Ultrasound-Induced Aqueous Removal of Nitric Oxide from Flue Gases: Effects of Sulfur Dioxide, Chloride, and Chemical Oxidant

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The effects of sulfur dioxide (SO_2), sodium chloride (NaCl), and peroxymonosulfate or oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ with active ingredient, HSO_5^-) on the sonochemical removal of nitric oxide (NO) have been studied in a bubble column reactor. The initial concentration of NO studied ranged from about 500 to 1040 ppm. NaCl in the concentration range of 0.01−0.5 M was used as the electrolyte to study the effect of ionic strength. At the low NaCl concentration (0.01 M), the percent fractional removal of NO with initial concentration of 1040 ppm was enhanced significantly, while as the NaCl concentration increased, the positive effects were less pronounced. The presence of ∼2520 ppm SO_2 in combination with 0.01 M NaCl further enhanced NO removal. However, with a NO initial concentration of 490 ppm, the addition of NaCl was detrimental to NO removal at all NaCl concentration levels. The combinative effect of sonication and chemical oxidation using 0.005−0.05 M oxone was also studied. While the lower concentrations of HSO_5^- enhanced NO removal efficiency, higher concentrations were detrimental depending on the initial concentration of NO. It was also demonstrated that in the presence of ultrasound, the smallest concentration of oxone was needed to obtain optimal fractional conversion of NO.

Introduction

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the major species of the six compounds of nitrogen and oxygen jointly referred to as NO_x.[1] NO_x, together with sulfur dioxide (SO_2), is the major contributor to acid rain that harms forest crops and buildings, as well as aquatic life.[2,3] NO_x also constitutes one of the main ingredients involved in the formation of ground-level ozone and urban smog through photochemical reactions, which can trigger serious respiratory problems.[4,5] Unlike SO_2 and NO_2, NO emission from industrial and other stationary combustion sources is difficult to control by scrubbing because of its low solubility in aqueous solutions, which greatly increases the liquid-phase resistance to mass transfer.[1,6−7] In a previous study in a bubble column scrubber, the result of a blank test to determine the solubility of NO in Milli-Q water with no chemical additives (and in the absence of ultrasonic irradiations) using 1003 ppm of NO in N_2 bubbled at a flow rate of 1.7 standard liters per minute (slpm), indicated that the NO was not absorbed and NO gas breakthrough was instantaneous.[1]

One of the promising NO_x control strategies is the conversion of NO into NO_2 (or other more reactive and water-soluble species) followed by the simultaneous scrubbing of NO_2 and SO_2 from the flue gases. Numerous liquid adsorbents have been used for this purpose in various gas−liquid contactors.[1,7−12] We previously reported the absorption and oxidation of NO_x in aqueous solutions of peroxymonosulfate or oxone (with active ingredient, HSO_5^-) in a bubble column reactor using NO feed concentrations of about 500 or 1000 ppm.[7] It was shown that (1) the fractional removal ranged from 60 to 86%; (2) the highest removal of NO occurred at the lowest gas flow rate of 0.1 slpm for the range of flow rates (0.1−1.0 slpm) tested; (3) the NO removal efficiency was not significantly affected by temperature in the range of 22−55 °C; (4) the presence of SO_2 increased the overall fractional conversion of NO; and (5) the optimal fractional conversion occurred with 0.02 M oxone in the pH range of 6.5 to 8.5. The rate of reaction of NO with HSO_5^- was found to be first order with respect to NO and zero order with respect to HSO_5^-. Our results demonstrated the feasibility of removing NO_x and SO_x simultaneously by low-temperature aqueous scrubbing using oxone. Nevertheless, the additional costs of chemicals and the complexity of some aqueous scrubbing systems have, in general, discouraged commercial applications.[1,7−12] Still, scrubbing of NO_x with aqueous solutions promises to be less expensive than competing postcombustion dry processes for NO_x removal such as selective catalytic reduction (SCR) and thermal NO_x removal.[13−15] Thus, there is need in the aqueous scrubbing arena for environmentally friendly and cost-effective alternatives for comprehensive treatment of NO_x from industrial flue gases.[16]

In the atmosphere, gas-phase reactions primarily responsible for the effective oxidation of SO_2/NO_x to H_2SO_4/HNO_3 both involve the $^\bullet OH$ radical.[5] Photochemical methods involving the use of hydrogen peroxide (H_2O_2) to produce homogeneous distribution of hydroxyl ($^\bullet OH$) radicals at low temperature for postcombustion flue gas treatment have also been reported.[17−19] One promising method for the removal of nitric oxide from flue gases involving the in situ generation of $^\bullet OH$ radicals in aqueous systems at low temperature is sonochemical oxidation. Sonochemical techniques utilize ultrasound to produce an oxidative environment via acoustic cavitation due to the formation and subsequent collapse of microbubbles from acoustical wave-induced compression/rarefaction.[20] The collapse of these bubbles leads to local transient high temperatures (≥5000 K) and pressures (≥1000 atm), resulting in the generation of highly reactive species including $^\bullet OH$, hydrogen ($H^\bullet$) and hydroperoxyl

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($HO_2^•$) radicals, and H_2O_2.[20−26] Solute gas molecules near the collapsing bubbles react with the radicals and are readily oxidized. We recently demonstrated the feasibility of developing an innovative aqueous sonochemical scrubber to provide an environmentally conscious method for the control of NO_x and SO_2.[27,28] The results of the sonochemical removal of NO at a fixed frequency of 20 kHz in a sonochemical bubble column reactor operated in both semibatch and continuous countercurrent flow at about room temperature (23 ± 2 °C), and the effects of the flow rate of flue gas, intensity of ultrasound, and the presence of SO_2 on the fractional conversion of NO were reported. The concentration of NO studied ranged from 50 to 1040 ppm while that of SO_2 ranged from about 52 to 4930 ppm. It was shown that the fractional conversions of NO ranged from 60 to 85%, while complete removal of SO_2 was observed for all the concentrations studied. It was shown that increasing ultrasonic intensity from 55.2 to 86.8 W/cm^2 improved NO removal. Also, more enhanced absorption of NO was observed for the case of continuous countercurrent gas−liquid flow compared with semibatch flow. In addition, the presence of low to moderate concentrations of SO_2 (990−2520 ppm) was found to enhance NO removal. Material balance analyses also indicated that the main products of sonochemical oxidation or chemical oxidation by oxone were nitrite, nitrate, and sulfate.[7,27]

However, in general, the use of ultrasound by itself for the treatment of pollutants, is highly energy intensive since sonication is relatively inefficient with respect to total input energy and is therefore, not by itself, economically attractive. The coupling of ultrasound with chemical oxidation or intensification with inorganic salts and oxides presents interesting and unique chemistry, and offers significant advantage of improved functionality.[29−34] Recent studies have shown that increasing the ionic strength of the air-saturated aqueous solutions by the addition of salt enhances product yields in certain ultrasonic systems.[35−38] The extent of intensification of the sonochemical activity will depend on the type of reactants. When the pollutant is an organic compound, studies have shown that increasing the ionic strength of the aqueous solution by the addition of salt (or electrolyte) increases the extent of degradation because of the enhanced effect of the organic pollutants being driven toward the bubble-bulk interface (i.e., the so-called "salting out effect") where they are able to interact more effectively with $^•OH$ radicals upon collapse of the bubble.[32,33] The presence of dissolved salts can also intensify the cavitational activity by altering the physicochemical properties of the cavitating medium; the salt decreases the vapor pressure and increases the surface tension; though marginal this can help in promoting a more violent collapse of the cavitating bubble.[37] The presence of sodium chloride (NaCl) has also been shown to be highly beneficial to the mass-transfer of gases under ultrasonic irradiation. Kumar et al.[31] found the overall gas−liquid mass-transfer coefficient of oxygen (K_La, s^{-1}) was about 3−5 times more (depending on the ultrasonic power dissipation) in the presence of NaCl as compared to that obtained in the absence of NaCl. This beneficial effect was attributed to the fact that aqueous NaCl (or the electrolyte) is noncoalescing, leading to the generation of many small bubbles in the system, which increases the available gas−liquid interfacial area. However, in the sonochemical and sonophotocatalytic isolation of hydrogen from water, it was shown that the sonochemical process was influenced by the addition of NaCl (as Cl^- ions scavenged $^•OH$ radicals and also reduced H_2O_2 production).[39,40] Considering the prevalence of different types of inorganic salts and anions (especially NaCl and Cl^-) in flue gas scrubbing systems, additional research is needed to generalize and quantify the effects of ionic strength, cations, and anions on the sonochemical oxidation process. To understand the effects of ionic strength of the scrubbing solution and exploit the advantages of combinative sonochemical and chemical oxidation systems on NO fractional conversion, we have extended our previous study[27] to include the effects of NaCl and oxone (i.e., HSO_5^-) in the presence and absence of SO_2.

Experimental Section

Reagents. The reagent gases used were separate mixtures of NO and SO_2 in ultrapure nitrogen obtained from Air Products and Chemicals Company. The NO cylinders contained gases ranging from about 500 to 1040 ppm NO, while the SO_2 cylinders contained about 2520 ppm SO_2, all in ultrapure nitrogen as the carrier gas. The peroxymonosulfate (also known as monopersulfate), a triple salt of potassium ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ with catalog no. 21988-6) used, was obtained from Sigma Aldrich Chemical Co. and was used without further purification. The pulverized NaCl used, which had a purity of greater than 99.5%, and phosphate buffers consisting of separate compounds of potassium dihydrogen phosphate (KH_2PO_4 with catalog no. 22130-9) and disodium hydrogen phosphate (Na_2HPO_4 catalog no. 21988-6) were also obtained from Sigma-Aldrich. Milli-Pore water was used for all the sonication experiments in order to reduce the presence of impurities. The Milli-Q included electrodeionizing (ELIX) and reverse osmosis (RiOs) water purification systems from the Millipore Corporation. The combination system is capable of producing purified water with a resistivity of ≤18.2 MΩ·cm at 25 °C and reducing the total organic carbons (TOC), silicates, and heavy metals to very low part per billion levels, if any. Samples of the purified water were analyzed prior to use in the experimental runs using a Dionex-DX 500 ion chromatograph (IC) and found to be free of trace amounts of sulfates, nitrites, and nitrates.

Apparatus and Procedure. The sonochemical bubble column scrubbing system used for this work consists of a jacketed bubble column reactor made of 10 cm i.d. by 30 cm long Pyrex glass, a sparger dispersion tube with a 25 mm diameter disk (porosity of grade C, 25−50 μm, ACE Glass), a digital sonifier, a flue gas blending system, and an analytical train as shown in Figure 1. The entire experimental setup has been discussed in details elsewhere.[27] The experiments could be performed in both the semibatch mode of run (in which the liquid phase is stationary, while the gas phase flows continuously) and continuous mode of run (where both liquid and gas phases flow continuously in countercurrent flow). The upward flow of the gases through the liquid produces bubbles that promote mixing of the liquid and the flue gas. At the same time ultrasonic waves from the sonifier are emitted into the solution. The total volume of liquid water used was 1.2 L, corresponding to a liquid height of about 0.24 m. An extender allows the probe of the sonicator to extend about 0.15 m below the surface of the solution in the reactor. The ultrasonic system consists of a digital sonifier model 450 obtained from Branson with a maximum power output of 400 W at a fixed frequency of 20 kHz and a variable amplitude that increases directly with power. According to the manufacturer's recommendation the amplitude was not to exceed 70%. As a result, the maximum amplitude used for this work was set at 70%, corresponding to a power output of about 110 W (power intensity of 86.8 W/cm^2 or power density of about 0.1 W/ml for our system). The power density (i.e., power/volume of liquid) gives an idea about the energy dissipated in the solution to bring

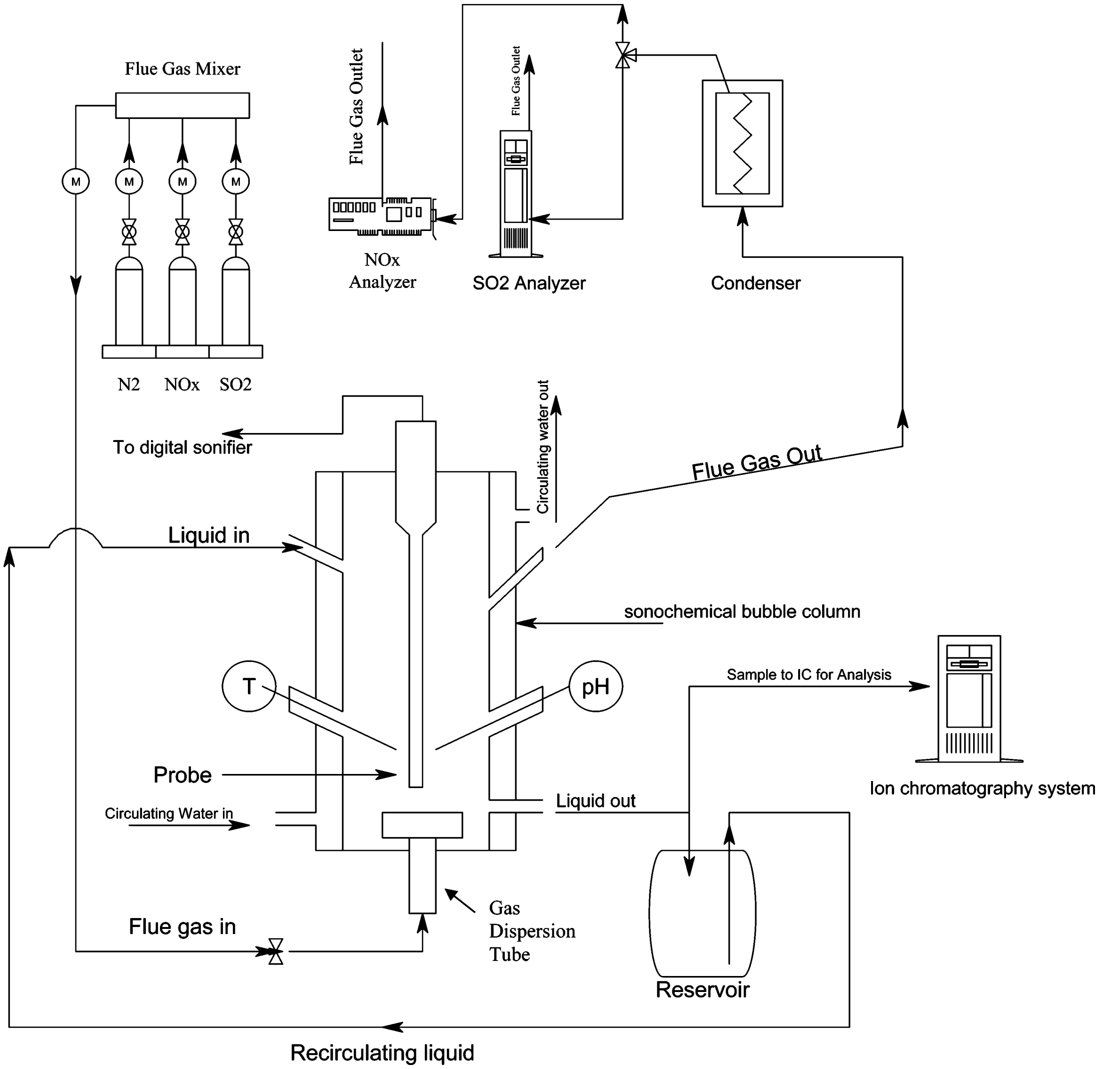


Figure 1. Experimental setup of sonochemical bubble column scrubber.

the desired change. Power intensity (i.e., power/vibration area or transducer's tip surface area) and power density both indicate the energy requirement of the process and assist in proper utilization of energy for a given chemical reaction. The concentration of NaCl used ranged between 0.01 and 0.5 M, while the concentration of oxone ranged between 0.005 and 0.05 M. The aqueous solutions used for the combinative ultrasound–oxone experiments were buffered with 0.025 M each of KH_2PO_4 and Na_2HPO_4 buffers. The oxone solution makes the scrubbing water acidic, but simultaneous NO/SO_2 scrubbing is effective in the pH range of 6–8 and so it was necessary to buffer the aqueous solution for oxone runs.[7] The aqueous solutions used for all other sonochemical scrubbing experiments were not buffered.

The experiments were run at approximately room temperature (23 ± 2 °C), with the heat generated from the ultrasonic irradiation removed via the water jacket of the reactor. The experiments in this study were conducted in the continuous countercurrent mode with the aqueous phase being circulated at approximately 0.475 L/min. The results of our previous work suggest that the cumulative effect of bulk mixing caused by both the mechanical circulation in the continuous mode of operation and, more importantly, the uniform mixing and interfacial turbulence at microscopic level created by the ultrasound enhanced the NO removal.[27] Also, the continuous accumulation of reactive radicals available for reaction with NO gas improves as the liquid is continuously recirculated. The flow rate of the gas mixture was maintained at 0.1 slpm or superficial velocity of 0.0034 m/s for all experimental runs. The exiting gas from the reactor is passed through a condenser that is cooled to about 1 °C or less. The cold trap, serves to remove any moisture carried in the gas mixture before exiting the reactor into the analyzer. The concentrations of input and output gases were analyzed using a chemiluminescence $NO-NO_2-NO_x$ analyzer and a fluorescence SO_2 analyzer. Solution pH values and ion concentrations were measured by an Orion pH meter and a Dionex-DX 500 IC, respectively.

Theoretical Background. The primary process of sonolysis of water results in the formation of $^\bullet$H and $^\bullet$OH radicals with the possibility of these active species reacting with each other to produce hydrogen (H_2) and H_2O_2 according to the following reactions:[20,29–30]

$$H_2O \xrightarrow{)))} {}^\bullet H + {}^\bullet OH \tag{1}$$

$${}^\bullet H + {}^\bullet H \rightarrow H_2 \tag{2}$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \tag{3}$$

Nitrite and nitrate are known sonochemical products in N_2-containing solutions. Wakeford et al.[35] found that the sonication of nitrogen- and air-saturated water at 35 kHz generated nitrite and nitrate as well as hydrogen peroxide. However, there was a dramatic improvement in the yields of nitrite and nitrate from the ultrasonic irradiation of air-saturated water compared to yields from nitrogen-saturated water. The rate of hydrogen peroxide was found to be approximately twice the rate of nitrite formation, which in turn was approximately twice the rate of nitrate formation. The yields of nitrite and nitrate in nitrogen-saturated water were only 10−15% of those in air-saturated water; the presence of molecular oxygen appears to enhance product yields. Kruus et al.[41] studied the formation of nitrite and nitrate ions in water under irradiation with 900 kHz (27W) ultrasound as a function of time, temperature, and gas (oxygen/nitrogen) composition. With 100 mL of water at 278 K sparged with nitrogen/oxygen gas mixtures with a total flow of 2.9 mL s^{-1} of gas (superficial velocity and sparger dimension are not given in this study) for 20 min, the highest rate of total nitrate plus nitrite (NO_x^-) obtained (measured as nitrate after treating solution with H_2O_2) was 1.6×10^{-4} M. They found that the reaction needed O_2 in order to proceed to a significant degree; no NO_x^- was detected in the absence of oxygen gas. Petrier et al.[42] proposed pathways to explain the sonochemical oxidation of nitrogen inside the cavitation bubble at high temperatures involving oxygen atoms produced by oxygen dissociation ($O_2 \rightarrow 2O$) reactions.

Nitric oxide undergoes either gas-phase reactions in the acoustic cavities or with hydroxyl radicals in the interfacial zone and in bulk solution, ultimately resulting in the formation of nitrous and nitric acids:[20,27] On the basis of the results of our previous study, we hypothesized the following reaction pathways for the sonochemical oxidation of NO, most likely taking place in the bubble-liquid interface.[27]

$$NO + {}^{\bullet}OH \rightarrow HNO_2 \tag{4}$$

$$HNO_2 + {}^{\bullet}OH \rightarrow HNO_3 + H^{\bullet} \tag{5}$$

$$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O \tag{6}$$

Overall:

$$NO + 3{}^{\bullet}OH \rightarrow HNO_3 + H_2O \tag{7}$$

The oxidation of the nitrite to nitrate by the sonochemically generated H_2O_2 was also thought to proceed in the liquid-bubble interface or in the bulk solution via[27,43−44]

$$H_2O_2 + NO_2^- \rightarrow NO_3^- + H_2O \tag{8}$$

Kruus et al.[41] also found that the differences in the NO_2^-/NO_3^- ratio found between various studies could be explained through a mechanism where HNO_2 and HNO_3 were formed in the gas phase of the imploding cavity, and then dissolved in the water and dissociated to ions, with NO_2^- species substantially favored initially as considerably more NO was formed than NO_2; the NO_2^- subsequently reacting with hydrogen peroxide to give NO_3^- (eq 8) much like the process used to convert nitrite to nitrate for total fixed nitrogen determination. They observed that this conversion was favored at lower pH values, and the pH decreased with time of sonication, suggesting that the conversion occurs in the aqueous phase rather than in the imploding cavity. They also found that the rate of H^+, NO_3^-, and NO_x^- ion concentrations after 20 min of irradiations decreased as a function of temperature between 25 °C and 40 °C. In our previous study, the determination of NO_2^-/NO_3^- produced by NO_x oxidation was obtained by subtracting the amount produced in a controlled reaction with only N_2 flow from the amount obtained with NO-containing N_2 flow.[27]

A similar mechanism for the oxidation of SO_2 by ${}^{\bullet}OH$ radical in the bubble-liquid interface was also provided as[27]

$$SO_2 + {}^{\bullet}OH \rightarrow HSO_3 \tag{9}$$

$$HSO_3 + {}^{\bullet}OH \rightarrow H_2SO4 \tag{10}$$

Overall:

$$SO_2 + 2{}^{\bullet}OH \rightarrow H_2SO_4 \tag{11}$$

The overall stoichiometry for the simultaneous oxidation of both NO and SO_2 by ${}^{\bullet}OH$ in the bubble-liquid interface was summarized as

$$SO_2 + NO + 5{}^{\bullet}OH \rightarrow H_2SO_4 + HNO_3 + H_2O \tag{12}$$

Also, the oxidation of HSO_3^- in the bubble-liquid interface or bulk solution by sonochemically generated H_2O_2 was also thought to be possible via[24,27]

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O \tag{13}$$

Oxone is the first neutralization salt of peroxymonosulfuric acid H_2SO_5 (also known as Caro's acid), a triple salt of potassium ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) consisting of a 2:1:1 mixture of the active ingredient $KOSO_2OOH$, along with $KHSO_4$ and K_2SO_4, and is written in aqueous solutions as HSO_5^-.[7,45−46] It is a strong oxidant that may be regarded as a monosubstituted derivative of hydrogen peroxide but with an oxidation potential greater than that of hydrogen peroxide (H_2O_2), ($E_{HSO_5^-/HSO_4^-} = 1.82$ eV) versus ($E_{H_2O_2/H_5O} = 1.776$ eV). The peroxymonosulfate ion (HSO_5^-) is also a strong acid with $pK_{a1} < 0$ and $pK_{a2} = 9.88 \pm 0.1$ at 15 °C. It is stable in acidic to neutral pH range but decomposes fairly rapidly to yield oxygen when pH = pK_{a2}. In our previous study we proposed the following scheme of reactions to describe the absorption−oxidation of NO by HSO_5^- in the absence of SO_2.[7]

$$NO_{(g)} \rightarrow NO_{(aq)} \tag{14}$$

$$NO_{(aq)} + HSO_5^- \rightarrow NO_{2(aq)} + HSO_4^- \tag{15}$$

$$2NO_{2(aq)} + HSO_5^- + H_2O \rightarrow 2NO_3^- + 2H^+ + HSO_4^- \tag{16}$$

$$2NO_{(aq)} + HSO_5^- + H_2O \rightarrow 2NO_2^- + HSO_4^- + 2H^+ \tag{17}$$

$$HSO_5^- + NO_2^- \rightarrow SO_4^{2-} + HOONO \tag{18}$$

$$HOONO \xrightarrow{\text{fast}} H^+ + NO_3^- \tag{19}$$

The stoichiometry for the moles of the oxidant, peroxomonosulfate ion, consumed to the moles of reactant, NO, converted to nitrate ion in solution was obtained by combining the reaction pathways outlined in eqs 15−19. Consider the oxidation of $NO_{(aq)}$ to $NO_{2(aq)}$ by HSO_5^- in eq 15 followed by further oxidation of $NO_{2(aq)}$ to nitrate ion by HSO_5^- as in eq 16, then combine eq 15 with eq 16 to give the overall reaction

$$2NO + 3HSO_5^- + H_2O \rightarrow 2NO_3^- + 3HSO_4^- + 2H^+ \qquad (20)$$

Also, consider the oxidation of NO to nitrite ion by HSO_5^- (eq 17) and subsequent oxidation of the nitrite ion to nitrate ion via eqs 18 and 19 to give the overall reaction

$$2NO + 3HSO_5^- + H_2O \rightarrow 2NO_3^- + HSO_4^- + 2SO_4^{2-} + 4H^+ \qquad (21)$$

In the presence of SO_2, peroxomonosulfate reacts predominantly with bisulfite species in the pH range of 3.8−7.9 according to the reaction[45]

$$HSO_5^- + HSO_3^- \rightarrow 2SO_4^{2-} + 2H^+ \qquad (22)$$

Betterton and Hoffmann studied the oxidation of aqueous SO_2 by HSO_5^- and H_2O_2.[46] It was reported that the rate of S (1 V) oxidation by HSO_5^- was comparable to the oxidation by H_2O_2 and that HSO_4^- was the only detectable oxidation product; they concluded that peroxomonosulfate reacts predominantly with the bisulfite species.

Results and Discussion

The efficiency (E_f) of the sonochemical scrubber is determined from the percent fractional removal of feed gas, NO or SO_2, that is, the fractional conversion defined as

$$E_f = 1 - \left(\frac{[\text{gas}]_{\text{out}}}{[\text{gas}]_{\text{in}}}\right) \qquad (23)$$

where $[\text{gas}]_{\text{in}}$ and $[\text{gas}]_{\text{out}} = [\text{gas}]_{\text{in}} \times (1 - \text{conversion})$ are steady state gas concentration values as recorded from the analyzers and corrected with a calibrating curve. The effectiveness of the sonochemical removal of pollutants was evaluated by measuring the breakthrough times (i.e., the time when the absorption capacity of the sonicated solution is exhausted and significant amount of the gas passes through without being removed). Typical experimental conditions and results of tests conducted are illustrated in Figures 2−8. In general, there are initial dips in the concentrations of NO partly attributable to mixing and dilution effects of purge gas (i.e., N_2). Similar observations were made in our previous studies.[1,7,27] These initial dips lasting about 3 min here and representing almost complete removal of NO are followed by actual absorption induced by ultrasound. Also, it is important to note that despite the thermostatic control of the experiments, the bulk liquid temperatures for all experiments increased slightly from 23 ± 2 °C initially and stabilized at 33 ± 2 °C. Higher temperatures decrease cavitation threshold by reducing surface tension and viscosity, resulting in the formation of higher number of cavitation sites. However, the increase in vapor pressure of the liquid now allows vapor to enter the forming bubbles more easily, thus cushioning their implosions and resulting in lower internal temperatures at the end of bubble collapse. On the other hand, the increased amount of water vapor in the bubble can also promote formation of free radicals from dissociation of water molecules. An optimum reaction temperature is typical in sonochemical processes with the optimum temperature dependent on the reaction medium and specific reaction. In general, at temperatures well below the boiling point of water (i.e, <60 °C), an increase in temperature leads to an increase in degradation rate assuming the temperature reached in the bubble is not influenced by aqueous-phase temperature. However, at temperatures >60 °C, the effectiveness of aquasonolysis decreases as temperature increases because of the higher vapor pressure of water.[47] The effects of temperature on sonochemical reaction rates and mechanisms are discussed in more detail elsewhere.[20,24,47−50] On the basis of the mechanisms of NO oxidation (eqs 4−6) discussed earlier, the increase in liquid temperature (from about 23 ± 2 °C to 33 ± 2 °C) would be expected to increase the rate of diffusion of NO from the bulk liquid to the reaction zone (i.e., bubble-liquid interface) to react with a higher concentration of $^{\bullet}OH$ radicals resulting from the dissociation of water molecules, resulting in an increased transformation of NO_x to product. However, the effects of temperature on the sonochemical oxidation of NO_x will need to be studied in detail and these suggestions verified experimentally, but this is beyond the scope of the current study.

Sonochemical Oxidation of NO in the Presence of NaCl and SO_2. Typical flue gas contains up to 100 ppmv of chlorides depending on the coal and method of combustion.[17] It is also well-known that NaCl is the principal mineral constituent of seawater (the most available water on earth) and its concentration is 2.7%.[40] The effect of ionic strength on the sonochemical removal of NO was investigated by absorbing about 500 or 1040 ppm NO in aqueous solutions containing 0.01−0.5 M NaCl irradiated with ultrasound at a power of 110 W and intensity of 86.8 W/cm^2. The results of these experiments are illustrated in Figures 2 and 3 along with that of ultrasonic irradiation in the absence of NaCl. Figure 2 shows the decrease of the outlet NO concentration with time in the presence of different solution concentrations of NaCl. Figure 3 depicts the steady-state percent fractional conversions of NO observed after about 10 min as a function of NaCl solution concentrations. As shown in Figure 2, the percent fractional removal of NO (with inlet concentration of 1040 ppm) was observed to increase from 64.9 (in the absence of NaCl) to 76% in the presence of 0.01 M NaCl. However, as the concentration of NaCl was varied from 0.01 to 0.5 M, the fractional NO removal decreased gradually with increasing NaCl concentration. Recent studies have described possible effects of the NaCl on sonochemical reactions.[35,39] In the presence of NaCl, the following complex reactions occurring with the sonolytically generated $^{\bullet}OH$ radical and H_2O_2 are possible:

$$^{\bullet}OH + Cl^- \rightarrow OH^- + Cl^{\bullet} \qquad k_{24} = 4.3 \times 10^9\ M^{-1}\ s^{-1} \qquad (24)$$

$$H_2O_2 + Cl^{\bullet} \rightarrow HO_2^{\bullet} + HCl \qquad k_{25} = 4.5 \times 10^7\ M^{-1}\ s^{-1} \qquad (25)$$

$$^{\bullet}OH + Cl^- \rightarrow ClOH^{\bullet -} \qquad k_{26} = 4.3 \times 10^9\ M^{-1}\ s^{-1} \qquad (26)$$

$$ClOH^{\bullet -} \rightarrow {}^{\bullet}OH + Cl^- \qquad k_{27} = 6.1 \times 10^9\ M^{-1}\ s^{-1} \qquad (27)$$

$$ClOH^{\bullet -} + Cl^- \rightarrow Cl_2^{\bullet -} + OH^- \qquad k_{28} = 2.5 \times 10^5\ M^{-1}\ s^{-1} \qquad (28)$$

$$ClOH^{\bullet -} + H^+ \rightarrow Cl^{\bullet} + H_2O \qquad k_{29} = 1.0 \times 10^9\ M^{-1}\ s^{-1} \qquad (29)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -} \qquad k_{30} = 8.5 \times 10^9\ M^{-1}\ s^{-1} \qquad (30)$$

$$Cl_2^{\bullet -} + {}^{\bullet}OH \rightarrow HOCl + Cl^- \qquad k_{31} = 1.0 \times 10^9\ M^{-1}\ s^{-1} \quad (31)$$

$$Cl_2^{\bullet -} + H_2O_2 \rightarrow HO_2^{\bullet} + 2Cl^- + H^+ \qquad k_{32} = 4.1 \times 10^4\ M^{-1}\ s^{-1} \quad (32)$$

$$Cl_2^{\bullet -} + HO_2^{\bullet} \rightarrow 2Cl^- + H^+ + O_2 \qquad k_{33} = 3.0 \times 10^9\ M^{-1}\ s^{-1} \quad (33)$$

$$Cl^{\bullet} + HO_2^{\bullet} \rightarrow HCl + O_2 \qquad k_{34} = 3.1 \times 10^9\ M^{-1}\ s^{-1} \quad (34)$$

The presence of chloride leads to the rapid formation of various reactive chlorinated inorganic radicals ($Cl^{\bullet}$, $HClOH^{\bullet}$/$ClOH^{\bullet -}$, $Cl_2^{\bullet -}$) similar to those described in atmospheric chemistry.[4−5,51−58] Because of the scavenging of $^{\bullet}OH$ radicals, eq 24 and eq 26 (k for both is $4.3 \times 10^9\ M^{-1}\ s^{-1}$), it is thought that the probability of the collisions for $^{\bullet}OH$ radicals (eq 3, $k_3 = 6.0 \times 10^9\ M^{-1}\ s^{-1}$) would be reduced and the dimerization (and hence formation of H_2O_2) would be impeded.[39] Also, electron transfer between chloride anions and one of the strongest oxidants known, $^{\bullet}OH$ radicals (eq 24) followed by proton transfer (eq 30), leads to the formation of chlorine radicals ($Cl^{\bullet}$, $Cl_2^{\bullet -}$), which are less oxidative than $^{\bullet}OH$ radicals, an effect referred to as anion scavenging of $^{\bullet}OH$ radicals. For example, the reactivity of $Cl_2^{\bullet -}$ in general is lower than that of the $^{\bullet}OH$ radical since its reduction potential is low: 2.09 V versus NHE compared with $^{\bullet}OH$ ($^{\bullet}OH + H^+ + e^- \rightarrow H_2O$, $E° = 2.33$ V).[53,55] This would explain the decrease in the oxidative removal of NO in the bubble-liquid interface (based on eqs 4 and 5) as chloride concentration increases. However, the hypochlorous acid ion ($ClOH^{\bullet -}$) in eq 26 is a very effective oxidizing agent and once formed, it is capable of reacting with both NO and dissolved NO_2 to form both nitrous and nitric acids according to the reactions

$$ClOH^{\bullet -} + NO \rightarrow HNO_2 + Cl^- \quad (35)$$

$$ClOH^{\bullet -} + NO_{2(aq)} \rightarrow HNO_3 + Cl^- \quad (36)$$

Also, the hypochlorous acid (HOCl) in eq 31 with an oxidizing potential of 1.49 V ($HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$)[59] is known to react with nitrite ion (NO_2^-) in aqueous solutions as in eq 37 with second-order rate constant, $k\ (M^{-1}\ s^{-1}) = (3.82 \times 10^5)e^{-6450/RT}$, where $R = 1.987$ cal/mol K and T is in Kelvin:[59−60]

$$NO_2^- + HOCl \rightarrow NO_3^- + Cl^- + H^+ \quad (37)$$

These side reactions are believed to be also responsible for the enhanced fractional removal of the NO in the presence of low concentration of NaCl since chloride is nonvolatile and so would not be expected to enter the gas-phase of the cavity to any appreciable extent. However, the decline in the fractional removal of NO at high NaCl concentration could be due to a progressive increase in chloride ions that penetrate the interfacial zone and are more susceptible to the scavenging effect of $^{\bullet}OH$ radicals.

The results of our study are consistent with the effects of chloride on sonochemical oxidation reactions reported by other investigators. In a study on the effect of NaCl on the sonochemical formation of H_2O_2 formation in the presence of ultrasonic irradiation, it was reported that the decline in peroxide yield that was observed at high chloride concentrations might be due to the scavenging of $^{\bullet}OH$ radicals by chloride ions.[35,39−40]

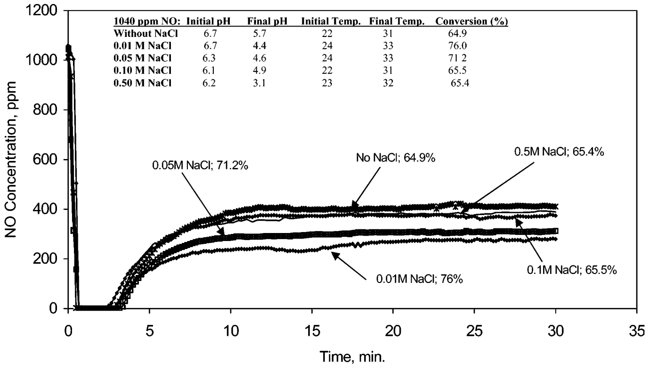
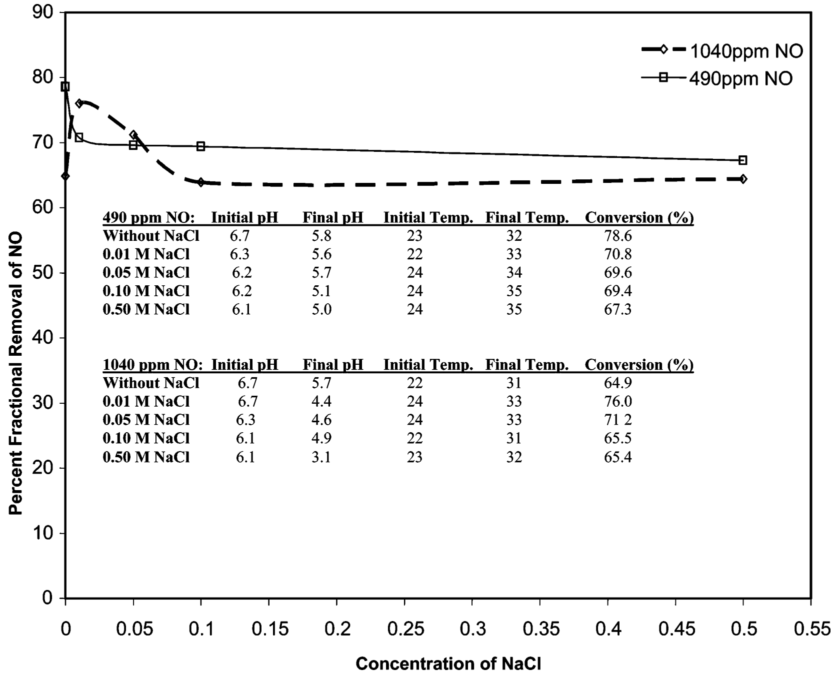


Figure 2. Effect of varying concentrations of NaCl on the absorption of NO during ultrasonic irradiation ($[NO]_0$, = 1040 ppm, gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; $I = 86.8$ W/cm^2).

Wakeford et al.[35] also investigated the effect of ionic strength (with NaCl and sodium sulfate) on the acoustic fixation of nitrogen and the rate of nitrite production using a 35 kHz ultrasound on a 659 mL sample at 293 K, but no power data was provided. The initial rapid decrease in H_2O_2 yields in argon-saturated NaCl solution (20% w/v) was attributed to the scavenging of those $^{\bullet}OH$ radicals, which are relatively accessible to the chloride ions at the liquid/bubble interface. It was indicated that, for air-saturated NaCl solutions, reactive chlorine species generated within the collapsing cavities could conceivably react in the interfacial zone with nitrogen oxides produced, leading to enhanced concentration of nitrite and nitrate. Using NaCl as the electrolyte, it was shown that the nitrite concentration resulting from sonication increased from 0.25 μmol dm^{-3} min^{-1} at zero ionic strength up to 1.25 μmol dm^{-3} min^{-1} at ionic strength of 3.5 mol dm^{-3} after which the nitrite concentration began to fall. It has also been shown in the degradation of formic acid (HCOOH) at 590 kHz and 40 W (3.2 W/cm^2 or 0.05 W/ml) in the presence of NaCl that the extent of intensification increased with the increase in the concentration of NaCl until an optimum concentration of 4 wt % was obtained, beyond which the increase is either marginal (for initial HCOOH concentration of 500 mg/l) or the extent of degradation decreased (for 1000 mg/l initial concentration).[36] These observations are consistent with our results for the initial NO equal to 1040 ppm depicted in Figure 3, which shows significant increase in the fractional conversion of NO in the presence of 0.01 M NaCl, followed by a decline in fractional conversion with increase in NaCl concentration. However, with lean initial NO concentration (490 ppm), the presence of 0.01 M NaCl slightly lowers the fractional conversion from about 78.6% (without NaCl) to 70.8%, beyond which the changes in fractional conversion as the NaCl concentration increases become insignificant. It appears that in the presence of lean initial concentration of NO, the hypochlorous acid anion is not as effective an oxidant for the NO_x, and the scavenging of the $^{\bullet}OH$ radicals by the chloride ion reduces the oxidation of NO_x, resulting in the lowering of the NO fractional conversion.

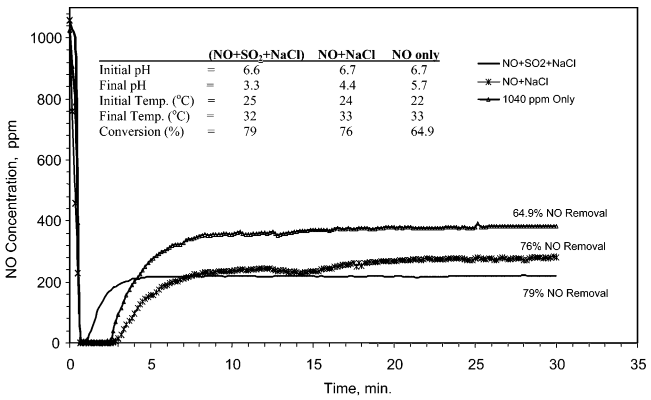
The effect of ionic strength on NO removal in the presence of SO_2 was also studied. The concentration−time graph is shown in Figure 4. On the same plot are shown the removal of 1040 ppm NO alone, 1040 ppm NO in the presence of 0.01 M NaCl, and 1040 ppm NO in the presence of 2520 ppm SO_2 and 0.01 M NaCl. Since the concentration of NaCl was optimized at the lowest concentration (0.01 M) by investigating the effect over a range of concentrations (0.0−0.5 M) as shown in Figures 2 and 3, our goal here was to study the possible synergistic effects of SO_2 at the optimal NaCl concentration and not at the



490 ppm NO:	Initial pH	Final pH	Initial Temp.	Final Temp.	Conversion (%)
Without NaCl	6.7	5.8	23	32	78.6
0.01 M NaCl	6.3	5.6	22	33	70.8
0.05 M NaCl	6.2	5.7	24	34	69.6
0.10 M NaCl	6.2	5.1	24	35	69.4
0.50 M NaCl	6.1	5.0	24	35	67.3

1040 ppm NO:	Initial pH	Final pH	Initial Temp.	Final Temp.	Conversion (%)
Without NaCl	6.7	5.7	22	31	64.9
0.01 M NaCl	6.7	4.4	24	33	76.0
0.05 M NaCl	6.3	4.6	24	33	71 2
0.10 M NaCl	6.1	4.9	22	31	65.5
0.50 M NaCl	6.1	3.1	23	32	65.4

Figure 3. Effect of varying concentrations of NaCl on NO fractional conversion for different inlet NO concentrations during ultrasonic irradiation (gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; I = 86.8 W/cm^2)



		(NO+SO_2+NaCl)	NO+NaCl	NO only
Initial pH	=	6.6	6.7	6.7
Final pH	=	3.3	4.4	5.7
Initial Temp. (°C)	=	25	24	22
Final Temp. (°C)	=	32	33	33
Conversion (%)	=	79	76	64.9

Figure 4. Combinative effect of 0.01 M NaCl and 2520 ppm SO_2 on the fractional conversion of NO during ultrasonic irradiation ($[NO]_0$ = 1040 ppm, gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; I = 86.8 W/cm^2).

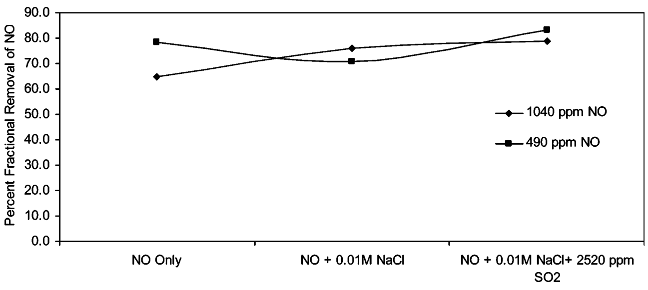


Figure 5. Comparison of the combinative effect of 0.01 M NaCl and 2520 ppm SO_2 on the fractional conversions of NO during ultrasonic irradiation for two different initial Cconcentrations ($[NO]_0$ = 490 and 1040 ppm, gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; I = 86.8 W/cm^2).

concentration where NaCl effects are marginal or detrimental. As shown in Figure 4, the fractional NO conversions were 64.9%, 76%, and 79%, respectively, for sonication alone, sonication in the presence of NaCl, and sonication in the presence of both NaCl and SO_2. For the same experimental conditions as in Figure 4 but with the lean initial concentration of NO of 490 ppm, the fractional conversion of NO was 83.3% in the presence of 2520 ppm SO_2 and 0.01 M NaCl as shown in Figure 5. The results suggest that the positive effects of the moderate amount of both SO_2 and NaCl on the sonochemical oxidation NO are additive. Also, it should be mentioned that, in aqueous chemical systems containing S(IV) and NO_x species (without the influence of ultrasound irradiation), the possibility of other side reactions between the bisulfite ion (HSO_3^-) and $NO_{2(aq)}$, nitrite (NO_2^-), or nitrous acid (HNO_2) in the pH range 3−8 resulting in the formation of N−S intermediates such as hydroxylamine disulfonate ($HON(SO_3)_2^=$ or HADS) and nitrososulfonic acid ($ONSO_3^-$ or NSS), and hence leading to enhanced NO removal, has been reported.[7] Hence, the observed enhanced NO removal in the presence of ultrasound and SO_2 could also be partially due to the reaction of NO_2 (from the sonochemical oxidation of NO) with HSO_3^- ion from dissolved SO_2 to form N−S complexes.

Sonochemical Oxidation of NO in the Presence of Oxone. The efficiency of using oxone for the simultaneous removal of NO and SO_2 has been demonstrated as discussed earlier.[7] In this work, we intend to investigate the combinative effect (if any) of the chemical oxidation by oxone and ultrasonic irradiation. The experiments were carried out by absorbing 490 and 1040 ppm NO separately in the sonochemically irradiated water in the presence or absence of 0.02 M oxone at an intensity of 86.8 W/cm^2 (110 W) in the continuous mode. The choice of the 0.02 M oxone concentration level was based on the results of previous work, which indicated that oxone in the concentration range of 0.015−0.02 M was optimal for scrubbing NO in the simulated flue gases of the same inlet concentrations of NO used in this study.[7] It was therefore of interest to test if this will also be the case in the presence of ultrasound. The results of this study are illustrated in Figures 6 and 7. At the lower inlet concentration of NO, the presence of oxone did not show an improvement. Fractional removal was 78.6% for the case with ultrasonic irradiation alone compared with 65.3% for the combined ultrasound and 0.02 M oxone system (Figure 6). However, for the higher inlet concentration of NO (1040 ppm), the oxone appears slightly detrimental initially, and the marginal

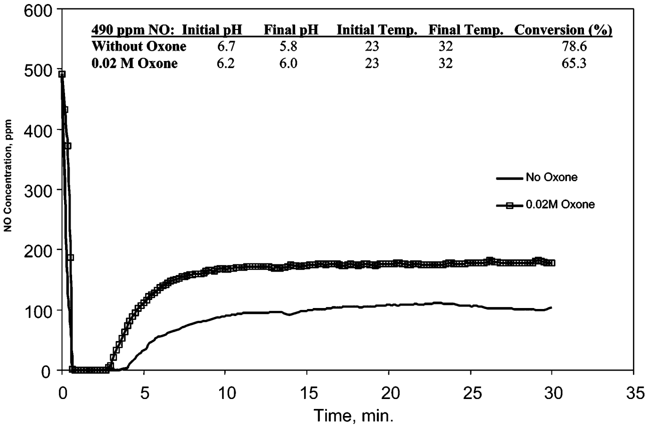


Figure 6. Combined effect of ultrasound and 0.02 M oxone on the removal of 490 ppm NO (gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; $I = 86.8$ W/cm^2).

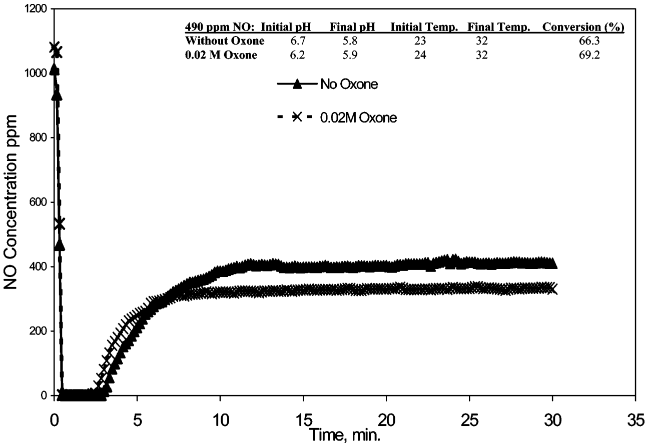


Figure 7. Combined effect of ultrasound and 0.02 M oxone on the removal of 1040 ppm NO (gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; $I = 86.8$ W/cm^2).

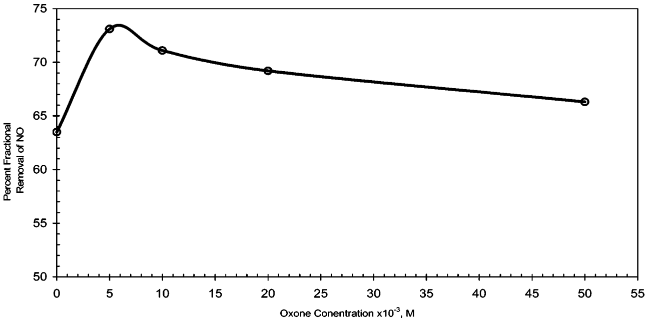


Figure 8. Combined effect of ultrasound and different concentrations of oxone (0.005, 0.01, 0.02, 0.05 M) on the NO fractional conversion ($[NO]_0 = 1040$ ppm, gas flow rate = 0.1 slpm; liquid flow rate = 0.475 L/min; $I = 86.8$ W/cm^2).

beneficial effect was not obvious until after 10 min when the outlet concentration of NO reached steady state. The fractional removal of NO of 69.2% in the combinative ultrasound−oxone system was slightly higher than the 66.3% obtained for ultrasonic irradiation alone after steady state (Figure 7). As illustrated in Figure 8, in the combined ultrasound−oxone scrubbing of feed gas containing 1040 ppm NO in continuous mode using different oxone concentrations of 0.005, 0.01, 0.02, and 0.05 M, the highest fractional removal of NO was obtained at the low oxone concentration of 0.005 M. In our previous study of NO absorption into the same concentration range of oxone but in the absence of ultrasound, a similar optimal fractional conversion for NO was observed but at a higher oxone concentration of 0.02 M.[7] The results obtained in this study indicate that, in the presence of ultrasound, while low concentrations of oxone improves the fractional removal of NO, higher concentrations of oxone are detrimental to NO removal. The results also indicate that in the presence of ultrasound, a smaller amount of the chemical oxone is needed to obtain optimal fractional conversion of NO.

Finally, it is important to discuss the possible effects of the phosphate buffers used in the ultrasound−oxone system. It has been reported that at the surface of the collapsed bubble, the $^{\bullet}OH$ concentration is a maximum and is estimated between 4×10^{-3} and 10^{-2} M.[25,41,61−62] The second rate constants for the recombination of the $^{\bullet}OH$ radicals (generated from sonolysis) to form H_2O_2 according to eq 3 is $k = 6.0 \times 10^9$ M^{-1} s^{-1}. This is comparable to that of the reaction of $^{\bullet}OH$ with NO (eq 4), NO_2^-, and HNO_2 (eq 5), which are 1.0×10^{10} M^{-1} s^{-1}, 1.0×10^{10} M^{-1} s^{-1}, and 2.6×10^9 M^{-1} s^{-1}, respectively.[63−68] On the other hand, the various phosphate species react with $^{\bullet}OH$ radicals at rates generally lower than the rates of $^{\bullet}OH$ with the NO_x species, and the rates depend on the particular species present according to the following reactions:[61]

$$^{\bullet}OH + PO_4^{3-} \rightarrow \text{product} \qquad k_{38} < 1.0 \times 10^7\ M^{-1}\ s^{-1} \quad (38)$$

$$^{\bullet}OH + HPO_4^{2-} \rightarrow \text{product} \qquad k_{39} = 1.5 \times 10^5\ M^{-1}\ s^{-1} \quad (39)$$

$$^{\bullet}OH + H_2PO_4^{-} \rightarrow OH^- + H_2PO_4^{\bullet} \qquad k_{40} = 2.0 \times 10^4\ M^{-1}\ s^{-1} \quad (40)$$

$$^{\bullet}OH + H_3PO_4 \rightarrow H_2O + H_2PO_4^{\bullet} \qquad k_{41} = 2.7 \times 10^6\ M^{-1}\ s^{-1} \quad (41)$$

Therefore, the competition for $^{\bullet}OH$ radicals could be expected to be least in the pH region of $H_2PO_4^-$ and HPO_4^{2-} used in our buffer system; hence, the impact on our ultrasound−oxone system is expected to be minimum. For comparison, it is also important to discuss briefly, the results from our previous study using oxone alone (buffered with 0.025 M phosphate solution) at 22°C for the oxidation of NO. For the cases in which the inlet concentrations of NO are 490 ppm and 1040 ppm (flow rate = 0.1 slpm) but in the absence of SO_2, the results indicated that the NO was initially almost completely absorbed in both cases but breakthrough times were short (<5 min) and the exit gas concentrations rapidly rose and stabilized at 450 ppm (8% conversion) and 770 ppm (26% conversion), respectively.[7] However, with the same inlet NO concentrations but in the presence of 2520 ppm SO_2, the instantaneous removals of NO were over 99%, and the exit concentrations of NO stabilized at 70 ppm and 170 ppm representing fractional conversion efficiencies of 86% and 84%, respectively, and there were no breakthroughs observed for over 30 min or the duration of the experiments. These results are explained in detail elsewhere.[7]

Among promoters, H_2O_2 is characterized by the generation of hydroxyl radicals, while oxone is capable of inducing the formation of sulfate and hydroxyl radicals.[57] The kinetic parameters of the first-order oxone decomposition, i.e., the rate constant and activation energy, have been calculated to be 111.3 kJ mol^{-1} and 3.1×10^{13} s^{-1}, respectively, the former being similar to the value reported for the auto-decomposition of H_2O_2 (i.e., 99.5 kJ mol^{-1}).[57,69−72] Under sonication conditions, it is plausible that the breakdown of a HSO_5^- molecule occurs in a way similar to that reported extensively for a H_2O_2 molecule, that is, a scission of the type[57−58]

$$HSO_5^- \xrightarrow{)))} {}^\bullet OH + SO_4^{\bullet -} \qquad (42)$$

leading to the formation of additional hydroxyl radicals and the sulfate radical anion ($E° = 2.6$ eV or between 2.5 and 3.1 vs NHE), which can act as a very strong one-electron oxidant in aqueous solutions and can also abstract a hydrogen from water to give hydroxyl radicals:[69−70]

$$SO_4^{\bullet -} + H_2O \rightarrow HSO_4^- + {}^\bullet OH \qquad (43)$$

On the other hand, an excess of oxone might behave as a scavenger of the free radicals generated according to[69−71]

$$HSO_5^- + SO_4^{\bullet -} \rightarrow SO_5^{\bullet -} + HSO_4^- \qquad (44)$$

$$HSO_5^- + {}^\bullet OH \rightarrow SO_5^{\bullet -} + H_2O \qquad (45)$$

The reactions expressed in eqs 42−45 could explain the enhancement effect of oxone at the lower concentrations and the detrimental effect at higher oxone concentrations observed in the sonochemical removal of NO.

Conclusion

The ultrasound-induced aqueous absorption of NO and the positive effects of SO_2, an electrolyte (NaCl) and chemical oxidant (peroxymonosulfate or OXONE) on the sonochemical removal of NO have been demonstrated. NaCl in the concentration range of 0.01−0.5 M was used as the electrolyte to study the effect of ionic strength on the sonochemical removal of NO. The presence of low concentration of NaCl (0.01 M) enhanced significantly the percent fractional removal of NO with inlet gas concentration of 1040 ppm. The presence of about 2520 ppm SO_2 in combination with 0.01 M NaCl further enhanced NO removal. However, with a NO initial concentration of 490 ppm, the addition of NaCl was detrimental to NO removal at all NaCl concentration levels. The combinative effect of sonication and chemical oxidation using 0.005−0.05 M oxone was also studied. It was demonstrated that lower concentrations of HSO_5^- enhanced NO removal efficiency. It was also demonstrated that in the presence of ultrasound, a smaller amount of oxone was needed to obtain optimal fractional conversion of NO. The results of this study suggest the feasibility of developing an innovative, cost-effective and low-temperature aqueous sonochemical scrubber for the simultaneous removal of NO_x and SO_2, leading to the reduction or elimination of chemical usage and associated disposal problems. Also, the use of minimum amounts of additives or chemicals as intensifying parameters under optimized conditions could help in reducing the cost of operation.

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References and Notes

(1) Adewuyi, Y. G.; He, X.; Shaw H. *Chem. Eng. Commun.* **1999**, *174*, 21.

(2) Hileman, B. *Environ. Sci. Technol.* **1984**, *18*, 8A.

(3) Cosby, B. J.; Hornberger, G. M.; Galloway, J. N. *Environ. Sci. Technol.* **1985**, *19*, 1144.

(4) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; John Wiley & Sons: New York, 1998.

(5) Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution*; John Wiley & Sons: New York, 1986.

(6) Oikawa, K.; Yongsiri, C.; Takeda, K.; Harimoto, T. *Environ. Prog.* **2003**, *22*, 67.

(7) Adewuyi Y. G.; Owusu S. O. *Ind. Eng. Chem. Res.* **2003**, *42*, 4084.

(8) Brogren, C.; Karlsson, H. T.; Bjerle, I. *Chem. Eng. Technol.* **1998**, *21*, 61.

(9) Yang, C.; Shaw H.; Perlmutter, H. *Chem. Eng. Commun.* **1996**, *143*, 23.

(10) Brogren, C.; Karlsson, H. T.; Bjerle, I. *Chem. Eng. Technol.* **1997**, *20*, 396.

(11) Littlejohn, D.; Chang, S. *Ind. Eng. Chem. Res.* **1990**, *29*, 1420.

(12) Long, X.-L.; Xiao, W.-D.; Yuan, W.-K. *Ind. Eng. Chem. Res.* **2005**, *44*, 686.

(13) Bradford, M.; Grover, R.; Paul, P. *Chem. Eng. Prog.* **2002**, *98*.

(14) Bradford, M.; Grover, R.; Paul, P. *Chem. Eng. Prog.* **2002**, *98*.

(15) Baukal, C. E.; Hayes, R.; Grant, M.; Singh, P.; Foote, D. *Environ. Prog.* **2004**, 23, 19.

(16) Barman, S.; Philip, L. *Environ. Sci. Technol.* **2006**, *40*, 1035.

(17) Lee J. Y.; Pennline H. W.; Markussen J. M. *Flue Gas Cleanup with Hydroxyl Radical Reactions*; National Technical Information Services: Pittsburgh, PA, DOE/PETC, 1990.

(18) Kasper, J. H.; Clausen III, C. A.; Cooper, C. D. *J. Air Waste Manage. Assoc.* **1996**, 46, 127.

(19) Haywood, J. M.; Cooper, C. D. *J. Air Waste Manage. Assoc.* **1998**, *48*, 238.

(20) Adewuyi, Y. G. *Ind. Eng. Chem. Res.* **2001**, *40*, 4681**.**

(21) Suslick, K. *Science* **1990**, *247*, 1439.

(22) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397.

(23) Thompson H.; Doraiswamy, L. K. *Ind. Eng. Chem. Res.* **1999**, *38*, 1215.

(24) Adewuyi, Y. G.; Appaw, C. *Ind. Eng. Chem. Res.* **2002**, *41*, 4957.

(25) Hoffmann, M. K.; Hua, I.; Hochemer, R. *Ultrason. Sonochem.* **1996**, 3, S163.

(26) Appaw C.; Adewuyi, Y. G. *J. Hazard. Mater. B* **2002**, *90*, 237.

(27) Owusu, S. O.; Adewuyi, Y. G. *Ind. Eng. Chem. Res.* **2006**, *45*, 4475.

(28) Owusu, S. O. Simultaneous Absorption and Oxidation of NO_x and SO_2 by Chemical and Sonochemical Methods. MS Thesis, North Carolina Agricultural and Technical State University, NC, 2001.

(29) Adewuyi, Y. G. *Environ. Sci. Technol.* **2005**. *39*, 3409.

(30) Adewuyi, Y. G. *Environ. Sci. Technol.* **2005**, *39*, 8557.

(31) Kumar, A.; Gogate, P. R.; Pandit, A. B.; Delmas, H.; Wilhelm A. M. *Ind. Eng. Chem. Res.* **2004**, *43*, 1812.

(32) Seymour, J. D.; Gupta, R. B. *Ind. Eng. Chem. Res.* **1997**, *36*, 3453.

(33) Mahamuni, N. N.; Pandit, A. B. *Ultrason. Sonochem.* **2006**, *13*, 165.

(34) Niemczewski, B. *Ultrason. Sonochem.* **1999**, *6*, 211.

(35) Wakeford, C. A.; Blackburn, R.; Lickiss, P. D. *Ultrason. Sonochem.* **1999**, *6*, 141.

(36) Gogate, P. R.; Pandit, A. B.; Wilhelm, A.; Ratsimba, B.; Delmas, H. *Water Res.* **2006**, *40*, 1697.

(37) Gogate, P. R.; Pandit, A. B. *Ultrason. Sonochem.* **2004**, *11*, 105.

(38) Dukkanci, M.; Gunduz, G. *Ultrason. Sonochem.* **2006**, *13*, 517.

(39) Harada, H. *Intl. J. Hydrogen Energy* **2001**, *26*, 303.

(40) Harada, H. Jpn. *J. Appl. Phys.* **2000**, *39*, 2974.

(41) Kruus S. P. *Ultrason. Sonochem.* **2000**, *7*, 109.

(42) Petrier, C.; Micolle, M.; Merlin, G.; Luche, J.-L.; Reverdy, G. *Environ. Sci. Technol.* **1992**, *26*, 1639.

(43) Moisy, P.; Bisel, I.; Genvo, F.; Rey-Gaurez, F.; Venault, L.; Blanc, P. *Ultrason. Sonochem.* **2001**, *8*, 175.

(44) Mead, E. L.; Sutherland, R. G.; Verrall, R. E. *Can. J. Chem.* **1976**, *54*, 1114.

(45) Connick, R. E.; Lee, S.; Adamic, R. *Inorg. Chem.* **1993**, *32*, 565.

(46) Betterton, E. A.; Hoffmann, M. R. *J. Phys. Chem.* **1988**, *92*, 5962.

(47) Lifka, J.; Ondruschka, B.; Hofmann, J. *Eng. Life Sci.* **2003**, *6*, 253.

(48) Sochard, S.; Wilhelm, A. M.; Delmas, H. *Ultrason. Sonochem.* **1997**, *4*, 77.

(49) Sochard, S.; Wilhelm, A. M.; Delmas, H. *Chem. Eng. Sci.* **1998**, *53*, 239.

(50) Vichare, N. P.; Senthikumar, P.; Moholkar, V. S.; Gogate, P. R. *Ind. Eng. Chem.* **2000**, *39*, 1480.

(51) Graedel, T. E.; Goldberg, K. I. *J. Geophys. Res.* **1983**, *88*, 10865.

(52) McElroy, W. J. *Atmos. Environ.* **1986**, *20*, 323.

(53) Yu, X.-Y.; Barker, J. R. *J. Phys. Chem.* **2003**, *107*, 1313.

(54) Yu, X.-Y.; Barker, J. R. *J. Phys. Chem.* **2003**, *107*, 1325.

(55) Truong, G. L.; Laat, J. D.; Legube, B. *Water Res.* **2004**, *38*, 2384.

(56) Moraes, J. E. F.; Silva, D. N.; Quina, F. H.; Chiavone-Filho, O.; Nascimento, C. A. O. *Environ. Sci. Technol.* **2004**, *38*, 3746.

(57) Rivas, F. J.; Beltran, F.; Carvalho, F.; Alvarez, P. M. *Ind. Eng. Chem. Res.* **2005**, *44*, 749.

(58) Anipsitakis, G. P.; Dionysiou, D. D.; Gonzalez, M. A. *Environ. Sci. Technol.* **2006**, *40*, 1000.

(59) Masschelein, W. J.; Rice, R. G. *Chlorine Dioxide: Chemistry and Environmental Impact of Oxychloride Compounds*; Ann Arbor Science Publishers: Ann Arbor, MI, 1979.

(60) Lahoutifard, N.; Lagrange, P.; Lagrange, J. *Chemosphere* **2005**, *50*, 1349.

(61) Jiang, Y.; Petrier, C.; Waite, T. D. *Ultrason. Sonochem.* **2002**, *9*, 163.

(62) Tauber, A.; Schuchamann, H.-P.; von Sonntag, C. *Ultrason. Sonochem.* **2000**, *7*, 45.

(63) Harris, G. W.; Wayne, R. P. *J. Chem. Soc.*, *Faraday Trans.* **1975**, *71*, 610.

(64) McElroy, W. J. *Atmos. Environ.* **1986**, *20*, 323.

(65) Vione, D.; Maurino, V.; Minero, C.; Borghesi, D.; Lucchaiari, M.; Pelizzetti, E. *Environ. Sci. Technol.* **2003**, *37*, 4635.

(66) Clifton, C. L.; Altstein, N.; Huie, R. E. *Environ. Sci. Technol.* **1988**, *22*, 586.

(67) Misik, V.; Riesz, P. *J. Phys. Chem.* **1996**, *100*, 17986.

(68) Mack, J.; Bolton, J. R. *J. Photochem. Photobiol. A* **1999**, *128*, 1.

(69) Dlyamandoglu, V.; Marinas, B. J.; Selleck, R. E. *Environ. Sci. Technol.* **1990**, *24*, 1711.

(70) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(71) Neta, P.; Huie, R. E.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

(72) Rivas, F. J.; Beltran, F.; Carvalho, F.; Gimeno, O.; Frades, J. *Ind. Eng. Chem. Res.* **2005**, *44*, 2871−2878.