NITRIC OXIDE REMOVAL BY AQUEOUS PERSULFATE ACTIVATED BY TEMPERATURE AND Fe (II) IN A BUBBLE COLUMN REACTOR: REACTION KINETICS AND MECHANISTIC MODELING

Yusuf G. Adewuyi, Chemical, Biological and Bioengineering Department, North Carolina A&T State University, Greensboro, NC

Biography

Dr. Yusuf G (Debo) Adewuyi is a Professor of Chemical, Biological and Bioengineering Department at North Carolina A&T State University, where his research is in sustainable production of energy & chemical products; synthesis of nanoscale materials for energy and environmental applications; sonochemistry, cavitation and advanced oxidation processes for pollution treatment; liquid-phase chemistry and kinetics of NOx, SO2 and Hg removal; and ultrasound-assisted biofuels synthesis and fuels desulfurization.

Summary

The chemistry and kinetics of nitric oxide (NO) removal by aqueous solutions of sodium persulfate (Na2S2O8) simultaneously activated by temperature and Fe2+ have been studied in a bubble column reactor. The effects of Na2S2O8 (0.01−0.2 M), Fe2+ (0−0.1 M), gas-phase NO (500−1000 ppm) concentrations and temperatures (23 ºC – 90 ºC) were investigated. In general, the NO fractional conversion at all temperatures in or without the presence of Fe2+ increased sharply with persulfate concentration up to about 0.1 M before leveling off. Increased temperature led to increased conversions of NO at all persulfate levels, and Fe2+ further enhanced NO conversion by about 10% at all temperatures. At 0.1M Na2S2O8 and 0.01M Fe2+ concentrations, conversions of up to 79% and approximately 100% were observed at 70ºC and 90ºC, respectively. Mechanistic reaction pathways were proposed and a mathematical model utilizing the pseudo-steady-state-approximation (PSSA) technique and film theory of mass transfer were developed. The model was solved numerically using fourth order Runge-Kutta (RK) method in Matlab to obtain species concentrations; correlate experimental data; and estimate mass transfer and kinetic rate parameters.

Introduction

The combustion of fossil fuel (e.g., in coal-fired plants) releases a large amount of NOx (mainly NO and NO2) and SO2 into the atmosphere. Both NOx and SO2 contribute to the formation of ground-level ozone, urban photochemical smog, acid rain, eutrophication, respiratory and cardiovascular diseases.[1, 2] Also, whereas SO2 and NO2 are quite
easily removed by wet scrubbing mechanisms, NO is much more difficult to remove.[2] Currently, available control technologies popularly used for NO\textsubscript{x} abatement include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) with urea injection or ammonia injection (thermal deNO\textsubscript{x}), flue gas recirculation (FGR) and low-NO\textsubscript{x} burners (LNB).[3] Although multi-pollutants' reductions from flue gas using different processes, for NO\textsubscript{x}, SO\textsubscript{2}, and Hg removal by high-temperature SCR, lime/limestone wet flue gas desulfurization (WFGD) and activated carbon, respectively, are efficient purification techniques, they are involved with high construction and operational cost, as well as large installation space and disposal with associated environmental problems, for the complex treatment processes.[4]

Aqueous scrubbing with chemical agents either to oxidize insoluble NO into a more soluble NO\textsubscript{2} or form a complex with NO, which can be subsequently removed, provides alternative treatment techniques. Various chemicals including water-soluble ferrous-chelating agents (e.g., Fe(II)EDTA) and oxidants such as H\textsubscript{2}O\textsubscript{2}, sodium chlorite (NaClO\textsubscript{2}) and potassium permanganate (KMnO\textsubscript{4})[2, 5-9] have been studied for their effectiveness in removing NO\textsubscript{x} by aqueous wet scrubbing. The mechanism of SO\textsubscript{2} removal in the wet scrubbing method is not a novel idea, whereas the mechanism of NO removal has unknown areas to be developed. We previously demonstrated the feasibility of removing NO\textsubscript{x} and SO\textsubscript{x} simultaneously by low-temperature aqueous scrubbing using oxone (with the active ingredient HSO\textsubscript{5}\textsuperscript{-}).[5] We also investigated the use of advanced oxidation process utilizing ultrasound for aqueous removal of NO\textsubscript{x}.[10-12] We recently evaluated sodium persulfate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) which is water-soluble, environmentally friendly and safe to handle, as a wet-scrubbing agent.[13] The persulfate anion (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}) is a strong and non-selective oxidant (E\textsubscript{o} = 2.01 V) comparable to O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2}, both of which are widely used in water and wastewater treatment.[14]

\begin{equation}
\text{HSO}_5^- + \text{NO} \rightarrow \text{H}^+ + \text{NO}_2^- + \text{SO}_4^{2-}
\end{equation}

Although persulfate is a strong oxidizing agent, it is kinetically slow at ordinary conditions, but can be activated by heat, light, ultrasound or transition ions such as Fe(II) to generate intermediate sulfate free radical (\textbullet\textsuperscript{SO}_4\textsuperscript{2+}) as represented by the generalized eq 2 and eq 3, respectively.[13, 15]

\begin{equation}
\text{HSO}_5^- + \text{Fe}^{2+} \rightarrow \text{H}^+ + \text{Fe}^{3+} + \text{SO}_4^{2-}
\end{equation}

\begin{equation}
\text{HSO}_5^- + \text{HSO}_5^- \rightarrow \text{H}_2\text{SO}_4 + \text{SO}_4^{2-}
\end{equation}

We recently investigated for the first time the potential of using Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} activated by temperature in aqueous scrubbing of NO\textsubscript{x}, and showed that up to 0.2 M persulfate significantly reduced 1000 ppm of NO in a simulated flue gas in a bubble column reactor.[13] The influence of different process variables such as the concentration of persulfate (0.01 - 0.2 M), temperature (23-90°C), the effects of pH (4-12), NO concentration (500-1000 ppm) and the effects of SO\textsubscript{2}, were studied.[13, 16] Analysis of liquid samples to reveal the presence and amounts of nitrite, nitrate and sulfate and the results of material balances showing mainly NO\textsubscript{3}\textsuperscript{-} as products from the
temperature-only activated persulfate oxidation of NO, were also discussed.[13, 17] A number of studies have reported synergistic effects of temperature and Fe$^{2+}$ on persulfate oxidation and remediation of organic pollutants.[18, 19] However, to the best of our knowledge, the simultaneous and synergistic application of temperature and Fe$^{2+}$ activation of aqueous persulfate for the removal of NO has never been studied. In this work, we extended our recent studies to exploit the advantages of simultaneous temperature and Fe$^{2+}$ activation of aqueous persulfate for the conversion of NO; and to elucidate the reaction pathways, and estimate the kinetic rate parameters.

**Experimental Procedures**

The scrubbing system consisted of a jacketed bubble column reactor made of pyrex glass (5.1-cm i.d. × 61-cm length; Ace Glass, Inc., Vineland, NJ), a flue gas blending system consisting of a Dynablender mass flow controller (Matheson Tri-gas, Montgomeryville, PA) with two flow transducers calibrated to allow a maximum flow of 5 standard liters per minute (SLPM) gas, and an analytical train of an Fourier Transform Infra-red (FTIR) spectrometer (Tensor 27; Bruker Optics, Billerica, MA), shown in Figure 1, and described in details in a previous study[13]. The total volume of scrubbing solution used was 1 L, corresponding to a liquid height of about 0.5 m.

Figure 1: Schematic diagram of the experimental setup

The column was filled initially with 750 ml water and the temperature was allowed to stabilize. Pure, dry nitrogen gas was then bubbled through the scrubber for at least 15 min to remove any dissolved oxygen; at the same time, the simulated flue gas was passed through a bypass line until a stabilized reading was obtained.
Immediately before the start of the experiment, persulfate of required quantity to make 1 L of the desired concentration of scrubbing solution was added directly to the reactor, and water was then added to make the total volume 1 L. For Fe$^{2+}$ activation experiments, the deionized water in the column was first adjusted to pH between 3.0 and 3.5 (± 0.1) with 5.0 N sulfuric acid. This maintained the both the initial and final reaction pH in the range of 2.5-2.6 and minimized the possibility of Na$_2$S$_2$O$_8$ oxidation of Fe$^{2+}$ to Fe$^{3+}$, which, at a pH above 4, is insoluble. The gas exiting from the reactor passed through a membrane dryer to remove moisture prior to analysis with the FTIR spectrometer equipped with a custom gas cell made by FTIR.com, where the outlet concentrations (in ppm) were analyzed. The details of the analytical procedures, including the analysis of gas-phase NO$_x$ and anions in solution, are reported in a previous study.[13] Liquid samples were collected through the side syringe as quickly as 30 s for up to 1 h, and the concentrations of ferrous iron and total iron were determined by the 1, 10-phenanthroline colorimetric method by measuring absorbance at 510 nm (to determine Fe$^{2+}$) and at 396 nm where absorbance are additive (ferrous and ferric complexes) with a Beckman DU-7000 spectrophotometer. Fe$^{3+}$ concentrations were calculated from the difference between the total Fe and Fe$^{2+}$.[20]

**Model Formulation**

The principal kinetic species for NO$_x$ oxidation are assumed to be the hydroxyl and sulfate radicals, which provide the driving force in the liquid phase for the absorption of NO.[13] Based on the findings of previous studies, reactions (4 – 15), with their corresponding rate constants documented in the literature,[21] were hypothesized as reaction pathways responsible for NO consumption in the presence of non-excess amount of Fe$^{2+}$.[22]

(4)

(5)

(6)

(7)

(8)

(9)

(10)

(11)

(12)
Applying the Bodenstein or pseudo-steady-state approximation (PSSA) approach to reactions (4 – 15), and considering the , , and as intermediates, these reaction pathways result in the following overall rate expressions for the liquid-phase reactions of NO, persulfate and Fe$^{2+}$:[13]

\[ \text{Equation 16} \]

\[ \text{Equation 17} \]

\[ \text{Equation 18} \]

where , (eq 5), , , , , and is from eq 11. The first three terms on the right-hand of eq 16 represent the contributions from heat activation, direct oxidation of persulfate, and Fe$^{2+}$ activation, respectively; and the last three terms result from the interaction of free radicals ( and ) generated from persulfate activation with heat and Fe$^{2+}$, and their intercombinations and self-combinations of sulfate radicals ( ).

Assuming the gas and liquid are completely back-mixed and the transfer of NO from gas to liquid is liquid-phase controlled, the rate of transfer of NO from gas to liquid, using film theory, is given by.[2, 5, 13]

\[ \text{Equation 19} \]

where \( k_m \) is the mass-transfer coefficient, \( H \) is the Henry's law coefficient, \( P_{NO} \) is the partial pressure of NO at the outlet, and \( C_{NO} \) is the aqueous concentration of NO. PNO is calculated as \( P_{NO} = 10^{-6} \ P_{total} \) where \( P_{total} \) is 1 atm and \( C_{NO} \) is the NO concentration molar parts per million (ppm)[5, 13]. The material balance of NO in the gas phase yields

\[ \text{Equation 20} \]

where \( V_g \) is the gas holdup volume, \( R \) is the gas constant, \( T \) is the temperature, \( F \) is the gas flow rate, \( P_{NO} \) is the partial pressure of NO at the inlet, \( V_l \) is the liquid volume. Substituting eq 19 in eq 20 gives

\[ \text{Equation 21} \]
From eq 16 and eq 19 the material balance for aqueous NO yields the following equation

\[ (22) \]

Equations 21 and 22 are now solved simultaneously with eqs 17 and 18 using fourth order Runge-Kutta (RK) numerical method in Matlab with varying values of the parameters \( , , , , , , , \) until a good fit for the data was obtained.

**Results and Discussion**

The fractional conversion of NO is calculated using the final steady state attained as:

\[ (23) \]

where \( \) and \( \) are the steady state concentrations [in parts per million (ppm)] of NO at the inlet and outlet of the bubble column, respectively.

Figure 2 shows the experimental and model plots in the presence of 0.01 M Fe\(^{2+}\) persulfate concentrations of 0.10 M at different temperatures (23 – 90 °C). As shown in Figure 2, the model appears to adequately fit the experimental data, especially at the higher temperatures. Higher temperatures accelerates rate of activation and can result in very aggressive oxidizing conditions. At lower temperatures of 23 and 30 °C, where temperature activation is limited, the fit is not as good as higher temperatures.

**Figure 2** Comparison of experimental and model-predicted NO concentration profiles at different temperatures for 0.10 M Na\(_2\)S\(_2\)O\(_8\) in the presence of initial 0.01 M Fe\(^{2+}\).

6
The calculated activation energies for $k'_1$, $k'_2$, $k'_3$, $k'_4$, $k'_5$, $k'_6$ and $k'_7$, based on the Arrhenius plots using eq. 25 shown in Figure 3 are given in Table 2.

![Image](image_url)

**Figure 3** Arrhenius plots of the model predicted reaction rate constants ($k'_1$, $k'_2$, $k'_3$, $k'_4$, $k'_5$, $k'_6$ and $k'_7$) and mass transfer coefficient ($K_La$).

<table>
<thead>
<tr>
<th>Rate Values</th>
<th>$K_La$</th>
<th>$k'_1$</th>
<th>$k'_2$</th>
<th>$k'_3$</th>
<th>$k'_4$</th>
<th>$k'_5$</th>
<th>$k'_6$</th>
<th>$k'_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A$ kJ/mol</td>
<td>13.88</td>
<td>32.83</td>
<td>25.68</td>
<td>46.46</td>
<td>41.83</td>
<td>24.45</td>
<td>36.41</td>
<td>29.95</td>
</tr>
</tbody>
</table>

**REFERENCES**