REACTION KINETICS AND MECHANISTIC STUDIES OF NITRIC OXIDE REMOVAL BY COMBINED PERSULFATE AND FERROUS-EDTA SYSTEMS

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Biography

Md Arif Khan obtained his BS in chemical engineering from Bangladesh University of Engineering and Technology (BUET) in 2008. Arif is currently a Chemical Engineering graduate student at North Carolina A&T State University. He completed his coursework in 2012, and is working on his thesis entitled: “Chemical Reactive Separations in Energy and Environmental Processes”, under the supervision of Dr. Adewuyi. He plans to pursue a Ph.D upon graduation.

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 and chemical products; synthesis of nanoscale materials for energy and environmental applications; sonochemistry, cavitation and advanced oxidation processes (AOPs) for pollution treatment; liquid-phase chemistry and kinetics of NOx, SO2 and Hg removal; and ultrasound-assisted biofuels synthesis and fuels desulfurization.

Summary

The removal of nitric oxide (NO) from simulated flue gas in a bubble column reactor at atmospheric pressure is investigated using combined aqueous persulfate (Na2S2O8) and ferrous ethylenediamine tetraacetic acid (FeII-EDTA) systems. The results show significant improvement in NO removal compared with thermally and Fe2+ activated persulfate systems. Almost 100% NO conversion can be achieved at 70 °C compared to temperature and Fe2+-activated persulfate systems, which could attain 100% conversions only at ≥ 90 °C, suggesting the possibility of significant reduction in energy costs. The pH for optimal NO removal was found to be near neutral (~6.5). A mathematical model, based on proposed reaction pathways and film theory of mass transfer, has been developed, and will be used to correlate the experimental data and evaluate the reaction kinetic parameters and mass transfer coefficients.

Introduction

Nitrogen oxides (NOx – mainly NO2 and NO) and sulfur oxides (SOx – mainly SO2) are the most prominent acid gases emitted from the burning of fossil fuel, especially from the coal fired power plants, and are responsible for widespread problems of air pollution, health hazards, acid rains etc [1, 2]. Of these oxides, NO2 and SO2 are very soluble in water and can be separated easily from the exhaust stream by simple scrubbing, but nitric oxide (NO) is sparingly soluble in water and cannot be separated easily [3]. It is well known that the
commonly practiced methods of removing NO such as selective catalytic and non-catalytic processes have high capital costs and undesirable problems with high temperatures and handling of harmful chemicals. Therefore, alternative cost-effective and environmentally friendlier processes, such as scrubbing suitable oxidizing agents capable of significantly increasing the solubility of NO in water, are of ardent interest [1-5]. Hence, the use of aqueous hydrogen peroxide [6], sodium chlorite [7], aqueous NaClO₂ solution, KMnO₄ solutions [8-10] and various other reagents is widespread in the literature. In a previous study, we used oxone or potassium hydrogen peroxymonosulfate (2KHSO₅·KHSO₄·K₂SO₄) in the removal of NO in absence or presence of SO₂ and reported detailed experimental and kinetic aspects of this process, including feasibility, stoichiometry, reaction pathways and the effects of various process parameters [4]. This was followed by work on NO absorption by aqueous hydrogen peroxide [6], sodium chlorite [7], aqueous NaClO₂ solution, KMnO₄ solutions [8-10] and various other reagents is widespread in the literature. In a previous study, we used oxone or potassium hydrogen peroxymonosulfate (2KHSO₅·KHSO₄·K₂SO₄) in the removal of NO in absence or presence of SO₂ and reported detailed experimental and kinetic aspects of this process, including feasibility, stoichiometry, reaction pathways and the effects of various process parameters [4]. This was followed by work on NO absorption by aqueous peroxymonosulfate (Na₂S₂O₆) activated by temperature. The use of peroxymonosulfate was suggested to reduce the process costs as peroxymonosulfate is comparatively cheaper than oxone and also, significant amount of NO removal could be achieved (up to 90% at 90 °C) [3]. In a recent study involving the removal of NO in presence of SO₂ by the aqueous persulfate systems, we demonstrated that the absorption of NO was greatly enhanced in the presence of SO₂ (70-80% NO removal at 23-70 °C), while the SO₂ itself was completely removed [2]. In our most recent study on the removal of NO using persulfate systems simultaneously activated by temperature and Fe²⁺ ion, we showed that NO removal further increased by almost 10% in presence of Fe²⁺ at all temperatures compared to temperature-only activation [1]. In our discussions of the results, we proposed that the thermal and Fe²⁺ ion activation of the persulfate anion leads to the production of the sulfate radicals (SO₄²⁻), which is responsible for the production of hydroxyl radical (OH⁻) that acts as the main oxidant for the conversion of NO in the aqueous solution [1, 3]. The following major pathways were suggested.

(1)
(2)
(3)
(4)
(5)
(6)
(7)

It was shown that almost 100% NO removal is attainable by this system but only at very high temperature (90 °C). Hence, the energy requirement for the higher temperature process could be the main stumbling block that impedes further development. A number of reports have suggested NO removal by iron chelating agent, especially ferrous ethylenediamine tetraacetic acid (Fe²⁺-EDTA) with or without some other reagents (Na₂SO₃, MgSO₃, Na₂S₂O₄), where NO is combined with Fe²⁺-EDTA by reversible binding and separated from the solution [11-16].

(8)
The main drawbacks of this process include removal of the Fe\textsuperscript{II}-EDTA(NO) complex, fast oxidation of Fe\textsuperscript{II}-EDTA to the inert Fe\textsuperscript{III}-EDTA and high cost of EDTA. The problems can be somewhat overcome in BioDeNOx process where Fe\textsuperscript{II}-EDTA(NO) is broken down by denitrifying bacteria and Fe\textsuperscript{III}-EDTA is reduced by iron reducing bacteria and resultant Fe\textsuperscript{II}-EDTA is recycled back to the reactor [17-20]. But the process was impeded by the slow action of the biological process, uncertainty involving bacteria culture and the additional cost of installing another unit. Some researchers have suggested reducing Fe\textsuperscript{III}-EDTA by the catalytic activity of activated carbon [21, 22] or bio-film electrode reactor [23, 24] but the requirement for additional unit still persists. It is widely reported in the literature that Fe\textsuperscript{III}-EDTA can also be reduced by S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}, SO\textsubscript{4}\textsuperscript{-}, and bisulfate and bisulfide ions, and the resulting Fe\textsuperscript{II}-EDTA recycled for reuse [16, 25-27]. It has also been suggested that the Fe\textsuperscript{III}-EDTA can also activate persulfate anion [28, 29], thus producing a complete synergistic relationship with the persulfate in NO removal process. However, to the best of our knowledge the simultaneous and synergistic application of S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} and Fe\textsuperscript{II}-EDTA for NO removal has never been studied.

**Experimental Procedures**

**NO Absorption**

The schematic diagram for the NO absorption, consisting of a thermally jacketed bubble column reactor with flue gas blending system and analytical train of Fourier Transform Infrared (FTIR) spectrometer, is shown in Figure 1, and is discussed in details elsewhere [1-3].

![Schematic diagram of the experimental setup](image)

**Figure 1.** Schematic diagram of the experimental setup

Initially, the column was filed with 750 ml of de-ionized water and dry nitrogen gas was passed through it for at least 15 min to purge it of all dissolved oxygen. Then, persulfate and
Fe(II)-EDTA solutions were added to the water and additional water was added to make the total volume of solution 1 L before the bubbling of the gas through the solution was started. Finally, the outlet concentration in ppm level was analyzed in the FTIR and recorded using a software program where gas concentration profiles were generated. The experiments were performed at 23-70 °C. To maintain the solution, pH buffer solution was used for pH of 4.0-10.0, concentrated NaOH solution for pH 12.0 and concentrated H₂SO₄ solution for pH 2.0.

Spectrophotometric Determination of Iron Species’

Iron species’ (Fe²⁺, Fe³⁺ and Fe-EDTA) were determined spectrophotometrically using Beckman DU-7500 spectrophotometer. Fe²⁺ and (Fe²⁺+Fe³⁺) ion concentration was determined at 506-512 nm and 393-399 nm wavelength spectra by classical 1, 10-phenanthroline colorimetric method and Fe³⁺ concentration was determined from the difference. At low wavelength (270-330 nm) Fe-EDTA compound shows absorbance and can be determined spectrophotometrically. At first, the calibration curves were drawn from the absorption of known samples at 506-512 nm, 393-399 nm and 270-330 nm. The samples were taken quickly from the reactor by the side syringe and the absorbance was found from the spectrophotometer. From these absorbance data using the calibration curves, the concentration of Fe²⁺, Fe³⁺ and Fe-EDTA can be measured. For better accuracy the samples were diluted to enable correct spectrophotometric determination and more than one wavelength were used and final concentration was found by averaging the data.

Results and Discussion

Determination of Optimum Fe²⁺:EDTA Ratio

The optimum ratio for Fe²⁺:EDTA has been investigated at different temperatures (40, 50 and 60 °C), and widely reported in the literature to be around 1:1 in the removal of organic and inorganic pollutants. [13, 22, 30]. However, to the best of our knowledge, this is the first time Fe²⁺-EDTA is used with persulfate system. Fe²⁺ and EDTA react with one another by the following reversible reaction:

\[ \text{(9)} \]

It was previously shown that the optimum Fe²⁺ concentration needed for activation of 0.1M NaS₂O₈ was 0.01 M Fe²⁺, as higher concentration of Fe²⁺ acted antagonistically with resultant reduction of NO conversion [1]. Hence, these concentration levels were used to determine the optimum Fe²⁺:EDTA ratios as shown in Table 1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0 M EDTA</th>
<th>0.005 M EDTA</th>
<th>0.01 M EDTA</th>
<th>0.015 M EDTA</th>
<th>0.02 M EDTA</th>
<th>0.025 M EDTA</th>
<th>0.03 M EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>52.99</td>
<td>58.17</td>
<td>65.28</td>
<td>64.10</td>
<td>63.21</td>
<td>61.52</td>
<td>60.62</td>
</tr>
<tr>
<td>50</td>
<td>71.45</td>
<td>74.05</td>
<td>77.82</td>
<td>76.63</td>
<td>74.18</td>
<td>71.46</td>
<td>67.45</td>
</tr>
<tr>
<td>60</td>
<td>82.07</td>
<td>83.45</td>
<td>86.99</td>
<td>85.56</td>
<td>82.12</td>
<td>81.16</td>
<td>78.13</td>
</tr>
</tbody>
</table>
Table 1 shows the NO conversion for the different concentrations of EDTA using 0.01 M Fe\textsuperscript{2+} and 0.1 M persulfate. It can be seen that the highest NO removal was obtained when Fe\textsuperscript{2+}:EDTA ratio was 1:1, thus confirming the prior literature results.

**Effect of EDTA Addition and Temperature on NO removal**

Using the optimum initial Fe\textsuperscript{2+} and EDTA concentrations established with 0.1 M persulfate solution (0.01M Fe\textsuperscript{2+} and EDTA), the effect of Fe\textsuperscript{II}-EDTA addition was compared to the temperature-only activated persulfate system [3] and the Fe\textsuperscript{2+}-persulfate systems.

![Figure 2](image)

**Figure 2.** The effect of EDTA addition: (a) Comparative NO profiles at 30 °C, (b) NO conversion at different temperature; -♦- persulfate only, -▲- persulfate with Fe\textsuperscript{2+}, -*- persulfate with both Fe\textsuperscript{2+} and EDTA

In Figure 2, NO absorption for combined persulfate and Fe\textsuperscript{II}-EDTA system is compared with Fe\textsuperscript{2+} activated system and persulfate-only system [1, 3]. Figure (a) shows the comparative NO absorption profiles for three systems, indicating higher removal for combined persulfate and Fe\textsuperscript{II}-EDTA system. In Figure (b), NO conversion at 23-70 °C is compared for the three systems. As shown in Figure (b) NO absorption is very high compared to Fe\textsuperscript{2+} activated system at lower temperature but at higher temperature the advantage appears to diminish. This may be attributed to the reversible binding of NO with Fe\textsuperscript{II}-EDTA in reaction (8).

As the literature values suggest, the forward reaction constant, k\textsubscript{8} (6 x 10\textsuperscript{7} at 25 °C) is higher than the lower temperature. At higher temperature k\textsubscript{8} becomes lower (3.7 x 10\textsuperscript{7} at 50 °C) where the backward reaction constant, k\textsubscript{-8} increases, resulting in a lower value of equilibrium constant K\textsubscript{8} [11, 30]. But the comparative advantage still holds (around 5% higher NO conversion at 70 °C) due to the synergistic effect of Fe\textsuperscript{II}-EDTA on persulfate oxidation of NO.

**Effect of pH on NO Removal**

The effect of pH on NO removal by combined persulfate and Fe\textsuperscript{II}-EDTA system was investigated at 50 °C (a situation that mimics industrial condition). Khan and Adewuyi observed the best NO removal for persulfate-only systems at near neutral pH [3]. Also, Adewuyi and Sakyi reported that acidic pH (3.0 to 4.0) is best for Fe\textsuperscript{2+} activated persulfate system as higher pH will result in Fe(OH)\textsubscript{2} precipitate, which is severely detrimental to NO absorption [1]. On the other hand, studies suggesting a neutral pH optimum for the Fe\textsuperscript{II}-EDTA systems abound in the open literature [30, 31]. Therefore, a pH study for combined persulfate and Fe\textsuperscript{II}-EDTA system was undertaken. Figure 3 shows NO conversion for pH 2.0-12.0 and...
comparison to the pH study of Khan and Adewuyi for persulfate system only [3]. As seen in Figure 3 shows, whereas there is no significant difference in NO removal with pH for the persulfate-only system, the combined persulfate and Fe$^{II}$-EDTA system shows optimal pH of around 6.5 for maximum of NO removal.

![Figure 3.](image_url) Comparative pH dependence of combined persulfate and Fe$^{II}$-EDTA system

**Speciation and Material Balance of Iron**

The iron species present in the solution (Fe$^{2+}$, Fe$^{3+}$ and Fe-EDTA) is determined spectrophotometrically as discussed earlier. Total measured iron is the sum of Fe$^{2+}$, Fe$^{3+}$ and Fe-EDTA and undetermined Fe is the difference between initial iron concentration (0.01M) and total measured iron. Figure 4 shows the profiles of all the iron species at 50 °C. It can be seen from Figure 4 that Fe$^{2+}$ concentration remains close to zero throughout the experiment suggesting near complete reaction with both persulfate and EDTA. The undetermined Fe consists of non-labile iron hydroxides, Fe$^{II}$-EDTA(NO) and other non-labile iron species presents in very small amounts. Since all other non-labile species except Fe$^{II}$-EDTA(NO) remain constant throughout the experiment, the increase in the undetermined Fe suggests increase in Fe$^{II}$-EDTA(NO) concentration, resulting reaction (8) progression.

![Figure 4.](image_url) Concentration profiles and material balance for iron species at 50 °C

**Conclusion**

The chemistry and removal rates of NO by combined aqueous solution of persulfate and Fe$^{II}$-EDTA was studied and reaction pathways proposed. The removal of NO by combined
persulfate and Fe$^{II}$-EDTA system seems to be very promising as persulfate and Fe$^{II}$-EDTA act simultaneously and synergistically to boost the NO conversion by almost 30% over Fe$^{2+}$ activated persulfate system at lower temperature and by 5% at the highest temperature. However, at very low or high pH the absorption of NO decreases as the optimum pH is near neutral. Also, a very high concentration of Fe$^{II}$-EDTA is detrimental to NO removal due to the antagonistic effects of Fe$^{2+}$ and/or Fe$^{II}$-EDTA on persulfate activation and subsequent NO absorption. We are currently working on a mathematical model based on proposed reaction pathways to fit experimental results and obtain mass transfer and kinetic rate parameters.

References


