INTRODUCTION

SO$_2$ and NO$_x$ as gaseous pollutants are released from different sources, especially from coal-fired power plants and cause serious environmental and health problems. These gases can form acid rain and photochemical smog, causing great harm to human health and ecosystems.$^{[1-10]}$

SO$_2$ and NO$_x$ emissions can be controlled by combining of flue gas desulfurization and denitrification equipment.

However, the large and complex systems and high capital and operating costs limit the application of such combined systems. Recently, studying new and low-cost approaches for simultaneous removal of NO$_x$ and SO$_2$ has become important issues in the field of gas purification.$^{[1,3-5,10]}$

Wet scrubbing is the most widely used approach in flue gas desulfurization (WFGD) process which ending in high SO$_2$
removal efficiencies. A conventional WFGD process is based on using a chemical absorbent like lime or limestone slurry to converting SO$_2$ into waste solids which must be removed from absorbing slurry. The final product in calcium absorbent-based FGD is calcium sulfate (CaSO$_4$) which present many operational problems. For solving this problem, air is blown into the slurry which oxidizes CaSO$_4$ to CaSO$_4$.\(^{[14]}\)

However, this process fails to reach high NO$_x$ removal efficiency because of very low solubility of nitric oxide (NO) which is a key component of NO, and constitutes about 90–95% of the entire emission.\(^{[8,9]}\) This low solubility greatly increases the liquid phase resistance in relation to the mass transfer of NO.\(^{[8,9]}\) A solution to overcome this drawback could be application of complex agents such as Fe$^{[1]}$EDTA, Fe$^{[II]}$ (CYS)$_3$, and Co$^{[III]}$ (en)$_3$, and oxidants such as KMnO$_4$, Na$_2$S$_2$O$_8$, NaClO, H$_2$O$_2$, and Fenton and using sonochemical oxidation in order to increase the absorption rate of NO in solutions,\(^{[1,7,13,15‑17]}\) while these technologies are still not developed because of high cost or existing technical problems.\(^{[1,10]}\)

Advanced oxidation processes (AOPs) are based on producing an oxidizing agent such as hydroxyl radicals to simultaneously oxidize and remove multiple pollutants. The ultraviolet (UV)/H$_2$O$_2$ process due to its strong oxidation ability, simplicity, and environmentally friendly character is widely used in wastewater treatment field.\(^{[3,4,18‑20]}\) UV light is applied for photochemical decomposition of H$_2$O$_2$ (based on Eq. (1)) to produce hydroxyl free radicals. These radicals are very strong oxidizing agents. The redox potential of hydroxyl radicals is 2.80 eV while this value for H$_2$O$_2$ is 1.77 eV.\(^{[5,6]}\)

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{UV light(hv)}} 2\cdot\text{OH} \quad (1)
\]

Recently, it is found that this process can be applied for simultaneous oxidizing of SO$_2$ and NO$_x$ into sulfuric and nitric acid without the generation of any secondary pollution.\(^{[10]}\) Considering the aforementioned advantages of UV/H$_2$O$_2$ process, if applied effectively in improving the existing WFGDs, it may significantly reduce the costs related to the simultaneous removal of NO$_x$ and SO$_2$.\(^{[1,10]}\)

The absorption of NO by UV/H$_2$O$_2$ process is essentially a reactive absorption process; therefore, the process performance is affected by chemical reaction.\(^{[10]}\) The study of reaction kinetics in the presence of mass transfer is an important issue. Knowing the mass transfer and kinetic parameters are essential for the numerical simulation of the process and the process development.

To the author’s knowledge, there are a few studies on modeling of reaction kinetics of NO removal using UV/H$_2$O$_2$ process. Liu et al.,\(^{[1]}\) based on two-film theory, investigated the mass transfer–reaction kinetics of NO absorption from flue gas by UV/H$_2$O$_2$/NaOH process. Their findings revealed that the absorption process of NO from flue gas using UV/H$_2$O$_2$/NaOH process is a pseudo-first-order fast reaction with respect to NO. The NO absorption rate described based on the cooperative effect of mass transfer and chemical reaction by a simple rate equation. The value of Ha numbers and rate constants are calculated in different experimental conditions.

Liu et al.\(^{[6]}\) studied the kinetic of simultaneous removal of NO and SO$_2$ from a simulated flue gas by the UV/H$_2$O$_2$ AOP without considering the mass transfer effect. Their results showed that the removal process of NO from SO$_2$-containing simulated flue gas using UV/H$_2$O$_2$ AOP is a pseudo-first-order reaction for NO. The effects of several parameters, including H$_2$O$_2$ initial concentration, UV lamp power, NO initial concentration, and reaction temperature on reaction rate constant were studied as well.

The focus of this study is on calculating the mass transfer-reaction kinetic parameters of NO absorption from SO$_2$-containing flue gas through UV/H$_2$O$_2$ AOP. The kinetic parameters are obtained and reported in terms of empirical reaction rate constants and Ha numbers. This study is based on experimental data reported by Liu et al.\(^{[1]}\) The kinetic parameters are obtained as a function of the concentration of the involved components and UV radiation intensity. Mass transfer-reaction kinetic parameters are important in process modeling, design or scale up procedures.

**KINETIC MODELING APPROACH**

In this section, the calculation procedure for obtaining the rate constant and Hatta number is presented. The major reaction pathway for the removal of NO from flue gas using UV/H$_2$O$_2$ includes the removal of NO by the oxidation of OH free radicals and the removal of NO by the oxidation of H$_2$O$_2$. The total reaction rate of NO absorption through UV/H$_2$O$_2$ process can be expressed as the sum of the oxidative removal rate of NO by OH free radical, and oxidative removal rate of NO by H$_2$O$_2$ by Eq. (2):

\[
\begin{aligned}
r_{\text{NO}} &= -\frac{dC_{\text{NO}}}{dt} \\
&= r_{\text{OH,NO}} + r_{\text{H2O2,NO}}
\end{aligned}
\]

where, $r_{\text{NO}}$ is the total reaction rate of NO removal by using UV/H$_2$O$_2$, (mol/Ls); $r_{\text{OH,NO}}$ is the oxidative removal rate of NO by OH free radical, (mol/L s); and $r_{\text{H2O2,NO}}$ is the oxidative removal rate of NO by H$_2$O$_2$, (mol/L s)\(^{[7]}\)

The oxidative removal rate of NO by OH free radicals could be presented as Eq. (3):

\[
r_{\text{OH,NO}} = k_{\cdot \text{OH}} C_{\cdot \text{OH}} C_{\text{NO}}
\]

where, $m$ and $n$ are the reaction orders for H$_2$O$_2$ and NO, respectively. In addition, it is found that the oxidative removal rate of NO by H$_2$O$_2$ is a reaction with an overall order of two,
where the order of reaction with respect to each reactant is one. This reaction rate can be expressed as Eq. (4):

\[ r_{D_{NO}} = k_{H2O2} C_{H2O2} C_{NO} \]  
(4)

The OH free radical has very low concentration because of its very short lifetime, so the concentration of OH free radical can be approximately assumed as a constant based on the steady-state approximation theory. Moreover in all experimental studies, the initial concentration of H2O2 (C_{H2O2}) is adjusted in the range of 10^-1 - 10^1 mol/L, which is much greater than that of the NO (10^-4 - 10^-5 mol/L). Therefore, the concentration of H2O2 can be approximately regarded as a constant, as well.6-7 accordingly Eq. (4) is changed into the following Eq. (5):

\[ r_{D_{NO}} = k_{H2O2} C_{H2O2,0} C_{NO} \]  
(5)

Thus, the total rate of NO absorption can be written as Eq. (6):

\[ r_{NO} = -\frac{dC_{NO}}{dt} = k_{obs} C_{NO} \]  
(6)

Based on the two-film theory, schematically shown in Figure 1, a mass balance for NO within a layer with the thickness of δ, under the steady state condition, leads to Eq. (7):

\[ D_{NO, L} \frac{d^2C_{NO}}{dx^2} = r_{NO} \]  
(7)

where, \( D_{NO, L} \) is the molecular diffusion coefficient of NO in the liquid phase (m^2/s); \( x \) is the differential element thickness in the liquid film (m).

The Eq. (7) can be solved based on the following boundary conditions:21

At \( x = 0 \), \( C_{NO} = C_{NO, i} \) and \( x = \delta \), \( C_{NO} = C_{NO, L} \).

It is assumed that the absorption of NO by UV/H2O2 is a fast reaction. Therefore, the concentration of NO in the bulk of liquid equals 0 (\( C_{NO, L} = 0 \)).1,7

Solving the Eq. (7) leads to NO concentration distribution in liquid as described by Eq. (8)

\[ C_{NO} = \frac{C_{NO,G} \sinh(\delta - x) \sqrt{\frac{k_{obs}}{D_{NO,L}}}}{\sinh(\delta \sqrt{\frac{k_{obs}}{D_{NO,L}}})} \]  
(8)

The rate of transfer or flux of NO into the liquid film, \( N_{NO}(x = 0) \), equals the diffusion rate at the gas-liquid interface.21

\[ N_{NO}(x = 0) = -D_{NO,L} \frac{dC_{NO}}{dx} \bigg|_{x=0} = \frac{C_{NO,G} \sqrt{k_{obs} D_{NO,L}}}{\tan(\sqrt{k_{obs} D_{NO,L}})} \]  
(9)

where, \( k_{obs} / D_{NO,L} \) and \( C_{NO,G} \) are the liquid phase mass transfer coefficient (m/s) and the interface concentration, (mol/L), respectively. In the case of a fast reaction (i.e., very large value of \( k_{obs} \)), the denominator in Eq. (9) is almost one and this equation can be rewritten as Eq. (10):

\[ N_{NO} = C_{NO,G} \sqrt{k_{obs} D_{NO,L}} \]  
(10)

It should be noted that the argument of tanh function in the denominator of Eq. (11) is a definition of Hatta number for a first-order reaction.

\[ Ha = \left( \frac{\sqrt{k_{obs} D_{NO,L}}}{k_{obs}} \right) \]  
(11)

The two-film theory holds that under steady-state condition, the absorption rate of NO removal can be described as the following Eq. (12):

\[ N_{NO} = k_{NO,G} (P_{NO,G} - P_{NO,i}) = E k_{NO,L} (C_{NO,G} - C_{NO,L}) \]  
(12)

where, \( N_{NO} \) is the absorption rate of NO, (mol/m^2s), \( k_{NO,G} \) is the gas phase mass transfer coefficient, (mol/s m^2Pa); \( P_{NO,G} \) is the NO partial pressure in bulk of gas, (Pa); \( P_{NO,i} \) is the NO partial pressure in gas-liquid interface, (Pa); \( C_{NO,L} \) is the NO concentration in the bulk of liquid, (mol/L); \( k_{NO,L} \) is the liquid phase mass transfer coefficient (m/s), and \( E \) is the chemical reaction enhancement factor.

\( C_{NO,G} \) can be correlated to \( P_{NO,G} \) based on Henry’s law (Eq. (13)):

\[ P_{NO,G} = H_{NO,L} C_{NO,G} \]  
(13)

where, \( H_{NO,L} \) is Henry constant (Pa.m^3/mol), which can be calculated by Eq. (14)

\[ \log \left( \frac{1}{H_{NO}} \right) = \frac{-146.32}{T} + 2.178 \]  
(14)
The Eq. (14) is the Van Krevelen and Hofitzer empirical equation where, $H_{NO,L}$ is the solubility of NO in the liquid phase (mol/L. atm).\(^1\)

Through manipulation of Eq. (12), $C_{NO,i}$ can be calculated by Eq. (15):

$$C_{NO,i} = \frac{1}{H_{NO,L}} \left( P_{NO,G} - \frac{N_{NO}}{k_{NO,G}} \right) \tag{15}$$

The NO diffusion coefficient in the liquid phase is calculated using Wilke and Chang empirical Eq. (16) as follows.\(^1\)

$$D_{NO} = 7.4 \times 10^{-16} \left( \frac{\theta_s M}{\mu_s} \right)^{0.15} \frac{T}{V_A} \text{ m}^2 / \text{s} \tag{16}$$

where, $\theta_s$ is the association factor, 2.6 for water; $V_A$ is the molar volume of gas, 23.9 cm\(^3\)/mol for NO; $D_A$ is the diffusion coefficient of the solute A at very low concentrations in water (m\(^2\)/s); and $T$ is temperature in K.

The value of $D_{NO,L}$, $H_{NO,L}$, and the value of $k_{NO,G}$ are summarized in Table 1. The value of the gas phase mass transfer is the same as reported by Liu et al.\(^7\)

The values of $k_{obs}$ under different experimental conditions are calculated through Eq. (10), where $N_{NO}$ is calculated based on experimental data from Liu et al.\(^4\) by Eq. (17) and $C_{NO,G}$ can be calculated by Eq. (15). The experimental values are reported in Table 2.

The following correlations (Eqs.(20-22)) are developed by López-López et al.\(^22\) for gas hold-up and liquid phase mass transfer.

$$\varepsilon_g = 4.86 U_g \tag{20}$$

$$d_{12} = 0.14 U_g + 0.0031 \tag{21}$$

where, $d_{12}$ is the suture diameter of gas bubbles.

$$k_i a = 3.6 U_g \tag{22}$$

The gas-liquid interfacial area can be calculated by Eq. (23):

$$a = \frac{\varepsilon \varepsilon_g}{d_{12}} \tag{23}$$

The values of calculated parameters are tabulated [Table 3].
RESULTS

The values of reaction rate constant are calculated based on Eq. (10) where CNO and NNO are obtained by Eq. (15) and Eq. (17), respectively. These values are fitted into the following empirical Eqs. (24) to (27) with NO concentrations, H2O2 concentrations, SO2 concentrations and UV radiation intensities. The results are also illustrated in [Figure 2 a-e].

\[ k_{o,b:NO} = 2.21 \times 10^7 \exp(-8 \times 10^{-4} C_{NO}) \text{ s}^{-1} \]
\[ R^2 = 0.971, \quad 200 \leq C_{NO} \leq 1100 \text{ ppm} \]

\[ k_{o,b:H_2O_2} = [0.623 \ln(C_{H_2O_2}) + 0.978] \times 10^5 \text{ s}^{-1} \]
\[ R^2 = 0.995,0.3 \leq C_{H_2O_2} \leq 2.5 \text{ mol} / \text{ L} \]

\[ k_{o,b:SO_2} = 2.45 \times 10^5 C_{SO_2}^{0.76} \text{ s}^{-1} \]
\[ R^2 = 0.973, \quad C_{SO_2} \geq 1000 \text{ ppm} \]

\[ k_{o,b:UV} = \left\{ \begin{array}{ll}
(7094 UV^2 - 20.01 UV + 0.045) \times 10^5 \text{ s}^{-1}, & \quad R^2 = 0.993,0 \leq UV \leq 0.012 \text{ W} / \text{ mL}, \\
(30.89UV + 0.916) \times 10^5 \text{ s}^{-1}, & \quad 0 < UV < 0.03 \text{ W} / \text{ mL}.
\end{array} \right. \]

As observed the \( k_{o,b} \) increases with an increase in \( H_2O_2 \) concentrations and UV radiation intensities, while it decreases with an increase in NO concentrations and SO2 concentrations. Since the NO absorption by UV/H2O2 process is a pseudo first order reaction, the NO absorption rate is proportional to the \( k_{o,b} \). Therefore the NO removal follows the same trend as \( k_{o,b} \) with different parameters. This trend emphasizes the fact that the NO absorption rate increases with an increase in \( H_2O_2 \) concentrations and UV radiation intensities, while decreases with an increase in NO concentrations and SO2 concentrations as indicated by Liu et al.[6]

DISCUSSION

As can be seen from Eq. (24) to (27) and [Figure 2 b-e], the rate constant values increase by increasing the \( H_2O_2 \) concentration and UV light intensity per liquid volume. It is obvious that an increase in \( H_2O_2 \) concentration or UV intensity means more \( OH \) free radicals and consequently more NO absorption. However, an increase in NO concentration results in decrease in rate constant value. Increasing in NO content means more NO molecules compete for absorbing by specified amount of hydroxyl radicals which results in a decrease in NO absorption rate. Also, Eq. (26) and [Figure 2c] confirm that the values of rate constant decrease with an increase in SO2 concentration. It reveals that at SO2 concentration higher than 1000 ppm the rate of NO absorption is decreased when SO2 concentration decreases which can be related to competitive behavior of this gas in consumption of hydroxyl radicals. It means that

| \( U_g \times 10^3 \) (m/s) | \( a_{NO,L} \) (1/m) | \( k_{NO,L} \times 10^4 \) (m/s) |
|-----------------|-----------------|------------------|
| 1.7             | 15.1            | 4.1              |

Table 3: The values of gas superficial velocity, gas-liquid interfacial area and liquid phase mass transfer

Figure 2: The effect of concentration of involved components in the reaction and radiation intensity on \( k_{o,b} \); (a) Effect of nitric oxide concentration, (b) Effect of \( H_2O_2 \) concentration (c), Effect of SO2 concentration and (d and e) Effect of Ultraviolet radiation intensity
in presence of SO$_2$, lower amount of hydroxyl radicals are available for NO oxidation.

The values of $N_{\text{NO}}$ are calculated by Eqs. (10) and (24) to (27) and compared with the experimental values obtained by Eq. (17) [Table 4]. It is observed that there is a good agreement between calculated and experimental values where the maximum absolute error is 16.18%. This error relates to the values of $N_{\text{NO}}$ calculated from different UV intensities between zero to 0.012 W/mL. The value of absolute error is obtained by Eq. (28):

$$\text{Absolute error} = \frac{\sum |N_{\text{NO,cal}} - N_{\text{NO,exp}}|}{n} \times 100$$

(28)

where, $n$ is the number of data points in each experiment.

Thus, the Eqs. (10) and (24) to (27) can be used to simulate the absorption process of NO by using UV/H$_2$O$_2$ advanced oxidation process.

Based on calculated $k_{\text{obs}}$, the Has are calculated by Eq. (11) under different experimental conditions where, $k_{\text{NO,1}}$ is taken from Table 3. The results are shown in Figure 3a-d, where all of the Ha numbers are greater than 3. This reveals that the removal process of NO through UV/H$_2$O$_2$ wet scrubbing is a fast reaction.

| Absolute error, $N_{\text{NO}}$ | Absolute error, H$_2$O$_2$ | Absolute error, SO$_2$ | Absolute error, UV First equation | Absolute error, UV Second equation |
|-------------------------------|--------------------------|-----------------------|----------------------------------|----------------------------------|
| 2.18                          | 1.38                     | 2.29                  | 16.18                            | 0.41                             |

Table 4: The values of errors relates to the values of $N_{\text{NO}}$ calculated by Eqs. (9) and (24) to (27)

in UV/H$_2$O$_2$ AOP are obtained. The calculations reveal that under different experimental conditions, the values of Ha numbers are > 3, confirming that the removal of NO by absorption through the liquid film is a fast reaction. The values of reaction rate constants $k_{\text{obs}}$ are calculated as well. These values are fitted by empirical equations, and the NO absorption rates are calculated through these equations under different conditions. The calculated values of $N_{\text{NO}}$ are in good agreement with experimental ones. The maximum value of absolute error is 16.18% which is reasonable in this context.

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**Conflicts of interest**

There are no conflicts of interest.

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