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Article

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Research paper

Removal of high concentrations of NOx and SO₂ from diesel off-gases using a hybrid electron beam technology

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ABSTRACT

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Keywords: SO₂ NOx Electron beam Wet-scrubber Diesel off-gases The removal of high inlet concentrations of NOx (>1000 ppm) and SO₂ (>500 ppm) from diesel engine off-gases was studied using hybrid electron beam technology, i.e. electron beam combined with a wet scrubber method. Five different wet scrubbing solutions were examined: 3.5% NaCl solution (simulated sea water), NaOH solution, NaCl-NaClO₂-phosphate buffer solution, NaCl-NaClO₂ solution, and NaCl-H₂O₂ solution. The SO₂ removal efficiency for all hybrid experiments was 100% at 10.9 kGy irradiation dose for inlet concentrations of SO₂ varying between 501 ppm and 723 ppm. The NOx removal efficiency also increased with increasing the absorbed dose and decreased with increasing the gas flow rate. NOx removal efficiency also increased with increasing the oxidant concentration (NaClO₂) in the wet scrubber solution. The order of the NOx removal efficiency from lowest to highest in the hybrid system with the different scrubber solution increased NOX removal efficiency. An NOX removal efficiency of greater than 89.6% was achieved at 10.9 kGy irradiation dose for inlet NOX concentrations around 1500 ppm when 3.5% NaCl-5mMNaClO₂-phosphate buffer solution was used. After treatment, the cleaned off-gases can be released into the atmosphere.

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1. Introduction

Air pollution is an important issue for present day society and people living in big cities are at the greatest risk of harm. Despite the fact that air quality has risen significantly in comparison to the last century, there is still a lot of room for improvement. According to WHO (World Health Organisation), more than 80% of people living in cities and towns are affected by air pollution which exceeds safe norms set by WHO (2019). Countries of low economic status suffer the most from toxic pollutants. Recently, there has been significant concern about pollution from marine sources which currently utilise low quality diesel fuels. As a result, research and development projects have focused heavily on creating a cost effective technology that can clean off-gases with a high level of efficiency.

The abatement of harmful pollutants such as NO_x and SO_2 has become an urgent issue in the marine industry since stringent regulations came into force. Based on the IMO (International Marine Organisation) MARPOL Annex VI (International Maritime Oganization, 2019), the emission limit of 0.1% S has been applied in the SECA (sulphur emission control area) and the emission the IMO MARPOL Annex VI Tier III will be applied in NECA (NOx emission control area) in Europe in 2020; it requires a 75% reduction of the NOx emission from the current Tier II NOx emission limit, and NOx emission must be below 2 g NOx/kWh at marine engine speeds over 1200 rpm. During the combustion of heavy oils used on cargo ships, a significant amount of highly concentrated NO_x and SO₂ is produced. SO₂ concentration is proportional to the fuel sulphur content; NOx concentration is related to the engine load. Taking MAN B&W two-stroke diesel engines as an example, when 1.75 g/kWh fuel (3% S) and 8.5 kg/kWh air were used for combustion, the typical exhaust gas composition was 13% O₂, 75.8% N₂, 5.2% CO₂, 5.35% H₂O, 1500 ppmv NOx, 600 ppmv SOx, 60 ppm CO, 180 ppm hydrocarbon (HC), and 120 mg/N m³ particulate matter (PM) (MAN B & W Diesel A/S, 2019). Based on our own work done in December 2018 at the Riga Shipyard on flue gas emitted from a marine type four stroke five cylinder turbo diesel engine NOHAB POLAR SF15RS with 560 horse power. the exhaust gas composition for 0% S fuel (desulphurised fuel) at 75% engine load was 12.4% O₂, 1444 ppmv NO, 141 ppmv NO₂, 162 ppm CO, 400 ppm HC, and NOx concentration was 1585ppm, about 91.1% NOx was NO. Currently, there are no cost-effective, efficient technologies available to simultaneously remove sulphur

limit of S in global areas (excluding SECA) will be reduced from the current 3.5% S to 0.5% S in 2020. Concerning NOx emission,

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and nitrogen oxides at such high concentrations. Two separate technologies, wet scrubber for removal SO_2 and SCR (selective catalytic reduction) for NOx removal from off-gases have been implemented on board.

Although good removal efficiency of SO₂ (99%) and NOx (90%) are achieved using these two separate technologies, they possess of number of drawbacks: high installation cost, high maintenance cost, and a large space needed for two separate installations and ammonia storage (EGCSA, 2012; Jurgens et al., 2012). Besides, high temperature (300–400 °C) is needed for NOx reduction using the SCR method, so the flue gas after the wet scrubber for SO₂ reduction needs to be reheated. Otherwise, the catalyst might be deactivated in a short time when the temperature is below 250 °C, especially when a high concentration of SO₂ and PM are present in the off-gases (Magnusson et al., 2012).

A new technology has to be searched for. Electron beam (EB) technology is one of the promising technologies being investigated. EB dry scrubber technology has been successfully applied to simultaneously remove SO₂ and NOx from flue gas in coal-fired power plants (Chmielewski et al., 2004; Kim et al., 2011). High removal efficiency of SO₂ and NOx were achieved and benign by-products were generated. However, this technology cannot be directly transferred from stationary sources to marine sources due to the special requirements of ships. These include the limitations of ship space and weight and the need to store a large amount of ammonia water and its solid products.

It is not so efficient to remove high concentrations of SO₂ and NOx using only an electron beam without a scrubber. In order to improve the electron energy efficiency, electron beam (EB) + microwave wave (MW) has been studied as a means to remove NOx and SOx from marine diesel engine exhaust and a high removal efficiency of SO₂ and NOx were theoretically predicted (Manivannan et al., 2014). Taking into consideration the good solubility of SO₂ and NO₂ and the availability of sea water, EB combined with a wet scrubber system may provide an answer to the reducing SO₂ and NOx emissions from global and in marine engine and ships. There are two main stages involved: (1) SO₂ and NO_x (mainly NO) oxidation during irradiation by the electron beam from the accelerator (NO is oxidised into NO₂ and higher oxides. SO_2 is oxidised into SO_3 and higher oxides) and (2) NO_2 . SO_3 and their higher oxides in the gas phase are absorbed into aqueous solution via wet scrubbing to form HNO₂, HNO₃, H₂SO₃ and H₂SO₄. The cleaned off-gas after EB-wet scrubber treatment can be released into the atmosphere. EB-hybrid technology may remove SO₂ and NOx simultaneously, it does not need an additional set-up for NOx removal and it can save space and weight for NOx removal using an SCR installation.

An electron beam combined with the wet-scrubber method takes advantage of both technologies: SO_2 and NO_x (mainly NO) oxidation using electron beam and removal of soluble oxidised pollutants using a wet scrubber. EB combined with the wet-scrubber method to remove SO_2 and NOx from diesel off-gases was first proposed by our laboratory.

In this work, we studied the removal efficiency of SO_2 and NOx using an EB-hybrid system under various conditions: different inlet concentrations of pollutants, EB hybrids with different kinds of wet-scrubber solutions (with or without oxidant), different concentrations of the selected scrubber solutions, and different gas flow rates, dose levels, etc. This was done in order to identify the optimum conditions (irradiation dose, type of the wet-scrubber and its concentration) that are needed to achieve high removal efficiency of SO_2 and NOx while taking into consideration the cost and energy efficiency.

2. Experimental

2.1. Chemicals

The following chemical reagents were used to make scrubber solutions: NaCl (Solid, ACS reagent) was purchased from CHEMPUR, Poland; NaClO (Liquid, 6%–14% active chlorine, density 1.22–1.25 g/cm³), NaClO₂ (solid, ACS reagent), NaClO₃ (solid, ACS reagent) and NaOH (solid, ACS reagent) were purchased from SIGMA ALDRICH, USA; Na₂HPO₄ (solid, ACS reagent) and KH₂PO₄ (solid, ACS reagent,) were purchased from VWR CHEMICALS, USA.

Gas cylinders of NO (99.5% purity) and SO₂ (99.98% purity) were provided by AIR LIQUIDE, Poland.

Calibration NO (1715 ppm in N_2) and SO₂ (1810 ppm in N_2) gas were purchased from MESSER, Germany. NO (99.5% purity), SO₂ (99.98% purity), and N₂ (99.999% purity) were used for making calibration gas.

2.2. Preparation of the simulated flue gas and wet scrubber solutions

The experiment was conducted in the laboratory scale installation constructed in the Institute of Nuclear Chemistry and Technology (INCT). The flow diagram of the experimental set-up is presented in Fig. 1.

The installation and the experimental procedure were described in a previous publication (Chmielewski et al., 2018). The simulated flue gas was generated from an oil-fired burner (type LG 40/60, 24 kW, Scheer-Heizsysteme & Produktionstechnik GmbH, German) by burning Polish light fuel oils with addition of NO and SO₂ from the respective gas cylinders. Five N m³/h flue gas was conducted into a reaction vessel for irradiation and inlet flue gas was kept at 90 °C. A pulse ILU-6M electron beam accelerator (2 MeV, 20 kW) was used for irradiation, 800 keV was applied for irradiation of the flue gas. A CTA (Cellulose Triacetate) film dosimeter was applied to measure the applied dose. For the wet scrubber method (without irradiation) or EB hybrid method, a small amount of the flue gas after the reaction vessel was passed through two wet scrubbers connected in series with a flow rate of 100–220 d m^3/h ; each wet scrubber contained 600 mL of liquid. The rest of the flue gas after the reaction vessel was passed through the retention chamber and the bag filter before it was released into the atmosphere through the chimney.

Liquids for the wet scrubbers were freshly prepared before use. The simulated sea water solution (3.5% w/w NaCl) was obtained by dissolving 35.0 g of NaCl into 1 L of the deionised water. The solutions with the sea water and each additive were obtained by preparing the solution described above and adding 200 mL of the additive solution. The additive of NaOH was obtained by dissolving the appropriate amount of NaOH into 200 mL of deionised water. The 1 L of 0.81 M solution of phosphate buffer (pH = 6.5) was achieved by dissolving 42.6 g of Na₂HPO4 and 69.4 g of KH₂PO4 in the appropriate amount of water to complement a 1L volumetric flask. The additive of buffered NaClO₂ was prepared by mixing an appropriate amount of already prepared 1M NaClO₂ solution with the complemented amount of phosphate buffer (Na₂HPO₄-KH₂PO₄) to achieve 200 mL. The additive of non-buffered NaClO₂ was prepared exactly the same as above but the buffered solution was replaced with pure, deionised water. Each prepared solution was precisely mixed and divided into two 600 mL volumes for each scrubber The scrubbers were connected in series.

The scheme of wet scrubber system is presented in Fig. 2.

When valves V1, V3, & V4 were opened and V2, V5 were closed, SO_2 and NOx removal efficiency after only the electron beam process was measured; when valves V1, V2 & V5 were opened and V3 & V4 were closed, the removal efficiency of SO_2 and NOx after EB combined with the wet scrubber system was measured.



Fig. 1. Flow diagram of the experimental set-up.



Fig. 2. Scheme of the wet scrubber system.

2.3. Analytical methods

An NO/NO_x analyser (Model 10 A/R, chemiluminescent, Thermo Environmental Instruments Co. USA), an SO₂ analyser (Model 40, pulsed fluorescent, Thermo Environmental Instruments Co. USA) and a portable flue gas analyser Lancom Series II (Land Combustion, U.K.) were used to measure the concentration of the components of the flue gas.

Continuous measurement of SO₂ and NOx concentration in the simulated gas was carried out by two independent extractive monitoring systems at the process inlet point (before irradiation, point 6 in Fig. 1) and at the outlet point (after treatment, point 12 in Fig. 1). These two independent extractive monitoring systems were heated up to 180 °C to prevent SO₂ condensation. Heated ceramic filters were used to trap particulate matter (PM) before the flue gas entered into the analysers.

Before the flue gas (before and after treatment) was analysed, calibration gases of NO (1715 ppm in N₂) and SO₂ (1810 ppm in N₂) were used to calibrate the NO/NO_x analyser and SO₂ analyser, respectively. An air compressor (model: pole position OL 190 REMO, ABAC company, Italy) was used to generate "zero" air, it was also used to dilute flue gas (usually 20 times) before the flue gas entered into SO₂ and NOx analysers.

For the NO/NO_x analysis in this work within the range of 0–1715 ppm NO, the lower detectable concentration was 0.5 ppm, accuracy was \pm 1.1%, and the relevant standard error was 0.3%.

For the SO₂ analysis in this work within the range of 0–1810 ppm SO₂, the lower detectable concentration was 1.0 ppm, accuracy was \pm 2.2%, and the relevant standard error was 1.0%.

The removal efficiency of the pollutant (R%) is defined by Eq. (1),

$$R\% = \frac{(C_o - C_t)}{C_o} \times 100\%$$
(1)

where C_o denotes the initial concentration of a certain kind of pollutant in the flue gas before treatment, C_t denotes the concentration of a certain kind of pollutant in the flue gas after treatment.

The pH value of the scrubber solution was measured using a pH meter (pH 3210 Set 2, WTW company, Germany).

3. Results and discussion

The research was divided into two main parts concerning liquids used for the wet scrubber, the use of absorbents only, and the addition of oxidants.



Fig. 3. Changes in the efficiency of removing pollutants during the hybrid process with simulated sea water. Initial concentration of the pollutants: NO-1271 ppmv, NO₂-52 ppmv, NO_x-1323 ppmv and SO₂-694 ppmv; gas flow rate in the wet scrubber-138 d m.

3.1. The hybrid process with non-oxidant scrubbing solution

The absorption of pollutants in the EB-hybrid water system was examined with the addition of two compounds: sodium chloride (NaCl) and sodium hydroxide (NaOH). Typical seawater contains 3.5% (w/w) of NaCl, so a 3.5% NaCl solution was chosen to represent sea water which is easily available for the shipping industry, and an NaOH solution has been reported to be an effective absorbent (Zhang et al., 2014).

3.1.1. The hybrid process with simulated sea water

To provide a more detailed investigation of the hybrid process, an experiment lasting 2.5 h was carried out. The aim of this research was to determine the absorption capacity of the simulated sea water and to observe how the process proceeds over time. Fig. 3 shows that the whole process for SO₂ removal is relatively stable between 4–90 min, the G/L (gas/liquid) ratio was 172.5:1 at 90 min. The results indicate that SO₂ concentration decreases very rapidly during the first several minutes. Its removal efficiency remains at 100% (Fig. 3) for up to 95 min in the wet scrubber process, the G/L ratio was 182:1. With the wet scrubber process going on, the G/L ratio was also increasing and this decreased the gas-liquid contact time and SO₂ concentration started to increase further. At the end of experiment (150 min), the G/L ratio was 287.5:1.

 SO_2 and NOx removal in hybrid system includes two stages. The first stage is SO_2 and NOx removal under an electron beam; the second stage is their absorption (including their oxidation products after EB irradiation) in the liquid phase. In the case when a liquid oxidant is used, it also includes oxidation in liquid phase.

SO₂ removal in the gas phase during EB irradiation has already been described (Dors et al., 2000; Matzing and Paur, 1992); the main reactions are listed below:

$$SO_2 + \cdot OH + M \rightarrow HSO_3 + M$$

M is a third body in the reaction system (2)

$$\cdot OH + HSO_3 \rightarrow SO_3 + H_2O \tag{3}$$

$$\mathrm{HO}_{2}\cdot + \mathrm{SO}_{2} \to \mathrm{SO}_{3} + \mathrm{OH} \tag{4}$$

$$\cdot OH + H_2O + SO_2 \rightarrow HSO_3 + H_2O \tag{5}$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2$$
 (6)

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{7}$$

$$SO_2 + \cdot OH \rightarrow HOSO_2$$
 (8)

$$HOSO_2 + \cdot OH \rightarrow H_2SO_4$$
 (9)

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{10}$$

The removal of SO_2 and SO_3 (product of SO_2 after EB irradiation) from the gas is through an absorption process. The chemical reactions of these two compounds in the liquid phase are given below:

$$SO_2(g) \leftrightarrow SO_2(aq)$$
 (11)

$$SO_2(aq) + H_2O = H_2SO_3$$
 (12)

$$SO_3(g) \leftrightarrow SO_3(aq)$$
 (13)

$$5O_3 + H_2O = H_2SO_4$$
 (14)

Fig. 3 notes graphically that the NO_x removal efficiency initially increases, which is followed by a very slow decrease from 37.47% (at 5 min) to 32.0% as the process continues. The connection between SO₂ and NO₂ removal is clear after 95 min. The SO₂ removal efficiency begins to decrease from 99.3% (at 96 min) to 82.3% (at 150 min); and the NO₂ removal efficiency starts its increase, from -5.0% (at 96 min) to 18.3% (at 150 min). The pH value of the scrubber solution is decreasing during the time of the scrubbing process. At the end of the experimental process (150 min), the pH of the solution decreased from 5.408 (before the experiments) to 1.930 (the first scrubber) and 2.393 (the second scrubber), respectively. pH values lower than 3 are unfavourable for the removal of SO₂ and beneficial for the removal of NO₂ (Zhang et al., 2014). This may explain why the removal efficiency of SO₂ is decreasing while the removal efficiency of NO₂ is increasing after 95 min. The initial NO removal efficiency remains almost the same through the whole process at the level of 32.7% \pm 3.2% (Fig. 3) and the trends note a correlation of the NO_x removal and the NO removal efficiency.

Previous studies show that the removal of NO_x in the gas phase during the electron beam process mainly goes through an oxidation pathway. The most important reactions (15)–(21) involving NO oxidation to NO₂, N₂O₃, N₂O₄, & NO₃ are given below (Matzing and Paur, 1992; Zwolińska et al., 2015).

$$\cdot OH + NO + M \rightarrow HNO_2 + M \tag{15}$$

$$\cdot OH + HNO_2 \rightarrow NO_2 + H_2O \tag{16}$$

$$O(^{3}P) + NO_{2} + M \rightarrow NO_{3} + M$$
(17)

$$NO + O(^{3}P) + M \rightarrow NO_{2} + M$$
(18)

$$NO_2 + \cdot OH + M \to HNO_3 + M \tag{19}$$

$$2NO_{2(g)} \leftrightarrow N_2O_{4(g)} \tag{20}$$

$$NO_{(g)} + NO_{2(g)} \leftrightarrow N_2O_{3(g)}$$
 (21)

The main reactions of nitrogen oxides in liquid phase are given below (Loutet et al., 2011).

$2NO_{2(g)} + H_2O_{(l)} \rightarrow$	\rightarrow HNO _{2(l)} + HNO _{3(l)}	(22)
		(

$$N_2O_{3(g)} + H_2O_{(l)} \rightarrow 2HNO_{2(l)}$$
 (23)

$$N_2O_{4(g)} + H_2O_{(l)} \to HNO_{3(l)} + HNO_{2(l)}$$
 (24)

$$3HNO_{2(l)} \rightarrow HNO_{3(l)} + H_2O_{(l)} + 2NO_{(g)}$$
 (25)

To form comparisons between the hybrid, wet scrubbing, and electron beam technology, the current study also conducted a wet scrubbing experiment without the electron beam. For all of these three process, the NO initial concentration was about 1500 ppm, SO₂ initial concentration was 700 ppm, NaCl concentration was 3.5%, gas flow rate in the wet scrubber was 140 d m³/h, and the time of each experiment was 60 min. The G/L ratio in wet scrubber process was 116.7:1 at 60 min. The results show that the SO₂ removal efficiency reached 100% immediately in the wet scrubber filled with simulated sea water, which is similar to the "EB-sea water" hybrid technology's results. However, the NO_x



Fig. 4. A comparison of the process efficiencies for the methods of sole electron beam, sole wet scrubbing, and a hybrid technology with simulated sea water. Initial NO concentration-1500 ppm, initial SO₂ concentration-700 ppm, NaCl concentration-3.5%, gas flow rate in the wet scrubber-140 d m^3/h , time of each experiment-60 min.

removal efficiency was significantly lower, with average of 23.6% \pm 1.3% after 60 min. In comparison over the same time frame, the NOx removal efficiency for the hybrid technology was 35.3% \pm 3.3% (Fig. 4). These results show that the oxidation of NO to NO₂ through the electron beam is necessary to achieve the higher removal efficiencies.

3.1.2. The hybrid process with NaOH solution

The second phase of the research concerned the increase of pollutant absorption in the wet scrubbing solutions. It was conducted with a NaOH solution. NaOH is an alkaline compound; it causes an increase in pH of the wet scrubber solution at the beginning of the process, potentially increasing the absorption of the acidic oxides and causing a higher pH solution at the end of the process. The latter is desirable as the limit of pH 6.5 applies for liquid wastes before they are discharged from the ships into the ocean.

3.1.2.1. Different concentrations of NaOH solutions. Experiments aimed to determine the optimal NaOH concentration were conducted with a starting value of 0.03% (0.34 g/1200 mL) solution. This concentration was selected based on the stoichiometric 1:1 ratio between NaOH and NO₂. This assumed that all NO_x is present in the form of NO_2 , the initial NO_x concentration is 1500 ppmv, the gas flow rate is 140 d m^3/h , and NO_x has the volume of an ideal gas at standard conditions. Three different concentrations of NaOH solutions were studied: 0.03%, 0.06% (0.68 g/1200 mL) and 0.23% (2.79 g/1200 mL). The G/L ratio was 116.7:1 at 60 min. Based on the experimental results, an increase in the NaOH concentration (from 0.03% to 0.23%) does not lead to a significant change in the removal efficiency of NOx, which varies from 33.1% to 34.73% (Fig. 5). Although the NaOH solution concentrations may not appear high, the calculations indicate that an excess is already present. Adding a greater amount of NaOH would result in further increasing the alkalinity of an already alkaline solution (pH = 12.293) and create difficulties when scaling up the process on an industrial scale. Finally, the 2.79 g/1200 mL solution was chosen as the optimal solution for treating gases with 1500 ppmv and with a flow rate of 140 d m³/h per hour. This decision was made based on the final pH values of the scrubbing solutions, which were 7.077 (I scrubber) and 7.262 (II scrubber). At this pH level, the scrubbing solutions after treatment potentially could be released into the ocean safely. When 0.03% NaOH and 0.06% NaOH scrubbing solutions were used, the pH value of the 0.03% NaOH scrubbing solution decreased from 11.335 to 2.408 (I scrubber) and 5.882 (II scrubber) after hybrid process, the pH value of the 0.06% NaOH scrubbing solution decreased from 11.411 to 5.405 (I scrubber) and 6.061 (II scrubber) after hybrid process, both of



Fig. 5. A comparison of the NO_x removal efficiency during hybrid process for different concentrations of NaOH solutions. NO-around 1330 ppmv, NO₂-around 70 ppmv, NO_x-around 1400 ppmv and SO₂-around 675 ppmv; gas flow rate in the wet scrubber-140 d m³/h, irradiation dose-10.9 kGy.

these scrubbing solutions after hybrid process cannot fulfil the limitation of pH 6.5 for liquid wastes before they are discharged from the ships into the ocean.

Besides those reactions described above, the reactions of SO_2 and NOx removal in NaOH solution includes following reactions (Zhang et al., 2014):

$50_2 + NaOH = NaHSO_2$	3 ((26))

 $SO_2 + 2NaOH = Na_2SO_3 + H_2O$ ⁽²⁷⁾

 $SO_3 + 2NaOH = Na_2SO_4 + H_2O$ ⁽²⁸⁾

 $NO + NO_2 + 2NaOH \rightarrow 2NaNO_2 + H_2O$ ⁽²⁹⁾

$$2NO_2 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$$
(30)

3.1.2.2. The pollutants' concentrations change vs. time during the EB process (first 10 min) and the hybrid process with NaOH solution. The process of pollutant removal was also examined in a 70 min experiment to determine if the removal efficiency changes overtime (Fig. 6). The initial 10 min was dedicated to the electron beam only process, where the average removal efficiency of NO_x reached 11.31% (\pm 1.0%). Similar to the hybrid technology that uses an NaCl solution, the removal efficiency forms a plateau and then slightly decreases overtime. The G/L ratio was 116.7:1 at the end of the experiment. Another similarity is that NO_x removal efficiency is determined in parallel by the NO removal efficiency with NO₂ having a very limited influence. Alternatively, the results show that the NO₂ concentration remains high, meaning that it has not been fully absorbed in the water. This could be due to the rapid oxidation of NO by the electron beam, where



Fig. 6. The removal efficiency of the pollutants during the EB process (first 10 min) and the hybrid process with NaOH solution. Initial pollutants concentrations: NO-1438 ppmv, NO₂-45 ppmv, NO₂-45 ppmv, NO₂-45 ppmv, and SO₂-723 ppmv; gas flow rate in the wet scrubber-140 d m³/h, irradiation dose-10.9 kGy.



Fig. 7. The influence of the gas flow rate on the NOx removal efficiency during a hybrid process with the use of 0.23% NaOH. Initial pollutants concentrations: NO-around 1400 ppmv, NO_2 -around 55 ppmv, NO_x -around 1450 ppmv and SO_2 -700 ppmv; irradiation dose 10.9 kGy.

up to 20% is converted into NO₂, NO₃ and N₂O₅, which cannot be fully absorbed in the liquid due to the concurrent absorption of the SO₂. As expected, SO₂ was removed and maintained at 100% efficiency over time from the initial stages of the process. The average NO_x removal efficiency was 34.7% (\pm 2.3%) and the starting pH of the scrubbing solution was as high as 12.293. During the process, a decrease in the pH level of the scrubbing solutions to 7.077 and 7.262 was noted. The average removal efficiency could be higher if the gas flow rate was lowered or the scrubbing solutions would be more voluminous. Surprisingly, there is little increase in the average removal efficiency of NOx in comparison to the hybrid technology with the NaCl solution. It was predicted that the absorption of nitrous acid and nitric acid in the liquid would be higher as the following two reactions have been reported to occur in an NaOH solution (reactions (31)-(32)) (Thomas and Vanderschurem, 1999).

$$HNO_2 + NaOH \rightarrow NaNO_2 + H_2O \tag{31}$$

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O \tag{32}$$

The lack of enhancement in the removal efficiency of NOx may be explained as follows: for NOx removal in hybrid process with NaCl solution or NaOH solution, NO is first oxidised into its' higher oxidation state compounds, e.g. NO_2 , N_2O_3 , N_2O_4 , & NO_3 (see reactions (15)–(21)); they are absorbed into water solution to form HNO₂ or HNO₃ in the second stage (see reactions (22)–(25)), which is the rate determining stage and determines the speed at which the overall reaction of NOx removal proceeds; although reactions of NaOH with HNO₂ (31) and HNO₃ (32) occur fast in the third stage, however, due to the absorption stage of

NOx being the rate determining stage and there is no enough contacting time between gas/liquid phase, therefore, the removal efficiency of NOx in EB hybrid system with 3.5% NaCl solution is similar to that in EB hybrid system with NaOH solution.

3.1.2.3. Gas flow rate. Gas flow rate appears to have a significant impact on the process's removal efficiency. This was noted with a direct comparison between the three experimental procedures where only the gas flow rate was changed (Fig. 7). The concentrations of NO_x and SO_2 were 1450 ppmv and 700 ppmv, respectively. The irradiation dose was 10.9 kGy, and each experiment lasted 5 min. The difference is 3.2%, which is based on the average NO_x removal efficiency values for 180 d m^3/h (G/L = 12.5: 1) being 31.5% (± 2.8%) and for 140 d m³/h (G/L = 9.7: 1) being 34.7% (\pm 2.3%). The effect is even more significant for a gas flow of 220 d m^3/h (G/L = 15.3: 1), where the average NO_x removal efficiency is only 27.4% (± 1.8%). The effect can be explained by the higher gas flow rate, which results in a higher amount of pollutants flowing into the wet scrubbing solutions. This also reduces the residence time between the gas and the liquid, which causes the removal efficiency of NOx to decrease. A similar phenomenon has been reported in other works (Kim et al., 2011). The flue gas flow rate will have to be taken into consideration and examined carefully during the scaling up process.

3.1.2.4. Irradiation dose of electron beam. The final parameter examined during the hybrid process with 0.23% NaOH was the influence of the dose. Two experiments with an irradiation dose of 10.9 kGy (solid line at Fig. 8) and 21.8 kGy (dashed line at Fig. 8) were conducted for an inlet NOx concentration of 1455 ppm



Fig. 8. A comparison of the NO and NO_x removal efficiency during the hybrid process with 0.23% NaOH solution under two irradiation doses: 10.9 and 21.8 kGy. Initial pollutants concentrations: NO-around 1400 ppmv, NO₂-around 55 ppmv, NO_x-around 1450 ppmv and SO₂-700 ppmv; gas flow rate in wet scrubber-140 d m^3/h .



Fig. 9. A comparison of the process efficiencies for the methods of sole electron beam, sole wet scrubbing, and a hybrid technology with 0.23% NaOH solution. Initial NO concentration-1500 ppm, initial SO₂ concentration-700 ppm, NaOH solution concentration-0.23%, gas flow rate in the wet scrubber-140 d m^3/h , time of each experiment-60 min.



Fig. 10. A comparison of process efficiencies for methods using solely an electron beam and a hybrid technology and coupling an electron beam with a wet scrubber in two cases: with simulated sea water and with simulated sea water and NaClO₂ addition with phosphate buffer. Initial NO concentration-1500 ppm, initial SO₂ concentration-700 ppm, NaClO₂ concentration-25 mM, gas flow rate in the wet scrubber-100 d m^3/h , time of each experiment-15 min.

with the presence of 700 ppm SO₂. Flue gas flow rate in the wet scrubber was 140 d m³/h, the ratio of G/L was 116.7:1 at the end of experiment. The graph shows that the irradiation dose has a significant impact on the NO and NO_x removal efficiencies. Both values significantly increased as the dose increased for both the electron beam and hybrid technologies. The average NO removal efficiency increased from 11.7% \pm 0.2% (EB only) and 38.8% \pm 2.2% (hybrid process) to 19.2% \pm 0.5% (EB only) and 51.4% \pm 1.9% (hybrid process), when the dose was doubled. Similarly, the average NO_x removal efficiency was enhanced from 10.83% \pm 0.2% and

 $34.7\% \pm 2.3\%$ to $16.4\% \pm 0.4\%$ and $48.56\% \pm 2.0\%$ for the electron beam only and the hybrid technology, respectively.

3.1.2.5. Comparison of EB, wet scrubber, and EB-wet scrubber process. To compare the efficiency of the three processes, a wet scrubbing experiment was carried out without the use of the electron beam. A comparison of all three methods was carried out under the following experimental conditions: NO initial concentration-1500 ppm, SO₂ initial concentration-700 ppm, NaOH solution concentration-0.23%, gas flow rate in the wet

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Fig. 11. The influence of NaClO₂ concentration on the NO_x removal efficiency. Initial NO concentration approximately 1500 ppm, initial SO₂ concentration-700 ppm, phosphate buffer pH-6.5, gas flow rate in the wet scrubber-100 d m^3/h , time of each experiment-15 min.



Fig. 12. Changes in removal efficiency of pollutants during the hybrid process with simulated sea water and buffered NaClO₂ addition. Initial pollutants concentrations: NO-1326 ppmv, NO₂-68 ppmv, NO_x-1394 ppmv and SO₂-713 ppmv; NaClO₂ concentration-5 mM, gas flow rate in wet scrubber-162 d m³/h, irradiation dose-10.9 kGy.



Fig. 13. Gas flow rate influence on the NO and NO_x removal efficiency during the hybrid process with simulated sea water and buffered NaClO₂ addition (5 mM). Initial pollutants concentrations: NO-1400 ppmv, NO₂-60 ppmv, NO_x-1460 ppmv and SO₂-700 ppmv; irradiation dose 10.9 kGy.

scrubber-140 d m³/h, time of each experiment-60 min. The ratio of G/L was 166.7:1. The results are depicted in Fig. 9. Graphically, the hybrid method depicts the highest levels of removal efficiency (34.7% \pm 2.3%), the difference between the wet scrubbing only and the hybrid technology is as high as 10.7%.

In conclusion, hybrid technology with an NaOH solution results in relatively high removal efficiencies. Process optimisation can be controlled by changing the irradiation dose, gas flow rate, or the composition of the scrubbing solution. Optimising all of these variables together enables a NO_x removal efficiency of 30%-50%, when the initial concentration of NO is above 1000 ppm.

3.2. Use of oxidants

The NO_x removal efficiency during the hybrid process significantly increased when compared with the process of electron

beam. The effect is significant, especially when the NO initial concentration is high. However, the NO_x removal efficiency imposed by the new regulations requires a 79% removal of NOx, which cannot be achieved by the hybrid process with absorbents alone. An alternative solution to further enhance NO_x removal is the addition of oxidants, which may increase NO to NO₂ oxidation. Two oxidants: NaClO₂ (sodium chlorite) and H₂O₂ (hydrogen peroxide) were chosen based on the previous literature. NaClO₂ is reported to be a highly effective oxidant (Guo et al., 2012a; Hutson et al., 2008; Krzyzyńska and Huston, 2012b,a; Yang et al., 2018), whereas H₂O₂ has the ability to prevent the creation of new pollutants in the exhaust liquids as it decomposes to water and oxygen. A series of studies were conducted with oxidants added to the simulated sea water.

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Fig. 14. Changes in the concentration of pollutants during the hybrid process with simulated sea water and $NaClO_2$ addition. Initial pollutants concentrations: NO-1356 ppmv, NO_2 -67 ppmv, NO_x -1423 ppmv and SO_2 -654 ppmv; $NaClO_2$ concentration-5 mM, gas flow rate in the wet scrubber-162 d m³/h, irradiation dose-10.9 kGy.



Fig. 15. A comparison of the process efficiencies for the methods of sole electron beam, sole wet scrubbing and a hybrid technology with simulated sea water and NaClO₂ addition with phosphate buffer. Initial NO concentration-1500 ppm, initial SO₂ concentration-700 ppm, NaClO₂ concentration-25 mM, gas flow rate in the wet scrubber-162 d m^3/h , time of each experiment-60 min.



Fig. 16. The removal efficiency of pollutants during the hybrid process with the simulated sea water and H₂O₂ addition. Initial pollutants concentrations: NO-1179 ppmv, NO₂-84 ppmv, NO₂-84 ppmv, NO₂-1263 ppmv and SO₂-501 ppmv; H₂O₂ concentration-0.5%, gas flow rate in the wet scrubber-140 d m³/h, irradiation dose-10.9 kGy.

3.2.1. Oxidation by sodium chlorite (NaClO₂)

The effectiveness of NaClO₂ as an oxidant has been well reported, and it has potential for use in the NO_x removal processes. However, the previous research was mostly based on low initial concentrations of NO. This research uses sodium chlorite as a second step of the process (after EB) for NO to NO₂ oxidation.

3.2.1.1. Irradiation dose of electron beam. The first parameter to be optimised was the irradiation dose (Fig. 10). The 25 mM NaClO₂ and the phosphate buffer (pH 6.5) were selected based on the work by Guo et al. (2012a), Hutson et al. (2008), Krzyzyńska and Huston (2012b) and Krzyzyńska and Huston (2012a). The

initial NO concentration was 1500 ppm, initial SO₂ concentration was 700 ppm, flue gas flow rate in the wet scrubber was 100 d m^3/h , the time of each experiment was 15 min. The G/L ratio was 20.8:1 when the wet scrubber was used. The results of the NO_x removal efficiency were also compared with the removal efficiency results for the electron beam only and the hybrid processes with the use of simulated sea water.

The data is very promising and shows a huge improvement in the NO_x removal efficiency compared to the other methods. Furthermore, the influence of the irradiation dose was minor above 10.9 kGy. Encouragingly, 90% NO_x removal efficiency was achieved even when the dose was as low as 6.5 kGy or 10.9 kGy.

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Fig. 17. The comparison of the process efficiencies for the methods of sole electron beam, sole wet scrubbing and a hybrid technology with simulated sea water and H_2O_2 addition. Initial NO concentration-1500 ppm, initial SO₂ concentration-700 ppm, H_2O_2 concentration-0.5%, gas flow rate in the wet scrubber-162 d m³/h, time of each experiment-60 min.



Fig. 18. The comparison of the NO_x removal efficiencies between all examined methods in the optimal conditions for 100 d m³ of flue gas with NO initial concentration-1500 ppm, SO_2 initial concentration-700 ppm.

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This value (90%) is much higher than that (less than 50%) when a similar concentration of active chlorine was used for 1000 ppm NO removal (Yang et al., 2018).

3.2.1.2. Concentration of $NaClO_2$ oxidant. The next stage of the research was the optimisation of the NaClO₂ concentration within a range of 5–25 mM (Fig. 11). The other experimental conditions were kept the same except for the NaClO₂ concentration. The addition of the oxidants and their ranges were selected on the basis of previous literature (Guo et al., 2012a).

The data represented graphically (Fig. 11) indicates that decreasing the NaClO₂ concentration even by 5 times (from 25 mM to 5 mM) has an insignificant influence on the removal efficiency of NOx, which decreases from 92.3% (\pm 0.5%) to 89.6% (\pm 0.5%). The 5 mM NaClO₂ concentration results in a very high efficiency, so it was chosen as the optimal concentration for further experimentation in the current research.

Removal efficiency of SO₂ and NOx versus time during the hybrid process with simulated sea water and buffered 5 mM NaClO₂ addition was studied (Fig. 12). Initial pollutant concentrations were as follows: NO-1326 ppmv, NO₂-68 ppmv, and SO₂-713 ppmv. Gas flow rate in the wet scrubber was 162 d m³/h, and irradiation dose was 10.9 kGy. The experiments lasted 140 min in total. The ratio of G/L was decreasing with the processing time. It was 315:1 at the end of the experiment. Fig. 12 shows that the SO₂ removal efficiency for all hybrid technology experiments was maintained at 100% for the whole duration of

the process. The trend of NO and NO_x removal efficiencies are completely opposite to the trends recorded when only absorbents are utilised. The graphical representation highlights the accelerated rise in both removal efficiencies to a high level of 90%. This increase is also noted with the NO₂ concentration, resulting in negative removal efficiency. The combination of NO oxidation with the electron beam and liquid oxidants causes a very high level of NO₂ production to the point that the volume of absorbing liquid (1.2 L) is not able to deal with the high concentrations of NO₂ over a limited time frame, as dictated by the high gas flow (162 d m³/h). However, the average NO_x removal efficiency after 1 h of experimentation (G/L = 135:1) was 81.1% (\pm 9.5%), which is a very high removal efficiency in comparison to the other methods we have explored. The pH of the solution decreased from 6.155 (before the scrubber process) to 5.147 (I scrubber) and 6.025 (II scrubber), respectively, at the end of the experiment. Similar to the experiments using NaOH, the NO_x removal efficiency trends with the NO removal efficiency due to the high percentage of NO (95%) present in inlet NOx.

The removal of SO_2 and NOx using a wet scrubber with the presence of NaClO₂ can be described by the following chemical reactions (Schwartz and White, 1983; Park et al., 2015; Adewuyi et al., 1999)

$$SO_2(g) + H_2O(I) \rightarrow HSO_3^{-}(aq) + H^+(aq)$$
(33)

$$ClO_2^{-}(aq) + HSO_3^{-}(aq) \rightarrow SO_4^{2-}(aq) + HClO(aq)$$
(34)

$$HClO(aq) + HSO_3^{-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + Cl^-(aq)$$
(35)

(36)

$$4NO + 3NaClO_2 + 2H_2O \rightarrow 4HNO_3 + 3NaCl$$

$$4NO + ClO_2^{-} + 4OH^{-} \leftrightarrow 4NO_2^{-} + Cl^{-} + 2H_2O$$
(37)

$$2NO + ClO_2^- + 2OH^- \leftrightarrow 2NO_2^- + ClO^- + H_2O$$

$$(38)$$

$$12NO_2 + 3CIO_2^- + 3H^+ + 6H_2O \leftrightarrow 12HNO_3 + 3HCI$$
(39)

$$5\text{ClO}_2^- + 4\text{H}^+ \leftrightarrow 4\text{ClO}_2 + \text{Cl}^- + 2\text{H}_2\text{O}$$

$$\tag{40}$$

$$5NO + 2ClO_2 + H_2O \leftrightarrow 5NO_2 + 2HCl$$
(41)

 $5\mathrm{NO}_2 + \mathrm{ClO}_2 + 3\mathrm{H}_2\mathrm{O} \leftrightarrow 5\mathrm{HNO}_3 + \mathrm{HCl} \tag{42}$

$$2NO_2^- + ClO_2^- \leftrightarrow 2NO_3^- + Cl^-$$
(43)

 $4\text{ClO}_2^- + 2\text{H}_3\text{O}^+ \to 2\text{ClO}_2 + \text{ClO}_3^- + 3\text{H}_2\text{O} + \text{Cl}^-$ (44)

It is seen that with the presence of NaClO₂, SO₂ removal was increased through reactions (34) and (35); for NOx removal, ClO_2/ClO_2^- are main active species and their formation strongly depends on the pH of the solution and the concentration of NaClO₂. With the consumption of NaClO₂, NOx removal efficiency decreases accordingly.

3.2.1.3. Gas flow rate. The importance of the influence of the gas flow rate has been highlighted in the literature (Kim et al., 2011; Yang et al., 2018; Park et al., 2015), and it was investigated in the current study. Two experiments with two different gas flow rates $(162 \text{ d m}^3/\text{h} \text{ and } 220 \text{ d m}^3/\text{h})$ were conducted for an NOx inlet concentration of 1460 ppm (NO-1400 ppm, NO₂-60 ppmv) with 700 ppmv SO₂ present. The irradiation dose was 10.9 kGy. Each of the experiments lasted 60 min. The G/L ratio at 60 min was 135:1 (162 d m^3/h) and 183:1 (220 d m^3/h). Results are presented in Fig. 13. It is evident that the higher gas flow rate results in a lower removal efficiency of NO and NO_x; this observation agrees well with other work (Park et al., 2015; Paiva and Kachan, 2004). The average NO_x removal efficiency after one hour of the experiment, when the flow was 220 d m³/h (G/L = 183:1), was $61.8\% \pm 15.3\%$, which represents a 17.3% decrease compared with a gas flow rate of 162 d m^3/h (G/L = 135:1).

3.2.1.4. Buffer influence. Following this, the influence of a buffer on the process was analysed. An experiment was carried out within 60 min for 1423 ppm NOx removal with the presence of 5 mM NaClO₂ but without buffer addition. The gas flow rate in the wet scrubber was 162 d m³/h and the irradiation dose was 10.9 kGy. The G/L ratio was 135:1 at the end of the experiment. The graph (Fig. 14) shows that the process without a buffer is very turbulent in comparison to the process with a buffer present (Fig. 12). As we described above (Section 3.2.1.2), ClO_2/ClO_2^- are the main active species for NOx removal. The ratio of ClO₂/ClO₂⁻ formation strongly depends on the pH of the solution and the concentration of NaClO₂. In the buffered solution, the pH of the scrubber solution is relatively stable. Without the buffered NaClO₂ solution, the ratio of ClO_2/ClO_2^- formation varies with the pH value of the solution which dynamically changes during the formation of the products. The influence of the pH value of the absorption solution on NO removal efficiency has been reported (Kim et al., 2011; Park et al., 2015).

By comparison, processes without a buffer lead to a decrease in removal efficiency of NO_x to an average of 56.9% (\pm 15.8%). Interestingly, the results show a correlation between the NO_x removal efficiency and the NO₂. Following the exhaustion of the oxidant (which is shown as a very sharp increase of NO concentration in Fig. 14), the NO_x removal efficiency is once again dependent on the NO removal efficiency. Similar results were reported by Adewuyi et al. (1999), where NO₂ significantly increased during the process of NO_x absorption in the NaClO₂ solution without the addition of a buffer. The authors suggested that the absorption of NO₂ is significantly higher in solutions with higher pH and the addition of the buffer avoids a rapid increase in the NO₂ concentration. Moreover, the pH of the scrubbing solution decreased from 9.021 to 2.136 (I scrubber) and 2.808 (II scrubber). This acidic post-process liquid would be difficult to handle and it would be impossible to directly release this liquid into the ocean without treatment. These latter points clearly identify the necessity of a buffer.

3.2.1.5. Comparison of EB, wet-scrubber, and hybrid process. A comparison of the process efficiencies between method of sole electron beam, sole wet scrubbing and a hybrid technology with simulated sea water and NaClO₂ addition with phosphate buffer was carried out. The initial NO concentration was 1500 ppm, initial SO₂ concentration was 700 ppm, NaClO₂ concentration was 25 mM, gas flow rate in the wet scrubber was 162 d m³/h, and the time of each experiment was 60 min. The G/L ratio was 135:1 at the end of the experiment. NOx removal efficiency using three different processes was 12.3% (EB), 61.6% (scrubber solution with buffered NaClO₂) and 81.8% (EB hybrid wet scrubber with a buffered NaClO₂ solution) (Fig. 15). EB hybrid technology with the use of a buffered NaClO₂ solution greatly enhances the NOx removal efficiency; it is very promising.

3.2.2. Oxidation by hydrogen peroxide (H_2O_2)

To examine the influence of a weaker but cheaper oxidant compared to NaClO₂, experiments assessing the impact of H_2O_2 were conducted. As already discussed, hydrogen peroxide does not add any new species into the system. The literature suggest that the beneficial effect of the H_2O_2 oxidation is not only achieved by the oxidation of nitrogen oxides (reaction (45)) (Paiva and Kachan, 2004), but also by oxidation of nitrous acid according to reaction (46), which prevents its decomposition (reaction (47)) (Thomas and Vanderschurem, 1999).

$2NO \pm 3H_2O_2 \rightarrow 2HNO_2 \pm 2H_2O_2$	(15	۱
$2INO + 3\Pi_2O_2 \rightarrow 2\Pi NO_3 + 2\Pi_2O$	43	J

$$H_2O_2 + HNO_2 \rightarrow HNO_3 + H_2O \tag{46}$$

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \tag{47}$$

By analogy to the previous experiments, the hybrid process with 0.5% H₂O₂ addition in wet scrubber solution was studied for an NOx inlet concentration of 1263 ppm (NO-1179 ppmv, NO₂-84 ppmv) with 501 ppm SO₂ present. A 10.9 kGy absorbed dose was applied, gas flow rate in the wet scrubber was 140 d m³/h, the experiment lasted 2 h, and the G/L ratio was 233:1 at the end of the experiment. The NO_x removal trends remain stable throughout the whole process (Fig. 16). Similar to the other wet scrubbing techniques, the SO₂ removal efficiency was maintained at 100%. The NO₂ shows a slow increase over time which is an indication that the scrubbing solution might become saturated with nitrogen oxides. The average removal efficiency after one hour of the experiment is 50.1% (\pm 2.7%). A disadvantage of the process with 0.5% H₂O₂ addition is the low starting scrubbing solution pH of 4.316, which decreases to a pH of 1.820 (I scrubber) and 2.795 (II scrubber) after the two hour process.

A comparison of three processes (EB, wet scrubber with 0.5%, H_2O_2 , hybrid process with 0.5%, H_2O_2) for NOx removal was carried out for 1500 ppm NOx with 700 ppm SO₂ present. The gas flow rate in the wet scrubber was 162 d m³/h, each experiment lasted 60 min, and the G/L ratio was 135:1 at the end of experiment when a wet-scrubber was used. As previously noted in other cases, the hybrid technology's dominance is clear as shown by the significant difference of 10.2% between wet scrubbing only (40.9%) and the hybrid technology (51.1%) (Fig. 17).

3.3. Comparison of all methods

The current research has explored a variety of techniques to determine the most optimal method for cleaning NO_x and SO_2 with high efficiency, whilst accounting for variations in parameter values. Fig. 18 presents a comparison of the different technologies under the most optimal conditions. To objectify the results, the average removal efficiencies were calculated for 100 d m³ of the flue gas with an initial NO_x concentration of 1500 ppmv.

Fig. 18 shows the superiority of the hybrid technology with the simulated sea water and with the addition of buffered NaClO₂. The second best is the wet scrubbing method without electron beam However, the faster rate of oxidant exhaustion means that the expenditure of NaClO₂ reagent will increase, in comparison to the hybrid process. Another promising method is the hybrid method with the addition of H_2O_2 to the simulated sea water. Although this oxidant does not fulfil the expectations and regulations concerning NO_x removal efficiency, it might be improved with the addition of NaOH; one mole of H_2O_2 can oxidise 2 moles of NO in alkaline solutions instead of the 3 moles of H_2O_2 needed to oxidise NO in acid solution (Paiva and Kachan, 2004). Furthermore, good results have been recorded when the hybrid methods using NaCl and NaOH solutions are used, with slight superiority of the NaCl solution. However, the difference between the methods is less than the uncertainty of measurements, so it is not possible to determine which is truly dominant. Fig. 18 also demonstrates that the addition of the electron beam to the wet scrubbing methods increases their efficiency by around 10%.

Two of the scrubbing solutions that used the hybrid technology were selected as the most promising and practically feasible for industrial use: the simulated sea water and the simulated sea water with the addition of buffered $NaClO_2$. The former is the easiest to scale up and implement in the marine industry. Whereas, the latter has the most encouraging results as the NO_x removal efficiency is above 80% when the optimal conditions are applied.

Wet scrubber solutions with a liquid oxidant to remove NO have been studied in recent years in many laboratories. Most of these studies were limited to low inlet concentrations of NO (<1000 ppm). There have been several studies at high inlet concentrations of NO (1000 ppm-1200 ppm). However, NOx removal efficiency was less than 63% when the initial concentration of NO was 1200 ppm (Guo et al., 2015). The NO_x removal efficiency using hybrid technology with 5 mM NaClO₂ addition (89.6%) is higher than results obtained using SNCR (selective noncatalytic reduction, where only low concentrations of NO can be treated) (Liang et al., 2014), ozone injection (70% NO_x removal efficiency) (Sun et al., 2011), a bioprocess (15%-20% removal efficiency for pilot plants) (Jin et al., 2005), and other plasmas methods (e.g., EB is more energy efficient than pulsed corona discharge). Technologies that recorded similar NO_x removal efficiencies are SCR (selective catalytic reduction) and absorption methods. The SCR method enables a very high NOx removal efficiency for high inlet concentrations of NO, but this technology is very expensive (Guo et al., 2012b). Furthermore, only NO_x can be treated with this technology. Additionally, the absorption methods cannot treat NO_x at high inlet concentrations because of the poor solubility of NO, meaning that the addition of oxidants is necessary. By contrast, the hybrid method enables a significant reduction in reagent consumption compared with the liquid oxidant absorption of NO. The addition of the electron beam increases the average removal of the wet scrubbing technology by 10%–20% depending on the dosage used.

4. Conclusions

This work has investigated the removal of a high inlet concentration of NO_x and SO₂ from diesel engine off-gases by using a hybrid technology which couples an electron beam with wet scrubbing methods. Five different wet scrubbing solutions were examined: 3.5% NaCl solution (simulated sea water), NaOH solution, buffered NaCl solution with NaClO₂, non-buffered NaCl solution with NaClO₂, and NaCl solution with H_2O_2 . The SO₂ removal efficiency for all hybrid experiments was 100% due to its excellent solubility in water. The NO_x removal with hybrid technology is dependent on the irradiation dose and gas flow rate. Higher process efficiency was achieved by increasing the dose or by decreasing the gas flow rate. However, dose impact is lower than its influence with the electron beam only method. The hybrid technology with scrubbing solutions without the oxidants resulted in a similar NO_x removal efficiency regardless of the utilisation of NaCl or NaOH. All scrubbing solutions achieved their best results with the buffered NaCl solution with the addition of NaClO₂ and over 89.6% NOx was removed. This can be increased further with a semi-batch or flow reactor in which a scrubbing solution could be renewed continuously.

The reported process is based on the application of a hybrid of physical and chemical means of oxidising pollutants. Therefore, knowledge regarding kinetics and equilibrium constants of chemical reactions plays an important role. These are fundamentals for this and other pollutant removal technologies. Further research will consider the application of a two phase system (liquid droplets–flue gas) in the electron where the equilibrium of the reversible reactions will be shifted to the product side by continuously scrubbing the NO₂ formed. In this case, a decrease in the quantity of oxidant necessary to run the absorption process is expected and the height of scrubber will be lower, which will reduce investment and operational costs.

A self-shield accelerator might be used in this EB-wet scrubber system. Although an accelerator needs some additional space and weight, the wet-scrubber solution after treatment can be discharged into the sea when the "open loop" mode is used or recirculated back into the scrubber when the "closed loop" mode is used. The principle is the same as the wet scrubber for SO₂ removal. The results obtained in this work show that EBhybrid wet scrubber technology is a very promising technology for removal of high concentration of SO₂ and NOx from marine engine off-gases.

Declaration of competing interest

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

CRediT authorship contribution statement

Ewa Zwolińska: Investigation, Data acquisition, Formal analysis, Writing - original draft. **Yongxia Sun:** Conceptualization, Methodology, Supervision, Writing - review & editing. **Andrzej G. Chmielewski:** Funding acquisition. **Andrzej Pawelec:** Investigation. **Sylwester Bułka:** Investigation.

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