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NO₂ Absorption in Aqueous Solutions with Phenolic Additives: Hydroquinone and 4-Methylaminophenol Sulfate

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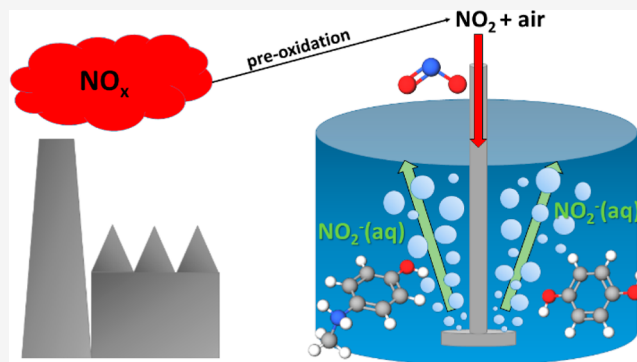
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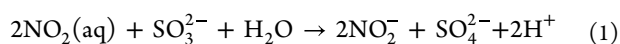
ABSTRACT: NO₂ absorption has recently gained attention as a promising alternative to conventional NO_x reduction methods. One key challenge in NO₂ absorption is that high amounts of additives are required to maintain satisfactory absorption efficiency. The present study investigates the absorption of NO₂ from flue gases in aqueous solutions with low concentrations of phenolic additives. Absorption tests with hydroquinone and 4-methylaminophenol sulfate were performed in a laboratory-scale absorption system with test gases containing 0 or 5% O₂ (N₂ as a balance gas) and 50, 100, or 150 ppm of NO₂, representing typical flue gas conditions in a range of industrial processes. The results show that NO₂ was absorbed efficiently with small concentrations of 4-methylaminophenol sulfate, both with 0 or 5% O₂ in the test gas.

Hydroquinone also enhanced NO₂ absorption but to a lesser degree than 4-methylaminophenol sulfate. Interestingly, the presence of O₂ did not influence the consumption of the phenolic additives, in contrast to commonly used additives such as sulfite that require oxidation inhibitors such as thiosulfate. With a 2 mM solution of 4-methylaminophenol sulfate, more than 90% of the incoming NO₂ was absorbed. Thus, NO₂ absorption with 4-methylaminophenol sulfate appears to be able to remove NO_x emissions from flue gases with high efficiency.

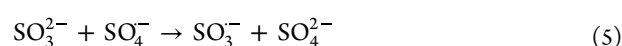
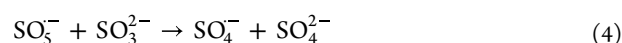
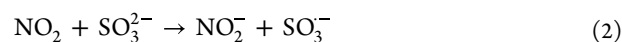


1. INTRODUCTION

NO₂ absorption in wet scrubbing systems is an effective method to reduce NO_x emissions from industrial combustion flue gases and other industrial processes.^{1–3} NO₂ absorption has several advantages as compared to conventional methods, e.g., selective catalytic reduction (SCR) is not suitable for flue gases with impurities, and selective non catalytic reduction (SNCR) is also sensitive to both impurities and may give rise to ammonia slip. In the combustion flue gases, the majority of NO_x is in the form of NO. Due to its low water solubility, NO is oxidized to NO₂ to enable absorption in aqueous solutions, as NO₂ has a higher water solubility.^{4,5} In spite of the higher water solubility of NO₂, additives are needed to achieve reasonable absorption rates. Sulfite is commonly used as an additive for converting NO₂(aq) to nitrite (NO₂⁻) and improving NO₂ absorption rates.⁶ In a recent laboratory absorption study with 50 ppm of NO₂ and 0% O₂ in the incoming gas, the NO₂ concentration was reduced to 25 ppm with 2 mM sulfite in the solution and to 10 ppm of NO₂ with 10 mM sulfite in the solution. Sulfite is consumed following the reaction⁷



In the presence of oxygen, the following NO₂⁻ and O₂-induced radical chain mechanism for sulfite oxidation has been suggested^{8,9}



The oxidation of sulfite to sulfate reduces the NO₂ absorption rate, requiring either additional sulfite or a sulfite oxidation inhibitor to maintain a high NO₂ absorption rate. One recently studied sulfite oxidation inhibitor is thiosulfate (S₂O₃²⁻).^{10,11} Thiosulfate is a radical scavenger and terminates

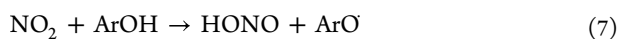
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the chain reaction of sulfite oxidation. Some studies proposed that the chain reaction is terminated by the reaction of thiosulfate with the $\text{SO}_5^{\cdot-}$ radical,^{6,9} whereas others proposed that it is terminated by a reaction with the $\text{SO}_3^{\cdot-}$ radical.^{12,13} Other radical scavengers that have shown to reduce the sulfite oxidation rate are, e.g., ascorbic acid,¹⁴ alcohols,¹⁵ and hydroquinone.¹⁶

Besides their ability to reduce sulfite oxidation, substituted phenols can also react directly with NO_2 . The reactions between phenols and NO_2 have been of interest due to their importance in atmospheric chemistry.^{17–19} Aromatic hydrocarbons represent a significant part of nonmethane hydrocarbons in the atmosphere.²⁰ In gas-phase reactions, NO_2 may react with phenols to form HNO_3 , NO , and nitrophenols.¹⁷ In the liquid phase, the solvent influences the reaction products.^{21,22} In order to understand the reactions of NO_2 in aqueous solutions containing phenolic compounds, Ammann et al. investigated hydroxy- and methoxy-substituted phenols in a wetted-wall reactor to obtain rate-constants for the NO_2 uptake under conditions relevant for atmospheric chemistry.²³ Rate constants for other substituted phenols with NO_2 have also been determined using pulse radiolysis.^{24,25} The reaction between phenolic compounds and NO_2 is initiated by a charge transfer from the phenolic compound (ArOH or ArO^- in the deprotonated form) to NO_2 .^{19,23}



The ArO^{\cdot} radical can react further with NO_2 to produce several reaction products. A mechanistic study by Coombes and Diggle observed the formation of 2-nitro-4-methylphenol and 6-nitrocyclohexa-2,4-dien-1-on from the reaction of 4-methylphenol with NO_2 .²² The reactivity of the phenolic compound toward NO_2 is influenced by the substituents. A theoretical study about the influence of various substituents in different positions of the phenol has been performed by Shenghur et al.¹⁹

In a recent study, we investigated thiosulfate as an oxidation inhibitor in aqueous sulfite solutions in a laboratory-scale NO_2 absorption system.¹⁰ While absorption solutions containing sulfite and thiosulfate show good performance in NO_2 absorption, the consumption of additives is still relatively high. To further increase the efficiency and decrease the environmental impact of the NO_x removal processes via NO_2 absorption, the consumption of additives should be further reduced. This may be achieved either by finding additives that decrease sulfite oxidation more efficiently than thiosulfate or by finding additives that react efficiently with NO_2 and are not consumed by oxygen in the flue gas. The present study investigates two phenolic additives, hydroquinone and 4-methylaminophenol sulfate, and their potential for usage in NO_2 absorption under industrially relevant conditions in comparison to the previously studied additives sulfite and thiosulfate.

2. EXPERIMENTAL SECTION

Figure 1 shows the experimental setup used for the NO_2 absorption experiments (a more detailed description can be found elsewhere^{8,10}). NO_2 was mixed with air and nitrogen to obtain a gas mixture containing 50, 100, or 150 ppm of NO_2 and 5 vol % O_2 , with N_2 as a balance gas. These NO_2 concentrations represent typical flue gas conditions of

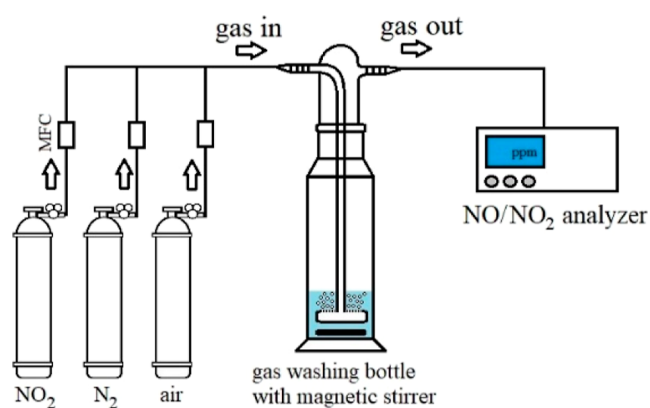


Figure 1. Experimental setup for laboratory-scale NO_2 absorption experiments; MFC = mass flow controller.

industrial processes. The total flow of the gas was 2.3 NL/min. The gas was bubbled through a gas washing bottle at room temperature. The gas washing bottle contained 50 mL of absorption liquid in all tests. At the bottom of the bottle, where the gas came in contact with the liquid, a porous glass sinter provided a high surface area for good contact between the gas and the absorption liquid. The absorption solution was magnetically stirred to avoid concentration gradients within the solution. The NO_2 concentration in the off-gas of the absorption system was continuously analyzed. In the first step, the NO_2 was reduced to NO on an SCC-K catalyst from ABB. The NO was then quantified with a chemiluminescence analyzer from Teledyne, model 200EM.

Absorption tests were done with 5% O_2 and 50–150 ppm NO_2 at pH 8 with sulfite; sulfite and thiosulfate; sulfite and hydroquinone; and sulfite and 4-methylaminophenol sulfate. In these tests, the sulfite, thiosulfate, and hydroquinone concentrations were 2 mM; the 4-methylaminophenol sulfate concentration was 1 mM (1 mol of 4-methylaminophenol sulfate contains 2 mol of the phenolic compound). In addition, tests were done with solutions containing only hydroquinone or 4-methylaminophenol sulfate at pH 5–8. The solutions were buffered with phosphate buffer ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} + \text{KH}_2\text{PO}_4$). The chemical structures of hydroquinone and 4-methylaminophenol sulfate are shown in Figure 2. 4-Methylaminophenol sulfate

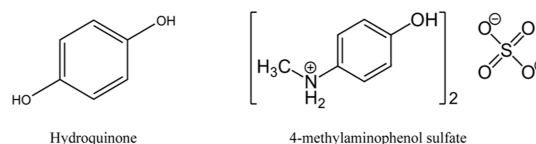


Figure 2. Chemical structures of hydroquinone and 4-methylaminophenol sulfate.

(also known commercially as Metol) is a chemical derived from hydroquinone and methylamine.²⁶ The hydroquinone (99% purity) was purchased from Sigma-Aldrich, and the 4-methylaminophenol sulfate (98% purity) was purchased from Acros Organics.

Hydroquinone and 4-methylaminophenol sulfate are commercially available solid chemicals with recommended storage temperatures of 15–25 °C. 4-Methylaminophenol sulfate needs to be stored protected from light, as it slowly decomposes under the influence of light. Both chemicals

dissolve rapidly in water, and the investigated solutions were prepared right before the experiment.

Absorption tests with 4-methylaminophenol sulfate and hydroquinone caused increased foam formation in the absorption solution when the experiments were run for a longer period of time. To ensure the reproducibility and accuracy of the reported experiments, experiments were run only for shorter periods of time during which no or only little foam was formed.

3. RESULTS

Figure 3 presents results from NO_2 absorption tests (5% O_2) in water with sulfite; sulfite and thiosulfate; sulfite and

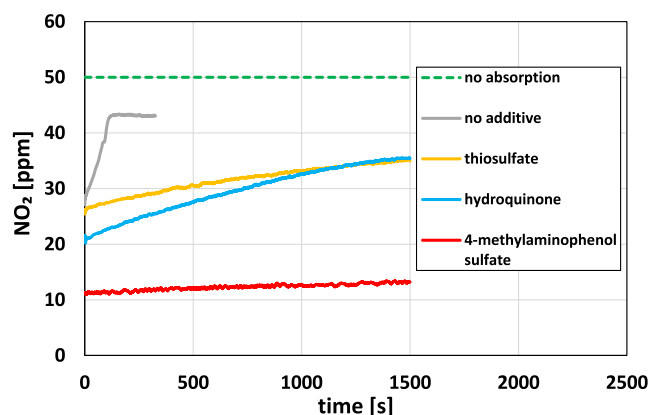


Figure 3. NO_2 concentrations from absorption tests with 2 mM sulfite with no additive or addition of 2 mM thiosulfate, 2 mM hydroquinone, or 1 mM 4-methylaminophenol sulfate at pH 8; 50 ppm of NO_2 inlet concentration shown as dotted line (5% O_2 , N_2 as balance gas).

hydroquinone; and sulfite and 4-methylaminophenol sulfate. In the case with only sulfite, around 40% of the NO_2 was absorbed initially. The NO_2 absorption rate decreased rapidly, and after less than 200 s, all of the sulfite had been consumed. At this point, the NO_2 absorption rate corresponded to that of pure water.⁸ With sulfite and thiosulfate in the solution, a similar absorption efficiency was observed initially in the experiment compared to the experiment with only sulfite. However, the decrease in the NO_2 absorption rate was slower, i.e., a higher absorption rate was maintained during the experiment. After 1500 s, the absorption efficiency was still 30%. The test with sulfite and hydroquinone gave similar results as compared to those with sulfite and thiosulfate. The

initial absorption rate was slightly higher with hydroquinone, but the absorption rate decreased at similar rates, and the NO_2 absorption was 30% after 1500 s. With 4-methylaminophenol sulfate, almost 80% of NO_2 was initially absorbed. The absorption rate remained almost constant during the time of the experiment. An absorption efficiency of 75% was observed even after 1500 s in this case. The high absorption efficiency with 4-methylaminophenol sulfate indicates a strong interaction between the additive and NO_2 .

To understand the higher NO_2 with the phenolic additives, hydroquinone and 4-methylaminophenol sulfate were investigated separately on their reactions with NO_2 . The results for the absorption tests with only hydroquinone or 4-methylaminophenol sulfate (no sulfite) are presented in Figure 4. In these tests, 2 mM of the respective phenolic compounds was dissolved at pH 5, 6, 7, and 8. Generally, the NO_2 absorption was significantly higher when using 4-methylaminophenol sulfate as compared to hydroquinone. The pH had a strong effect on the absorption efficiency as well. At pH 8, around 90% of the NO_2 was absorbed with the 4-methylaminophenol sulfate solution, while with hydroquinone only 25% of the NO_2 was absorbed. In the tests at a lower pH, lower NO_2 absorption was observed for both additives. At pH 5, the NO_2 absorption efficiency was around 45% with 4-methylaminophenol sulfate and 18% with hydroquinone. The difference in the reactivity toward NO_2 may be explained by the reaction mechanism and the influence of the different substituents on the phenol. As discussed in the introduction part, phenols may interact with NO_2 via a charge transfer or a hydrogen transfer, depending on if the $-\text{OH}$ group is protonated (ArOH) or deprotonated (ArO^-). Nitrite is formed as a product in this reaction (compare reactions 7 and 8). The phenoxide anions are thereby much more reactive, which explains the observed pH dependency of the NO_2 absorption. At a higher pH, a higher fraction of the phenolic compound is present in the deprotonated form. These observations are in agreement with earlier studies.²³ The role of the substituents on phenol in this reaction is to stabilize the aromatic radical. The reactivity of phenols is higher when a more stable radical is formed. This may explain why the NO_2 absorption is more effective with 4-methylaminophenol sulfate as compared to hydroquinone. The $-\text{NHCH}_3$ group is a better electron donor than the $-\text{OH}$ group in the para-position, which is in agreement with results from earlier studies on the effects of substituents on the reactivity of phenols.^{19,25}

Figure 5 shows the NO_2 concentrations from absorption tests with various concentrations of 4-methylaminophenol sulfate between 0 and 2 mM at pH 8. 0 mM represents the absorption

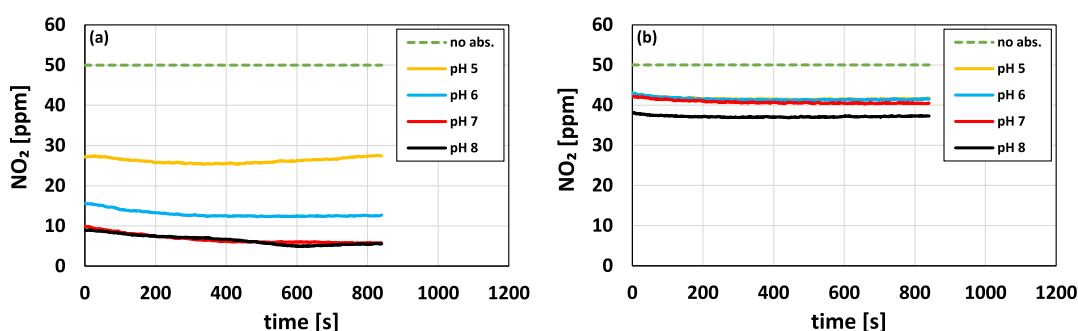


Figure 4. NO_2 concentrations from absorption experiments with 1 mM 4-methylaminophenol sulfate (a) and 2 mM hydroquinone (b) solutions at pH 5–8; 50 ppm of NO_2 inlet concentration shown as dotted line (5% O_2 , N_2 as the balance gas).

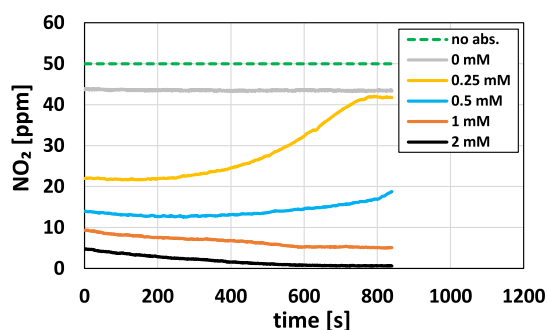


Figure 5. NO_2 concentrations from absorption experiments with 0–2 mM 4-methylaminophenol sulfate solution (pH 8); 50 ppm of NO_2 inlet concentration shown as dotted line (5% of the O_2 , N_2 as the balance gas).

with pure water (+buffer). With only water, the NO_2 concentration decreased from 50 ppm to around 43 ppm, corresponding to an absorption efficiency of 15%. With 0.25 mM 4-methylaminophenol sulfate, the NO_2 concentration decreased initially to 22 ppm, i.e., almost 60% of the NO_2 was absorbed. After around 300 s, the NO_2 concentration started to increase until it remained constant at around 800 s. At 800 s, the NO_2 absorption is similar to the NO_2 absorption in pure water, and it can be assumed that most of the 4-methylaminophenol sulfate has been consumed, and absorption reactions occur mainly with water. In the test with 0.5 mM 4-methylaminophenol sulfate, similar observations were made. Initially the NO_2 concentration decreased to 13 ppm and slowly increased after around 500 s. However, even after 800 s, the absorption was still higher than 60%. In the tests with 1 or 2 mM 4-methylaminophenol sulfate, NO_2 concentrations decreased from 10 or 5 ppm to 5 or 0 ppm, respectively. The slight decrease in the NO_2 concentration might be explained by the formation of a foam in the scrubber solution, which might have some effect on the absorption process. The foam formation was also the reason why experiments with higher additive concentrations were not run until all of the additive was consumed. From the experiments with 0.25 and 0.5 mM, it was estimated that it would take around 6000 s until all additive is consumed in the 2 mM solution. With the increasing foam formation, however, it was not possible to achieve reliable results for such long experiments.

Ion chromatography was used to quantify the reaction products nitrite and nitrate in the solutions after the tests with 0–2 mM 4-methylaminophenol sulfate. Table 1 shows results from these tests. The amount of absorbed NO_2 (in μmol) has been calculated from the results shown in Figure 5. Nitrite was the only reaction product of NO_2 that could be identified in

Table 1. Amount of Absorbed NO_2 and Nitrite Found in Solution after Experiments with 0–2 mM 4-Methylaminophenol Sulfate Solution (pH 8); 50 ppm of NO_2 Inlet, 15 min Test

additive conc. [mM]	additive total [μmol]	NO_2 input [μmol]	NO_2 absorbed [μmol]	found as nitrite (NO_2^-) [μmol]
0.25	25	66	29	38
0.5	50	66	47	53
1	100	66	57	61
2	200	66	63	69

the scrubber solutions, and no nitrate was found. Under the investigated conditions, nitrite solutions are stable for long periods of time, so the transformation of nitrate would not be expected when only nitrite is initially formed during NO_2 absorption.²⁷ Within the uncertainty of the measurements of around 10%, the amount of formed nitrite corresponds well to the amount of absorbed NO_2 , indicating that this is the main reaction product from the NO_2 absorption. The ion chromatograms and standard curve for nitrite can be found in Figures S1 and S2 in the Supporting Information, and the ion chromatogram for the test solutions with 4-methylaminophenol sulfate after the absorption tests can be found in Figure S3 in the Supporting Information.

Since the amount of nitrite found in the product solution corresponds well with the amount of absorbed NO_2 , it seems that no or only little NO_2 is reacting with the amine in 4-methylaminophenol sulfate. Amines (R_2NH) can also react with NO_2 when nitrogen oxides are absorbed into aqueous amines.^{28–30} When amines react with NO_2 , a radical ($\text{R}_2\text{N}^\bullet$) is formed, which can react further with NO_2 .³⁰ In this case, however, a lot of absorbed NO_2 should be bound to the additives and not be present in the solution. This supports that the amine is not the reactive group under the investigated conditions.

Figure 6 shows the NO_2 absorption as a function of the NO_2 inlet concentration. The gas inlet concentrations were 50, 100, or 150 ppm of NO_2 , and the absorption solution contained 2 mM 4-methylaminophenol sulfate. At the lowest concentration, a high absorption efficiency could be maintained for almost 1500 s before the level of NO_2 slowly started to increase. With 100 ppm of NO_2 , the NO_2 concentration increased after 700 s and with 150 ppm of NO_2 after 400 s. The results indicate that the absorption efficiency is not affected by the NO_2 inlet concentration. With all inlet concentrations, 50, 100, and 150 ppm, the absorption efficiency was the same. In addition, when the reactive additive was consumed and the NO_2 concentration reached a constant level at a higher concentration, the absorption efficiency was the same for different NO_2 inlet concentrations.

To investigate the influence of oxygen on the NO_2 absorption with 4-methylaminophenol sulfate, a 30 min test with and without oxygen in the test gas was performed. The results for this test are listed in Figure 7. Similar to the results in Figure 5, a decrease from initial NO_2 was observed. This is likely due to the formation of a foam on the absorption liquid that might have an influence on the absorption efficiency. The foam formation was observed both with and without oxygen in the test gas. In both cases, the NO_2 initially dropped to around 10 ppm and decreased to less than 2 ppm after 1000 s and less than 1 ppm after 1500 s. Interestingly, the NO_2 absorption was almost identical in both cases, with and without oxygen in the test gas.

Based on the above presented results, it can be stated that phenolic additives can be a highly efficient additive for NO_2 absorption, especially with activating substituents. To evaluate the overall performance, however, costs of chemicals, safety issues, and waste treatment need to be considered as well. While 4-methylaminophenol sulfate has a higher price per ton as compared to conventionally used sulfite and thiosulfate, the much lower consumption and higher performance of this additive may still compensate for this. Concerning recovery of chemicals, neither the phenolic additives nor the sulfurous additives can be recovered for reuse in the process. Both

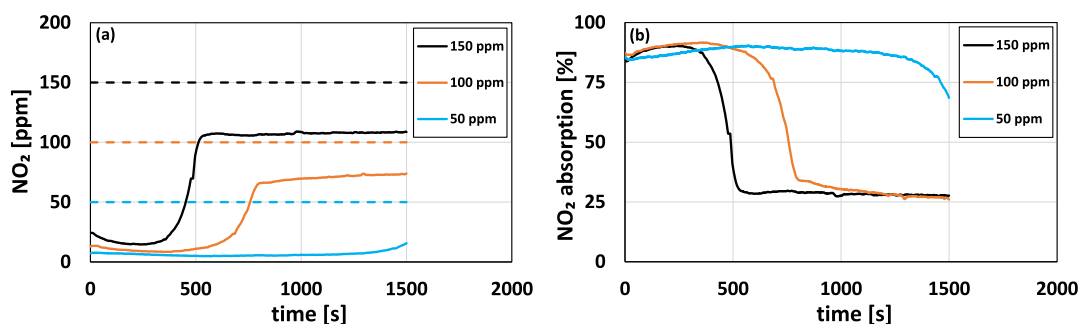


Figure 6. NO₂ concentrations (a) and NO₂ absorption (b) from the absorption experiment with 1 mM 4-methylaminophenol sulfate solution (pH 8) and 50–150 ppm of NO₂ inlet concentration (inlet concentrations marked with dotted lines).

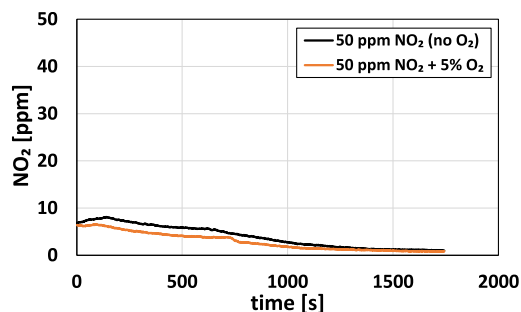


Figure 7. NO₂ concentrations from absorption experiment with 1 mM 4-methylaminophenol sulfate solution (pH 8) without or with 5% O₂; 50 ppm of NO₂ inlet (balance gas N₂).

hydroquinone and 4-methylaminophenol sulfate are harmful chemicals that are toxic to aquatic life and must therefore not be released into the environment. Wastewater treatment may include, e.g., treatment with UV-light and peroxide.³¹ Reaction products from the absorption process also need to be removed from the wastewater. The formation of different products in the wastewater is strongly dependent on the conditions of the process, since, e.g., the reactions of nitrite with other chemicals depend on the pH of the wastewater.²⁷ Further research is needed to better understand possible reactions in the wastewater.

4. CONCLUSIONS

The present study investigated sulfurous and phenolic additives for the absorption of NO₂ into aqueous solution for NO_x removal from flue gases. The sulfurous additives sulfite and thiosulfate were compared to the phenolic additives hydroquinone and 4-methylaminophenol sulfate.

Sulfite can effectively absorb NO₂ from the flue gas but is rapidly consumed in the presence of oxygen. The addition of thiosulfate, which acts as a sulfite oxidation inhibitor, significantly reduces sulfite consumption and enables NO₂ absorption with sulfite over extended periods of time. Hydroquinone had a similar effect to thiosulfate when added to a sulfite solution. However, increased NO₂ absorption with hydroquinone addition to the sulfite solution indicated that hydroquinone itself is interacting with NO₂. The addition of 4-methylaminophenol sulfate enhanced the NO₂ even more when it was added to the sulfite solution.

To investigate the interactions between the phenolic additives and NO₂, experiments were also performed without the presence of sulfite in the solution. Solutions containing 1 mM hydroquinone absorbed around 20–25% of the NO₂ in

the test gas, depending on the pH. The same amount of 4-methylaminophenol sulfate absorbed 50% of the incoming NO₂ at pH 5 and 80% at pH 8. When the concentration was increased to 2 mM, the NO₂ concentration was reduced from 50 to almost 0 ppm. Thus, it is concluded that 4-methylaminophenol sulfate has an exceptional capacity to improve NO₂ absorption and potentially even entirely eliminate NO_x from flue gas. Interestingly, the oxygen concentration in the test gas had no influence on the NO₂ absorption with 4-methylaminophenol sulfate, which is a great advantage in industrial processes. It eliminates the need for additional additives, which are required when, e.g., using sulfite solutions that need a sulfite oxidation inhibitor.

Further studies are needed to clarify the reaction mechanisms in detail and to understand the fate of reaction products in the absorption liquid. Due to the harmfulness of the phenolic additives, safety issues need to be addressed in future studies as well. However, wastewater treatment is also required when using conventional sulfurous additives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c03205>.

Ion chromatograms for the solutions from the NO₂ absorption tests with 4-methylaminophenol sulfate and standard solutions used for quantification (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Sharif, H. M. A.; Mahmood, N.; Wang, S.; Hussain, I.; Hou, Y. N.; Yang, L. H.; Zhao, X.; Yang, B. Recent Advances in Hybrid Wet Scrubbing Techniques for NO_x and SO₂ Removal: State of the Art and Future Research. *Chemosphere*; Elsevier Ltd June 1, 2021; p 129695.
- (2) Zhao, M.; Xue, P.; Liu, J.; Liao, J.; Guo, J. A Review of Removing SO₂ and NO_x by Wet Scrubbing. *Sustainable Energy Technologies and Assessments*; Elsevier Ltd October 1, 2021; p 101451.
- (3) Johansson, J.; Normann, F.; Andersson, K. Techno-Economic Evaluation of Co-Removal of NO_x and SO_x Species from Flue Gases via Enhanced Oxidation of NO by ClO₂—Case Studies of Implementation at a Pulp and Paper Mill, Waste-to-Heat Plant and a Cruise Ship. *Energies* **2021**, *14* (24), 8512.
- (4) Guo, R. T.; Hao, J. K.; Pan, W. G.; Yu, Y. L. Liquid Phase Oxidation and Absorption of NO from Flue Gas: A Review. *Sep. Sci. Technol.* **2015**, *50* (2), 310–321.
- (5) Brogren, C.; Karlsson, H. T.; Bjerle, I. Absorption of NO in an Aqueous Solution of NaClO₂. *Chem. Eng. Technol.* **1998**, *21* (1), 61–70.
- (6) Shen, C. H.; Rochelle, G. T. Nitrogen Dioxide Absorption and Sulfite Oxidation in Aqueous Sulfite. *Environ. Sci. Technol.* **1998**, *32* (13), 1994–2003.
- (7) Littlejohn, D.; Wang, Y.; Chang, S.-G. Oxidation of Aqueous Sulfite Ion by Nitrogen Dioxide. *Environ. Sci. Technol.* **1993**, *27*, 2162–2167.
- (8) Schmid, D.; Karlström, O.; Kuvaja, V.; Vuorinen, I.; Paavola, M.; Hupa, M. Role of Sulfite Oxidation in NO₂ Absorption in a PH-Neutral Scrubber Solution. *Energy Fuels* **2022**, *36* (5), 2666–2672.
- (9) Sapkota, V. N. A.; Fine, N. A.; Rochelle, G. T. NO₂-Catalyzed Sulfite Oxidation. *Ind. Eng. Chem. Res.* **2015**, *54* (17), 4815–4822.
- (10) Schmid, D.; Hupa, M.; Paavola, M.; Vuorinen, I.; Lehtikoinen, A.; Karlström, O. Role of Thiosulfate in NO₂ Absorption in Aqueous Sulfite Solutions. *Ind. Eng. Chem. Res.* **2023**, *62* (1), 105–110.
- (11) Rochelle, G. T.; Owens, D. R.; Chang, J. C. S.; Bma, T. G. Thiosulfate as an Oxidation Inhibitor in Flue Gas Desulfurization Processes: A Review of R&D Results. *J. Air Pollut. Control Assoc.* **1986**, *36* (10), 1138–1146.
- (12) Chang, J. C. S.; Brna, T. G. Pilot Testing of Sodium Thiosulfate. *Environ. Prog. Sustain. Energy* **1986**, *5* (4), 225–233.
- (13) Mo, J.-S.; Wu, Z. b.; Cheng, C.-J.; Guan, B.-H.; Zhao, W. r. Oxidation Inhibition of Sulfite in Dual Alkali Flue Gas Desulfurization System. *J. Environ. Sci.* **2007**, *19*, 226–231.
- (14) Lidong, W.; Yongliang, M.; Wendi, Z.; Qiangwei, L.; Yi, Z.; Zhanchao, Z. Macrokinetics of Magnesium Sulfite Oxidation Inhibited by Ascorbic Acid. *J. Hazard. Mater.* **2013**, *258–259*, 61–69.
- (15) Alyea, H. N.; Bäckström, H. L. J. The Inhibitive Effect of Alcohols on the Oxidation of Sodium Sulfite. *J. Am. Chem. Soc.* **1929**, *51* (1), 90–109.
- (16) Li, S.; Huang, W.; Xu, H.; Liu, K.; Wang, J. n.; Sun, Y.; Qu, Z.; Yan, N. Enhanced simultaneous absorption of NO and SO₂ in oxidation-reduction-absorption process with a compounded system based on Na₂SO₃. *J. Environ. Sci.* **2022**, *111*, 1–10.
- (17) Mondal, K.; Biswas, S.; Chattopadhyay, A.; Chatterjee, P.; Chakraborty, T. Gas-Phase Oxidation of NO₂ to HNO₃ by Phenol: Atmospheric Implications. *ACS Earth Space Chem.* **2021**, *5* (8), 2131–2141.
- (18) Sosedova, Y.; Rouvière, A.; Gäggeler, H. W.; Ammann, M. Uptake of NO₂ to Deliquesced Dihydroxybenzoate Aerosol Particles. *J. Phys. Chem. A* **2009**, *113* (41), 10979–10987.
- (19) Shenghur, A.; Weber, K. H.; Nguyen, N. D.; Sontising, W.; Tao, F. M. Theoretical Study of the Hydrogen Abstraction of Substituted Phenols by Nitrogen Dioxide as a Source of HONO. *J. Phys. Chem. A* **2014**, *118* (46), 11002–11014.
- (20) Koch, R.; Knispel, R.; Elend, M.; Siese, M.; Zetzsch, C. Consecutive reactions of aromatic-OH adducts with NO, NO₂ and O₂: benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline. *Atmos. Chem. Phys.* **2007**, *7* (8), 2057–2071.
- (21) Astolfi, P.; Panagiotaki, M.; Greci, L. New Insights into the Reactivity of Nitrogen Dioxide with Substituted Phenols: A Solvent Effect. *Eur. J. Org. Chem.* **2005**, *2005* (14), 3052–3059.
- (22) Coombes, R. G.; Diggle, A. W.; Kempell, S. P. The Mechanism of Nitration of Phenol and 4-Methylphenol by Nitrogen Dioxide in Solution. *Tetrahedron Lett.* **1994**, *35* (34), 6373–6376.
- (23) Ammann, M.; Rössler, E.; Strekowski Present address Universi, R.; George, C. Nitrogen Dioxide Multiphase Chemistry: Uptake Kinetics on Aqueous Solutions Containing Phenolic Compounds. *Phys. Chem. Chem. Phys.* **2005**, *7* (12), 2513–2518.
- (24) Miao, J.-L.; Wang, W.-F.; Pan, J.-X.; Lu, C.-Y.; Li, R.-Q.; Yao, S.-D. The Scavenging Reactions of Nitrogen Dioxide Radical and Carbonate Radical by Tea Polyphenol Derivatives: A Pulse Radiolysis Study. *Radiat. Phys. Chem.* **2001**, *60* (3), 163–168.
- (25) Alfassi, Z. B.; Huie, R. E.; Neta, P. Substituent effects on rates of one-electron oxidation of phenols by the radicals chlorine dioxide, nitrogen dioxide, and trioxosulfate(1-). *J. Phys. Chem.* **1986**, *90*, 4156–4158.
- (26) Harger, R. N. The Preparation of Metol (N-Methyl-p-Amidophenol Sulfate). *J. Am. Chem. Soc.* **1919**, *41* (2), 270–276.
- (27) Cai, Q.; Zhang, W.; Yang, Z. Stability of Nitrite in Wastewater and Its Determination by Ion Chromatography. *Anal. Sci.* **2001**, *17*, 917–920.
- (28) Chen, C.-I.; Rochelle, G. T. Amine Oxidation Catalyzed by NO₂. *Proceedings of the 16th Greenhouse Gas Control Technologies Conference*, 2022.
- (29) Peterson, G. W.; Mahle, J. J.; Decoste, J. B.; Gordon, W. O.; Rossin, J. A. Extraordinary NO₂ Removal by the Metal-Organic Framework UiO-66-NH₂. *Angew. Chem. Int. Ed.* **2016**, *55* (21), 6235–6238.
- (30) Fine, N. A.; Rochelle, G. T. Absorption of Nitrogen Oxides in Aqueous Amines. *Energy Procedia* **2014**, *63*, 830–847.
- (31) Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. The Oxidation of Metol (N-Methyl-p-Aminophenol) in Aqueous Solution by UV/H₂O₂ Photolysis. *Water Res.* **2000**, *34* (2), 463–472.