NITRIC OXIDE REMOVAL BY COMBINED PERSULFATE AND FERROUS-EDTA REACTION SYSTEMS

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ABSTRACT

Nitric oxide (NO) removal from simulated flue gas is investigated using combined aqueous persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and ferrous ethylenediaminetetraacetate (Fe^{2+} -EDTA) systems. The results at 23-70 °C showed significant improvement in NO removal using the optimally obtained molar ratio of 1:1 for the Fe^{2+} and EDTA compared with temperature-only and combined temperature- Fe^{2+} activated persulfate systems with 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ and 0.01 M Fe^{2+} in the absence of EDTA. Almost 100% NO conversion can be achieved at 70 °C (flue gas treatment inlet temperature generally at 50-70 °C) compared to temperature and Fe^{2+} -activated persulfate systems which require ≥ 90 °C for such high removal efficiency. The percentage increases in NO removal were dependent on temperature, 25-30% and 5-10% at the lower (< 40 °C) and higher (> 40 °C) temperatures, respectively. A very high concentration of Fe^{II} -EDTA appears to negatively impact NO removal. However, this process operates at an optimal NO removal pH of near neutral (~ 6.5) with efficiency decreasing at very low or high pH. This should reduce the use of auxiliary chemical for pH adjustment and help mitigate the important technological hurdle of undesired ferric product formation associated with Fe^{2+} -only activated persulfate and other Fenton-like systems at pH (> 3.5). The material balance on iron species (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) was determined to better understand the chemistry of persulfate with Fe^{2+} -EDTA for NO removal. The results demonstrate the feasibility of near complete NO removal at relatively lower temperatures (with the advantage of reduced energy usage), and sustained longtime high NO absorption capability.

Keywords: Nitric Oxide; Absorption; Oxidation; Persulfate, Ferrous-EDTA; Activation.

1. INTRODUCTION

Nitrogen oxides (NO_x – mainly NO_2 and NO) and sulfur oxides (SO_x – mainly SO_2) released from the burning of fossil fuel, especially from the coal-fired power plants, cause considerable environmental and health problems.[1, 2] Of these oxides, NO_2 and SO_2 are very soluble in water and can be separated easily from the exhaust stream by simple scrubbing, but nitric oxide (NO) is sparingly soluble and cannot be separated easily. 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 using wet scrubbing agents, capable of significantly increasing the solubility of NO in water, are of ardent interest.[3-7] As a result, the uses of aqueous solutions of H_2O_2 , NaClO_2 , KMnO_4 , iron and cobalt chelated compounds, and sonochemical oxidation processes for NO removal, are the subjects of a number of recent studies.[8-15] In 2010, Khan and Adewuyi reported, for the first time, the use of aqueous sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) activated by temperature for NO removal, and commented on its safety, stability and environmental benign nature.[6] The persulfate or peroxydisulfate anion ($\text{S}_2\text{O}_8^{2-}$) is a strong and non-selective oxidant ($E^\circ = 2.01 \text{ V}$) comparable to O_3 and H_2O_2 , both of which are widely used in water and wastewater treatment.[16-19]

However, it is kinetically slow at ordinary conditions and often activated by heat, light, ultrasound or transition metal ions such as Fe(II) (or its chelate complexes) to generate intermediate sulfate free radical ($\text{SO}_4^{\bullet-}$) as represented by the generalized eq 2 and eq 3, respectively.

The decomposition reactions of the persulfate anion also vary with persulfate concentration, pH, and oxygen, and hydrogen peroxide or peroxymonosulfate can be produced.[20]

In 2013, Adewuyi and Sakyi investigated the removal of NO in presence of SO₂ by the aqueous persulfate systems, showing that the absorption of NO was greatly enhanced in the presence of SO₂ (70-80% NO conversion in the temperature range of 23-70 °C), while the SO₂ itself was completely removed.[4] Adewuyi and coworkers, in their most recent studies on the removal of NO using Na₂S₂O₈ (0.1 M) simultaneously activated by temperature and Fe²⁺ ion, also found that NO removal further increased by almost 10% in presence of Fe²⁺ (0.01 M) at all temperatures (23-90 °C) compared to a prior study involving temperature-only activation.[5, 21] However, in these studies, initial solution pH was kept between 3.0 and 3.5 (± 0.1) to prevent Fe²⁺ oxidation to Fe³⁺ and subsequent precipitation as Fe(OH)₃. The thermal and Fe²⁺ ion activation of the persulfate anion leads to the production of the sulfate radicals (SO₄^{•-}), which is responsible for the production of OH[•] that acts as the main oxidant for the conversion of NO in the aqueous solution.[5, 6, 21-23] The following major pathways have been proposed:

A number of reports have suggested NO removal by iron chelating agent such as ferrous nitrilotriacetic acid (NTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentacetic acid (DPTA), and cobalt ethylenediamine solutions.[24, 25] But the use of chelated ferrous ethylenediaminetetraacetic acid (Fe²⁺-EDTA) with or without some other reagents (Fe²⁺-citrate, Na₂SO₃, MgSO₃, Na₂S₂O₄) is the most widespread and prevalent in literature, where NO is combined with Fe²⁺-EDTA by reversible binding and separated from the solution.[25-28] Although Fe²⁺-EDTA can obtain a high NO removal efficiency, it is easily oxidized (by NO, NO₂ and O₂ in the flue gas) to Fe³⁺-EDTA that is not capable of binding NO. As a result, the concentration of the active Fe²⁺-EDTA in the scrubbing solutions decreases quickly as the absorption proceeds. Hence, the main drawbacks of this process include removal of the Fe²⁺-EDTA(NO) complex, fast oxidation of Fe²⁺-EDTA to the inert Fe³⁺-EDTA and high cost of EDTA. The problems can be somewhat overcome in BioDeNOx process where Fe²⁺-

EDTA(NO) is broken down by denitrifying bacteria and Fe^{3+} -EDTA is reduced by iron reducing bacteria and resultant Fe^{2+} -EDTA is recycled back to the reactor.[29] But the process has been impeded by the slow action of the biological process, uncertainty involving bacteria culture, detrimental effect of sulfur compounds present in flue gas and the costs of installing additional unit.[30-32] Also, many methods have been put forward to regenerate Fe^{2+} -EDTA to sustain the NO removal through denitrification and/or reduction using sulfur derived ions, from Na_2SO_3 , MgSO_3 , $\text{Na}_2\text{S}_2\text{O}_4$ etc.), in combinative processes.[26, 28] It has also been suggested that both Fe^{2+} -EDTA and Fe^{3+} -EDTA can also activate persulfate anion, like ferrous ion, thus producing a complete synergistic relationship with the persulfate.[33] Ahmad et al. [34] investigated extensively the Fe-EDTA activated persulfate systems using reactant-specific probes and electron spin resonance (ESR) and concluded that both Fe^{2+} -EDTA and Fe^{3+} -EDTA decompose persulfate more rapidly than only $\text{Na}_2\text{-EDTA}$. Thus, it is widely reported in the literature that Fe^{3+} -EDTA can also be reduced by $\text{S}_2\text{O}_8^{2-}$, $\text{SO}_4^{\bullet-}$, and bisulfate and bisulfide ions, and the resulting Fe^{2+} -EDTA recycled for reuse. Liang et al.[35] reported that Fe^{3+} -EDTA can maintain persulfate activation by promoting recycling of Fe much as in catalyzed H_2O_2 propagation (i.e., modified Fenton's reagent), suggesting an interaction of an intermediate organic radical with Fe^{3+} to recycle Fe^{2+} which was then complexed again with EDTA. Additionally, Li et al. [36], by measuring hydroxyl radical formation, suggests that Fenton and Fenton like reactions were never suppressed by iron-chelating agents. Also, the use of chelating agents has been shown to increase the Fe^{2+} solubility, maximizing its availability in groundwater remediation processes.[35]

However, to the best of our knowledge, the simultaneous and synergistic application of persulfate anion ($\text{S}_2\text{O}_8^{2-}$) and Fe^{2+} -EDTA for NO removal has never been studied. In this work, the removal of nitric oxide (NO) from simulated flue gas in a bubble column reactor at

atmospheric pressure is investigated using combined aqueous persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and ferrous ethylenediaminetetraacetate (Fe^{2+} -EDTA) systems to demonstrate the significance and advantages over Fe^{2+} -only activated systems previously reported.[5, 21] The effects of different process variables, such as the molar ratio of Fe^{2+} and EDTA, temperature and pH, on the fractional conversion of NO were determined. The material balance on the iron species (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) has been determined to understand the simultaneous and synergistic relationship between persulfate and Fe^{2+} -EDTA on NO removal.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Reagents. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, powder, >98%), iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, >99%), concentrated sulfuric acid (95-98%) and 1.0 N sodium hydroxide solution were obtained from Acros Organics, Morris Plains, NJ; disodium ethylenediaminetetraacetate (Na_2 -EDTA, reagent grade), 1, 10-phenanthroline monohydrate (PTM), hydroxylamine hydrochloride (96%), acetic acid (99.7%), anhydrous sodium acetate (99%), fuming nitric acid (90%) and sodium hydroxide (solid) were obtained from Fisher Chemical, Fair Lawn, NJ; and 5.0 N sulfuric acid from LabChem Inc., Pittsburg, PA. Extra-dry nitrogen (N_2) and standard mixtures of NO in ultrapure nitrogen were obtained from Airgas National Welders, Charlotte, NC. Deionized water was obtained by using a Milli-Q Advantage A 10 purifier with Elix 5 system from Millipore Corporation, Bedford, MA. The resistivity of the water was always greater than 18.2 M Ω .cm and total organic contents (TOC), silicates and heavy metals contents were minimized to a very low parts per billion (ppb) levels.

2.2. Experimental Procedure for NO Removal. The schematic diagram (Figure 1) for the NO absorption consisted of a thermally jacketed bubble column reactor made of pyrex glass (5.1 cm i.d. $\times$ 61-cm length; Ace Glass, Inc., Vineland, NJ), flue gas blending system consisting

of a Dynablender mass flow controller (Matheson Tri-gas, Montgomeryville, PA) with two flow transducer calibrated to allow a maximum flow of 5 standard liters per minute (SLPM) gas, and analytical train of Fourier Transform Infrared (FTIR) spectrometer (Tensor 27; Bruker Optics, Billerica, MA), and was discussed in details elsewhere.[4-6]

The scrubber was operated in a semibatch mode with the simulated gas flowing upward continuously at a rate of 0.1 SLPM through the 1 L total volume of stationary scrubbing solution (corresponding to a liquid height of ~0.5 m). The experiments were performed in the range of 23-70 °C with each temperature setting maintained with the jacketed cooling/heating system of a refrigerated bath (Neslab RTE 7D1, Thermo Scientific, Newington, NH). Initially, the column was filled with around 750 ml of de-ionized water and temperature was allowed to reach the desired level and stabilize. Pure, dry nitrogen gas was passed through it for at least 15 min to purge it of all dissolved oxygen and then through a bypass line until a stable reading was obtained. Freshly prepared Fe^{2+} , Na_2EDTA and persulfate solutions of appropriate quantity to make 1.0 ± 0.05 L total volume of solution of desired concentration were added to the water consecutively. To maintain the solution pH at neutral level, NaOH and/or H_2SO_4 solution were used, the additional volume so small compared to total volume as to significantly affect the overall liquid volume or height of the reactor. It should be noted that phosphate buffer solution were used for the studies at pH 4.0, 8.0 and 10.0, and for pH 2.0 and 12.0, H_2SO_4 and NaOH (1.0 N) solutions were used, respectively, until the pH reach the desired value. Once all the reagents dissolved completely and the solution observed to turn greenish, the simulated flue gas was switched to the inlet of the reactor and bubbling through the solution issued. The dissolution of persulfate seemed rapid and even vigorous at higher temperature aided by the gas mixing action. The outlet gas reached the FTIR almost instantaneously and data acquisition was started.

The exit gas from the reactor passed through a membrane dryer (MD-050-48P, Perma Pure, Inc.) to remove moisture prior to analysis with the Fourier transform infrared (FTIR) spectrometer equipped with a custom gas cell made by FTIR.com. Both the FTIR and membrane dryer were purged with dry, CO₂ free air from laboratory gas generator (Parker Balston, Haverhill, MA) to continuously remove the moisture. NO_x concentration in the outlet gas was continuously monitored and recorded by proprietary software, Enformatic FTIR Collection Manager (EFCM) from FTIR.com, calibrated with standards of different gas species obtained from Airgas National Welders. The scrubbing solution was analyzed before and after the experiment using a Dionex ICS 3000 ion chromatographic system (Dionex Corporation, Sunnyvale, CA) for anions. The solution pH was monitored continuously using Accumet pH meter 50. Initial and final pH was recorded for each of the experiments. The details of the analytical procedures, including the analysis of gas-phase NO_x and anions in solution and the results of material balances showing mainly NO₃⁻ (and not NO₂⁻) as the main products of Na₂S₂O₈ oxidation, are reported in previous studies.[6, 37]

2.3. Spectrophotometric Determination of Fe Species in Solution. Iron species (Fe²⁺, Fe³⁺ and Fe²⁺-EDTA) were determined spectrophotometrically using Beckman DU-7500 spectrophotometer (Beckman Coulter, Inc., Fullerton, CA). For better accuracy, the concentrations of Fe²⁺ and total Fe (i.e., Fe²⁺ + Fe³⁺) were determined at peak absorbance ranges of 506-512 nm and 393-399 nm, respectively, by a modified 1, 10-phenanthroline colorimetric method, and the Fe³⁺ calculated from the difference.[5, 38] Also, at low wavelength, Fe²⁺-EDTA compound shows higher absorbance and the concentration can be determined spectrophotometrically.[39] From the UV-vis spectrum of Fe²⁺-EDTA, it can be seen that there

is no clear absorbance peak and a wide range of wavelength (270-300 nm) is selected for absorbance measurement.

2.3.1. Determination of calibration curves. Standard Fe^{2+} and Na_2EDTA solutions were prepared in different concentrations and dilution ratios. Previously prepared hydroxylamine hydrochloride and 1, 10-phenanthroline solutions were added to the standard Fe^{2+} solutions and pH was adjusted to 4.5 using acetic acid-sodium acetate buffer. The standard solutions in quartz cuvettes (Spectrocell Corporation, Orelan, PA) were taken to sampling compartment of the spectrophotometer already blanked using base solution (i.e., sample solution without the Fe^{2+}), and absorbance was measured multiple times and recorded for each of the samples with concentrations and dilutions ratios at seven different wavelengths ranging from 506-512 nm. The corresponding absorbance of a particular concentration was found by discarding outlier data and then averaging the retentions. The calibration curves of Fe^{2+} were obtained at different wavelengths by plotting absorbance against the respective concentration. The same procedure was followed to determine ($\text{Fe}^{2+} + \text{Fe}^{3+}$) calibration curves except for the addition of hydroxylamine hydrochloride, as it is used to regenerate Fe^{2+} oxidized to Fe^{3+} . In this case, pH was kept at 3.9 and the wavelength range was 393-399 nm. Fe^{2+} -EDTA was prepared by mixing standard Fe^{2+} and Na_2EDTA solutions (molar ratio 1:1) and adding few drops of concentrated sulfuric acid. The calibration curves of Fe^{2+} -EDTA were obtained by repeating the same procedure at the 270-330 nm wavelength range.

2.3.2 Determination of concentrations of Fe species. Samples of 10-15 mL were taken quickly from the side syringe of the reactor into a number of small test tubes as soon as 30 s and at subsequent allowable intervals for up to about 1 h. Each of the samples was then diluted from one-half up to one-128th of the original strength. For the Fe^{2+} and ($\text{Fe}^{2+} + \text{Fe}^{3+}$) determination 1,

10-phenanthroline was added to the samples, and absorbance was measured in the range of 506-512 nm and 393-399 nm, respectively. For Fe²⁺-EDTA determination, absorbance was measured directly with the spectrophotometer in the range of 270-330 nm, where the molar extinction coefficients are significant.[40, 41] From these absorbance data, and using the previously determined calibration curves, the concentrations of Fe²⁺, Fe³⁺ and Fe-EDTA were recorded. Finally, the respective concentration values were multiplied by their respective dilution factors, and then averaged to determine the concentration of a particular sample. The concentration profiles of the species were then obtained. It should be noted that the persulfate anion by itself is not expected to interfere with these measurements in these wavelength ranges.[42]

3. RESULTS AND DISCUSSION

Based on the results of a previous study, different NO inlet concentrations (500-1000 ppm) have no significant effects on NO removal using 0.10 M Na₂S₂O₈, found to be the optimum concentration for aqueous removal and fractional conversion of NO.[6] As a result, 753 ppm inlet NO concentration was used for this study as it is the average NO concentration in typical industrial flue gases. Several sets of absorption-oxidation experiments at several temperatures (23, 30, 40, 50, 60 and 70 (±1 °C) and Na₂S₂O₈ (0.1 M (± 0.5%)) were conducted in the absence and presence of Fe²⁺ (0.005-0.02 M (± 0.5%)) and Na₂-EDTA (0.005-0.03 M (± 0.5%)) at pH near neutral to acidic region pH of about 6.5). Experiments were also conducted at 50 °C in the pH range of 2.0 - 12.0 to evaluate the pH effects on NO removal. From the FTIR's EFCM recorded data, outlet gas concentration-time profiles were obtained and using the initial and final steady state value of NO concentration, percent conversion of NO is defined as

$$X_{NO} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100\% \quad (17)$$

where $[\text{NO}]_{\text{in}}$ and $[\text{NO}]_{\text{out}}$ are the steady state concentration in parts per million (ppm) of NO at the inlet and outlet of the reactor, respectively. The steady state outlet concentrations of NO were calculated by averaging the values of the outlet concentration after 3000 s. It should also be noted that the concentration-time profiles show the characteristic initial sharp drop in NO exit concentration due to absorption in an unsaturated solutions, and mixing and dilution effects of the purge gas (i.e., N_2 filling the void above the liquid level in the column), which was also observed and discussed in previous studies.[3, 6, 8]

3.1. Determination of Optimum Fe^{2+} /EDTA Ratio. The optimum molar ratio for Fe^{2+} /EDTA has been investigated and widely reported in the literature to be around 1:1 in the removal of organic and inorganic pollutants.[31] Fe^{2+} and EDTA react with one another according to the reversible reaction presented in eq 18.

The kinetics of this reversible reaction fixes the amount of Fe^{2+} -EDTA produced in the solution. The Fe^{2+} /EDTA molar ratio of 1:1 is desirable according to the stoichiometry of this reaction, but, a different molar ratio other than 1:1 has also been observed, when Fe^{2+} -EDTA is used with other reagents in a combined NO absorption process.[43] Because, aqueous Fe^{2+} -EDTA with persulfate is being studied for the very first time for the absorption of NO, the optimum molar ratio of Fe^{2+} and EDTA was deemed necessary to be determined experimentally.

The influence of 0.01 M Fe^{2+} (with no EDTA), and with various EDTA concentration levels (0, 0.005, 0.01, 0.015, 0.02, 0.025, and 0.03 M or Fe^{2+} -EDTA molar ratios of 2.00, 1.00, 0.667, 0.500, 0.400, and 0.333) on NO concentration profiles for three temperatures (40, 50, and 60 °C) is shown in Figure 2. At lowest temperature of 40 °C (Figure 2a) the concentration profiles were smooth and steady, while at 50 °C and 60 °C (Figure 2b and 2c, respectively), the

results were not as stable, suggesting higher activation and greater interaction between reaction species at the higher temperatures. For a better interpretation of the effect of EDTA concentration and Fe^{2+} -EDTA molar ratios, the respective NO percent conversion results are plotted as a function of EDTA concentration in Figure 3 for the different temperatures. At all three different temperatures, the NO conversion values showed an increase up to 0.01 M EDTA concentration, beyond which they decrease steadily with the increase in EDTA concentration, clearly demonstrating that the 1:1 Fe^{2+} -EDTA molar ratio is optimal at all three temperatures. These results also show improved NO removal efficiencies using the combined persulfate- Fe^{2+} -EDTA system compared to persulfate- Fe^{2+} process without EDTA.

Recently, Adewuyi and Sakyi reported the results of the simultaneous temperature and Fe^{2+} activation of aqueous persulfate for use in NO removal.[5] It was shown that NO conversion at all temperatures in or without the presence of Fe^{2+} increased sharply with persulfate concentration up to about 0.10 M before leveling off, and 0.10 M $\text{Na}_2\text{S}_2\text{O}_8$ and 0.01 M Fe^{2+} were established as optimum concentrations for the process. NO fractional conversions of up to 79% and approximately 100% were observed at 70 and 90 °C, respectively, including the ~10% further improvement attributable to the Fe^{2+} activation at all temperatures. [5] As shown in Figure 3, NO conversion increases with increase in EDTA concentration up to 0.01 M before decreasing with the additional increase in EDTA. At 40 °C, it is seen that even for 0.03 M EDTA the NO conversion (61.62%) does not drop below the conversion level of no EDTA (i.e., 0.01 M Fe^{2+} only, 0.00 M EDTA), that is, 52.99%. But at 50 and 60 °C at 0.03 M EDTA, NO conversions are 67.45% and 78.13% respectively, which are much lower than the case of without EDTA, which are 71.45% and 82.07% respectively, suggesting that at higher temperatures excess EDTA may have antagonistic effects on NO removal. The results in Figures 2 and 3 and

Table 1 also clearly show that the optimum molar ratio for Fe^{2+} and EDTA needed with 0.1 M persulfate for the combined persulfate- Fe^{2+} -EDTA process is 1:1 (i.e., 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$). As indicated before from prior literature studies, Fe^{2+} -EDTA absorbs NO by a reversible binding producing nitrosyl compound as presented in eq 19. [25-28, 43, 44]

Fe^{2+} not only reacts with EDTA according to reaction 18 to produce Fe^{2+} -EDTA, which is then combines with NO in reaction 19, but Fe^{2+} also activates persulfate in the solution as shown in reaction 5. The results suggest that at higher EDTA doses, EDTA depletes Fe^{2+} to the point of significantly lowering the amount of Fe^{2+} available for persulfate activation. From Figure 3, it can be seen that the absorption capability of the solution for NO did not drop drastically but instead a gradual decrease was observed at a given temperature, indicating that excess EDTA mainly affects iron activation of persulfate by scavenging available Fe^{2+} , but not the temperature activation of persulfate to any significant extent.

3.2. Synergistic Effect of Fe^{2+} -EDTA with Persulfate, and Temperature Effect on NO Removal. Using the optimal concentrations of persulfate (0.1 M), Fe^{2+} (0.01 M), and molar ratio of Fe^{2+} -EDTA (1:1) established for NO removal, the effect of the Fe^{2+} -EDTA addition was compared to the temperature-only and temperature- Fe^{2+} activated persulfate systems. A prior study of the effects of the different injection methods of Fe^{2+} and persulfate on the absorption of NO in a bubble column concluded that both persulfate and Fe^{2+} simultaneously introduced at the top of the reactor at the beginning of reaction gave the best NO removal efficiencies.[5] Because EDTA reacts with Fe^{2+} by reaction 18, Fe^{2+} solution was first added to the de-oxygenated water

followed by $\text{Na}_2\text{-EDTA}$ solution. Upon the complete reaction between Fe^{2+} and EDTA, persulfate is added from the top of the reactor. The reversible nature of the reaction presented in eq 18, dictates the presence of Fe^{2+} , EDTA and $\text{Fe}^{2+}\text{-EDTA}$ in the solution, and enough Fe^{2+} is expected to remain in the solution for persulfate activation. Figure 4 showing the NO concentration profile at 30 °C, compares the NO removal efficiency of the combined persulfate- Fe^{2+} -EDTA system to those of persulfate only and persulfate with Fe^{2+} . The conversion for 0.1 M persulfate only at 30 °C is about 25.13%. The addition of 0.01 M Fe^{2+} increases the conversion up to 30.81%, a 5.68% increase in the NO removal efficiency. When 0.01 M Fe^{2+} and 0.01 M EDTA are added to 0.1 M persulfate solution, the fractional conversion is 55.64%, an additional 24.83% increase in NO removal efficiency. Figure 5 illustrates the comparison of NO concentration profiles at six different temperatures (23, 30, 40, 50, 60 and 70 °C) of the results of persulfate activated by Fe^{2+} ion and by the combined Fe^{2+} -EDTA. The addition of 0.01 M EDTA increases NO conversion efficiency by almost 28% at 23 °C, while at 30 °C, the conversion increases by almost 25%. As shown in Figure 5, the NO conversion increases by approximately 13, 7, 5, and 4 % at 40, 50, 60, and 70 °C, respectively.

In Figure 6, the NO conversion in the temperature range of 23-70 °C is compared for the three absorptive systems, where NO fractional conversion data for the persulfate-only system were taken from our previous work.[6] It can be seen that, at higher temperature, the increase in NO removal efficiency due to the presence of 0.01 M EDTA become less significant but maintains a higher value with increase in temperature. As a result, close to 100% NO removal is obtained at 70 °C compared with the Fe^{2+} activated persulfate system, which requires up to 90 °C for the same level of NO removal efficiency.[5] It is observed that the effectiveness of the NO removal is temperature-dependent, gradually diminishing from the lower temperature (28% at 23

°C) to higher temperature (4% at 70 °C). This could be attributed to the reversible binding of NO with Fe²⁺-EDTA in reaction 19. As indicated from prior literature, the forward reaction constant, k_{19} is higher in the lower temperature ($6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C) compared to the value at the higher temperature ($3.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ at 50 °C). At 50 °C, the backward reaction constant, k_{-19} increases from 6 to 60 s⁻¹, resulting in a lower value of equilibrium constant K_{19} at the higher temperature.[43] However, the comparative advantage still holds (around 5% higher NO conversion at 70 °C) due to the synergistic effect of Fe²⁺-EDTA on persulfate oxidation of NO. Because at 23 °C, NO removal increased by almost 30% and at 70 °C by 4-5% and the Fe²⁺-EDTA reversible binding with NO (reaction 19) is slower at higher temperature as backward reaction rate increases, it should be expected that there will be little or no increase in NO removal. However, the NO removal increased instead by almost 4%. This can be attributed to the comparative advantage of using Fe²⁺-EDTA over Fe²⁺ only activated persulfate. It has been reported in the literature that iron chelating prevents or minimizes the scavenging of hydroxyl radical, and hence, prevents suppression of Fenton or Fenton-like reactions.[36] Thus, in reactions 14 and 15, where Fe²⁺ was responsible for the scavenging of hydroxyl and sulfate radicals, such reactions are suppressed when Fe²⁺-EDTA is used instead of Fe²⁺ only. In 2004, Liang et al.[33], in their study on the destruction of TCE using persulfate, concluded that the chelated iron compound is far superior to unchelated Fe²⁺ in persulfate activation. The superiority of Fe²⁺-EDTA over Fe²⁺ as a persulfate activator was also confirmed by ESR spectroscopy and probe compounds investigation to track different free radicals.[34] As shown in Figure 6, the Fe²⁺ activated persulfate system gives higher NO removal at higher temperature compared to persulfate only system, which is due to the higher activation of persulfate at higher temperature. The difference between NO removals of Fe²⁺-EDTA activated persulfate system

and the persulfate-only system is almost the same at every temperature (i.e., 35-40%). It could be deduced that activation effect from the presence of Fe^{2+} -EDTA is about 5% and the remaining 22-25% increase is due to the direct absorption of Fe^{2+} -EDTA. It has also been reported that NO binds to $FeSO_4$ in solution according to reaction 20.[27] However, the order of magnitude of the reaction constant is four times less than that of reaction 19.

Reaction 20 is relatively very slow compared to reaction 19 and considered insignificant in the removal of NO by the Fe^{2+} -EDTA only system, nonetheless, it can play a significant role in combined persulfate and Fe^{II} -EDTA systems. In Fe^{2+} -activated persulfate system, all the Fe^{2+} reacts very quickly and remains virtually non-existent in the solution and the possibility of reaction 20 is negligible to nil. However, in the combined persulfate and Fe^{2+} -EDTA systems, the concentration of Fe^{2+} is determined by the equilibrium reaction in eq 19 (measured by spectrophotometric method) and the possibility of reaction 20 is reinvigorated and could aid the removal efficiency of NO.

As noted earlier, O_2 in the flue gas continuously oxidizes the Fe^{2+} in the coordinated EDTA during the NO absorption process by Fe^{2+} -EDTA, producing inert Fe^{3+} -EDTA by reaction in eq 21.[43]

Because the ferric complex does not react with NO, the suppression of this undesired oxidation processes is currently a very important technological problem to be overcome. As stated earlier, a number of methods have been adopted to regenerate Fe^{2+} -EDTA to sustain the NO removal using reductive agents such as sulfite (SO_3^{2-}) and dithionite ($S_2O_4^{2-}$) ions.[26] In 1988, Sada et

al.[45] studied this reaction system and found it to be first order in O_2 and half order in Fe^{2+} -EDTA, and that the reaction could be suppressed by as much as 20% by the addition of excess Fe^{2+} -EDTA. In our experiment water was de-aerated completely by purging with dry nitrogen before starting the NO absorption experiment, and also Fe^{2+} and Na_2 -EDTA were added to the system separately without producing Fe^{2+} -EDTA outside the reactor. Therefore, the system remained completely oxygen free throughout the experiments to avoid or minimize the possibility of reaction 19. Moreover, there was no O_2 that could be determined in the FTIR's inlet and outlet spectra and no Fe^{3+} -EDTA found in spectrophotometric determination of iron species. The goal here at this stage of the study is to understand the chemistry of the combined $Na_2S_2O_8$ and Fe^{2+} -EDTA process without the complexity introduced by the presence of O_2 .

It has been reported in the literature that Fe^{2+} -EDTA also reacts with NO_2^- and NO_2 by reaction presented in eqs 22 and 23, respectively, producing both Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA.[43, 46]

The denitrification of Fe^{2+} -EDTA(NO) can be done in biological processes where ethanol acts as a electron donor compound but, Fe^{2+} -EDTA can also acts an electron donor. It has been reported that denitrification using Fe^{2+} -EDTA as an electron donor is chemical reaction rather than biological in nature, thus probable in our reaction system.[43, 47]

If these reactions were to occur in our system, and Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA are produced, the absorption capability of the solution would be expected to decrease with the progression of time. The success of an effective NO removal process by Fe^{2+} -EDTA lies in the

efficient reduction of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA, and regeneration of Fe^{2+} -EDTA into the system. Sulfate and other persulfate derived ions in our system can effectively accomplish this task. It has been reported in the literature that HSO_3^- and/or SO_3^{2-} can be used to reduce Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA in NO removal process.[27, 28, 44] It should also be noted that in a neutral medium NO_2^- could react with Fe^{3+} -EDTA, serving as an electron donor to reduce it to Fe^{2+} -EDTA as in eq 25, and thus aiding iron recycling to maintain persulfate activation.[48]

On the basis of these studies, the following reactions involving sulfate anions are proposed in our system for the reduction of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA back to Fe^{2+} -EDTA.

However, to the best of our knowledge, no kinetic study for these reactions has been conducted in the open literature and would need to be undertaken in future studies. With these hypothesized reduction reaction pathways (reactions 25-28), it could be implied that the persulfate system also helps Fe^{2+} -EDTA chemistry, producing a complete synergistic and simultaneous relationship. Also, based on these potential pathways, eq 28 could also yield the Caro's acid, which is a known powerful oxidant for both NO_x and S(IV) in the pH range of 6.5-8.5, with regeneration of Fe^{2+} -EDTA.[3] The results of prior studies on NO removal by Fe^{2+} -EDTA only solution indicate that with the passage of time Fe^{2+} -EDTA solution losses NO absorption capability and the NO conversion drops significantly as early as 2-3 hours.[43] The long time viability of the absorbent solution was tested at 30 °C for both Fe^{2+} -persulfate and the combined persulfate and Fe^{2+} -EDTA processes. For the prolonged period of time (6 h), NO fractional conversion was found to

be 28.07% for Fe^{2+} activated persulfate system and 56.88% for the combined persulfate and Fe^{2+} -EDTA system. The longtime viability of the combined solution to better sustain absorption-oxidation capability for NO suggests the possibility of continuous reduction of and both Fe^{3+} -EDTA and Fe^{2+} -EDTA(NO) to Fe^{2+} -EDTA (with the formation of N_2 in eq 28 as the reduction product of NO) such as the hypothesized reactions in eqs 25 - 28, confirming the beneficial action of persulfate and its derived radicals and ions on Fe^{2+} -EDTA at longtime period. As a result, close to 100% removal is obtained at 70 °C compared with the Fe^{2+} activated persulfate system, which requires up to 90 °C for the same level of NO removal.

3.3 Effect of Initial Fe^{2+} -EDTA Concentration and Temperature on NO Removal:

The persulfate oxidation chemistry of NO in the presence of Fe^{2+} -EDTA is complex, since it takes place through direct electron transfer from the persulfate anion, free radical reactions via the sulfate radical generated by activation, and the direct reaction of the NO_x species with Fe^{2+} -EDTA, which results from the reversible reaction of Fe^{2+} and EDTA^{2-} . Hence, the removal of the NO is also thought to be dependent on the consumption of the dissolved NO by the various reactive species in the liquid phase, which maintains the driving force needed for the absorption process. Figure 7 shows the synergistic and antagonistic aspects of the combined effects of increase in both the initial concentration of Fe^{2+} -EDTA and temperature on NO removal. The graphs in Figure 7 show the effect of different Fe^{2+} -EDTA concentration (0.005 to 0.05 M) on NO fractional conversion at the different temperatures (23-70 °C). At all temperatures, NO conversion increases with increase in Fe^{2+} -EDTA concentration up to 0.01 M, peaking at 96.28% at 70 °C. However, as the Fe^{2+} -EDTA concentration increases from 0.01 M to 0.02 M, the NO conversion increases very slightly in the temperature range 23-40 °C, but decreases from 50-60 °C, while with Fe^{2+} -EDTA concentration of 0.02 M at 70 °C, the drop in NO removal is even more

pronounced. With further increase in Fe^{2+} -EDTA concentration to 0.05 M, its antagonistic effects on the aqueous persulfate removal of NO occurs at all temperatures except those at the lower temperatures of 23 and 30 °C. The solution appears to completely lose its absorption capability for NO at the higher temperatures of 60 and 70 °C in the presence of 0.05 M Fe^{2+} -EDTA. These results are similar to those obtained with the use of excess Fe(II) concentration levels in the absence of EDTA.[5, 21]. The results appear to suggest that, while NO conversion increases with Fe^{2+} -EDTA concentration at lower temperatures (23 to 30 °C) increases beyond 0.01 M are detrimental at the higher temperatures (40 to 70 °C).

As indicated earlier in reactions (7-16), in addition to the direct oxidation of NO by persulfate, direct interactions of radicals generated from persulfate activation with Fe^{2+} and self-recombination and intercombination of oxidative sulfate and hydroxyl free radicals reactions (15 – 16), which might tend to reduce NO_x oxidation, could play a significant role depending on reaction conditions. Higher temperatures accelerate rate of activation and can result in very aggressive oxidizing conditions. At higher temperatures and in the presence of optimal amount of Fe^{2+} -EDTA, the decomposition of persulfate is faster and so is the rate of generation of oxidative species. Also, it is well known that the hydroxyl radical also reacts with Fe-EDTA as in reactions 29 and 30 with rate constants (at about pH 6) ranging from 4.0×10^8 to $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.[49-51]

However, the $OH^\bullet$ generated in reaction 6 is more likely to react with NO since reaction 7 is 10 - 100 times higher than reactions 29 and 30 at the optimal concentrations of Fe^{2+} -EDTA and lower temperatures. Also, the $OH^\bullet$ and $SO_4^{\bullet-}$ generated in reactions 5 and 6 are more likely to react directly with NO in reactions 7 and 8, and not other reactions. However, reactions 29 and 30 could be significant at higher Fe^{2+} -EDTA concentrations and higher reaction temperatures. In addition, self-recombination ($SO_4^{\bullet-}/SO_4^{\bullet-}$) and intercombination of oxidative free radicals ($SO_4^{\bullet-}$ and $OH^\bullet$), resulting from higher production of sulfate radicals possibly due to the effects of higher temperatures, are also possible. The explanation is supported in part by the fact that the reaction between $OH^\bullet$ and NO (reaction 7) is a factor of 100 faster than reaction between $OH^\bullet$ with Fe^{2+} (reaction 13), and a factor of 10 faster than even its self-recombination reaction ($OH^\bullet + OH^\bullet \rightarrow H_2O_2$, $k = 5.5 \times 10^9 M^{-1}s^{-1}$). However, the scavenging reactions by $SO_4^{\bullet-}$ and $OH^\bullet$ could be significant at higher Fe^{2+} doses and temperatures and compete with the $SO_4^{\bullet-}/NO_x$ reactions in solution. In addition, the presence of high levels of Fe^{2+} EDTA results in the pronounced scavenging of the $SO_4^{\bullet-}$ and/or $OH^\bullet$ radicals and also the sulfate/bisulfate ions and radicals that are available for the reversible binding of NO to reduce the Fe^{3+} EDTA back to Fe^{2+} EDTA. The combinative effects of these reactions could explain why where at lower Fe^{2+} -EDTA concentration, persulfate and Fe^{2+} -EDTA act synergistically to boost the NO removal to an unprecedented level, but act completely antagonistically to each other at the higher Fe^{2+} -EDTA concentration and higher temperature to significantly depletes the absorption capacity of the solution as observed in Figure 7.

3.4. Effect of pH on NO Removal: The effect of pH on NO removal by combined persulfate and Fe^{II} -EDTA system was investigated at 50 °C (a temperature that mimics typical industrial flue gas inlet condition). Figure 8 illustrates the effect of different solution pH (2.0 -12.0) on NO

removal at 50 °C for the combined $\text{Na}_2\text{S}_2\text{O}_8$ (0.1 M) and Fe^{2+} -EDTA (0.01 M) system and comparison with our prior results showing pH effect on NO removal for $\text{Na}_2\text{S}_2\text{O}_8$ -only system at the same concentration.[6] As seen in Figure 8, whereas there is no significant difference in NO removal with pH in the range 4-9 for the persulfate-only system; however, the combined persulfate and Fe^{II} -EDTA system shows optimal pH of around 6.5 for maximum of NO removal, with significantly improved removal efficiencies. It should also be noted that the typical pH limitation of $\text{Na}_2\text{S}_2\text{O}_8$ - Fe^{2+} only system (operational pH of ≤ 3.5 , which is the drawback for using such a system for improving NO removal) is completely overcome by using Fe^{2+} -EDTA instead of Fe^{2+} only with the persulfate solution. Adewuyi and Sakyi reported that acidic pH (3.0 to 4.0) is best for Fe^{2+} activated persulfate system as higher pH will result in $\text{Fe}(\text{OH})_2$ precipitate, which is severely detrimental to NO absorption.[5]

Persulfate is known to be highly reactive at low pH (< 3), but it is also highly reactive at pH's greater than 10.[16] Khan and Adewuyi (2010) studied the effects of pH on the persulfate-only oxidation and removal of NO and provided extensive discussions on the chemistry involving the roles of the persulfate anion and the generated sulfate and hydroxyl radicals resulting from its reactions in the 3-12 pH range.[6] It was concluded that a decrease in solution pH will accelerate the persulfate decomposition but will not produce an increase in the amount of reactive radicals generated, resulting in an insignificant change in NO absorption rate at low pH; but that neutral to alkaline condition is much more effective in NO removal than acidic condition. This was attributed to the predominance of $\text{OH}^\bullet$ as the oxidative radical at the high pHs. It was stated that since $\text{OH}^\bullet$ reacts with NO at almost diffusion controlled rate ($k = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$), the consumption of NO in the liquid phase was expected to be much higher at alkaline conditions

than in an acidic one. However, it was noted that at very high pH, the effectiveness might be reduced due to the rapid dissociation of $OH^\bullet$ in alkaline solutions as illustrated by eq. 31.

where $k_f = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for forward and $k_b = 9.3 \times 10^7 \text{ s}^{-1}$ for backward reaction and the oxide radical ion ($O^{\bullet-}$) is known to react more slowly with the same substrate than $OH^\bullet$. Also, the effects of the competition for $OH^\bullet$ and $SO_4^{\bullet-}$ by the phosphate species in the buffer was discussed and it was concluded to be marginal in the pH region of $H_2PO_4^-$ and HPO_4^{2-} used in the buffer system, hence, the impact on persulfate- NO_x system was expected to be minimum. Liang and Bruell in 2004[52], also showed that phosphate-buffered systems (e.g. phosphate anion species) did not have significant effect on persulfate oxidation of trichloroethylene (TCE).

The effect of pH value on NO removal rate for the combined $Na_2S_2O_8$ and Fe^{2+} -EDTA system can be explained by the impacts of pH on the complex formation constant of EDTA and ferrous iron. With pH changing, there may be four kinds of Fe and EDTA.[50] It can be represented by:

where Y is the EDTA ligand.

The Fe^{2+} -EDTA and Fe^{3+} -EDTA are reported to be the predominant species in the mid-pH range ($pH > 3.8 < 6.8$).[53] The formation constants (LogK) for the various complexation forms of Fe^{2+} and EDTA under the range of pH studied have been reported to be 2.8, 14.25, 4.87 and 4.1 at pH 1, 6, 9, and 10.5, respectively. It can be concluded that the complex formation constant of Fe^{2+} -EDTA reached the largest value at about pH of 6.0. At more acidic or more alkaline solution, the complex formation constant becomes much smaller. This would explain the optimal

and much improved NO removal obtained with the combined $\text{Na}_2\text{S}_2\text{O}_8$ and Fe^{2+} -EDTA system at pH around 6.5. In addition, Dwibedy et al.[54] in 2000, reported rate constants of $\text{OH}^\bullet$ with acid-base conjugates of EDTA to be 1.8×10^9 , 1.2×10^9 , 5.0×10^8 , 3.3×10^9 and $5.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively, at pH 2 (H_4Y), 3 (H_3Y^-), 5 (H_2Y^{2-}), 8 (HY^{3-}) and 11 (Y^{4-}). The data also suggest the the protonated Fe^{3+} -EDTA and Fe^{2+} -EDTA complexes predominant in the mid-pH range are less susceptible to $\text{OH}^\bullet$ oxidation, which is in consistent with the result in Figure 8 indicating NO removal optimal in the the mid-pH range. The $\text{OH}^\bullet$ is electrophilic in its reactions with with acids, and more strongly with amines; its rate of reaction is reduced when the substrate is protonated.[50]

3.5. Studies on Iron Speciation and Material Balance. The concentration of the iron species present in the solution (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) is determined spectrophotometrically at 50 °C using 0.1 M persulfate concentration and three different Fe^{2+} and EDTA (Fe^{2+} :EDTA = 1:1) concentration, 0.005, 0.010 and 0.020 M, as discussed earlier. Total measured Fe is the sum of Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA and undetermined Fe is the difference between initial iron concentration and total measured iron. Figure 9 shows the profiles of all the iron species at 50 °C. It can be seen from Figure 9 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^{2+} -EDTA(NO) and other non-labile iron species presents in very small amounts. Because all other non-labile species except Fe^{2+} -EDTA(NO) remain essentially constant throughout the experiment, the increase in the undetermined Fe suggests increase in Fe^{2+} -EDTA(NO) concentration, resulting from the progression of reaction 19. Also, the Fe^{2+} -EDTA(NO) concentration increases very slightly and slowly throughout the experiment, suggesting that its accumulation in the solution is very small.

Hence, this would indicate its reduction back to Fe^{2+} -EDTA by persulfate and radicals in the system, thus confirming the synergistic action of persulfate with Fe^{2+} -EDTA.

The comparison between the concentration of iron species in Fe^{2+} activated persulfate system and combined persulfate and Fe^{2+} -EDTA system is illustrated in Figure 10, and Table 1 shows the respective steady state maximum, minimum and average values. In Figure 10a, Fe^{2+} ion concentration is plotted for both of Fe^{2+} activated persulfate and persulfate with both Fe^{2+} and EDTA with initial concentrations of 0.005, 0.01 and 0.02 M. Ferrous ion concentration for both systems is similar, that is, upon addition of oxidant, Fe^{2+} concentration quickly diminishes to very low level indicating it has been oxidized to Fe^{3+} ion. Figure 10b is plotted to observe the difference between the Fe^{2+} concentration profiles of the two processes more closely, and is a truncation of Figure 10a from 500 s to 4000 s to show the comparative Fe^{2+} concentration more clearly. As shown in Figure 10b, Fe^{2+} ion increases (1×10^{-5} to 2.8×10^{-4} M on average) with the initial Fe^{2+} concentration (0.005 to 0.02M) for Fe^{2+} activated persulfate systems. However, for combined persulfate and Fe^{2+} -EDTA system, the concentration of Fe^{2+} remains the same (1×10^{-4} M on average) for 0.005, 0.010 and 0.020 M initial concentration. This can be explained by the reversible reaction in eq 18, where, the forward and backward reactions stabilize Fe^{2+} concentration in the system that facilitates the Fe^{2+} activation of persulfate. Figure 10c shows the Fe^{3+} ion concentration profiles determined by 1,10-phenanthroline method. Compared to Fe^{2+} activated persulfate system, Fe^{3+} ion concentration decreases significantly in the combined Fe^{2+} -EDTA system during the absorption process. As shown in Table 1, the concentration of Fe^{3+} in Fe^{2+} activated persulfate systems is almost equal to sum of the concentration of Fe^{3+} and Fe^{2+} -EDTA in combined persulfate and Fe^{2+} -EDTA systems. This implies that the addition of EDTA actually formed Fe^{2+} -EDTA by taking up Fe^{2+} ion that are supposed to be converted into Fe^{3+}

anyway, thus, the presence of EDTA increases the NO removal without necessarily affecting the persulfate activation by temperature and Fe^{2+} , further confirming that Fe^{2+} -EDTA does not suppress persulfate activation as discussed earlier. Figure 10d shows the concentration profile for undetermined Fe species. In the persulfate systems with only Fe^{2+} the undetermined Fe consists of only non-labile iron species. In combined persulfate and Fe^{2+} -EDTA systems, undetermined Fe also consists of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA. Because in the spectrophotometric determination significant amount of Fe^{3+} -EDTA was never found, the difference between undetermined Fe concentration in the two systems is Fe^{2+} -EDTA(NO) assuming that the concentration of the non-labile iron species remains the same for same initial Fe^{2+} concentration.[55] As shown Table 1, the Fe^{2+} -EDTA(NO) concentration (difference between two systems) is 0.001 M. Fe^{2+} -EDTA(NO) does not change when Fe^{2+} -EDTA increased from 0.01 to 0.02 M, suggesting no further NO removal occurred for the increase in initial Fe^{2+} concentration from 0.01 to 0.02 M, thus, confirming previously chosen optimum Fe^{2+} concentration of 0.01 M. Again, presence of only 10% of initial Fe^{2+} as Fe^{2+} -EDTA(NO) and absence of Fe^{3+} -EDTA indicate the role sulfate ions play in the reduction of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA is significant in the combined system as suggested earlier.

3.6 Some Perspectives on Solution Regeneration and Reaction Products. In the removal of NO with iron chelates, the nitrosyl complexes (i.e., nitrogen-sulfur or N-S compounds or intermediates such as sulfamate and amine sulfonate), formed from interaction between nitrite and bisulfate, are usually treated or converted to useful products. An important aspect of this process is the ability of nitrosyl complexes to regenerate the metal chelate (i.e., Fe^{3+} -EDTA is reduced by HSO_3^- to produce Fe^{2+} -EDTA and dithionate ion) in a scrubber system by reacting with absorbed SO_2 in aqueous solutions with simultaneous production of sulfate and

nitrogen species such as N_2 . N_2O has been observed in strong acid solutions, but which in O_2 deficient solutions reacts with H_2O to form N_2 and HNO_2 (that is subsequently oxidized to HNO_3). Nitrates are not very toxic themselves compared to nitrites, and if treatment is necessary, practical full-scale processes include evaporation (or distillation), ion exchange, biological denitrification, reverse osmosis, and catalytic liquid-phase methods.[56, 57] In general, the N-S compounds can be removed from the scrubbing solution as alkaline-metal salt precipitates (e.g. potassium salt precipitates) of commercial value, SO_3^-/SO_4^{2-} ions as calcium salts (gypsum) by reaction with lime/limestone, and sodium nitrite and nitrate can be manufactured by the addition of NaOH.[55] The complex Fe^{2+} -EDTA(NO) can be decomposed to regenerate Fe^{2+} -EDTA and recover NO as a rich gas.[58] Also, Suchecki et al. in 2004, showed that the use of iron powder as a reducing agent has merit in that maximum concentration of NO_3^- and SO_4^{2-} in liquid absorbent can be automatically controlled by crystallization of ferric nitrate ($Fe(NO_3)_3$) and ferric sulfate ($Fe_2(SO_4)_3$).[59] Both $Fe(NO_3)_3(s)$ and $Fe_2(SO_4)_3(s)$ can be removed as the filter cake in the filtration unit. Most of the scrubbing liquors leaving the reducing tank or filtration units (which may still contain such ion species as free Fe^{2+} , free Fe^{3+} , Fe^{2+} -EDTA, $[Fe^{3+}$ -EDTA free EDTA, NO_3^- , SO_4^{2-} and so forth) are recycled to the absorber. As noted recently by Liu and coworkers (2014), boiler flue gas contains large amounts of waste heat and the temperature is often more than 120 °C. They suggested that this reservoir of waste heat from the boiler can completely provide the energy needed for thermal persulfate activation in their $(NH_4)_2S_2O_8$ -only process to simultaneously oxidize NO, SO_2 and Hg^0 . [60] The resulting products, $(NH_4)_2SO_4$ and NH_4NO_3 (obtained by partial addition of ammonia to neutralize the H_2SO_4 and the HNO_3 in mixed solution) could also be concentrated and crystallized by using the flue gas waste energy. A number of catalytic liquid-phase methods are also under development to remove both nitrates

and nitrites using palladium (Pd) to reduce them to N_2 . [61-63] Hence, the development of the combined $Na_2S_2O_8$ - Fe^{2+} -EDTA technology could make it possible to combine the environmentally friendly utilization of coal with the improvement of agricultural productivity via binary N+S fertilizer supply from neutralization of sulfate/nitrate with ammonia to produce ammonium sulfate/ammonium nitrate and hence, converting the liability of pollution problem advantageously into assets. However, further studies are necessary in the future to better demonstrate the potential applications and cost benefits of the combined process. This is beyond the scope of the current study.

4. CONCLUSION

The simultaneous and synergistic action of persulfate and Fe^{2+} -EDTA for the removal of NO is demonstrated along with the temperature effects (23-70 °C) in a bubble column reactor operated in semi-batch mode. Using 0.1 M $Na_2S_2O_8$ and 0.01 M Fe^{2+} previously determined as the best concentrations of $Na_2S_2O_8$ - Fe^{2+} system for NO absorption and oxidation at different temperatures (23-90 °C), the molar ratio of Fe^{2+} and EDTA was found to be 1:1 for maximum NO conversion in combined persulfate and Fe^{2+} -EDTA process. The results showed significant improvement in NO removal compared with temperature-only and combined temperature- Fe^{2+} activated persulfate systems with almost 100% NO conversion achieved at 70 °C compared to temperature and Fe^{2+} -activated persulfate systems, which required a temperature ≥ 90 °C for the same conversion. This higher removal should provide a remarkable advantage in the treatment of industrial flue gas, which is generally received at the treatment plant in the temperature range of 50-70 °C. Also, the percentage increases in NO removal for the $Na_2S_2O_8$ - Fe^{2+} -EDTA were dependent on temperature range, 25-30% and 5-10% at the lower (< 40 °C) and higher (> 40 °C)

temperatures, respectively. The absorption of NO decreases at very low or high pH and found to be optimal at near neutral pH (~6.5), which should reduce the use of auxiliary chemical for pH adjustment. 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.

In this study the material balance on the iron species (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) was determined spectrophotometrically to understand the simultaneous and synergistic relationship between persulfate and Fe^{2+} -EDTA on NO removal, and reaction pathways to better explain the results. However, this investigation also indicates a number of areas in which additional research is needed. These include O_2 effects; mass-transfer reaction kinetics; determination of reactants, intermediates and final products in the complex chemical system (using ion chromatograph, IC and electron spin resonance, ESR, and other analytical methods) for more comprehensive material balance; and the regeneration of the scrubbing liquor. We are currently working on the effects of other flue gas constituents (O_2 , SO_2 , CO_2), and additional studies on the effects of persulfate and EDTA concentrations and pH at different temperatures, and the results will be reported in future publications.

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Table 1. Iron species concentration for different initial Fe²⁺ and/or EDTA concentration with 0.1

M persulfate at 50 °C

Iron Species'	Types of Values		Concentration (M)					
			Fe ²⁺ Only	Fe ²⁺ / EDTA	Fe ²⁺ Only	Fe ²⁺ / EDTA	Fe ²⁺ Only	Fe ²⁺ / EDTA
Initial Concentration			0.005		0.01		0.02	
Fe ²⁺	Range	Minimum	0	0.000052	0.00008	0.000076	0.00012	0.000081
		Maximum	2.20 x 10 ⁻⁵	0.000099	0.00022	0.00023	0.0005	0.00016
	Steady State Average		1.05 x 10 ⁻⁵	0.000078	0.00013	0.00012	0.00028	0.00011
Fe ³⁺	Range	Minimum	0.00457	0.00264	0.00929	0.00569	0.01838	0.01279
		Maximum	0.00494	0.00315	0.00986	0.00628	0.01918	0.01423
	Steady State Average		0.00474	0.00286	0.00957	0.00599	0.01884	0.01337
Fe ^{II} -EDTA	Range	Minimum	-	0.00111	-	0.00247	-	0.00468
		Maximum		0.00132		0.00277		0.0059
	Steady State Average			0.00123		0.00261		0.00518
Total Measured Fe	Range	Minimum	0.00458	0.00381	0.00937	0.0084	0.0185	0.01825
		Maximum	0.00495	0.0045	0.01	0.00919	0.01956	0.0194
	Steady State Average		0.00475	0.00416	0.00969	0.00872	0.01911	0.01866
Undetermined Fe	Range	Minimum	0.00005	0.005	0	0.00031	0.00022	0.0011
		Maximum	0.00042	0.00119	0.00063	0.00151	0.00075	0.00175
	Steady State Average		0.00025	0.00084	0.00031	0.00128	0.00044	0.00144

Figure Caption

Figure 1. Schematic diagram of the experimental set-up.

Figure 2. NO concentration profiles at 40, 50 and 60 °C for $\text{Na}_2\text{S}_2\text{O}_8$ concentration of 0.1 M and Fe^{2+} concentration of 0.01 M for different $\text{Na}_2\text{-EDTA}$ concentration (0-0.03 M): (a) 40 °C, (b) 50 °C and (c) 60 °C.

Figure 3. NO fractional conversion at 40, 50 and 60 °C for different $\text{Na}_2\text{-EDTA}$ concentration for $\text{Na}_2\text{S}_2\text{O}_8$ concentration of 0.1 M and Fe^{2+} concentration of 0.01 M.

Figure 4. Comparative NO concentration profiles at 30 °C for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution system, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution in presence of 0.01 M Fe^{2+} , and 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution with 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$.

Figure 5. Comparative NO concentration profiles for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution in presence of 0.01 M Fe^{2+} , and 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution with 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$ at various temperature (23-70 °C): (a) 23, (b) 30, (c) 40, (d) 50, (e) 60 and (f) 70 °C.

Figure 6. Dependence of NO fractional conversions on temperature (23-70 °C) for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution system, 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution in presence of 0.01 M Fe^{2+} , and 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution with 0.01 M Fe^{2+} ion and 0.01 M $\text{Na}_2\text{-EDTA}$.

Figure 7. Effect of different initial Fe^{2+} -EDTA concentration (0.0 – 0.05 M) and various temperatures (23 – 70 °C) on NO removal in the presence of 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$.

Figure 8. Effect of pH (2 – 12) on NO removal for the 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution in presence and absence of combined 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$ at 50 °C

Figure 9. Iron species ($\text{Fe}^{2+}/\text{Fe}^{3+}/\text{Fe}^{\text{II}}\text{-EDTA/Undetermined Fe}$) profiles at 50 °C for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution and different initial $\text{Fe}^{2+}/\text{Na}_2\text{-EDTA}$ ($\text{Fe}^{2+}:\text{EDTA}=1:1$) concentration: (a) 0.005 M $\text{Fe}^{2+}/\text{Na}_2\text{-EDTA}$, (b) 0.01 M $\text{Fe}^{2+}/\text{Na}_2\text{-EDTA}$, and (c) 0.02 M $\text{Fe}^{2+}/\text{Na}_2\text{-EDTA}$.

Figure 10. Comparative Fe^{2+} and Fe^{3+} concentration profiles at 50 °C for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution in presence of 0.01 M Fe^{2+} , and 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution with 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$: (a) Fe^{2+} profiles, (b) Truncated and enlarged Fe^{2+} profiles (≥ 500 s), (c) Fe^{3+} profiles and (d) Undetermined-Fe profiles.

Figure 1.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10