mechanism (Eq. 1 to 6), flue gas
114 desulphurization through wet processes is generally performed using an alkaline solution
115 as absorbent for chemical absorption.

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 SO₂ can be
118 dissociated following Eq. 2, a first order reaction with a reaction rate of $3.4 \cdot 10^6 \text{ s}^{-1}$ at
119 20°C (Chang and Rochelle 1981). The dissolved SO₂ reacts in the presence of hydroxide
120 ions through the second order reaction presented in Eq. 3 with a rate constant exceeding
121 $10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 25°C, 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.



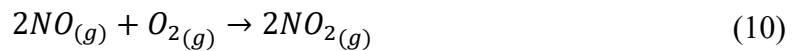
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129 The wet-type processes can be implemented using other alkaline reagents such as
 130 calcium compounds (Sakai et al. 2002) or NaHCO₃/Na₂CO₃ solutions (Ebrahimi et al.
 131 2003). The absorption of SO₂ into HCO₃⁻/CO₃²⁻ solutions and concomitant CO₂
 132 desorption is presented in Eq. 9. For this reason, it is important to also consider CO₂
 133 hydrolysis both at pH below 8 (Eq. 7) and at pH above 10 (Eq. 8).



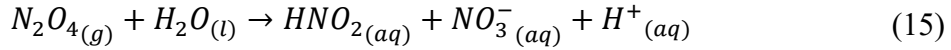
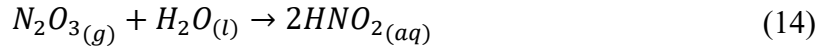
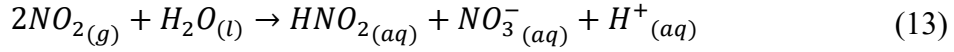
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135 Gaseous NO_x is a complex mixture of nitrogen species of different oxidation states.
 136 Several reactions in gas phase can be considered in a NO_x mixture (Newman and Carta
 137 1988; Suchak et al. 1990; Thomas and Vanderschuren 1997). Reactions of NO and NO₂
 138 in presence of oxygen are shown in Eq. 10-12, and include NO oxidation to NO₂ and the
 139 instantaneous production of nitrogen species such as N₂O₃ and N₂O₄.



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 NO₂, N₂O₃ and N₂O₄ 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:



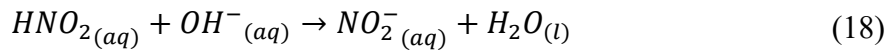
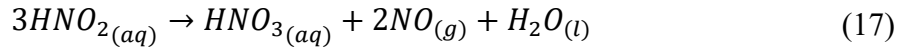
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146 Nitrous oxide can also be generated from NO. Despite NO is sparingly insoluble and
147 non-reactive with water, under low concentrations reacts with NO₂ (Joshi et al. 1985)
148 forming nitrous acid (Eq. 16).



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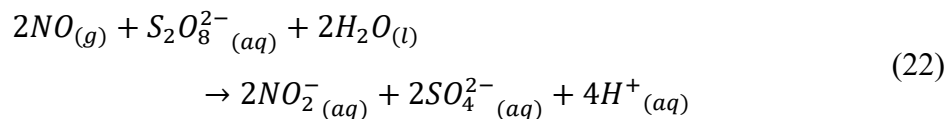
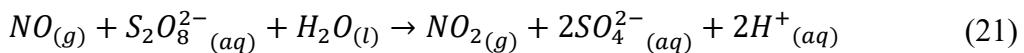
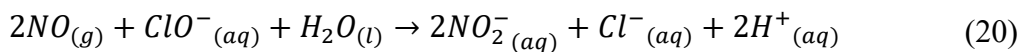
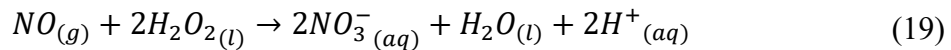
150 In aqueous solution and especially under high nitric acid concentrations, nitrous acid
151 is very unstable and can be decomposed to NO (Eq. 17) that can be desorbed. In strong
152 alkaline solutions HNO₂ decomposes through an instantaneous proton transfer reaction
153 (Eq. 18) preventing NO release.

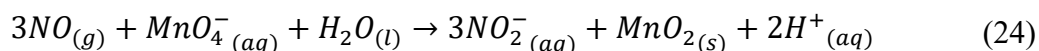
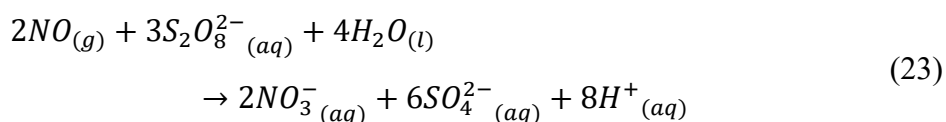


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155 2.1.2. Chemistry of NO oxidation

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 H₂O₂, NaClO, Na₂S₂O₇ and KMnO₄ solutions has been explored. Such oxidation
161 reactions are presented in Eq. 19-24.





162

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 SO₂ 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 SO₂ 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 SO₂ 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 competitiveness 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 H₂S release. The operation of CSTR
200 resulted in a sulfur productivity 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 biosulfur 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 100°C.

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 SO₂/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 ($\text{SO}_2\text{-B4}$, Alphasens, UK), an electrochemical NO sensor (4NO-2000 , EuroGas,
234 UK) and an electrochemical NO_2 sensor ($4\text{NO}_2\text{-2000}$, 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 $^\circ\text{C}$ and atmospheric pressure. Absorption
242 efficiency was evaluated for each pollutant by means of the following expression:

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

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), SO₂ 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 80°C. 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 NO₂. For this reason, NO_x absorption
260 was performed considering NO_x concentration as the sum of NO and NO₂ concentration
261 and assessing NO_x RE considering both NO RE and NO₂ 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 NaHCO₃
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 CO₂
266 concentration in the biological process effluent ranged between 0.05 and 0.20 g C-
267 HCO₃·L⁻¹. The suitability of reusing the biological process effluent for flue gas spray
268 scrubbing was assessed quantifying the SO₂ RE using NaHCO₃-based absorbents of 0.05
269 and 0.2 g C-HCO₃·L⁻¹. The UASB HCO₃⁻ concentration range was selected for the study
270 because no carbonate lost was detected during elemental sulphur production in CSTR.
271 Both NaHCO₃-based were prepared by dissolving NaHCO₃ in distillate water and
272 adjusting pH at the CSTR outlet pH (pH 7.5). The spray scrubbing using NaHCO₃
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·m⁻³) and SO₂ 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 KMnO₄ (0.3 M), NaClO (0.4 M), Na₂S₂O₇ (0.2 M), H₂O₂
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·m⁻³.

287

288 3. RESULTS

289 3.1. Flue gas wet-absorption

290 3.1.1. Characterization of SO₂ wet-absorption

291 Several sets of experiments were performed to characterize SO₂ wet absorption.
292 Results shown in Figure 2 depict the effect of the tested operating variables on SO₂
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·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 SO₂ mass transfer to
300 the liquid bulk. According to these results, SO₂ 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 SO₂ RE but a higher energy consumption and operating costs. The L/G ratio in
307 spray absorbers for the removal of SO₂ is typically set between 8 L·m⁻³ and 25 L·m⁻³.
308 Considering the high performance of NaOH solutions, the desulphurization efficiency
309 was evaluated between 5 L·m⁻³ and 15 L·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·m⁻³ to 12 L·m⁻³, and
312 from 68.7% to 79.8% when L/G ratio rose from 12 L·m⁻³ to 15 L·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 SO₂ 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 Na₂SO₃
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 SO₂ 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, SO₂ 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 SO₂ 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 SO₂ 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 SO₂ inlet concentration on sulphur removal efficiency. Results presented
339 in Figure 2e showed that the SO₂ 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 SO₂ 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 SO₂ inlet concentrations.

347 The effect of temperature on SO₂ absorption process is complex. Temperature rise can
348 reduce the solubility of SO₂ but improve mass transfer coefficient and also accelerate
349 chemical reactions rates (Wang et al. 2012). For this reason, the flue gas influence on SO₂
350 RE was evaluated. The liquid temperature at the beginning of the experiments was kept
351 at 25°C. A flue gas temperature effect on RE was not observed within the tested range
352 (Figure 2f), since liquid phase temperature and thus SO₂ solubility, kept steady during
353 absorption.

354 3.1.2. Characterization of NO_x 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 H₂O). 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 NO_x 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 NO_x 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ and NO_x
403 abatement treating a gas stream with 2000 ppm_v of SO₂ 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 SO₂ absorption was enhanced but NO_x
408 absorption capacity was strongly limited. Removal efficiencies obtained in the first
409 scrubber for SO₂ and NO_x absorption are presented in Table 2. Higher SO₂ 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·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 NO_x removal of 50.5%. Results
418 showed that most of SO₂ 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 SO₂ 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 SO₂ 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. SO₂ absorption using recovered NaHCO₃/Na₂CO₃*

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 NaHCO₃/Na₂CO₃ 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 NaHCO₃
433 solutions as absorbent for SO₂ 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 SO₂ concentration on system RE.

437 Results obtained in the characterization of SO₂ absorption using mimicking absorbents
438 of biological origin are presented in Fig. 4. NaHCO₃ absorbent, both with low and with
439 high concentration, showed a RE for SO₂ 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 SO₂
441 concentration on absorption capacity was also observed. Experimental results obtained

442 working with an absorbent of $0.05 \text{ g C}\cdot\text{L}^{-1}$ concentration showed that a L/G ratio increase
443 from 5 to $15 \text{ L}\cdot\text{m}^{-3}$ 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 $15 \text{ L}\cdot\text{m}^{-3}$, 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 $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ 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 NO₂ as well as in N₂O₃ and N₂O₄
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 H₂O₂, NaClO and Na₂S₂O₇ presented similar oxidation efficiencies, ranging from 12
486 to 18%. However, Na₂S₂O₇ 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 NO₂ absorption, close to the 30% and higher than the exhibited for most of
491 the tested oxidants. On the other hand, the KMnO₄ 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 Nm³·h⁻¹ with a SO₂ 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 CO₂ 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 NaHCO₃ 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·year⁻¹. On the other hand, the biological treatment of the 76.94 kg SO₂·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 O₂·g⁻¹ S. The operation of both biological reactors under these
518 conditions gives rise to a process effluent with an average dissolved CO₂ concentration
519 of 0.10 g C·L⁻¹, equivalent to an annual amount of 2558 Tn. The reuse of the NaHCO₃
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 SO₂ and NO_x from flue gas. The SO₂ 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 SO₂ working at low RT
529 (below 2 s) and at moderate L/G ratios (7.5 L·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

546 **REFERENCES**

547 Adewuyi YG, Sakyi NY (2013) Simultaneous absorption and oxidation of nitric oxide
548 and sulfur dioxide by aqueous solutions of sodium persulfate activated by
549 temperature. *Ind Eng Chem Res* 52:11702–11711.
550 <https://doi.org/10.1021/ie401649s>

551 Ađar A, Küçükataş V, Yargıçođlu P, et al (2000) The effect of sulfur dioxide inhalation
552 on visual evoked potentials, antioxidant status, and lipid peroxidation in alloxan-
553 induced diabetic rats. *Arch Environ Contam Toxicol* 39:257–264.
554 <https://doi.org/10.1007/s002440010103>

555 Altuđ H, Gaga EO, Döđerođlu T, et al (2013) Effects of air pollution on lung function
556 and symptoms of asthma, rhinitis and eczema in primary school children. *Environ*
557 *Sci Pollut Res* 20:6455–6467. <https://doi.org/10.1007/s11356-013-1674-1>

558 An T, Wan S, Li G, et al (2010) Comparison of the removal of ethanethiol in twin-
559 biotrickling filters inoculated with strain RG-1 and B350 mixed microorganisms. *J*
560 *Hazard Mater* 183:372–380. <https://doi.org/10.1016/j.jhazmat.2010.07.035>

561 Bai J, Meng Z (2005) Effects of sulfur dioxide on apoptosis-related gene expressions in
562 lungs from rats. *Regul Toxicol Pharmacol* 43:272–279.
563 <https://doi.org/10.1016/j.yrtph.2005.09.002>

564 Chang CS, Rochelle GT (1981) SO₂ absorption into aqueous solutions. *AIChE J* 27:292–
565 298. <https://doi.org/10.1002/aic.690270217>

- 566 Chen JC, Liu ZS, Huang JS (2007) Emission characteristics of coal combustion in
567 different O₂/N₂, O₂/CO₂ and O₂/RFG atmosphere. *J Hazard Mater* 142:266–271.
568 <https://doi.org/10.1016/j.jhazmat.2006.08.021>
- 569 Ding J, Zhong Q, Zhang S, et al (2014) Simultaneous removal of NO_x and SO₂ from
570 coal-fired flue gas by catalytic oxidation-removal process with H₂O₂. *Chem Eng J*
571 243:176–182. <https://doi.org/10.1016/j.cej.2013.12.101>
- 572 Ebrahimi S, Picioreanu C, Kleerebezem R, et al (2003) Rate-based modelling of SO₂
573 absorption into aqueous NaHCO₃/Na₂CO₃ solutions accompanied by the
574 desorption of CO₂. *Chem Eng Sci* 58:3589–3600. [https://doi.org/10.1016/S0009-
575 2509\(03\)00231-8](https://doi.org/10.1016/S0009-2509(03)00231-8)
- 576 Fernández-Palacios E, Lafuente J, Mora M, Gabriel D (2019) Exploring the performance
577 limits of a sulfidogenic UASB during the long-term use of crude glycerol as electron
578 donor. *Sci Total Environ* 688:1184–1192.
579 <https://doi.org/10.1016/j.scitotenv.2019.06.371>
- 580 Gao H, Li C, Zeng G, et al (2011) Flue gas desulphurization based on limestone-gypsum
581 with a novel wet-type PCF device. *Sep Purif Technol* 76:253–260.
582 <https://doi.org/10.1016/j.seppur.2010.10.013>
- 583 Han Y, Li X, Fan M, et al (2015) Abatement of SO₂–NO_x binary gas mixtures using a
584 ferruginous active absorbent: Part I. Synergistic effects and mechanism. *J Environ
585 Sci* 30:55–64. <https://doi.org/10.1016/j.jes.2014.10.012>
- 586 Hao R, Yang S, Yuan B, Zhao Y (2017) Simultaneous desulfurization and denitrification
587 through an integrative process utilizing NaClO₂/Na₂S₂O₈. *Fuel Process Technol*
588 159:145–152. <https://doi.org/10.1016/j.fuproc.2017.01.018>
- 589 Hikita H, Asai S, Tsuji T (1977) Absorption of sulfur dioxide into aqueous sodium
590 hydroxide and sodium sulfite solutions. *AIChE J* 23:538–544.
591 <https://doi.org/10.1002/aic.690230419>
- 592 Hu Y, Naito S, Kobayashi N, Hasatani M (2000) CO₂, NO_x and SO₂ emissions from
593 the combustion of coal with high oxygen concentration gases. *Fuel* 79:1925–1932.
594 [https://doi.org/http://dx.doi.org/10.1016/S0016-2361\(00\)00047-8](https://doi.org/http://dx.doi.org/10.1016/S0016-2361(00)00047-8)
- 595 Jiang F, Zhang L, Peng G-L, et al (2013) A novel approach to realize SANI process in

596 freshwater sewage treatment - Use of wet flue gas desulfurization waste streams as
597 sulfur source. *Water Res* 47:5773–5782.
598 <https://doi.org/10.1016/j.watres.2013.06.051>

599 Jin Y, Veiga MC, Kennes C (2005) Bioprocesses for the removal of nitrogen oxides from
600 polluted air. *J Chem Technol Biotechnol* 80:483–494.
601 <https://doi.org/10.1002/jctb.1260>

602 Joshi JB, Mahajani VV, Juvekar VA (1985) Absorption of NO_x Gases. *Chem Eng*
603 *Commun* 33:1–92. <https://doi.org/10.1080/00986448508911161>

604 Kan H, Wong C-M, Vichit-Vadakan N, et al (2010) Short-term association between sulfur
605 dioxide and daily mortality: The Public Health and Air Pollution in Asia (PAPA)
606 study. *Environ Res* 110:258–264. <https://doi.org/10.1016/j.envres.2010.01.006>

607 Karatepe N (2000) A comparison of flue gas desulfurization processes. *Energy Sources*
608 22:197–206. <https://doi.org/10.1080/00908310050013983>

609 Lee KH, Sublette KL (1991) Simultaneous combined microbial removal of sulfur dioxide
610 and nitric oxide from a gas stream. *Appl Biochem Biotechnol* 28–29:623–634.
611 <https://doi.org/10.1007/BF02922637>

612 Lens PNL, Gastesi R, Lettinga G (2003) Use of sulfate reducing cell suspension
613 bioreactors for the treatment of SO₂ rich flue gases. *Biodegradation* 14:229–240.
614 <https://doi.org/10.1023/A:1024222020924>

615 Li Y, Zhong W, Ju J, et al (2014) Experiment on simultaneous absorption of NO and SO₂
616 from sintering flue gas by oxidizing agents of KMnO₄/NaClO. *Int J Chem React*
617 *Eng* 12:539–547. <https://doi.org/10.1515/ijcre-2014-0066>

618 Lin J, Li L, Ding W, et al (2015) Continuous desulfurization and bacterial community
619 structure of an integrated bioreactor developed to treat SO₂ from a gas stream. *J*
620 *Environ Sci (China)* 37:130–138. <https://doi.org/10.1016/j.jes.2015.05.029>

621 Liu Y, Bisson TM, Yang H, Xu Z (2010) Recent developments in novel sorbents for flue
622 gas clean up. *Fuel Process Technol* 91:1175–1197.
623 <https://doi.org/10.1016/j.fuproc.2010.04.015>

624 Majeed JG, Korda B, Békássy-Molnár E (1995) Comparison of the efficiencies of sulfur
625 dioxide absorption using calcium carbonate slurry and sodium hydroxide solution in

626 an ALT reactor. *Gas Sep Purif* 9:111–120. <https://doi.org/10.1016/0950->
627 4214(95)93948-J

628 Mathieu Y, Tzanis L, Soulard M, et al (2013) Adsorption of SO_x by oxide materials: A
629 review. *Fuel Process Technol* 114:81–100.
630 <https://doi.org/10.1016/j.fuproc.2013.03.019>

631 Moore DJ (1987) Conditions in which power stations contribute to high ground level SO₂
632 concentrations in the U.K. *Atmos Environ* 21:1849–1853.
633 [https://doi.org/10.1016/0004-6981\(87\)90126-0](https://doi.org/10.1016/0004-6981(87)90126-0)

634 Mora M, Fernández-Palacios E, Guimerà X, et al (2020) Feasibility of S-rich streams
635 valorization through a two-step biosulfur production process. *Chemosphere* 253:1–
636 10. <https://doi.org/10.1016/j.chemosphere.2020.126734>

637 Mora M, Lafuente F javier, Gabriel D (2018) Screening of biological sulfate reduction
638 conditions for sulfidogenesis promotion using a methanogenic granular sludge.
639 *Chemosphere* 210:557–566. <https://doi.org/10.1016/j.chemosphere.2018.07.025>

640 Newman BL, Carta G (1988) Mass transfer in the absorption of nitrogen oxides in alkaline
641 solutions. *AIChE J* 34:1190–1199. <https://doi.org/10.1002/aic.690340715>

642 Ottengraf SPP, Diks RMM (1992) Process technology of biotechniques. *Biotechniques*
643 *Air Pollut Abat Odour Control Policies* 51:17–31. <https://doi.org/10.1016/S0166->
644 1116(08)70673-3

645 Perry RH, Green DW (1997) Perry's chemical engineer's handbook, 7 Edition. Mc Graw-
646 Hill

647 Philip L, Deshusses MA (2003) Sulfur dioxide treatment from flue gases using a
648 biotrickling filter - Bioreactor system. *Environ Sci Technol* 37:1978–1982.
649 <https://doi.org/10.1021/es026009d>

650 Qian J, Lu H, Jiang F, et al (2015) Beneficial co-treatment of simple wet flue gas
651 desulphurization wastes with freshwater sewage through development of mixed
652 denitrification-SANI process. *Chem Eng J* 262:109–118.
653 <https://doi.org/10.1016/j.cej.2014.09.066>

654 Rahmani F, Mowla D, Karimi G, et al (2014) SO₂ removal from simulated flue gas using
655 various aqueous solutions: Absorption equilibria and operational data in a packed

656 column. Sep Purif Technol 153:162–169.
657 <https://doi.org/10.1016/j.seppur.2014.10.028>

658 Rao AG, Ravichandra P, Joseph J, et al (2007) Microbial conversion of sulfur dioxide in
659 flue gas to sulfide using bulk drug industry wastewater as an organic source by
660 mixed cultures of sulfate reducing bacteria. *J Hazard Mater* 147:718–725.
661 <https://doi.org/10.1016/j.jhazmat.2007.01.070>

662 Sakai M, Su C, Sasaoka E (2002) Simultaneous removal of SO_x and NO_x using slaked
663 lime at low temperature. *Ind Eng Chem Res* 41:5029–5033

664 Shen TT, Ayer LG (1975) Determination of SO₂ Emission from Oil Combustion Sources
665 by Fuel Analyses and SO₂ /CO₂ Relations. *J Air Pollut Control Assoc* 25:851–855.
666 <https://doi.org/10.1080/00022470.1975.10470150>

667 Srivastava RK, Jozewicz W (2001) Flue gas desulfurization: The state of the art. *J Air*
668 *Waste Manag Assoc* 51:1676–1688.
669 <https://doi.org/10.1080/10473289.2001.10464387>

670 Suchak NJ, Jethani KR, Joshi JB (1990) Absorption of Nitrogen Oxides in Alkaline
671 Solutions: Selective Manufacture of Sodium Nitrite. *Ind Eng Chem Res* 29:1492–
672 1502. <https://doi.org/10.1021/ie00103a059>

673 Sun J, Li L, Zhou G, et al (2018) Biological Sulfur Reduction to Generate H₂ S As a
674 Reducing Agent to Achieve Simultaneous Catalytic Removal of SO₂ and NO and
675 Sulfur Recovery from Flue Gas. *Environ Sci Technol* 52:4754–4762.
676 <https://doi.org/10.1021/acs.est.7b06551>

677 Sun Y, Zwolińska E, Chmielewski AG (2016) Abatement technologies for high
678 concentrations of NO_x and SO₂ removal from exhaust gases: A review. *Crit Rev*
679 *Environ Sci Technol* 46:119–142. <https://doi.org/10.1080/10643389.2015.1063334>

680 Thomas D, Vanderschuren J (1998) Removal of tetravalent NO_x from flue gases using
681 solutions containing hydrogen peroxide. *Chem Eng Technol* 21:975–981.
682 [https://doi.org/10.1002/\(SICI\)1521-4125\(199812\)21:12<975::AID-
683 CEAT975>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1521-4125(199812)21:12<975::AID-CEAT975>3.0.CO;2-H)

684 Thomas D, Vanderschuren J (1997) Modeling of NO_x absorption into nitric acid solutions
685 containing hydrogen peroxide. *Ind Eng Chem Res* 36:3315–3322.

- 686 <https://doi.org/10.1021/ie960436g>
- 687 Tian H, Gao J, Lu L, et al (2012) Temporal trends and spatial variation characteristics of
688 hazardous air pollutant emission inventory from municipal solid waste incineration
689 in China. *Environ Sci Technol* 46:10364–71. <https://doi.org/10.1021/es302343s>
- 690 Van Houten RT, Yun SY, Lettinga G (1997) Thermophilic sulphate and sulphite
691 reduction in lab-scale gas-lift reactors using H₂ and CO₂ as energy and carbon
692 source. *Biotechnol Bioeng* 55:807–814. [https://doi.org/10.1002/\(SICI\)1097-
693 0290\(19970905\)55:5<807::AID-BIT11>3.0.CO;2-8](https://doi.org/10.1002/(SICI)1097-0290(19970905)55:5<807::AID-BIT11>3.0.CO;2-8)
- 694 Wang J, Cao Y, Zhong Q (2013) Formulation and optimization of biological removal of
695 flue gas pretreatment wastewater and sulfur recycling process by Box-Behnken
696 design. *Water Sci Technol* 67:2706–2711. <https://doi.org/10.2166/wst.2013.175>
- 697 Wang W, Yang C, Zhang J (2012) Absorption of Sulphur Dioxide from Flue Gas with
698 Sodium Alkali Solution in Packed Columns. *Adv Mater Res* 383–390:6409–6415.
699 <https://doi.org/10.4028/www.scientific.net/AMR.383-390.6409>
- 700 Wang Z, Peng Y, Ren X, et al (2015) Absorption of sulfur dioxide with sodium hydroxide
701 solution in spray columns. *Ind Eng Chem Res* 54:8670–8677.
702 <https://doi.org/10.1021/acs.iecr.5b02146>
- 703 Winnes H, Fridell E (2010) Emissions of NO_x and particles from manoeuvring ships.
704 *Transp Res Part D Transp Environ* 15:204–211.
705 <https://doi.org/10.1016/j.trd.2010.02.003>
- 706 Zevenhoven, Kilpinen (2001) Chapter 2 Flue gases and fuel gases 2.1. *Flue Gases Fuel*
707 *Gases* 1–12
- 708 Zhao J, Jin B, Zhong Z (2007) The degree of desulphurization of a limestone/gypsum wet
709 FGD spray tower using response surface methodology. *Chem Eng Technol* 30:517–
710 522. <https://doi.org/10.1002/ceat.200600347>
- 711 Zhao Y, Han Y, Ma T, Guo T (2011) Simultaneous desulfurization and denitrification
712 from flue gas by ferrate(VI). *Environ Sci Technol* 45:4060–4065.
713 <https://doi.org/10.1021/es103857g>
- 714 Zhu Q, Van Teeffelen RM, Van Santen RA, Hensen EJM (2004) Effect of high-
715 temperature treatment on Fe/ZSM-5 prepared by chemical vapor deposition of FeCl₃

716 II. Nitrous oxide decomposition, selective oxidation of benzene to phenol, and
717 selective reduction of nitric oxide by isobutane. *J Catal* 221:575–583.
718 <https://doi.org/10.1016/j.jcat.2003.09.025>
719