Comparison of various chemical compounds for the removal of SO₂ and NO_x with wet scrubbing for marine diesel engines

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Abstract

Seawater, NaOH, NaClO, NaClO₂, H₂O₂, and KMnO₄ were used as scrubbing liquids to react with SO_x and NO_x separately in a customized wet scrubber. The absorption of SO₂ in the aqueous phase was influenced by three factors: pH, ionic concentration, and oxidation potential. For NO_x removal, the effectiveness of various chemical compounds can be ranked from least to most effective as follows: seawater, NaOH, H₂O₂ < NaClO < KMnO₄ < NaClO₂. This effectiveness was influenced by the chemical compound's ability to oxidize NO to NO₂, absorb the NO₂ that was formed, and retaining the nitrogen in the aqueous phase. High oxidation potential promoted the oxidation of NO to NO₂ but hindered the absorption of NO₂. NaClO₂ was superior compared to NaClO in all three categories of oxidizing, absorption and retention. NaClO could not retain a significant amount of NO₂ which it absorbed in the aqueous phase. The pH around 8 provided a good balance between oxidation versus absorption/retention and reactant utilization for the chlorine-based oxidants. KMnO₄ had the lowest reactant consumption rate; only half a mole was consumed for every mole of NO removed, compared to around 2–3 mol of chlorite or 3–5 mol of hypochlorite.

Keywords NO · SO₂ · Wet scrubbing · Marine emissions · NaClO · NaClO₂ · KMnO₄

Introduction

The combustion of fossil fuels in power plants, boilers, and diesel engines are known to generate large amounts of air pollutants in the form of sulfur oxides (SO_x) and nitrogen oxides (NO_x), among other polluting substances. Control of these pollutants are particularly more challenging in the marine sector where ocean-plying ships with large diesel engines depend on low-cost heavy fuel oil for propulsion (Deng et al. 2021; Marine 2015). The application of known land-based end-of-pipe technologies onboard ocean-plying vessels faces many constraints, including space, weight, and logistical limitations.

The simplest solution for complying with the SO_x cap set in “Annex VI—Prevention of Air Pollution from Ships” of the International Convention for the Prevention of Pollution from Ships (MARPOL) would be to switch to low-sulfur fuel (Lloyd's Register Marine 2015). However, this is estimated to cost the industry at least an additional several billion dollars per year due to the high cost of low sulfur fuel. Although once considered a fringe solution, the installation of wet scrubbers onboard vessels for SO_x removal is fast becoming mainstream (ABS Advisory On Exhaust Gas Scrubber Systems 2018).

Unfortunately, current commercial wet scrubbers are only effective for SO_x removal but not for NO_x. The control of the latter has always been more challenging as most of it is generated in the engine itself due to the high temperatures of the combustion process (thermal NO_x). Hence, it can be formed even if the fuel does not contain any nitrogen (Nevers 2000). Also, NO_x from engine combustion comprises around 90% of nitric oxide (NO), which is highly insoluble in the aqueous phase and cannot simply be scrubbed and solubilized from the gas to aqueous phase like SO_x. Therefore, engine medication techniques are mainly used to reduce the combustion temperature in the engine so that less NO_x will be formed. However, such methods also reduce the engine efficiency, thereby leading to higher fuel consumption (Deng et al. 2021).

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The acceptance of wet scrubbers onboard ships has already gained much traction—Wärtsilä itself has already built more than 700 units before 2019 (Ni et al. 2020). It is therefore justifiable to explore its potential to remove NO_x on top of SO_x . Already in the R&D scene, there are many upcoming methods for treating SO_x and NO_x simultaneously. Out of these, a significant amount of work focused on gas–liquid reactions where strong oxidizing agents were used to oxidize NO to a more soluble NO_2 form. The more common chemical compounds studied included chlorine-based oxidizing agents such as chlorite and hypochlorite (Brogren et al. 1998; Chien and Chu 2000; Chu et al. 2003; Deshwal and Lee 2009; Gong et al. 2020; Jin et al. 2006; Mondal and Chelluboyana 2013; Park et al. 2015; Wei et al. 2009; Yang et al. 2018; Zhao et al. 2010; Zhao et al. 2011; Zhao et al. 2015; Zhao et al. 2016), permanganates (Brogren et al. 1997; Chu et al. 2001; Fang et al. 2013), ozone (Han et al. 2020; Kang et al. 2020; Lin et al. 2016; Shao et al. 2019; Sun et al. 2017; Sun et al. 2015), and hydrogen peroxide (Liu et al. 2014; Liu and Zhang 2011; Wen et al. 2019; Wu et al. 2018; Xie et al. 2019).

Among these works, Yang et al. demonstrated that SO_2 and NO can be effectively removed in a wet scrubbing system using hypochlorite-based oxidants that were directly generated by electrolysis of NaCl solution of similar concentration to seawater (Yang et al. 2018). Han et al. recently showed that continual dosing of chlorite oxidant in a pH buffered aqueous system could improve the reactant utilization rate (Han et al. 2019).

Although desulfurization using wet scrubbers in onboard vessels can already be considered established, there has been several interesting developments that has taken place recently. One of them involved the use of a cascading design in a wet scrubber that allowed for higher L/G ratio without the risk of flooding, thereby achieving higher sulfur removal, lower pressure drop, and with lower alkalinity requirements when compared with a straight-through traditional open-loop scrubber (Kuang et al. 2020; Zhao et al. 2021). In addition, a square-shaped spray column which allowed for a smaller footprint, smaller pressure drop, and higher efficiency was also proposed (Van Duc et al. 2021). Although only focused on desulfurization, these studies are interesting as some their innovations may be transferable to simultaneous SO_2 and NO_x removal.

Although quite a few of these studies demonstrated full removal of SO_2 and relatively high NO removal, many challenges remain; these include high reactant utilization rate, difficulty in removing NO_2 that were generated from the oxidation of NO, potential release of toxic compounds in the exhaust (such as chlorine dioxide), and high nitrate content in the scrubbing wastewater. It is difficult to do an accurate comparison of these common wet scrubbing chemical compounds being studied because existing studies usually focuses on one of the substances that show potential but very little work

is done on comparing multiple substances in a single experimental platform.

In the present study, a broad range of widely reported substances, namely, seawater, sodium hydroxide (NaOH), sodium hypochlorite (NaClO), sodium chlorite (NaClO_2), hydrogen peroxide (H_2O_2), and potassium permanganate (KMnO_4), were systematically compared for their capacity to remove SO_x and NO_x and new insights were gained from comparing these reactions together instead of separately. These chemicals were selected for this study because they either showed potential in NO_x removal, are widely available in the industry at a reasonable cost, or are already currently used on ship-based wet scrubbers.

Besides a wide range of reactants being compared, other novelties in the work here include the comparison of the consumption rate and chemical cost among various reactants, and observations of the influence of oxidation reduction potential (ORP) values in the various reaction mechanisms, which are seldom reported in existing studies. Other important reaction characteristics such as removal efficiency, change in pH, change of ionic concentration in the aqueous phase before and after reaction, and reactant stability were compared and discussed here. Existing challenges faced in current research, especially the difficulty in absorbing the NO_2 that has been formed after the oxidation of NO, will be discussed thoroughly based on the comparison between the various chemical reactions from the wide range of compounds studied.

Materials and methods

Experimental system

The sodium hydroxide (NaOH) solution used was from Merck Millipore (Titripur series), 1 M concentration. Both sodium chlorite (NaClO_2) (80% assay) and potassium permanganate (98% assay) were from Acros Organics. Hydrogen peroxide (H_2O_2) was purchased from VWR Chemicals, with a concentration of 6% w/v in solution form. The sodium hypochlorite (NaClO) reagent grade solution used was purchased from Sigma-Aldrich, with available chlorine of 4.00–4.99%. Its actual concentration was determined by iodometric titration according to ASTM 15.04 D 2022. Seawater used for experiments were collected from the Labrador Park jetty, Singapore.

The sulfur dioxide (SO_2) and nitric oxide (NO) gases used in this experiment were blended at a concentration of 10,000 ppm(v) in nitrogen. These, together with the oxygen (99.99%) and nitrogen (99.995%) gases, were supplied by Singapore Oxygen Air Liquide Private Limited. The nitrogen dioxide (NO_2) gas at a concentration of 5000 ppm(v) was supplied by Leedon National Oxygen Ltd. Various gases from the gas cylinders were mixed in the appropriate ratio and are hence referred to as “simulated exhaust gas” (Fig. 1).

Fig. 1 Schematic diagram representing the experimental setup: (1–5) gas cylinders, N_2 , O_2 , SO_2 , NO , and NO_2 ; (6–10) mass flow controllers; (11) gas mixer; (12) ball valve; (13–14) three-way valves; (15) adjustable glass

scrubber; (16) flue gas analyzers; (17) datalogging computer; (18) scrubbing liquid tank; (19–20) peristaltic pumps; (21) pH meter; (22) conductivity meter; (23) ORP meter

Two different flue gas analyzers were used in this setup. The first was the Testo 350XL that used electrochemical cell sensors to measure O_2 , SO_2 , and NO . For NO_2 gas, it was observed that the values measured by the electrochemical cell were affected by the presence of chlorine-based gases. Therefore, a second analyzer was used, which was the MGA Luxx containing an NDIR-based NO_2 sensor. The NDIR-based NO_2 sensor was more accurate as it was not subjected to cross-referencing interferences experienced by electrochemical sensors. Moisture from the gas was removed by in-built moisture traps in both analyzers. Data from both the exhaust gas analyzers were data-logged with their respective software and the NO_x data was calculated by using $NO_x = NO + NO_2$.

The wet scrubber used is a custom-made glass wet scrubber with adjustable height and an internal diameter of around 100 mm. A filter disc was built at the top of the scrubber to function as a mist eliminator to retain the liquid in the scrubber. The pH, conductivity, and ORP probes used to measure and data-log the scrubbing liquid in the tank were from Thermo Fisher Scientific.

The Basic 792 Ion Chromatograph system by Metrohm was used for quantitative analysis of NO_2^- , NO_3^- , Cl_2^- , and ClO_2^- while the Libra S22 UV-VIS Spectrophotometer by Biochrome was used for ClO_2^- and MnO_4^- . MnO_4^- aqueous samples were analyzed with the UV-Vis only and not the ion chromatograph in order to protect the instrument and avoid any staining or damaging of the column.

Experimental procedure

A three-way valve was used to manually switch the simulated exhaust gas directly to the flue gas analyzers before reaction and from the exit of the wet scrubber during reaction. The experimental conditions used in this study are found in Table 1.

Two separate reactions were planned for the scrubbing liquid mixtures being studied—the first for SO_2 removal and the second for NO removal. In each experiment, 2.5 L of the scrubbing solution were recirculated through the wet scrubber to react with the simulated exhaust gas for 60 min. A third study involving the removal of NO_2 was added for selected scrubbing mixtures to obtain better clarity on the subject. A lower L/G ratio was also studied for reaction with NO , where the L/G ratio was reduced to 15 L/m^3 . Here, the gas flowrate was increased to 25 L/min, the spray nozzle used was the QPHA-1 (0.38 L/min) and the experiment time reduced to 30 min. The rest of the parameters remained as stated in Table 1.

The properties of the different types of chemicals used as scrubbing liquids for the gas–liquid reaction can be found in Table 2. Among the oxidizing agents used in the scrubbing liquid, it is known that the oxidation potential of both $NaClO$ and $NaClO_2$ are highly pH sensitive. Therefore, both the scrubbing liquids of these compounds were also adjusted to pH 6 and 8 before the start of the reaction using 0.1 M of hydrochloric acid. When prepared without any pH

Table 1 Experimental conditions used

Simulated exhaust gas properties	
Composition (for SO ₂ study)	SO ₂ : 500 ppm(v)/O ₂ : 14%/N ₂ balance
Composition (for NO study)	NO: 500 ppm(v)/O ₂ : 14%/N ₂
Gas flowrate	10 L/min
Temperature	Ambient (~25 °C)
Scrubbing liquid properties	
Volume used	2.5 L
Liquid flowrate	1.0 L/min
Wet scrubber parameters	
Spray nozzle type	Promax Quick Fulljet QPHA-3 (capacity 1.1 L/min)
Active height of wet scrubber	430 mm
Diameter	99 mm
Packing material	Nil
Space velocity	0.022 m/s
Residence time	19.9 s
Others	
Experiment duration	60 min

adjustments, the starting pH of NaClO and NaClO₂ were 10.9 and 10.6, so these liquid mixtures were designated as NaClO/pH10.9 and NaClO₂/pH10.6 respectively.

For reactions that were able to remove NO_x, aqueous samples were collected at the beginning, midpoint, and the end of the experiments (0, 30, and 60 min, respectively) for ionic analysis within 24 h of the experimental run.

Calculations

The removal efficiency (η_i) of SO₂, NO, NO₂, and NO_x by the various gas–liquid reactions were calculated according to Eq. (1):

$$\eta_i = \frac{C_{i,inlet} - C_{i,outlet}}{C_{i,inlet}} \times 100\% \quad (1)$$

where $C_{i, inlet}$ and $C_{i, outlet}$ refer to the concentrations of the gas pollutants at the inlets and outlets of the wet scrubber, as recorded by the flue gas analyzers. For Figs. 9 and 10, the values of *NO₂ formed* and *NO₂ absorbed* were estimated from the flue gas analyzer data—it was assumed that NO removed was equivalent to *NO₂ formed* and *NO₂ absorbed* was equivalent to NO_x removed.

The amount of NO_x removed (in mmol) by various scrubbing mixtures shown in Table 5 was calculated by taking the area under the curve in the graphs of NO_x removal versus time. The NO_x removed (in ppm(v)) was converted to moles using the ideal gas law ($PV = nRT$), at 1 atm and 25 °C.

Table 2 Composition and properties of the scrubbing liquid used to react with the exhaust gas in the wet scrubber for the SO₂ and NO studies, respectively

No	Scrubbing liquid composition	Concentration (M)	Total Alkalinity (mg/L CaCO ₃)	Starting measurement			SO ₂ study	NO study	NO ₂ study
				pH	ORP (mV)	Cond. (mS/cm)			
1	Seawater (SW)	NA	116	8.2	206	47.2	x	x	—
2	NaOH	0.05	2468	12.4	−5	11.2	x	x	x
		0.10	—	12.9	−15	21.1	—	—	x
		0.40	—	13.4	−32	75.7	—	—	x
		0.05	6	4.4	352	—	x	x	—
3	H ₂ O ₂	0.05	6	4.4	352	—	x	x	—
4	NaClO/pH10.9	0.05	436	10.9	625	10.4	x	x	—
5	NaClO/pH 8	0.05	—	7.9	880	10.5	—	x	—
6	NaClO/pH 6	0.05	—	6.0	1013	11.4	—	x	—
7	NaClO ₂ /pH10.6	0.05	350	10.6	432	6.0	x	x	x
8	NaClO ₂ /pH 8	0.05	—	8.3	483	5.8	—	x	x
9	NaClO ₂ /pH7	0.05	—	7.3	—	5.8	—	—	x
10	NaClO ₂ /pH 6	0.05	—	6.2	523	5.8	—	x	—
11	KMnO ₄	0.05	36	9.2	561	6.0	x	x	—
12	Deionized (DI) water	NA	4	6.2	353	0.006	x	—	x

Results and discussion

Removal of sulfur oxides (SO_x)

The reaction mechanisms for the absorption of SO₂ in the aqueous phase have been well documented and can be summarized as follows (Al-Enezi et al. 2001; Andreassen and Mayer 2007; Tokumura et al. 2006):

These series of equations can roughly be grouped into two categories, the first being the absorption of SO₂ into bisulfite or sulfite in the aqueous phase (Eqs. 3 and 4), followed by oxidation to sulfate, its most stable aqueous form (Eqs. 5 and 6). From the reactions, it can be seen that the absorption of 1 mol of SO₂ in the aqueous phase results in the release of 1 to 2 mol of protons, thereby causing the pH to reduce over time.

The removal of SO₂ by the gas–liquid reaction in the wet scrubber by various scrubbing mixtures can be seen in Fig. 2 while the corresponding pH and ORP values are shown in Figs. 3 and 4, respectively. It can be seen from Fig. 2 that all compounds used achieved 100% SO₂ removal for the entire duration of the experiments except for DI water and seawater.

The reduction in SO₂ removed seen in DI water and seawater can be explained by the gradual reduction of pH over time as the reaction progressed. Further comparison between DI water and seawater showed that the performance of the seawater in removing SO₂ dipped below that of DI water at about the halfway point of the experiment although its pH still remained higher than the pH of DI water. This showed that other mechanisms could be at play for SO₂ removal besides pH.

There are two possibilities for this. First, DI water was more oxidative compared to seawater (Fig. 4), which could have aided the oxidation of sulfite and bisulfite ions into sulfate ions (Eqs. 5 and 6) and helped in the overall removal of SO₂. Second, seawater is much more saturated with ions compared to DI water, and this can extensively lessen the solubility of gases in the aqueous phase (Black & Veatch Corporation, 2009). This vast difference in ionic saturation can be seen in their conductivity values—the conductivity of seawater at 47.2 mS/cm was more than 7400 times higher than the conductivity of DI water (Table 2). Furthermore, as typical seawater already contains around 2500–3000 mg/L of sulfate ions (Al-Enezi et al. 2001; Andreassen and Mayer 2007; Vidal

and Ollero 2001; Black & Veatch Corporation, 2009), the saturation level of sulfur ions in the aqueous phase will be reached more quickly due to the common ion effect compared with DI water, which was almost free of ions.

Although the scrubbing mixtures of KMnO₄ and H₂O₂ were on par or even more acidic than DI water and seawater in terms of pH, they both performed better in terms of SO₂ removal. Again, this could be due to the higher oxidation potential of KMnO₄ and H₂O₂, giving them an advantage in the oxidation of sulfite and bisulfite ions into sulfates. It can be summarized that the full removal of SO₂ proceeded quite readily and was achieved by nearly all types of scrubbing mixtures that were tested here. This is because SO₂ gas is very soluble in the aqueous phase (Table 3) (Sander 2015). It was observed that the absorption of SO₂ in the aqueous phase under the experimental conditions here were likely influenced by three factors, namely, pH/alkalinity, concentration of soluble sulfur ions already present in the solution, and oxidation potential (estimated by ORP). An effective scrubbing liquid for the removal of SO₂ gas should have a high pH or alkalinity, low in sulfate ions, and oxidative in nature. If equipment for the measurement and monitoring of sulfite or sulfate ions in the aqueous phase is not available, a conductivity meter could be used to determine the overall ionic content as a substitute of sorts to provide some indication.

Removal of nitrogen oxides (NO_x)

Under natural conditions, the removal of NO when it is released into the atmosphere is a two-part mechanism, according to the following reactions (Nevers 2000; Yang et al. 2018):

In the first step, NO is naturally oxidized into a more soluble form, NO₂ (Eq. 7), before it is subsequently solubilized (Eqs. 8 and 9). Although the oxidation of NO to NO₂ takes place spontaneously under atmospheric conditions, the rate of reaction is relatively slow and there is insufficient time for this to occur in the combustion process before the exhaust is discharged. Therefore, a substantial amount of research has focused on speeding up this oxidation process so that the absorption step in the aqueous phase can take place.

In addition to the reactions shown in Eqs. 8 and 9 for the absorption of NO₂, Brogren and Deshwal suggested additional pathways involving the formation of more soluble intermediate in N₂O₃ and N₂O₄ (Brogren

Fig. 2 Sulfur dioxide (SO₂) removal from the simulated exhaust gas with various scrubbing liquids

et al. 1998; Deshwal et al. 2008):

It was further demonstrated by Sun, Lin, and Shao that the formation of intermediate N_2O_5 was also very effective for the solubilization of nitrogen in the aqueous phase (Lin et al. 2016; Shao et al. 2019; Sun et al. 2015). It is generally accepted that the solubility of gaseous nitrogen in the aqueous phase increases with increasing nitrogen valency (Lin et al. 2016).

Oxidation of nitric oxide (NO)

The results of the removal of nitric oxide (NO) from the simulated exhaust gas from the gas–liquid reaction in the wet scrubber can be seen in Fig. 5. Since the removed NO could have been oxidized to NO_2 without the latter getting absorbed, it should be noted that NO removal does not necessarily translate to NO_x removal.

The outcome can be broadly categorized into three groups—ineffective, somewhat effective, and effective. In the ineffective group, it can be seen that seawater, H_2O_2 , NaOH, and NaClO/pH10.9 converted less than 5% of nitric oxide in the flue gas throughout the entire duration of the experiment. That is why existing commercial marine wet scrubbers which use seawater and NaOH are able to remove SO_2 effectively but not NO.

In the somewhat effective group, KMnO_4 , NaClO/pH6, and NaClO/pH8 removed around 50% of the nitric oxide in the simulated emission gas. In the effective group, NaClO_2 /

Fig. 3 pH of the scrubbing liquid in the tank during SO_2 removal

Fig. 4 ORP of the scrubbing liquid in the tank during SO₂ removal

pH6 and NaClO₂/pH8 achieved 100% nitric oxide removal for the duration of the experiment. The NaClO₂/pH10.6 aqueous mixture could only remove around 50% of nitric at the beginning, but its removal efficiency continued to increase as the reaction progressed until it eventually reached 100% removal.

As seen in the pH graph in Fig. 6, high pH (NaOH) has no effect on the removal of NO gas as this gas–liquid reaction does not seem to follow an acid–alkaline absorption reaction owing to its very low solubility (Table 3). Observation of the ORP change (Fig. 7) showed that NaClO mixtures had higher values than NaClO₂ and KMnO₄ but performed worse in the conversion of NO. This showed that solely using ORP values to predict the effectiveness of a liquid mixture to oxidize NO to NO₂ would be inaccurate. However, ORP values did give a good indication of NO conversion when predicting the effectiveness of the same chemical compounds under different mixing conditions (pH, concentration, etc).

Oxidation of nitric oxide by hydrogen peroxide (H₂O₂)

H₂O₂ was not effective in oxidizing NO to NO₂ in this study. On top of using a high concentration, studies involving H₂O₂ usually required some sort of activation either with UV radiation or

ozone (Wen et al. 2019; Xie et al. 2019). Without these, it can be seen that H₂O₂ was inferior compared to other types of chemical oxidants of the same concentration studied here.

Oxidation of nitric oxide by sodium hypochlorite (NaClO)

NaClO was ineffective in removing NO gas in the wet scrubber in high pH but was more effective when the starting pH was lowered to 8 and 6, respectively. It is widely known that hypochlorites will partition itself between its ionic and hypochlorous acid form according to pH. It exists as hypochlorous acid (HOCl) below pH 6, as hypochlorite (ClO[−]) above pH 10, and a mixture of two between pH 6 and 9 (Metcalf et al. 1991).

When NaClO was at pH 10.9, the chlorine existed in its hypochlorite form (ClO[−]) where it is a less powerful oxidizing agent. As the pH was decreased to 8, partitioning into the hypochlorous acid form began and the oxidation potential increased as a result (Fig. 7). This trend was also consistent with theoretical values shown in Table 4—the half reaction of the oxidation of hypochlorous acid was +1.49 V, much higher compared to its hypochlorite at +0.90 V (Tchobanoglous et al. 2013). However, further lowering of pH from 8 to 6 did not show additional improvement in removal effectiveness, which was consistent with the findings of Yang et al. (2016).

The reaction mechanism of nitric oxide conversion by sodium chlorite is likely via the following pathways (Mondal and Chelluboyana 2013; Yang et al. 2016; Yang et al. 2018):

Table 3 Henry's law constant for several gases of interest, at 1 atm and 25 °C (Sander 2015)

Gas	Henry's law constant, H _{CO2} (mol.m ^{−3} /Pa)	Solubility compared to NO
Carbon dioxide, CO ₂	3.3 × 10 ^{−4}	17.4
Sulfur dioxide, SO ₂	1.3 × 10 ^{−2}	684
Nitric oxide, NO	1.9 × 10 ^{−5}	1
Nitrogen dioxide, NO ₂	9.9 × 10 ^{−5}	5.2

Fig. 5 Nitric oxide (NO) removal from the simulated exhaust gas with various scrubbing liquids

Oxidation of nitric oxide by sodium chlorite (NaClO₂)

Chlorite's lower oxidation potential seen in the ORP readings (Fig. 7) was consistent with theoretical values seen in Table 4 (+0.76 vs. +0.90 to 1.49 V of the hypochlorite/hypochlorous combination). Yet, it outperformed hypochlorite in oxidizing NO to NO₂. This was likely due to the tendency of NaClO₂ to decompose into its more oxidative form, ClO₂, at more acidic pHs, according to the reactions shown in Eqs. 16 and 17 (Choudhury 2011; Gong et al. 2020; Zhao et al. 2015). This decomposition will occur slowly when the pH is from 5 to 7 and accelerate when the pH is below 5.

Further evidence of this decomposition can be seen from Fig. 6 where the pH for the scrubbing mixtures of NaClO₂/pH6 and NaClO₂/pH8 defied the common trend by increasing instead of decreasing as the reaction progressed even though the reaction with NO_x generates proton ions. This was likely

because the conversion of chlorite to chlorine dioxide absorbs proton ions, according to Eq. 16.

When the pH was in the alkaline range, it was likely that any decomposition from ClO₂⁻ into ClO₂ gas was likely to have occurred mainly at the gas-liquid boundary layer when the chlorite ion came into contact with the NO gas instead of the bulk phase (Gong et al. 2020). This mechanism enabled the chlorite solution to effectively oxidize NO to NO₂ without needing very high ORP values in the bulk solution.

It could be seen from Figs. 6 and 7 that in general, the ORP values increase with decreasing pH, due to the increasing decomposition of ClO₂⁻ to ClO₂. However, it can be seen that in the pH range of 6 to 8, the ORP values were quite similar, hovering at around 600 mV. This suggested that further pH adjustment below 8 seemed unnecessary and does not increase the oxidation potential of the solution. Higher than necessary formation of the more volatile ClO₂ would result in more reactant being lost to the exhaust, which is both wasteful and a potential safety hazard. The reaction mechanism for the conversion of NO to NO₂ by sodium chlorite is likely to have taken place in the following manner (Deshwal et al. 2008):

Fig. 6 pH of the scrubbing liquid in the tank during NO removal

Fig. 7 ORP of the scrubbing liquid in the tank during NO removal

Oxidation of nitric oxide by potassium permanganate (KMnO_4)

It can be seen from Fig. 5 that the KMnO_4 scrubbing mixture managed to convert about 45% of NO for the duration of the experimental run. The pH of the mixture reduced from 10.4 to 8.4 during the run, but this did not affect the oxidative power of the liquid solution much, as seen by the ORP values which hovered around 500–600 mV for the entire reaction. The drop in pH was probably due to the acidic nature of NO_2 when absorbed and the low buffering capacity of the KMnO_4 mixture. Unlike the chlorine-based oxidation agents, KMnO_4 did not seem as sensitive to pH change as both its ORP values and NO conversion remained relatively stable throughout the reaction. The reaction mechanism for the conversion of NO to NO_2 by KMnO_4 is likely to have been the following (Chu et al. 2001; Fang et al. 2013):

As can be seen, all reactions resulted in the formation of MnO_2 , which is a solid precipitate. In all the experiments involving KMnO_4 conducted here, a dark brown precipitate was observed from early on in the experiments. This dark brown MnO_2 precipitate was present everywhere in the setup and was etched in the tubings, the walls of the wet scrubber, and within the crevices of the spray nozzle. Cleaning was very challenging as the apparatus had to be dismantled and soaked in concentrated acid solution.

Overall NO_x removal

The removal of overall NO_x , which is made up of NO and NO_2 , is shown in Fig. 8. Seawater, NaOH, and H_2O_2 were omitted from the graphs here as these chemical compounds were ineffective in NO_x removal. For the overall removal of NO_x , the effectiveness of various oxidants or chemical compounds used under the present experimental conditions can be ranked as follows, from least to most effective:

It can be seen that the NO_x removal by NaClO was very low at pH 10.9, peaked when pH was lowered to 8, but then reduced slightly when pH was further lowered to 6. These NO_x removal figures were much lower compared to the oxidation rates of NO to NO_2 that it achieved, suggesting that a significant amount of NO which were oxidized to NO_2 could

Table 4 The oxidation potential of various chemical compounds of relevance in this study (Tchobanoglous et al. 2013)

Chemical compounds	Half reaction	Oxidation potential, V
Hydrogen peroxide	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$	+1.78
Permanganate	$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \leftrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.67
Chlorine dioxide	$\text{ClO}_2 + \text{e}^- \leftrightarrow \text{ClO}_2^-$	+1.50
Hypochlorous acid	$\text{HOCl} + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O}$	+1.49
Hypochlorite	$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{Cl}^- + 2\text{OH}^-$	+0.90
Chlorite	$\text{ClO}_2^- + \text{H}_2\text{O} + 4\text{e}^- \leftrightarrow \text{Cl}^- + 4\text{OH}^-$	+0.76

Fig. 8 NO_x ($\text{NO} + \text{NO}_2$) removal from the simulated exhaust gas using various scrubbing liquids

not be absorbed in the wet scrubber. As for the chlorites, both $\text{NaClO}_2/\text{pH}8$ and $\text{NaClO}_2/\text{pH}6$ exhibited very similar performances, managing around 65–70% of NO_x removal for the duration of their experiments. The fluctuation seen for $\text{NaClO}_2/\text{pH}10.6$ aqueous mixture was likely to do with the lowering of the pH of the liquid mixture as the reaction progressed, leading to an increase in its oxidative properties.

In order to get a better view of the NO_2 absorption ability, Figs. 9 and 10 are plotted to show the ratio of NO_2 absorbed over the amount of NO that was oxidized to NO_2 for the duration of the experiment.

Absorption and oxidation potential

From Fig. 10, a clear inverse relationship between NO_2 absorption and oxidation potential of the various chemical compounds can be seen. NO_2 absorption by NaClO showed the strongest inverse linear correlation with oxidation potential,

with the linear regression R^2 value at 0.99. However, it should not be expected that all the different points belonging to various compounds fit nicely into one linear trendline as different chemical compounds have different reaction pathways even though they all broadly followed the linear trendline.

The observations here is consistent with the work by Chang, Xi, and Zhang who used compounds which have very low oxidation potential such as Na_2SO_3 , NaS , $\text{Na}_2\text{S}_2\text{O}_8$, and NaHSO_3 to improve the absorption of NO_2 (Chang et al. 2004; Xi et al. 2020; Zhang et al. 2020). Chang and Xi further showed that in a low oxidation potential environment, NO_2 can even be directly reduced to N_2 gas, thereby avoiding the formation of nitrogen anions altogether (Chang et al. 2004; Xi et al. 2020).

It should also be pointed out here that these observations were in contradiction with the other school of thought which focused on increasing the oxidation potential in order to form high valency intermediates such as N_2O_3 , N_2O_4 , and N_2O_5 as these have higher solubility in aqueous solution (Brogren et al. 1998;

Fig. 9 Ratio of NO_2 absorbed over the total NO_2 that was formed (converted to %) versus reaction time

Fig. 10 Ratio of NO₂ absorbed over the total NO₂ that was formed (converted to %) versus the oxidation potential

Lin et al. 2016; Shao et al. 2019; Sun et al. 2015). The formation of these intermediates, especially N₂O₅, is heavily dependent on the residence time (Lin et al. 2016; Shao et al. 2019) and it was possible that the setup in this study could not provide sufficient residence time for these reactions to take place.

Absorption by NaClO

As shown in Figs. 9 and 10, NaClO's capacity to absorb NO₂ increased with decreasing oxidation potential values in the pH range of 6–11. If NaClO is to be the oxidant of choice, a balance would have to be struck between achieving high NO oxidation rate, favored by high oxidation potential, versus absorbing the NO₂ that will be formed, favored by a low oxidation potential. Compared with other oxidants, NaClO performed the poorest in terms of absorbing the NO₂ that it formed from the oxidation of NO. However, NaClO could be ideal if the process requires only oxidation but not absorption.

Absorption by NaClO₂

In general, NaClO₂ of various pH were more effective in absorbing the NO₂ compared to NaClO due to its lower oxidation potential, managing to remove between 65 and 80% of NO₂ that was formed during the reaction. In addition, it could also be that NaClO₂ has additional reaction pathways for the absorption of NO₂ in the aqueous phase on top of the reactions shown in Eqs. 8 and 9 (Brogren et al. 1997):

Absorption by KMnO₄

It can be seen from Fig. 9 that KMnO₄ was the most effective in the absorption of NO₂—almost all the NO that was oxidized to NO₂ was subsequently absorbed into the aqueous phase. One possibility was that KMnO₄ oxidized NO directly to nitrate ions in the aqueous phase as shown in Eqs. 20 and 21 instead of the other gaseous intermediates such as NO₂. Nevertheless, KMnO₄ still trailed chlorite ions in terms of overall NO_x removal and the staining of pipes, pumps, and nozzles among the wet scrubbing equipment poses a significant problem for it to be considered the oxidant of choice. Brogren reported that the formation of the MnO₂ precipitate can be avoided under very high alkaline conditions—when the solution contains more than 3 mol/L of hydroxide ions, MnO₄⁻ will be formed instead of MnO₂ (Brogren et al. 1997). However, it was also reported in the same study that NO_x removal will be suppressed under such high pH conditions. Furthermore, it will also be quite costly to maintain such a high pH in a large-scale operation.

Absorption of nitrogen dioxide (NO₂)

In this additional study, selected chemical compounds were reacted with NO₂ in the wet scrubber in order to gain a clearer understanding of its absorption and removal in the gas–liquid reaction. From Fig. 11, it can be seen that deionized (DI) water could only remove around 10% of the NO₂ in the exhaust gas. Addition of NaOH up to 0.40 M to increase the alkalinity of the scrubbing liquid did not improve the absorption of NO₂ at all. The results seen here are in contrast with some of the previous reported literature which suggested significant levels of NO₂ absorption in the aqueous phase is possible after the

Fig. 11 NO₂ gas removal from the simulated exhaust gas using DI water versus scrubbing mixtures of increasing alkalinity (NaOH 0.05–0.40 M)

oxidation of NO to NO₂ has been achieved (Brogren et al. 1998; Kurpoka 2011). In one such example, Brogren reported that around 50–60% of NO₂ was successfully removed by NaOH between pH 9 and 12 (Brogren et al. 1998). However, it was consistent in the study by Chang et al. which showed NaOH as high as pH 13 had no effect on absorbing NO₂ (Chang et al. 2004).

Brogren also reported that the addition of sodium chlorite under alkaline conditions increased the absorption of NO₂, up to almost 80% removed when 0.6 M was used. However, it can be seen from Fig. 12 that the addition of NaClO₂ in the scrubbing mixture decreased the amount of NO₂ absorbed. Since Fig. 11 already shows that NO₂ absorption was not directly dependent on pH, it follows that the diminishing capacity to absorb NO₂ seen in Fig. 12 when the pH of NaClO₂ was lowered from 10.6 to 6 likely has less to do with the increasing acidity of the aqueous solution but rather due to the increasing oxidation potential.

Although NO₂ gas is at least five times more soluble in the aqueous phase than NO (Table 3), its solubility was clearly still insufficient for the significant absorption and removal of NO_x from the exhaust. Absorption and removal of NO₂ required more

than can be provided by an alkaline mixture such as NaOH. Increasing the oxidizing potential in attempt to form higher valency nitrogen intermediates which have higher solubility such as N₂O₃, N₂O₄, and N₂O₅ did not improve the absorption but made it worse, contrary to reported literature (Brogren et al. 1998; Lin et al. 2016; Shao et al. 2019; Sun et al. 2015). This was consistent with the findings discussed previously Section 3.2.2.1.

Analysis of aqueous solution

The analysis of aqueous samples from scrubbing mixtures which could remove NO_x at least partially are presented here. NO and NO₂ gases captured in the gas–liquid reaction in the wet scrubber should end up as either nitrites or nitrates in the aqueous phase. From Fig. 13, it can be seen that the nitrogen existing in the aqueous phase were all in nitrate form. This was because the residue oxidizing agent in the liquid phase will oxidize all the nitrites into nitrates. This is advantageous as nitrates are the more stable in the aqueous phase. However, one area of concern is if part of the scrubbing liquid needs to be treated and discharged into the ocean during voyage. According to existing IMO

Fig. 12 NO₂ gas removal from the simulated exhaust gas using DI water versus scrubbing liquids of increasing oxidation potential (NaClO₂/pH10.9 < NaClO₂/pH8 < NaClO₂/pH7)

Fig. 13 Amount of aqueous nitrogen of various reactions using NaClO and NaClO₂ quantified by ion chromatography

guidelines for wastewater discharge from vessels to the ocean, high levels of nitrates may cause algae bloom, especially near the coastal areas, and are hence subjected to an upper discharge limit, in contrast to sulfates and chlorides which are considered to be naturally occurring in seawater and can be discharged freely (IMO 2015).

In Table 5, the amount of nitrates in the aqueous system was compared to the calculated theoretical amount of NO_x that was removed based on the results from the flue gas analyzer. It can be seen that for NaClO samples of various starting pH, only around 35–50% of the NO_x captured showed up as nitrates in the aqueous system. This range was around 70–80% for NaClO₂ samples.

The unaccounted nitrogen between the gaseous and aqueous phases could at least be partially attributed to the assumption that the system followed the ideal gas law when converting the gaseous concentration values from ppm(v) to mole. Second, it was also possible that the NO₂ that was

absorbed by the aqueous mixture was unstable and a portion of it could have desorbed from the scrubbing liquid before the quantitative analysis was carried out (within 24 h), on account of Eqs. 8 and 9 being reversible reactions. These unstable absorbed nitrogen includes non-anionic aqueous forms such as NO₂ (aq) or HNO₂ (aq) (Yang et al. 2016). Third, they could simply have been reduced to N₂ gas especially when under low oxidation potential conditions (Chang et al. 2004).

These results clearly showed that in the operating pH range from 6 to 11, NaClO₂ was more successful in not only oxidizing NO to NO₂ (Fig. 5), but also in absorbing (Figs. 9 and 13) and retaining (Table 5) the NO₂ in the aqueous phase, compared to NaClO. It could effectively oxidize NO to NO₂ without needing a high ORP environment in the bulk phase likely due to its ability to decompose to its more oxidative form, ClO₂, at the gas–liquid interface, so the subsequent absorption of NO₂ which required a lower ORP environment was not inhibited.

Table 5 Amount of NO_x removed by the various scrubbing liquids and the amount eventually converted to nitrate ions in the aqueous phase

Scrubbing liquid	Total amount of nitrates formed (mmol)	Total amount of NO _x removed (mmol)	Percentage of removed NO _x converted to nitrates (%)
NaClO	0.29	0.82	35.4
NaClO/pH 8	1.38	2.90	47.6
NaClO/pH 6	0.84	1.99	42.2
NaClO ₂	5.42	7.06	76.8
NaClO ₂ /pH 8	6.40	8.32	76.9
NaClO ₂ /pH 6	5.74	8.23	69.7
KMnO ₄	—	5.65	—

For both NaClO and NaClO₂, the reaction at pH 8 registered the highest amount of nitrates in the aqueous system. The balance between the ability to oxidize NO to NO₂ and absorb the NO₂ formed was seen around this pH region. Deshwal speculated a similar concept of this balance when studying NaClO₂ but without arriving at an optimal pH as the work carried out was in the acidic pH range (Deshwal et al. 2008). A study by Han et. al. on NO removal using NaClO₂ between the pH of 2.4 and 8.0 also showed that the absorption of NO₂ that was formed from the oxidation of NO was highest at pH 8.0 (Han et al. 2019).

Consumption of reactants

The mole ratio of the reactant consumed over the amount of NO_x that was removed is shown in Fig. 14. It can be seen that for NaClO, the consumption of reactants for every mole of NO_x removed increased with decreasing pH, for the pH range of 6–11. This was because as the pH shifted from 11 to 6, the dominant form of the chlorine oxidants also shifted from ClO[−] to HOCl. The latter, while having a stronger oxidation strength, was also more volatile, leading to significant losses to the scrubber exhaust and a high reactant consumption rate. If NaClO is the oxidant of choice, the operating pH should be in the region of 8, as this range provided a balance between effectiveness of NO_x removal versus reactant consumption rate. In this experimental setup, about 3 mol of ClO[−] oxidant was consumed for every mole of NO_x removed at this operating pH.

Except for NaClO/pH10.9 and NaClO₂/pH10.6, all reactions showed similar reactant consumption rates at the midpoint and end of reaction, suggesting that the consumption rates of reactants were linear throughout the experimental duration. These two liquid mixtures saw increasing reactant consumption because their pH started high but gradually dropped throughout the reaction, leading to higher reactant losses to the gaseous phase.

The various samples of NaClO₂ achieved between 2 and 3 moles of reactant consumed for every mole of NO_x removed; this was a better performance compared to NaClO, which ranged between 3 and 5 mol (with the exception of NaClO/pH10.9 as the NO_x removal for that sample was quite

insignificant). Of all the reactants studied here, KMnO₄ had the lowest reactant consumption rate, achieving around half a mole of reactant consumed for every mole of NO_x removed. Unlike chlorine-based oxidants which tended to partition into more volatile forms especially at lower pH, the permanganate oxidant tends to precipitate out of the aqueous phase as solid deposits instead. It is able to achieve this low reactant consumption rate since it is not volatilized and lost via the exhaust like chlorine-based oxidants.

Based on the amount of chemicals consumed in Fig. 14 and the cost of chemicals in Table 6, the estimated chemical cost per mole of NO_x removed was estimated in Fig. 15. It can be seen from Table 6 that the bulk cost of industrial chemicals from cheapest to most expensive is NaClO < NaClO₂ < KMnO₄. Although KMnO₄ is the most expensive chemical, it is still the most cost-effective after accounting for its high utilization rate, at approximately USD 0.15 per mole of NO_x removed. Although NaClO was less efficient than NaClO₂ in terms of reactant consumption, they did not differ significantly after accounting their cost—both lie around the range of USD 0.39–0.62 per mole of NO_x removed. Therefore, if these two compounds are being considered for usage in a system, the choice would likely be decided by other factors instead of costs.

Scalability

The optimal conditions for the best three scrubbing compounds, namely, NaClO₂, KMnO₄, and NaClO, were selected for further experimental runs at a significantly higher flowrate which are closer to industrial wet scrubbers. This was carried out to observe the behavior of each of these compounds when scaled to a liquid-to-gas ratio that is closer to industrial norms. Focus was placed on NO removal as it is the more challenging pollutant compared to SO₂. The L/G ratios were decreased from 100 to 15 L/m³ and the results are shown in Figs. 16 and 17.

It can be seen that the conversion of NO and removal of NO_x by NaClO₂ were very similar for both L/G ratios. However, this was not so for KMnO₄ and NaClO, which saw a reduction in capacity for the oxidation of NO and removal of NO_x when the L/G ratio was reduced to 15. KMnO₄

Fig. 14 The mole ratio of the reactant consumed per mole of NO_x removed

Table 6 Cost estimation of various scrubbing liquid systems used

No	Scrubbing liquid	Reactant cost (per mole)	Cost of HCl needed for pH adjustment (per mole)	Total cost (reactant + acid) (per mole)
1	NaClO	USD 0.124	USD 0.000	USD 0.124
2	NaClO/pH8	USD 0.124	USD 0.003	USD 0.127
3	NaClO/pH6	USD 0.124	USD 0.013	USD 0.137
4	NaClO ₂	USD 0.199	USD 0.000	USD 0.199
5	NaClO ₂ /pH8	USD 0.199	USD 0.001	USD 0.200
6	NaClO ₂ /pH6	USD 0.199	USD 0.002	USD 0.201
7	KMnO ₄	USD 0.392	USD 0.000	USD 0.392

Bulk cost of chemicals was estimated from industrial chemical aggregator sites, namely, chembid.com, alibaba.com, and diytrade.com

encountered a reduction of 40% in its capacity to oxidize NO to NO₂ and in the removal of NO_x. As for NaClO, this reduction of capacity was around 80% for both the oxidation of NO and removal of NO_x.

This kinetic limitation in the capacity of KMnO₄ and NaClO to oxidize NO and absorb NO_x when the L/G ratio was reduced (i.e., gas flowrate was increased and liquid flowrate reduced) showed that these two compounds were more limited in their mass transfer capacities compared to NaClO₂. As NaClO₂ showed a maximum conversion (100%) of NO to NO₂ for both high and low L/G ratios studied here, it is likely that it has the mass transfer capacity to remain effective at even lower L/G ratios. Therefore, NaClO₂ would likely be the most effective compound compared to KMnO₄ and NaClO when scaling up to industrial size requires much higher gas flowrates compared to liquid flowrates. The latter two compounds may still be used if a significant increase in concentration can improve their effectiveness, but further work is needed to verify this at low L/G ratios.

Conclusions

For the reaction with SO₂, full removal of SO₂ proceeded quite readily and was achieved by nearly all the different types

of scrubbing mixtures that were tested. This is because SO₂ gas is very soluble in the aqueous phase. The absorption of SO₂ in the aqueous phase by the various gas–liquid reactions were likely influenced by three factors, namely, pH, the ionic concentration in the scrubbing mixture in terms of both its overall ionic strength and concentration of sulfate ions, and oxidation potential. An effective scrubbing liquid for the effective removal of SO₂ gas should have high pH or alkalinity, low in ionic strength and sulfate ions, and oxidative in nature.

As for NO_x removal, the effectiveness of various chemical compounds used can be ranked as follows, from least to most effective: seawater, NaOH, H₂O₂ < NaClO < KMnO₄ < NaClO₂. The first three, seawater, NaOH, and H₂O₂, had little or no effect. NaClO was somewhat effective when the pH was lowered to 9 and below, when the hypochlorite ions shifted to its oxidative form, HOCl. Following that was KMnO₄ which was moderately effective, while NaClO₂ was the most effective, especially when the pH was below 10. When the L/G ratio was reduced from 100 to 15 L/m³, NaClO₂ showed no changed in its effectiveness for NO_x removal while NaClO and KMnO₄ showed a reduction in 80 and 40%, respectively. This showed that NaClO₂ is the most reactive and suitable for scaling up to industrial size (higher gas flowrate, lower liquid flowrate conditions) while NaClO and KMnO₄ would

Fig. 15 The estimated chemical cost of various reactant per mole of NO_x removed

Fig. 16 Nitric oxide (NO) re-removal from the simulated exhaust gas with various scrubbing liquids at L/G ratios of 100 L/m³ vs. 15 L/m³, respectively

probably require higher concentrations to make up for their kinetic and mass transfer limitations.

For achieving high NO_x removal, the scrubbing liquid mixture must be effective in (1) oxidizing NO to NO₂, (2) absorbing the NO₂ into the aqueous phase, and (3) retaining the nitrogen in the aqueous phase as anions. Seawater, NaOH, and H₂O₂ were ineffective in NO_x removal because they had difficulty oxidizing NO to NO₂. NaClO was effective in oxidizing NO to NO₂ after it partitioned into its HOCl form when the pH was reduced below 9. However, it was not very effective in absorbing and retaining NO₂ in the aqueous phase, especially when the pH was lowered to below 9—up to half of the NO₂ that was absorbed likely desorbed back into the atmosphere after a short period of time.

Successful oxidation of NO to NO₂ did not necessarily translate to high NO_x removal as the absorption of NO₂ proved to be a challenge although it is approximately five times more soluble than NO in the aqueous phase. Alkalinity was not a factor in the absorption of NO₂ into the

aqueous phase as increasing the NaOH concentration had no effect on it. Rather, NO₂ absorption showed an inverse relationship with oxidation potential in this study. The seeming relationship between NO₂ absorption and pH was likely coincidental since the oxidation potential of chlorine-based oxidants are also pH dependent.

NaClO₂ was superior compared to NaClO in all three categories of oxidizing, absorption, and retention of NO in the pH range of 6–11. It could effectively oxidize NO to NO₂ without needing a high ORP environment in the bulk phase likely due to its ability to decompose to its more oxidative form, ClO₂, at the gas–liquid interface, so the subsequent absorption of NO₂ which required a lower ORP environment was not inhibited.

In the pH range of 6–11 studied here, the pH at around the region of 8 provided an optimal balance between oxidation versus both absorption/retention and reactant utilization for NaClO and NaClO₂, respectively. Operating at an optimal pH was important as to minimize reactant losses to the

Fig. 17 NO_x (NO+NO₂) removal from the simulated exhaust gas using various scrubbing liquids

atmosphere as both NaClO and NaClO₂ partitioned into a gaseous state at lower pH.

Although KMnO₄ was less effective than NaClO₂ in terms of overall NO_x removal, it was very effective in absorbing and retaining the NO₂ in the aqueous phase. In fact, it was possible that this seemingly high NO₂ absorption could be because KMnO₄ was able to oxidize NO into the aqueous phase without forming gaseous intermediates such as NO₂. KMnO₄ also had the lowest reaction consumption rate, with only half a mole utilized for every mole of NO_x removed, compared to 2–3 mol of NaClO₂ or 3–5 mol of NaClO needed for every mole of NO_x removed. This was because unlike the chlorine-based oxidants, KMnO₄ does not partition into a more volatile form, leading to less reactant losses to the atmosphere. However, KMnO₄ has a tendency to precipitate in the form of MnO₂ which caused clogging and was very difficult to remove.

In terms of chemical cost per mole of NO_x removed, KMnO₄ is the most cost effective which NaClO and NaClO₂ were similar in range. As each of the chemical reactant compared here have their own advantages and disadvantages, the choice of the most suitable reactant will still depend on the actual design of the wet scrubbing system. Nevertheless, this comparison exercise enabled a deeper understanding of the reaction mechanisms and behavior of the reactants during reaction.

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Declarations

Competing interests The authors declare no competing interests.

Ethical approvals Since this study did not recruit any human and/or animal subjects, this section does not apply.

Consent to participate Since this study did not recruit any human subjects, this section does not apply.

Consent to publish Since this study is not attempting to re-publish/publish any third party or author's previously published material, this section does not apply.

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