Nitric Oxide Removal from Flue Gas by Combined Persulfate and Ferrous–EDTA Solutions: Effects of Persulfate and EDTA Concentrations, Temperature, pH and SO₂

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ABSTRACT: The effects of persulfate (PS) and ethylenediaminetetraacetate (EDTA) concentrations at different temperature and pH on the removal of NO were studied using combined Na₂S₂O₈ and Fe²⁺-EDTA aqueous solutions. The experiments were conducted in the temperature and pH ranges of 23–70 °C and 2–12, respectively, using 0.05–0.20 M PS and 0.01 M Fe²⁺ in the absence and presence of 0.005–0.050 M Na₂-EDTA. The effect of SO₂ was also preliminarily investigated. Increased temperature led to increased conversions of NO (percent inlet NO removed) at all PS levels but high concentrations of EDTA produced antagonistic effects with increasing temperature. With 0.10 M Na₂S₂O₈, 0.01 M Fe²⁺ and ≤ 0.01 M EDTA, NO conversion increased with temperature from 23 to 70 °C. At 70°C, NO conversion increased from 83.40 to 96.28 % as EDTA concentration increased from 0.005 to 0.01 M EDTA but decreased to 29.22 and 0.4 % with 0.02 and 0.05 M EDTA, respectively. The results at 40 and 50 °C showed optimal NO conversions in the pH range 6–8, and higher at 50°C. However, at higher pH (>11), NO conversion is higher at 40°C than at 50°C. The speciation and material balance of the iron species were determined at different Fe²⁺ and EDTA concentrations. The results, which showed sustained NO absorption at lower temperatures and mid-pH, could in practice minimize process pH adjustment and energy usage in wet scrubbers. The process could be applicable to the simultaneous cleanup of NO_x and SO₂ from oil- and coal-fired power plant and industrial boiler.

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

1. Introduction

The three primarily energy sources for generating electric power are coal, natural gas, and nuclear energy. NO_x (mainly NO_2 and NO) and SO_2 released from the combustion of coal, fuel oils and solid waste have significant impact on the health of humans and ecosystems. [1, 2] Stringent environmental laws and regulations have driven recent advances in air emission control technologies.[3] The U.S. Environmental Protection Agency (EPA), for example, established the Acid Rain Program (ARP) and Cross-State Air Pollution Rule (CSAPR) to curb SO_2 and NO_x emissions from thermal power plants.[4] Wet flue gas desulfurization (WFGD) and selective catalytic reduction (SCR) are deployed for the abatement of SO_2 and NO_x emissions, respectively.[5] It is well known that SCR has high capital and operational costs and large environmental footprint, and usually operates at high temperatures (200-400 °C).[6] One motivation behind wet scrubbing is to retrofit existing WFGD scrubber system to provide simultaneous multicomponent (SO_2 , NO_x and mercury) control, thereby lowering costs, along with smaller plant footprint.[7, 8] Therefore, processes using wet scrubbing agents such as strong oxidants and metal chelates, and for which existing plants can be retrofitted for multiple applications are emerging. [9-11] Results from some recent studies have demonstrated that the use of $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{Fenton-like}$ reacting systems are also effective for the simultaneous removal of NO and SO_2 . [12-14] In China, where there is a great dependence on coal as energy source, such processes for flue gas cleanup are gaining significant popularity.[15] These methods either involve the conversion of NO and SO_2 into soluble NO_2 and SO_3 , followed by absorption to form sulfuric and nitric acids and/or sulfates and nitrates, respectively, or coordination of NO with metal complexes to quickly form nitrosyls followed by liquid treatment.[16]

Adewuyi and coworkers reported the use of aqueous sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) activated by temperature only or with Fe^{2+} for both NO only and simultaneous NO/ SO_2 removal, and commented on its safety, stability and environmental benign nature.[17-20] The persulfate (PS) 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 waste treatment.[21-24]

However, it is kinetically slow at ordinary conditions and often activated by high/alkaline pH, 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 eq 2 and eq 3, respectively.[25]

The decomposition reactions of $\text{S}_2\text{O}_8^{2-}$ also vary with PS concentration, pH, and O_2 , and H_2O_2 or peroxymonosulfate (PMS) can be produced.[26] The thermal and Fe^{2+} ion activation of $\text{S}_2\text{O}_8^{2-}$ leads to the production of $\text{SO}_4^{\bullet-}$, which is responsible for the production of $\text{OH}^\bullet$ that acts as the main oxidant for the conversion of NO.[20, 27]

The use of chelated ferrous ethylenediaminetetraacetic acid (Fe^{2+} -EDTA) for NO removal has been extensively reported in the literature, where NO is combined with Fe^{2+} -EDTA by reversible binding and separated from the solution.[11, 28-32] Although Fe^{2+} -EDTA can obtain a high NO removal efficiency, it is easily oxidized (by NO, NO_2 and O_2 in the flue gas) to Fe^{3+} -EDTA that is not capable of binding NO. As a result, the concentration of the active

Fe^{2+} -EDTA in the scrubbing solutions decreases quickly with significant loss of NO absorption capability as early as 2-3 h.[28] Hence, the main drawbacks of this process include removal of the Fe^{2+} -EDTA(NO) complex formed, fast oxidation of Fe^{2+} -EDTA to the inert Fe^{3+} -EDTA and high cost of EDTA. It has also been suggested that both Fe^{2+} -EDTA and Fe^{3+} -EDTA can also activate the PS anion, thus producing a complete synergistic relationship with the PS.[33] Recently, Adewuyi and Khan (2015), for the first time, studied the effect of combined PS and ferrous EDTA reaction systems on NO removal, using 0.1 M PS and 0.01 Fe^{2+} . [25] The results showed that the presence of EDTA improved and sustained NO removal significantly compared with temperature-only and combined temperature- Fe^{2+} activated PS systems. Also, issues relating to spent solution regeneration, reaction products and conversion to benign or useful end-products, were discussed.[25] The proposed pathways for the NO_x - S_2O_8 - Fe^{2+} -EDTA system are depicted in Scheme 1. In this study, the goal was to understand the chemistry of the combined $\text{Na}_2\text{S}_2\text{O}_8$ and Fe^{2+} -EDTA process at wider ranges of concentrations of PS and Fe^{2+} for different concentrations of EDTA, without the complexity introduced by the presence of O_2 . The combinative effects of initial PS and EDTA concentrations, temperature and pH on NO conversion were studied to elucidate the interactive, synergistic and/or antagonistic relationships of these process parameters. The longtime viability of the absorbent solution was also evaluated, and implication of the study to energy and process applications discussed. The speciation and material balance of iron species (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) were determined at the different Fe^{2+} and EDTA concentrations to further evaluate the process chemistry. The effect of SO_2 on NO removal was also preliminarily investigated. This study should be useful for future scale-up and application to low-temperature, and hence, reduced-energy treatment of NO_x and SO_2 from oil/coal-fired power or steel plants, incinerators, combustors and industrial boilers.

Scheme 1: Schematic diagram of the NO-PS-Fe²⁺EDTA reacting systems

2. Experimental

2.1. Materials. Sodium persulfate (powder, >98%), iron (II) sulfate heptahydrate (FeSO₄·7H₂O, >99%), concentrated sulfuric acid (95-98%) and 1.0 N sodium hydroxide solution were obtained from Acros Organics, Morris Plains, NJ; disodium ethylenediaminetetraacetate (Na₂-EDTA, reagent grade), and sodium hydroxide (solid) were obtained from Fisher Chemical, Fair Lawn, NJ; and 5.0 N sulfuric acid from LabChem Inc., Pittsburg, PA. Ultrahigh purity (5.0-grade) nitrogen (N₂) and NO/SO₂ mixtures in ultrapure (4.8-grade) N₂ were obtained from Airgas National Welders, Charlotte, NC. Deionized water was obtained from a Milli-Q Advantage A 10 purifier with Elix 5 system from Millipore Corporation, Bedford, MA. The water had a resistivity of at least 18.2 MΩ.cm, and the total organic contents, silicates and heavy metals contents were reduced very low parts per billion (ppb) levels.

2.2. Methods. The schematic diagram for the NO absorption consisted of a thermally jacketed bubble column reactor made of Pyrex glass (5.1 cm i.d. × 61-cm length designed in-house and custom-built by 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). The temperature setting was maintained by circulating water through the jacketed column using the cooling/heating system of a refrigerated bath (Neslab RTE7D1, Thermo Scientific, Newington, NH). The scrubber was operated in a semibatch mode with the simulated gas flowing upward continuously at a rate of 0.1 SLPM. The column was initially filled with 750 ml of water and N₂ was passed through it for 15 min to purge it of dissolved oxygen. Freshly prepared Fe²⁺, EDTA and PS solutions of appropriate quantity to make 1.0 ± 0.05 L total volume of solution (corresponding to a liquid height of ~0.5 m) of desired concentration were added to the water consecutively at the top of the column, previously determined to be the best injection method from a previous study.[19] The experimental setup is shown in Figure 1 and is discussed in detail elsewhere.[10, 17, 25] NO_x and SO₂ concentrations in the outlet gas were continuously monitored and recorded by proprietary software, Enformatic FTIR Collection Manager (EFCM) from FTIR.com. The solution pH was monitored continuously, and the initial and final pH also recorded using Accumet pH meter 50 (Thermo Scientific) and pH semi micro tip probe (Orion 8103 BN). Liquid 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. The details of the analytical procedures, including iron speciation (Fe²⁺, Fe³⁺ and Fe²⁺-EDTA), analysis of gas-phase NO_x and anions (oxidation products of mainly NO₃⁻ and not NO₂⁻), and material balances in solution, are reported in previous studies.[17, 25, 34]

Several sets of experiments at various temperatures (23, 30, 40, 50, 60 and 70 (±1 °C), and acidic to alkaline pH (pH 2.0–12.0) were conducted to investigate the removal of NO (753 ppm initial gas-phase, typical average of industrial flue gases) using aqueous solutions

containing $\text{Na}_2\text{S}_2\text{O}_8$ (0.05, 0.10, and 0.2 M ($\pm 0.5\%$)) and Fe^{2+} (0.01 M ($\pm 0.5\%$)) in the absence and presence of $\text{Na}_2\text{-EDTA}$ (0.005, 0.01, 0.02, and 0.05 M ($\pm 0.5\%$)).

Figure 1. Schematic diagram of the experimental set-up

From the FTIR's EFCM recorded data, outlet gas concentration-time profiles were obtained and fractional percent conversion of NO obtained from,

$$X_{\text{NO}} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (4)$$

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. $[\text{NO}]_{\text{out}}$ was calculated by averaging the values of the outlet concentration after 3000 s. It should be noted that the concentration-time profiles show the characteristic initial sharp drop in NO exit concentration due to absorption in 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 previously observed and [discussed](#).[\[9, 10, 17\]](#)

3. Results and Discussion

3.1. Effects of $\text{Na}_2\text{S}_2\text{O}_8$ Concentrations and Temperature on NO Removal.

The influence of three PS concentration levels (0.05, 0.10, and 0.20 M) on NO concentration profiles in the presence of 0.01 M Fe^{2+} and 0.01 M EDTA at various temperatures (23, 30, 40, 50, 60 and 70 °C) is shown in Figure 2. The effects of temperature and PS concentration on the steady state conversion of NO (at time ≥ 3000 s) in the presence of 0.01 M Fe^{2+} and 0.01 M EDTA are illustrated in Figure 3. The NO conversion as a function of PS concentration for all temperatures up to 70 °C illustrated on Figure 3(a) indicates that, in general, conversion at all temperatures increases with PS up to 0.10 M, before appearing to level off. In addition, increased temperature led to increased conversion of NO at all PS concentration levels. Figure 3(b) shows the NO conversion as a function of temperature for the different PS concentrations in the presence of 0.01 M Fe^{2+} and 0.01 M EDTA. As shown in this figure, in general, NO conversion increases with temperature at all PS levels, with the marginal change in NO conversion more significant, going from 0.05 to 0.1M but diminishing beyond 0.1 M. For example, the conversions were found to be 92.4%, 95.4% and 97.3% at 70 °C respectively, for 0.05, 0.1 and 0.2 M PS compared with 67.7%, 77.2% and 78.2% at 50 °C and 42.8%, 48.5% and 51.5% at 23 °C, for the same PS concentration levels.

As summarized in Table 1 (reactions R1-R50) and in Scheme 1, the PS oxidation chemistry of NO in the presence of Fe^{2+} -EDTA is complex, since it takes place through direct electron transfer from the PS anion, and free radical reactions via the sulfate radical generated by activation (R5-R10), 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 2. NO concentration profiles for different initial $\text{Na}_2\text{S}_2\text{O}_8$ concentrations (0.05, 0.10 and 0.20 M) with 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$ at various temperatures (23-70 °C): (a) 23, (b) 30, (c) 40, (d) 50, (e) 60 and (f) 70 °C.

Figure 3. Dependence of NO fractional conversions on different initial $\text{Na}_2\text{S}_2\text{O}_8$ concentrations (0.05, 0.10 and 0.20 M) with 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$ at various temperatures (23-70 °C): NO conversion as a function of (a) $\text{Na}_2\text{S}_2\text{O}_8$ concentration and (b) temperature.

It is also obvious from these results that increasing the temperature of the system at the same persulfate level led to an increased conversion of NO. The rate constants of PS decomposition

have been reported to be $1.0 \times 10^{-7} \text{ s}^{-1}$ and $5.7 \times 10^{-5} \text{ s}^{-1}$ (measured at pH 1.3) at 25 °C and 70 °C, respectively, suggesting that the rate constant at 70 °C is 570 times greater than that obtained at 25 °C.[21] The activation energy for the PS thermolysis has been reported to be 33.5 kcal mol⁻¹, indicating that decomposition of PS is much faster at high temperature than at low temperature.[35] This means that the thermal activation simply enhances the rate of generation of reactive radicals at the same PS concentration. Therefore, it is expected that elevated temperature could promote the decomposition of PS to form more sulfate radicals, resulting in an increased removal of NO. As evidence from Table 1, oxidation in PS solution occurs through reactions with the radicals generated by the decomposition of PS (R1–R3). The reaction between $\text{OH}^\bullet$ and NO (R5) is about a factor of 100 faster than reaction between $\text{OH}^\bullet$ or $\text{SO}_4^{\bullet-}$ with Fe^{2+} (R11 and R12), and a factor of 10 faster than even its self-recombination reaction (R14). Also, $\text{OH}^\bullet$ and $\text{SO}_4^{\bullet-}$ generated are more likely to react directly with NO as in reactions (R4-R5). It is expected that further addition of PS dose from 0.10 to 0.20 leads to the production of larger amounts of sulfate radicals ($\text{SO}_4^{\bullet-}$), which became more pronounced at the higher temperatures.[20] On the other hand, in a PS-driven process, excess $\text{SO}_4^{\bullet-}$ (from PS overdose) may recombine into $\text{S}_2\text{O}_8^{2-}$ (R15), and additionally react with the PS anion (R16) or be scavenged by Fe^{2+} (R12). These reactions may become significant to compete with the $\text{SO}_4^{\bullet-}/\text{NO}_x$ reactions in solution. Therefore, the slowing down of the NO conversion with increasing PS and temperature (at optimal initial concentrations of both Fe^{2+} and EDTA, i.e., 0.01 M)[19, 25] can be attributed to the combined effects of excessive release of $\text{SO}_4^{\bullet-}$ resulting in the enhancement of self-recombination and inter-combination of radicals ($\text{SO}_4^{\bullet-}$ and $\text{OH}^\bullet$) as shown in reactions (R13–R17).

Table 1. Proposed Reaction Scheme for NO Removal by the Combined Persulfate and Fe²⁺-EDTA Systems

R#	Reaction	Kinetic Constant	Refs.
Persulfate Degradation and NO Consumption by Radicals			
R1	$S_2O_8^{2-} + \text{heat} \xrightarrow{k_1} 2 SO_4^{\bullet -}$	$1.0 \times 10^{-7} (25^\circ C)$ or $5.7 \times 10^{-5} s^{-1} (70^\circ C)$	18
R2	$S_2O_8^{2-} + Fe^{2+} \xrightarrow{k_2} SO_4^{2-} + SO_4^{\bullet -} + Fe^{3+}$	$1.7 - 2.7 \times 10^1 M^{-1} s^{-1} (70^\circ C)$	17
R3	$SO_4^{\bullet -} + H_2O \xrightarrow{k_3} HSO_4^- + OH^\bullet$	$6.6 \times 10^2 s^{-1}$	17
R4	$SO_4^{\bullet -} + NO + H_2O \xrightarrow{k_4} HSO_4^- + NO_2^- + H^+$		16
R5	$OH^\bullet + NO \xrightarrow{k_5} H^+ + NO_2^-$	$2 \times 10^{10} M^{-1} s^{-1}$	17
R6	$OH^\bullet + NO_2^- \xrightarrow{k_6} OH^- + NO_2$	$1 \times 10^{10} M^{-1} s^{-1}$	38
R7	$S_2O_8^{2-} + NO_2^- \xrightarrow{k_7} SO_4^{2-} + SO_4^{\bullet -} + NO_2$		28
R8	$NO_2^- + SO_4^{\bullet -} \xrightarrow{k_8} SO_4^{2-} + NO_2$	$9.8 \times 10^8 M^{-1} s^{-1}$	38
R9	$NO_2 + OH^\bullet \xrightarrow{k_9} H^+ + NO_3^-$	$4.5 \times 10^9 M^{-1} s^{-1}$	38
Direct Consumption of NO by Persulfate			
R10	$S_2O_8^{2-} + NO + H_2O \xrightarrow{k_{10}} 2 HSO_4^- + NO_2$	$2.59 \times 10^{-4} M^{-1} s^{-1} (23^\circ C),$ $1.5 \times 10^{-3} M^{-1} s^{-1} (90^\circ C)$	17
Reactions of Ferrous Ion with Radicals			
R11	$Fe^{2+} + OH^\bullet \xrightarrow{k_{11}} Fe^{3+} + OH^-$	$3.2 \times 10^8 M^{-1} s^{-1}$	28
R12	$SO_4^{\bullet -} + Fe^{2+} \xrightarrow{k_{12}} Fe^{3+} + SO_4^{2-}$	$4.6 \times 10^9, 3.0 \times 10^8 M^{-1} s^{-1}$	28
Radical inter/re-combination & persulfate Interaction			
R13	$SO_4^{\bullet -} + OH^\bullet \xrightarrow{k_{13}} HSO_4^- + 0.5 O_2$	$1 \times 10^{10} M^{-1} s^{-1}$	28
R14	$OH^\bullet + OH^\bullet \xrightarrow{k_{14}} H_2O_2$	$5.5 \times 10^{10} M^{-1} s^{-1}$	38

$R15 \text{ SO}_4^{\bullet-} + \text{SO}_4^{\bullet-} \xrightarrow{k_{15}} \text{S}_2\text{O}_8^{2-}$	$4.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	16
$R16 \text{ SO}_4^{\bullet-} + \text{S}_2\text{O}_8^{2-} \xrightarrow{k_{16}} \text{S}_2\text{O}_8^{\bullet-} + \text{SO}_4^{2-}$	$6.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	16
$R17 \text{ OH}^{\bullet} + \text{S}_2\text{O}_8^{2-} \xrightarrow{k_{17}} \text{S}_2\text{O}_8^{\bullet-} + \text{OH}^-$	$1.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	17
NO Absorption Reaction by FeSO_4		
$R18 \text{ FeSO}_4 + \text{NO} \xrightleftharpoons{K_{18}} \text{Fe(NO)SO}_4$		25
Reactions of Fe^{2+} -EDTA with NO_x		
$R19 \text{ Fe}^{2+} + \text{EDTA}^{2-} \xrightleftharpoons{K_{19}} \text{Fe}^{2+}\text{-EDTA}$		27, 31
$R20 \text{ Fe}^{2+}\text{-EDTA} + \text{NO} \xrightleftharpoons{K_{20}} \text{Fe}^{2+}\text{-EDTA(NO)}$	$3.6 \times 10^6 \text{ M}^{-1}(25^\circ\text{C}),$ $6.0 \times 10^5 \text{ M}^{-1}(50^\circ\text{C})$	27, 31
$R21 \text{ 2Fe}^{2+}\text{-EDTA} + \text{NO}_2^- + 2\text{H}^+$ $\xrightleftharpoons{K_{21}} \text{Fe}^{2+}\text{-EDTA(NO)} + \text{Fe}^{3+}\text{-EDTA} + \text{H}_2\text{O}$		31
$R22 \text{ 2Fe}^{2+}\text{-EDTA(NO)} + 2\text{Fe}^{2+}\text{-EDTA} + 4\text{H}^+$ $\xrightarrow{k_{22}} 4\text{Fe}^{3+}\text{-EDTA} + \text{N}_2 + 2\text{H}_2\text{O}$		31
$R23 \text{ 2Fe}^{2+}\text{-EDTA} + 2\text{NO}_2 \xrightleftharpoons{K_{23}} \text{Fe}^{2+}\text{-EDTA(NO)} + \text{Fe}^{3+}\text{-EDTA} + \text{NO}_3^-$		31
Radical Reactions Under Alkaline Condition		
$R24 \text{ SO}_4^{\bullet-} + \text{OH}^- \xrightarrow{k_{24}} \text{SO}_4^{2-} + \text{OH}^{\bullet}$	$1.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	14
$R25 \text{ OH}^{\bullet} + \text{OH}^- \xrightleftharpoons{K_{25}} \text{O}^{\bullet-} + \text{H}_2\text{O}$ (at very high pH)		14
Reactions Under Acidic Condition		
$R26 \text{ S}_2\text{O}_8^{2-} + \text{H}^+ \xrightarrow{k_{26}} \text{HS}_2\text{O}_8^-$		18, 30
$R27 \text{ HS}_2\text{O}_8^- \xrightarrow{k_{27}} \text{H}^+ + 2\text{SO}_4^{\bullet-}$		18, 30
$R28 \text{ S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \xrightarrow{\text{H}^+, k_{28}} \text{H}_2\text{SO}_5 + \text{SO}_4^{2-}$ (pH < 3)		18, 30
Reduction of Fe^{3+} -EDTA and Fe^{2+} -EDTA(NO)		

R29 $Fe^{3+}-EDTA + NO_2^- \xrightarrow{k_{29}} Fe^{2+}-EDTA + NO_2$		28
R30 $Fe^{3+}-EDTA + HSO_4^- \xrightarrow{k_{30}} Fe^{2+}-EDTA + 0.5S_2O_8^{2-} + H^+$		28
R31 $Fe^{3+}-EDTA + SO_4^{\bullet-} \xrightarrow{k_{31}} Fe^{2+}-EDTA + 0.5S_2O_8^{2-}$		28
R32 $Fe^{2+}-EDTA(NO) + 2HSO_4^- \xrightarrow{k_{22}} Fe^{2+}-EDTA + SO_4^{2-} + H_2SO_5 + 0.5N_2$		28
R33 $Fe^{2+}-EDTA(NO) + SO_4^{2-} \xrightleftharpoons{K_{23}} Fe^{2+}-EDTA(NO)SO_4^{2-}$		28
R34 $3Fe^{2+}-EDTA(NO) + 4HSO_4^- \xrightleftharpoons{K_{34}} 3Fe^{2+}-EDTA + 2HON(SO_4)_2^{2-} + 0.5N_2 + H_2O$		34, 45
R35 $4Fe^{2+}-EDTA(NO) + 4HSO_4^- \xrightarrow{k_{35}} 4Fe^{2+}-EDTA + 2HON(SO_4)_2^{2-} + H_2N_2O_2$		34, 45
R36 $H_2N_2O_2 \xrightarrow{k_{36}} N_2O + H_2O$		34, 35
R37 $2Fe^{2+}-EDTA(NO) + SO_4^{\bullet-} \xrightleftharpoons{K_{37}} 2Fe^{2+}-EDTA + (NO)_2SO_4^{2-}$		34, 45
R38 $(NO)_2SO_4^{2-} \xrightleftharpoons{K_{38}} N_2O + SO_4^{2-} + 0.5O_2$		34, 45
R39 $3N_2O + H_2O \xrightarrow{k_{39}} 2HNO_2 + 2N_2$ (O_2 deficient solution)		28, 46
R40 $Fe^{2+}-EDTA(NO) + SO_4^{\bullet-} \xrightleftharpoons{K_{40}} Fe^{2+}-EDTA(NO)SO_4^{2-}$		28
OH-Radical Induced Degradation of EDTA		
R41 $[Fe(edta)]^{2-} + OH^{\bullet} \xrightarrow{k_{41}} [Fe(edta)]^{\cdot-} + OH^-$	$0.4 - 5.0 \times 10^9 M^{-1}s^{-1}$	36, 37
R42 $[Fe(edta)]^{\cdot-} + OH^{\bullet} \xrightarrow{k_{42}} H_2O + \text{products}$	$0.52 - 2.0 \times 10^9 M^{-1}s^{-1}$	36, 37
Iron-EDTA pH-dependent Equilibrium and Speciation		
R43 $Fe^{2+} + EDTA^{4-} + H^+ \xrightleftharpoons{pH=1, LogK_{42}=2.8} FeHEDTA^-$		40
R44 $Fe^{2+} + EDTA^{4-} \xrightleftharpoons{pH=6, LogK_{44}=14.25} FeEDTA^{2-}$		40

R45 $FeEDTA^{2-} + OH^- \xrightleftharpoons{pH=9, LogK_{45}=4.87} FeEDTA(OH)^{3-}$		40
R46 $FeEDTA(OH)^{3-} + OH^- \xrightleftharpoons{pH=10.5, LogK_{46}=4.1} FeEDTA(OH)^{4-}$		40
R47 $FeEDTA(OH)^{4-} + OH^- \xrightleftharpoons{pH=10.5, LogK_{47}=4.1} Fe(OH)_2 \downarrow + EDTA^{4-}$		40
Reduction of Ferric Chelates by Bisulfite		
R48 $Fe^{3+} - EDTA + HSO_3^- \xrightarrow{k_{48}} FeSO_3^+ + H^+ + EDTA$		34
R49 $FeSO_3^+ \xrightarrow{k_{49}} Fe^{2+} + SO_3^{*-}$		34
R50 $SO_3^{*-} + OH^\bullet \xrightarrow{k_{50}} HSO_4^-$		34

3.2. Effect of EDTA Concentrations and Temperature on NO Removal.

Figure 4 illustrates the effects of different EDTA concentrations (0.005, 0.01, 0.02 and 0.05 M) with 0.1 M PS and 0.01 Fe^{2+} on NO concentration profiles at temperature range 23 – 70 °C. At 23 °C the steady-state NO conversion increases significantly (38.0% to 48.5%) as EDTA concentration increases from 0.005 to 0.01 M, with the marginal conversion increase getting smaller at 0.02 M (52.6%) but with decreasing to 51.3% as EDTA concentration further increased to 0.05 M. The trend of the results at 30 °C is similar to that of 23 °C, showing NO conversion of 48.7%, 55.6%, 61.8% and 61.2% with increasing EDTA concentrations. However, at higher temperatures, the antagonistic effect of increasing EDTA concentrations becomes more pronounced. At 40 °C, NO conversions are 60.7%, 65.1% and 66.2 with EDTA concentrations of 0.005, 0.01, and 0.02 M, respectively, but at 0.05 M EDTA the solution losses almost all its absorption capacity and NO profile showing a breakthrough and a steady-state conversion of only 19.1% as shown in Figure 4(c). This behavior was also observed at 50, 60 and 70 °C as shown in Figure 4 (d, e and f). For example, at 50 °C, NO removal increases from 70.7% to

77.8% when EDTA concentration is increased from 0.005 to 0.01 M, while at 0.02 M it actually decreased to 73.6%.

Figure 4. NO concentration profiles for different initial Na₂-EDTA concentrations (0.005, 0.01, 0.02 and 0.05 M) for 0.1 M Na₂S₂O₈ and 0.01 M Fe²⁺ solution system at various temperatures (23-70 °C): (a) 23, (b) 30, (c) 40, (d) 50, (e) 60 and (f) 70 °C.

But at 0.05 M EDTA the solution losses almost all its absorption capacity and NO profile could be seen to rise upward sharply after maintaining absorption for a short time, resulting in an eventual NO removal of only 13.3%. Also, at 70°C, NO conversion increased from 83.4 to 96.3 % as EDTA concentration increased from 0.005 to 0.01 M EDTA. However, it should be noted that, at 0.02 M EDTA the initial NO removal appears to be 78.0%, but the solution losses its absorption capacity significantly in about 2200 s, resulting in a sudden rise in NO profile before stabilizing at 29.2%. In Figure 5, the NO conversion is plotted as a function of temperature for the different EDTA concentrations. With 0.10 M Na₂S₂O₈, 0.01 Fe²⁺ and ≤ 0.01 M EDTA, NO conversion increased with temperature from 23 to 70 °C (with the rate highest for 0.01 M EDTA), and showed significant improvement over the case with no EDTA over the entire temperature range. Interestingly, it can be observed that with 0.01 EDTA, the increase in NO conversion with temperature is steep and linear over the whole temperature range. However, with 0.02 M EDTA, the NO conversion increases almost linearly up to 60 °C (76.0%) before dropping sharply at 70 °C with NO conversion of 29.2% (which is below the value observed in the absence of EDTA of about 69%;, and with 0.05 M EDTA, the rapid decline of NO conversion started even earlier at 30 °C.

In addition to the Fe²⁺ activation of PS in reaction (R2), Fe²⁺ and EDTA react with one another according to the reversible reaction (R19). This reaction dictates the presence of Fe²⁺, EDTA and Fe²⁺-EDTA in the solution, with enough Fe²⁺ expected to remain in the solution for PS activation. The kinetics of this reversible reaction fixes the amount of Fe²⁺-EDTA produced

in the solution. The Fe^{2+} -EDTA absorbs NO by a reversible binding producing nitrosyl compound as represented in reaction (R20). It is observed from both Figure 4 and Figure 5 that the effectiveness of the NO removal is dependent on both temperature and EDTA concentration. 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 PS activation. As noted at 40 °C and 50 °C (Figure 4c and 4d), the initial results for 0.05 M EDTA were not as stable, suggesting that higher PS activation predominates initially resulting in higher NO removal but absorption efficiencies are shortly lost as Fe^{2+} is depleted with time. As the temperature increases (Figure 4e and 4f) the loss of NO absorption efficiency appears to be immediate.

Figure 5. Dependence of NO fractional conversions on temperature (23-70 °C) for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ and 0.01 M Fe^{2+} solution system in the presence of different initial concentrations of $\text{Na}_2\text{-EDTA}$.

It should be noted that high temperature reduces the physical solubility of NO, which is unfavorable for gas-liquid mass transfer. On the other hand, the mass transfer coefficient (K_La) increases with temperature due to the acceleration of molecular diffusion, and the driving force

provided by chemical reaction in a reactive gas-liquid process. In a recent study, Adewuyi et al (2014) determined chemical reaction plays the dominant role in the temperature range of this study.[20] Therefore, these results could be partly attributed to the reversible binding of NO with Fe^{2+} -EDTA in reaction (20).[25, 36] The forward reaction constant, k_{18} (in R18) 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_{20} (in R20) increases from 6 to 60 s^{-1} , resulting in a lower value of equilibrium constant K_{20} at the higher temperature. However, the Fe^{2+} -EDTA reversible binding with NO (R20) is slower at higher temperature as backward reaction rate increases. It should be noted that the use of Fe^{2+} -EDTA has advantage over Fe^{2+} -only activated PS as iron chelating prevents or minimizes the scavenging of $\text{OH}^\bullet$, and hence, prevents suppression of Fenton or Fenton-like reactions. Thus, in reactions (R11-R12), where Fe^{2+} was responsible for the scavenging of $\text{OH}^\bullet$ and $\text{SO}_4^{\bullet-}$, such reactions are suppressed when Fe^{2+} -EDTA is used instead of Fe^{2+} only. It has also been reported that NO binds to FeSO_4 in solution in a relatively very slow reaction (R18) with the order of magnitude of the reaction constant four times less than that of reaction (R20), and hence, considered insignificant in the removal of NO by the Fe^{2+} -EDTA absorption system.[29] However, it may play a significant role in combined PS and Fe^{2+} -EDTA systems. In Fe^{2+} -activated PS system, all the Fe^{2+} reacts very quickly and remains virtually non-existent in the solution and the possibility of reaction (R18) is negligible to nil. But in the combined PS and Fe^{2+} -EDTA systems, the concentration of Fe^{2+} is determined by the equilibrium reaction (R20), and the possibility of reaction (R18) is reinvigorated and could aid the removal efficiency of NO. Fe^{2+} -EDTA also reacts with NO_2^- and NO_2 by reactions (R21) and R23), and acts as an electron donor in the denitrification of Fe^{2+} -EDTA(NO) in a chemical reaction (R22) much as in biological processes where ethanol is

known to act as a electron donor compound.[36] As previously observed, the production of both Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA could reduce the absorption capability of the solution with time. The success of an effective NO removal by Fe^{2+} -EDTA was attributed to the efficient reduction of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA, and regeneration of Fe^{2+} -EDTA into the system. Sulfate and other PS derived ions in the system are also thought to effectively accomplish this task. It has been reported that HSO_3^- and/or SO_3^{2-} can be used to reduce Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA.[37]

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 reaction (R29), and thus aiding iron recycling to maintain PS activation.[38] In addition, reactions (R30-R40) involving sulfate anions and radicals have been proposed as pathways for the reduction of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA back to Fe^{2+} -EDTA.[25, 39] Therefore, it could be implied that the PS system also helps Fe^{2+} -EDTA chemistry, producing a complete synergistic and simultaneous relationship. The possible formation of Caro's acid (H_2SO_5) with regeneration of Fe^{2+} -EDTA in reaction (R32) is noteworthy, since the PMS anion (HSO_5^-) is a known powerful oxidant for both NO_x and S(IV) in the pH range of 6.5-8.5.[10, 40]

The longtime viability of the absorbent solution was also tested at 30 °C for both Fe^{2+} -PS and the combined PS and Fe^{2+} -EDTA processes. For the prolonged period of time (6 h), NO conversion was found to be 28.07% for Fe^{2+} activated PS system and 56.88% for the combined PS and Fe^{2+} -EDTA system as shown in Figure 6. The longtime viability of the combined solution to better sustain NO absorption-oxidation capability suggests the possibility of continuous reduction of both Fe^{3+} -EDTA and Fe^{2+} -EDTA(NO) to Fe^{2+} -EDTA, confirming the beneficial action of PS and its derived radicals and ions on Fe^{2+} -EDTA rejuvenation.[25]

Figure 6. Comparative NO concentration profiles for a prolonged period of time (6.0 h) for 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ and 0.01 M Fe^{2+} solution system in the absence and presence of 0.01 M $\text{Na}_2\text{-EDTA}$ at 30 °C.

However, as indicated earlier, 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 PS is faster and so is the rate of generation of oxidative species. Also, it is well known that $\text{OH}^\bullet$ reacts with Fe-EDTA as in reactions (R41-R42), with rate constants (at about pH 6) ranging from 4.0×10^8 to $5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. [41-43] Also, as previously noted, the $\text{OH}^\bullet$ and $\text{SO}_4^{\bullet-}$ generated in the reacting system more likely to react with NO_x species since these reactions are 10 -100 times higher than reactions (R41 and R42) at the optimal EDTA concentrations and lower temperatures. But at higher EDTA concentrations and temperatures, the OH-induced degradation of EDTA could be significant. It has been reported that reaction (R41) has a large activation energy due to the large reorganization energy required. [41] Therefore, the decrease in NO removal with increase in EDTA may also be due to the effect of excessive chelating agents, which may inhibit the reaction of NO_x species by rapidly

scavenging $OH^\bullet$. The combinative effects of these reactions could explain why at lower EDTA concentration, PS and Fe^{2+} -EDTA act synergistically to significantly improve NO removal, but antagonistically at the higher EDTA concentration and higher temperature to completely depletes the absorption capacity of the solution for NO as observed in Figures 4 and 5. In general, the degradation of chelating agent by $OH^\bullet$ depends on various factors such as pH, oxidant's dose, concentration of target pollutants, and radical scavengers (e.g., bicarbonate ions).[44]

3.3 Effect of pH and Temperature on NO Removal:

The combined effects of pH and temperature on the NO conversion are illustrated in Figure 7 for $Na_2S_2O_8$ (0.1 M) and Fe^{2+} -EDTA (0.01 M) reaction system. Figure 7 (a and b) show the NO concentration profiles at 40 and 50 °C. In general, NO removal is lower for both temperatures at very low and high pH levels compared to mid-pHs. As shown in Figure (7c), the steady state NO conversion (at time ≥ 3000 s) increases with pH 2 up to pH 6.5 with the marginal increase steeper at 50°C compared to 40°C, but begin to drop for both temperatures beyond pH 6.5. However, from pH 6.5 to pH 12, the drop is more pronounced at 50°C than at pH 40°C, and by pH 12, the NO conversion is actually higher at 40°C than at 50°C. Compared with our previous studies with $Na_2S_2O_8$ -only and $Na_2S_2O_8$ - Fe^{2+} systems without EDTA) [17, 19], these results indicate significant improvement in NO removal. The removal is also optimal at pH around 6-8), avoiding the pH (≤ 3.5) limitation of $Na_2S_2O_8$ - Fe^{2+} only system, the main drawback for Fenton-like systems.

Persulfate is known to be highly reactive at low pH (< 3) (R26-R28), and also at high pH (>10) (R24-R25).[21] Khan and Adewuyi (2010) studied the effects of pH ($\leq 4, 7, 9$ and 12) on the aqueous PS-only removal of NO at different temperatures (23, 50 and 70°C). They observed that acidic pH did not influence the rate of absorption of NO, whereas at $pH \geq 9$, increased NO

conversion occurred at higher temperatures.[17] It was stated that since $OH^\bullet$ reacts with NO at almost diffusion controlled rate ($k = 2 \times 10^{10} M^{-1}s^{-1}$)(R5), the consumption of NO in the liquid phase was expected to be much higher at alkaline conditions due to the generation of $OH^\bullet$ (R24) than in an acidic one. However, it was noted that at very high pH, NO removal effectiveness might be reduced due to the rapid dissociation of $OH^\bullet$ in alkaline solutions as illustrated in reaction (R25), where $k_f = 1.2 \times 10^{10} M^{-1}s^{-1}$ and $k_b = 9.3 \times 10^7 s^{-1}$ for the forward and backward reaction, respectively, and the oxide radical ion ($O^{\bullet-}$) produced is known to react more slowly with the same substrate than $OH^\bullet$. The effects of possible competition for $OH^\bullet$ and $SO_4^{\bullet-}$ by the phosphate species in the buffer system used was reported to be insignificant, hence, the impact on persulfate-NO_x system was expected to be minimum.[17]

EDTA (ligand denoted by Y) is an amino polycarboxylic acid (APCA) with four carboxylate and two amino groups. It is a weak acid for which the fully protonated acid and fully ionized conjugate base are H_4Y and Y^{4-} , respectively, and hence, the conjugate base form is significantly affected by the pH of the solution. With pH changing, there may be four kinds of Fe-EDTA species: $FeHY^-$, FeY^{2-} , $FeY(OH)^{-3}$, and $FeYOH^{-4}$, with equilibrium reactions

Figure 7. Effects of temperature and pH (2 – 12) on NO removal for the 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ solution in presence of combined 0.01 M Fe^{2+} and 0.01 M $\text{Na}_2\text{-EDTA}$: (a) NO concentration profiles at 40 °C, (b) NO concentration profiles at 50 °C, (c) Dependence of NO conversion on pH.

(R43–R47).[42] The formation constants (LogK) for the various complexation forms of Fe^{2+} and EDTA have been reported to be 2.8, 14.25, 4.87 and 4.1 at pH 1, 6, 9, and 10.5, respectively.[45] It can be concluded that the complex formation constant of Fe^{2+} -EDTA reached the largest value at pH of about 6.0. The effect of pH value on NO removal rate for the combined $\text{Na}_2\text{S}_2\text{O}_8$ and Fe^{2+} -EDTA system can be explained by the impacts of pH on the complex formation constant of EDTA and ferrous iron. The predominant EDTA species at pH = 7 are H_2Y^{2-} and HY^{3-} .[46]

Also, the Fe^{2+} -EDTA and Fe^{3+} -EDTA are reported to be the predominant species in the mid-pH range ($\text{pH} > 3.8 < 6.8$).[45] 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. The OH radical is electrophilic in its reactions with acids, and more strongly with amines; its rate of reaction is reduced when the substrate is protonated. The protonation and deprotonation of N atoms of an APCA bring about a lot of change in the electron density on the molecule, especially the α -carbon atom of the acetic acid moiety, thus resulting in a higher rate constant for the deprotonated form.[47, 48] Hobel et al.[42] in 1998, reported its rate constants with EDTA to be $4.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ at pH 4 (H_2Y^{2-}); $2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, much faster due to deprotonation, at pH 9 (HY^{3-}); and $6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ at pH 11 where Y^{4-} predominates. In addition, Dwibedy et al.[47] 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 protonated Fe^{3+} -EDTA and Fe^{2+} -EDTA complexes that predominant in the mid-pH range are less susceptible to $\text{OH}^\bullet$ oxidation, which is in consistent with the results in Figure 5 indicating optimal NO removal in the mid-pH range. As stated earlier, reaction (R41) has a large activation energy, hence, the scavenging of $\text{OH}^\bullet$ is also more severe at higher temperatures. Therefore, it should be expected that at higher pH (>11), the combinative effects of pH and temperature on $\text{OH}^\bullet$ depletion should more negatively impact NO removal at 50°C than at 40°C , consistent with Figure 7(c).

3.4. Effects of Initial EDTA Concentrations on Fe Speciation and Material Balance.

The effects of initial Na_2EDTA concentrations on iron speciation and material balance for solutions of 0.1 M PS and different Fe^{2+} concentrations at 50°C are summarized in the

supplementary material (Table S1) as steady state maximum, minimum and average concentration values for the respective species. The concentration profiles are illustrated in Figure 8. Table S1 also shows the comparison between the concentration of iron species in Fe^{2+} activated PS system and combined PS and Fe^{2+} -EDTA system at various initial concentrations of Na_2EDTA (0 – 0.02 M) and Fe^{2+} (0.005 – 0.02 M). The sum of labile Fe (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) measured spectrophotometrically in solution is denoted as total measured Fe. The undetermined Fe is the difference between initial iron and total measured iron concentrations, and consists of non-labile iron hydroxides, Fe^{2+} -EDTA(NO) and other non-labile iron species present in very small amounts. In PS- Fe^{2+} system, the undetermined Fe consists of only non-labile iron species, but in PS- Fe^{2+} -EDTA systems, undetermined Fe also consists of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA. The results in Table S1 reveal that the concentration of Fe^{3+} in PS- Fe^{2+} systems is almost equal to the sum of the concentration of Fe^{3+} and Fe^{2+} -EDTA in combined PS- Fe^{2+} -EDTA systems. This would suggest 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 PS activation by temperature and Fe^{2+} , further confirming that Fe^{2+} -EDTA does not suppress PS activation. Also, 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 expected to be Fe^{2+} -EDTA(NO), assuming that the concentration of the non-labile iron species remains the same for same initial Fe^{2+} concentration.

The concentration profiles of Fe^{2+} is shown in Figure 8(a) and its enlarged form, Figure 8(b), drawn to enhance Fe^{2+} concentration. It can be seen from Figure 8(a) that Fe^{2+} concentration remains close to zero throughout the experiment suggesting near complete reaction

with both PS and EDTA. However, it appears from Figure 8(b) that the use of molar ratio of up to 1:1 (generally considered the optimal ratio for Fe^{2+} and EDTA)[36] does not have a significant effect on the eventual amount of Fe^{2+} presents in the solution, hence, the beneficial effects on NO removal as observed in Figure 4. Figure 8c shows Fe^{3+} concentration, which is much lower in PS- Fe^{2+} -EDTA systems compared to PS- Fe^{2+} only system. It can be observed from Figure 8d showing the Fe^{2+} -EDTA concentration profiles and Table S1 that, for 0.01 M Fe^{2+} and 0.005 M EDTA, 20.9 % Fe^{2+} was converted to Fe^{2+} -EDTA; for 0.01 M Fe^{2+} and 0.01 M EDTA, 25.5 % Fe^{2+} was converted to Fe^{2+} -EDTA; and for 0.01 M Fe^{2+} and 0.02 M EDTA, 28.2 % Fe^{2+} was converted to Fe^{2+} -EDTA. Increasing initial EDTA converts more Fe^{2+} to Fe^{2+} -EDTA but Fe^{2+} -EDTA formation seems to slow down with increasing EDTA concentration. The total labile Fe (Fe^{2+} , Fe^{3+} and Fe^{2+} -EDTA) and undetermined Fe (non-labile species) concentration profiles are illustrated in Figures 8(e) and 8(f), respectively. Although, undetermined Fe concentration increased in PS- Fe^{2+} -EDTA systems compared to PS- Fe^{2+} only system, mainly due to the formation of Fe^{2+} -EDTA(NO) and Fe^{3+} -EDTA, the formation of non-labile species is not significantly dependent on initial EDTA concentration. Because all other non-labile species except Fe^{2+} -EDTA(NO) remain essentially constant throughout the experiment, the increase in the undetermined Fe can be attributed to increase in Fe^{2+} -EDTA(NO) concentration, resulting from the progression of its formation reaction (R20). Also, the slow variation of Fe^{2+} -EDTA(NO) concentration increases throughout the experiment, suggest that its accumulation in the solution is very small. Therefore, this would indicate its reduction back to Fe^{2+} -EDTA by PS and radicals in the system, thus confirming the synergistic action of PS with Fe^{2+} -EDTA.

Figure 8. Speciation plots for different iron components for different initial Na_2EDTA concentration (0.005-0.02 M) with initial Fe^{2+} concentration of 0.01 M and initial persulfate concentration 0.1 M at 50 °C: (a) Fe^{2+} , (b) Truncated and enlarged Fe^{2+} (≥ 1000 s), (c) Fe^{3+} , (d) Fe^{2+} -EDTA, (e) Total measured Fe and (f) Undetermined Fe profiles.

3.5. Effect of SO₂ on NO Removal.

In general, Fe²⁺ ions and its complexes promote the interaction between NO or HNO₂ and HSO₃⁻/SO₃²⁻ via nitrosyl complexes, leading to the formation of hydroxylaminedisulfonate (HON(SO₃)₂²⁻ or HADS), sulfamate (H₂N(SO₃)⁻, N₂O and HSO₄⁻, and is accompanied by the oxidation of Fe²⁺ to Fe³⁺. Completion of the catalytic cycle occurs spontaneously in the presence HSO₃⁻/SO₃²⁻. [39, 49] An important consideration in the removal of NO with iron chelates in WFGD scrubber system is the ability of the nitrosyl complexes to regenerate the metal chelates by reacting with absorbed SO₂ and S(IV) species. Sada et al. demonstrated that the absorption rate of NO in the presence of SO₂ exceeded that in the absence of SO₂, and the absorption enhancement was attributed to the following reactions. [29, 30]

where eq 5 and eq 9 both show the regeneration of Fe²⁺EDTA through reduction by HSO₃⁻, H₂N₂O₂ further decomposes to N₂O and H₂O above pH > 7.5, and N₂O₂²⁻ reacts with H₂O to produce N₂O (plus 2OH⁻). The Fe³⁺-EDTA is also reduced by HSO₃⁻ to produce Fe²⁺ and EDTA as shown in reactions (R48-R50). The oxidation of S(IV) by OH[•], SO₄^{•-} and S₂O₈²⁻ have

been discussed in details elsewhere.[18] N_2O usually forms 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)(R39).[25, 50, 51]

Figure 9. Concentration profiles for the simultaneous removal of NO and SO₂ at 30 °C for 0.1 M Na₂S₂O₈ solution in the presence of combined 0.01 M Fe²⁺ and 0.01 M Na₂-EDTA.

We have preliminarily investigated the effect of SO₂ (1800 ppm) on NO (550 ppm) removal in 0.1 M PS and 0.01 M Fe²⁺-EDTA solution at 30°C, and the result is shown in Figure 9. It appears that the presence of SO₂ does not significantly affect NO removal efficiency (even with a feed ratio of over 3:1 SO₂ and NO) compared with the case without SO₂ (51.9 vs. 55.6), while SO₂ itself is completely removed. In our prior studies using PS-only solution and a flue gas mixture of 1000 ppm NO and 1550 ppm SO₂, we evaluated in details the effects of SO₂, and observed SO₂ significantly enhanced NO removal in the complex reacting system, especially in the pH range of 6.5-8.5.[18] The slight increase observed in this study in the presence of a large amount of SO₂ is likely due to the combinative effects of SO₂ and EDTA enhancement of NO removal, and the competition of NO and SO₂ for available oxidants. Also, using aqueous PMS

and flue gas containing NO, SO₂ and CO₂, we previously showed that 5-10% CO₂ had no significant effects on NO removal.[10]

3.6 Relevance of this study to energy and the application of the process. It is evident from the results of this work that the PS-Fe²⁺EDTA process offers enough incentive for utilization in the simultaneous control of NO_x and SO₂ from oil- and coal-fired power plants, incinerators, and industrial emission sources. The best conditions for chemical reactions of NO_x are indicated in this paper. In addition to its enhanced reactivity, this process appears to demonstrate the feasibility of sustained longtime high NO absorption capability at relatively lower temperatures, resulting in reduced energy usage. This higher removal should provide a remarkable advantage in the cleanup of industrial flue gas, which is generally received at the treatment plant in the temperature range of 50–70 °C. Also, Liu and coworkers (2014) noted that boiler flue gas contains large amounts of waste heat and the temperature is often more than 120 °C, and suggested that this reservoir of waste heat from the boiler can completely provide the energy needed for thermal persulfate activation.[15] On the basis of the results, it appears that very high concentrations of NO and SO₂ can be simultaneously and effectively scrubbed from the flue gas by proper balance of PS and EDTA concentrations, and process temperature and pH. Generally, 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. In addition, an important aspect of this process is the ability of nitrosyl complexes to regenerate the metal chelate in the scrubber system with simultaneous production of sulfate and nitrogen species such as N₂. In addition, the complex Fe²⁺-EDTA(NO) can be decomposed to regenerate Fe²⁺-EDTA and recover NO as a rich gas.[25] The progress in liquid treatment is expected to

promote the application of wet scrubbing using Fe^{2+} -EDTA, making the PS- Fe^{2+} -EDTA a promising solution to multicomponent gas cleanup.

The approach used in this study is appropriate for relatively small-scale operations involving limited volumes of waste, which provide sufficient residence times in the scrubber for NO_x to dissolve and react with chemicals in the scrubbing solutions. For example, there are over 650,000 small and medium size coal-fired boilers, industrial furnaces and refuse incinerators in China alone, where the proposed wet process for the simultaneous treatment of NO_x and SO_2 could have great prospect for potential practical applications.[15] The bubble column reactor is useful for laboratory investigations. The scale-up of small-scale bubble columns such as the ones used in this study to large-scale units is straightforward and is presented in detail elsewhere.[9] Contact times for commercial bubble columns and packed columns range from 0.01 to 1.0 s.[10] This technology might also be applicable as an emergency system when the ordinary de NO_x system is out of order or in chemical industries where the gas flow rates are normally smaller than those from oil- and coal-fired power plants. We also see this approach is desirable for small operations that wish to obviate the need to install additional costly control equipment or have limited space to build a new SO_2 scrubber and an SCR system for NO_x control. Hence, the development of the innovative $\text{Na}_2\text{S}_2\text{O}_8$ - Fe^{2+} -EDTA technology would be timely given the need for continuous use of coal as a source of electric energy. This study is expected to be useful for its scaling-up in the future in pilot plant tests to better demonstrate the potential applications and cost benefits of this process.

However, the current study also indicates a number of areas in which additional research is needed. These include a more detailed study on the effects of SO_2 and other flue gas constituents (O_2 , CO_2); mass-transfer reaction kinetics; the determination of

intermediates/products for a more comprehensive material balance; and modeling. For example, flue gases typically contain 2-15 % O₂ resulting from excess air introduced into the fossil fuel combustion system to ensure O₂ to fully consume the fuel. As noted earlier, O₂ in the flue gas continuously oxidizes the Fe²⁺ in the coordinated EDTA during the NO absorption process by Fe²⁺-EDTA, producing the ferric complex, which is does not react with NO, by reaction in eq 11[36];

On the other hand, it has been suggested that NO₂⁻ as could react Fe³⁺-EDTA serving as an electron donor back to Fe²⁺-EDTA as in reaction (R29), aiding iron recycling.[25, 38] However, as noted by several investigators, the oxidation kinetics of Fe²⁺-EDTA by dissolved oxygen is complex.[52-54] Therefore, its role in the PS-NO-SO₂-Fe-EDTA system will require a more thorough evaluation, which is beyond the scope of the current investigation.

4. Conclusion

The effects of initial concentrations of PS and EDTA at different temperatures and pH levels on the removal of NO from simulated flue gas is investigated using combined aqueous Na₂S₂O₈ and Fe²⁺-EDTA solutions in a bubble column reactor. The experiments were conducted in the temperature and pH ranges of 23-70 °C and 2-12, respectively, using 0.05, 0.10 and 0.20 M Na₂S₂O₈ and 0.01 Fe²⁺ in the absence and presence of 0.005, 0.01, 0.02, and 0.05 M Na₂-EDTA. The effect of SO₂ was also preliminarily studied. Increased temperature led to an increased fractional conversion of NO (percent of inlet NO removed) at all persulfate levels, with the increases almost linear with temperature. On the other hand, high concentration of EDTA was not useful with increasing temperature. With 0.10 M Na₂S₂O₈, 0.01 Fe²⁺ and EDTA

concentration of ≤ 0.01 M, NO conversion increases with temperature from 23 to 70 °C, with the rate highest for 0.01 M EDTA concentration. However, with 0.02 M EDTA, NO conversion deteriorates rapidly at 60 °C, and with 0.05 M EDTA, the rapid deterioration started even earlier at 30 °C. At 70°C, NO conversion increases from 83.40 to 96.28 % with EDTA concentration from 0.005 to 0.01 M EDTA but decreases to 29.22 % with 0.02 M EDTA, and to 0.4 % with 0.05 M EDTA, compared to about 69 % in the absence of EDTA. The results at temperatures of 40 and 50 °C indicate that the process operates at an optimal NO removal in the pH of 6 - 8 with efficiency decreasing at very low or high pH. Better NO removal was obtained at the temperature of 50 °C compared to 40 °C except at the highest pH of 12, where the removal is higher at 40 °C.

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- The diagram illustrates the chemical reaction network for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ catalyzed NO_x reduction process. The process involves the following components and reactions:
- Inlet Gas:** Contains $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{Fe}^{2+}\text{-EDTA}$.
 - Reactor:** A blue cylinder where the inlet gas is treated. The output is **Treated Flue Gas**.
 - Waste Heat:** A green flame-like shape at the bottom, providing energy to the system.
 - Chemical Species and Reactions:**
 - Fe^{2+} is oxidized to Fe^{3+} by $\text{S}_2\text{O}_8^{2-}$ (from waste heat) to form $\text{Fe}^{2+}\text{EDTA}$ and $\text{Fe}^{3+}\text{EDTA}$.
 - $\text{Fe}^{2+}\text{EDTA}$ reacts with NO to form $\text{Fe}^{2+}\text{EDTA}(\text{NO})$ and $\text{Fe}^{3+}\text{EDTA}$.
 - $\text{Fe}^{3+}\text{EDTA}$ reacts with HSO_4^- to form $\text{Fe}^{2+}\text{EDTA}$ and NO_2^- .
 - NO_2^- is further oxidized to NO_3^- .
 - $\text{SO}_4^{\bullet-}$ (formed from $\text{S}_2\text{O}_8^{2-}$) reacts with $\text{OH}^{\bullet}$ to form HSO_3^- and SO_2 .
 - HSO_3^- is oxidized to SO_2 and NO .

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