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Kinetic study on scrubbing on nitric oxide into sodium hypochlorite solution

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Abstract : Attempt has been made to investigate the reaction kinetics of scrubbing of nitric oxide into aqueous sodium hypochlorite scrubbing solution in a lab scale bubbling reactor. The effect of various operation variables such as nitric oxide and sodium hypochlorite concentration, initial pH, and temperature etc. was critically examined. Nitric oxide absorption reached to maximum value at an initial pH of 5.5 and thereafter absorption decreased slowly due to reduced oxidizing ability of scrubbing solution as higher pH. The absorption process followed first-order kinetics with respect to both nitric oxide as well as sodium hypochlorite. The pre-exponential frequency factor and activation energy were determined. The absorption rate of nitric oxide into aqueous sodium hypochlorite solution under the fast-reaction regime may be expressed by:

$$R_{NO} = \sqrt{k_2 \times D_{NO} \times C^2_{NO,i} \times C_{NaOCl}}$$

Keywords : Sodium hypochlorite; Nitric oxide; Order of reaction; Pre exponential factor; Activation energy.

INTRODUCTION

Nitrogen oxides (NO_x) and sulphur oxides (SO_x) are the main air pollutants found in the flue gases emitted from chemical plants and power plants. Technologies for removal of sulphur oxides has attained an advanced stage of development, however, it is not so in case of controlling NO_x emission. More than 90% of NO_x emitted from power plants consist of nitric oxide (NO) which is relatively inert.

Absorption of NO can be carried out either by using strong oxidative absorbent or by complex forming reagents. Wet scrubbers have been the workhorses of the chemical industry for decades and successfully used for removal of several acidic gases. In general, additives are added into scrubbing system to oxidize relatively inert NO into NO_2 which can be subsequently removed by alkaline absorbent. Aqueous solutions of numerous oxidative absorbents such as hydrogen peroxide[1], per acid[2], organic tertiary hydro peroxides[3], sodium chlorite[4 – 8], $KMnO_4$[9, 10] and chlorine dioxide[11, 12] have been investigated to determine their efficiency in the removal of NO_x.

Several other liquid absorbents, namely $FeSO_4$/H_2SO_4, Fe(II)EDTA, Na_2S/NaOH, $Na_2S_2O_4$/NaOH, Na_2SO_3, $FeSO_4$/Na_2SO_3, and urea have also been explored in the past to remove NO_x from the exhaust gases. Kustin et al[13] reported the absorption of NO in aqueous solution of $FeSO_4$ and found that the reaction follows first order kinetics both with respect to NO and $FeSO_4$. Sada et al[14] studied the kinetics of NO absorption in aqueous alkaline $KMnO_4$ solutions and reaction was found to be first order with respect to both NO and $KMnO_4$. Uchida et al[15] also studied NO absorption in aqueous alkaline solutions of $KMnO_4$ in a stirred tank absorber. Absorption of NO in aqueous mixed solutions of $NaClO_2$ and NaOH has been studied by Sada et al.[4, 5] The reaction was found to be second order with respect to NO and first order with respect to $NaClO_2$. Baveja et al[1] have studied the kinetics of liquid phase oxidation of NO in aqueous H_2O_2 solutions and reaction was found to be first order with respect to both NO and H_2O_2. Takeuchi et al[16] investigated that the absorption of NO in aqueous solutions of Na_2SO_3 was accompanied by a fast pseudo-second order reaction with respect to NO and zero order with respect to Na_2SO_3.

Teramoto et al[17] measured the absorption rates of NO in aqueous solutions of Fe (II) EDTA. The reaction was found to be first order with respect to both NO and Fe (II) EDTA. Warshaw[18] studied the absorption of nitrogen oxides into aqueous acidic urea solution. It is pertinent to mention here that aqueous acidic urea solution cannot be used for an exhaust gas which contains mostly NO (as in the case of flue gas from power plants). Khan and Adewuyi[19] studied the absorption-oxidation process of NO by aqueous solution of $Na_2S_2O_8$ in a bubbling reactor. $Na_2S_2O_8$ proved an economical agent for NO_x removal in gas-liquid contactors due to its low cost and environmentally benign nature. Guo et al[20] used Fenton reagent for NO removal. Kinetics of NO absorption in aqueous iron (II) thiochelate solutions were investigated by Shi et al[21] Recently, Mondal and Chelluboyana[22] investigated combined SO_2 and NO removal from simulated gas stream by NaOCl and observed 100% SO_2 and 92% NO removal efficiencies respectively. Chen et al[23] also used sodium hypochlorite as the oxidative absorbent for NO absorption.

Sodium hypochlorite has high oxidative ability in acidic medium and can be used as an effective additive for NO_x control in wet flue gas desulfurization scrubber. Inadequate studies have been made to investigate the oxidative absorption of NO into sodium hypochlorite solution; therefore, the present manuscript attempts to study the absorption kinetics of NO into sodium hypochlorite solution and to examine the effect of various operation variables such as concentration of NO and sodium hypochlorite, initial pH value, and reaction temperature etc.

THEORETICAL BACKGROUND

Henry's constant for NO in water is very small i.e. 1.218×10^{-3} M/atm at 45°C.[24] It suggests that NO has poor solubility in water. The relatively inert NO is firstly oxidized into NO_2 which is subsequently absorbed into scrubbing solution. Hypochlorous acid formed by acidic hydrolysis of sodium hypochlorite will oxidize NO into NO_2 (Eq. 2) followed by absorption (Eq. 3) of the later into aqueous HOCl solution. The plausible mechanism of reaction between NO and sodium hypochlorite in presence of sulphuric acid may be summarized as follows:

$$2NaOCl + H_2SO_4 \rightarrow 2HOCl + Na_2SO_4 \quad (1)$$

$$NO + HOCl \rightarrow NO_2 + HCl \text{ (oxidation)} \quad (2)$$

$$2NO_2 + HOCl + H_2O \rightarrow 2HNO_3 + HCl \text{ (absorption)} \quad (3)$$

From the above steps, the overall reaction between nitric oxide and aqueous sodium hypochlorite may be written as:

$$2NO + 3NaClO + H_2O \rightarrow 2HNO_3 + 3NaCl \quad (4)$$

EXPERIMENTAL

Kinetic study of scrubbing of NO into NaOCl solution was carried out in a lab scale lab scale bubbling reactor. A schematic diagram of the experimental system is shown in Figure 1. The flue gas cleansing unit included a simulated flue gas supply system, bubbling reactor, pH control system, and data acquisition system.

The simulated flue gas was obtained by con-

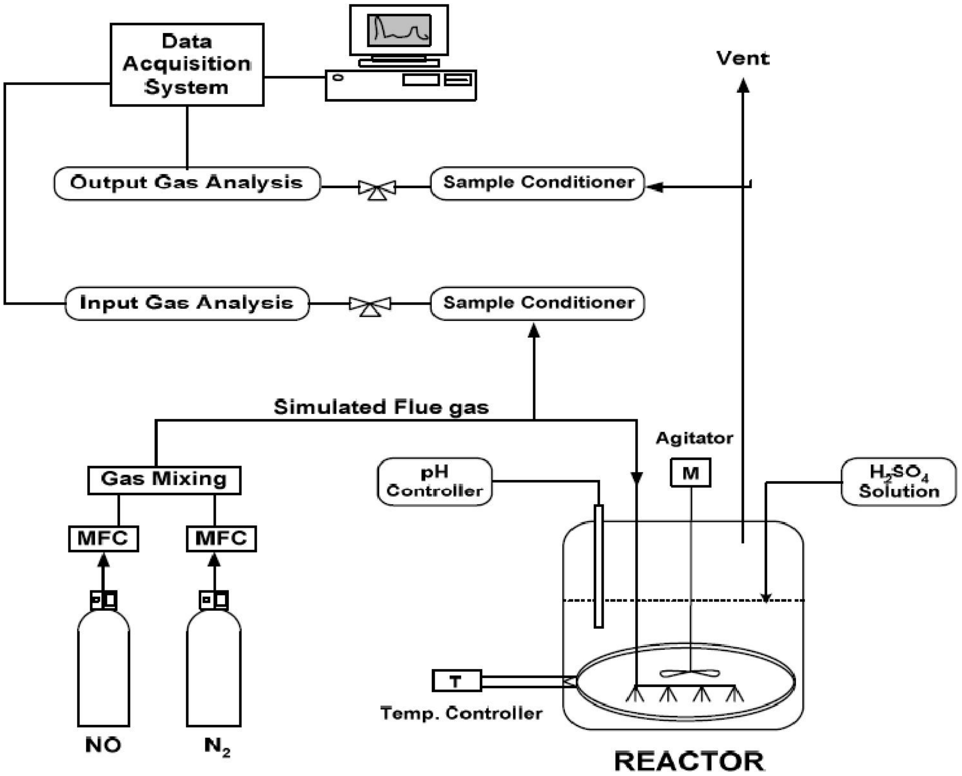

Figure 1 : A schematic diagram of the experimental apparatus

trolled mixing of NO and N_2 using mass flow controllers (MFC). The bubbling reactor is made up of acrylic material. The inner diameter and height of the reactor are 15 and 45 cm respectively. Continuous stirring was provided by mechanical agitator with a speed of 250 rpm. The temperature of the absorber and regeneration reactor was controlled by water thermostat (WBC-1506D, JEIO TECH, Korea). The pH of reaction solution was controlled by using an auto-pH control system (KFC-MK-250, Korea) by continuous addition of 0.2 M H_2SO_4 solution with the help of peristalsis pump (Cole-Palmer Co., USA). The simulated flue gas was obtained by controlled mixing of SO_2, NO, and N_2 using mass flow controllers (MFC). Air was introduced into reactor using air pump to maintain the dissolved O_2 concentrations at the desired level. The inlet and outlet NO_x concentrations were analyzed using the NO_x analyzer (Chemiluminiscent type, Model: 42C, Thermo Environmental Instruments, USA) after removing the moisture in the sample conditioner.

RESULTS AND DISCUSSION

Reaction kinetics

The absorption rate (R_{NO}) of NO into aqueous sodium hypochlorite solution can be expressed by:

$$R_{NO} = k_G(p_{NO,b} - p_{NO,i}) = Ek_L(C_{NO,i} - C_{NO,b}) \quad (5)$$

Here 'E' is the enhancement factor, which is a function of the Hatta number (H_a). Since concentration of NaOCl in the bulk liquid being much greater than the NO interfacial concentration, thus the kinetics of the reaction becomes pseudo-first order and in such instantaneous reaction, Hatta number is assumed to be equal to enhancement factor 'E'. The Hatta number can be calculated as follows:

$$H_a = \frac{1}{k_L}\sqrt{k_{(m+n)}D_{NO}C_{NaOCl}} \quad (6)$$

Further, k_G and k_L in Eq. (5) are the gas phase and liquid phase mass transfer coefficients respectively. The magnitude of and can be obtained by using the method as described by Deshwal and Lee[25]. Partial pressure of NO at interface i.e. can be calculated by using Henry's law:

$$p_{NO,i} = H_{NO}C_{NO,i} \quad (7)$$

Here is the interfacial concentration of NO in sodium hypochlorite scrubbing solution, which is related to the ionic strength (I) of the solution as follows:

$$\log\frac{C_{NO,i}}{C_{NO,iw}} = -(K_{NaOCl}I_{NaOCl} + K_{H_2SO_4}I_{H_2SO_4}) \qquad (8)$$

where and are the salting-out parameters for the electrolyte NaOCl and H_2SO_4 respectively. Due to small concentration of acid, the effects of H^+ and SOion on can be neglected, so Eq. (8) reduces to:

$$\log\frac{C_{NO,i}}{C_{NO,iw}} = -(K_{NaOCl}I_{NaOCl}) \qquad (9)$$

The salting-out parameter (K) of an electrolyte is obtained by addition of respective terms for the anions, cations and the gas. In short, it can be given by:

$$K = X_a + X_c + X_g \qquad (10)$$

The values of *X* for various species are available in literature:

$X_{Na^+} = -0.0183$ [26]

$X_{SO_4^{2-}} = 0.0183$ [26]

$X_{NO} = -0.1825$ [14]

However, is not available in the literature, thus the contribution of hypochlorite ion is assumed to be the same as that of chlorite ion:

$X_{ClO^-} = 0.3497$

The rate of reaction between nitric oxide and acidic sodium hypochlorite is assumed to be *m*th order with respect to NO and *n*th order with respect to NaOCl. Thus the absorption rate of NO into aqueous NaOCl solution could be expressed by the gas-liquid mass transfer theory as proposed by Danckwerts:[27]

$$R_{NO} = \sqrt{\left(\frac{2}{m+1} \times k_{(m+n)} \times D_{NO} \times C_{NO,i}^{m+1} \times C_{NaOCl}^{n}\right.} \qquad (11)$$

Whereis the diffusion coefficient of NO, which can be calculated from the Wilke-Chang equation as shown in Bird et al.[28] and its value was found to be **4.47×10^{-5} cm^2 s^{-1} at 50°C.**

After determining the value of *m* and *n*, the reaction rate constant can be calculated from Eq. (11). The value of rate constants were obtained at various temperatures ranging from 298 K to 328 K and then activation energy 'E_a' and pre-exponential frequency factor 'A' were obtained from Arrhenius Equation.

Order of Reaction with respect to NO

Experiments were performed to investigate the effect of gas-liquid NO concentration on its absorption rate at pH = 6.0, T = 328 K, and $C_{NaOCl,0}$ of zero, 0.04 M and 0.08 M. NO concentration was varied from 200 ppm to 1000 ppm. The effect of gas-liquid interfacial NO concentration on its absorption rate is shown in Figure 2, which clearly shows that the absorption rate of NO increased with the increasing gas-liquid interfacial NO concentrations. Danckwerts [27] indicated that during gas-liquid reac-

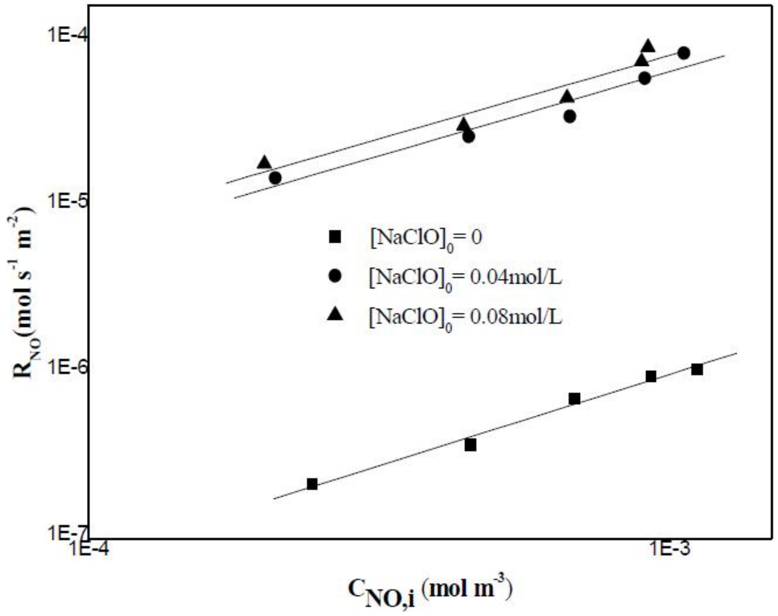

Figure 2 : Effect of gas-liquid NO conc. on its absorption rate at pH = 6.0 at 328K

tion, if $1 << \sqrt{M} << E_i$, then gas-liquid reaction can be assumed to be a pseudo m^{th} order reaction, where M is close to the fast reaction enhancement factor and E_i is the enhancement factor for instantaneous reaction. As shown in Figure 2, the values of the enhancement factor and the instantaneous enhancement factor for this study meet the requirement of $1 << \sqrt{M} << E_i$, as a result, the absorption rate of NO into aqueous sodium hypochlorite solution can be expressed by Eq. (11). It is obvious that there is a linear relationship between $\log R_{NO}$ and $\log C_{NO,i}$ and the average slope of these lines is close to 1, that is to say, $(m+1)/2$ is equal to 1, thus the value of m comes out nearly one i.e. the reaction is first-order with respect to NO.

Order of Reaction with respect to NaOCl

Experiments were performed to investigate the effect of NaOCl concentration on NO absorption rate at T = 328 K, pH = 6.0 and $C_{NO,i} = 8.58 \times 10^{-7}$ mol/L. NaOCl concentration was varied from 0.02 M to 0.1 M. Figure 3 shows the effect of NaOCl concentration on NO absorption rate. There is a linear re-

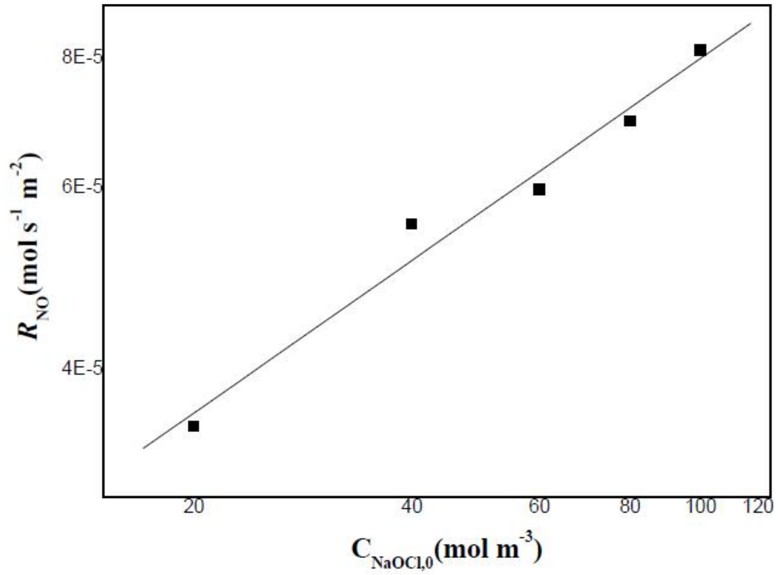

Figure 3 : Effect of NaOCl conc. on NO absorption rate at 328K, pH = 6.0 and $C_{NO,i} = 8.58\times10^{-7}$ mol/L respectively.

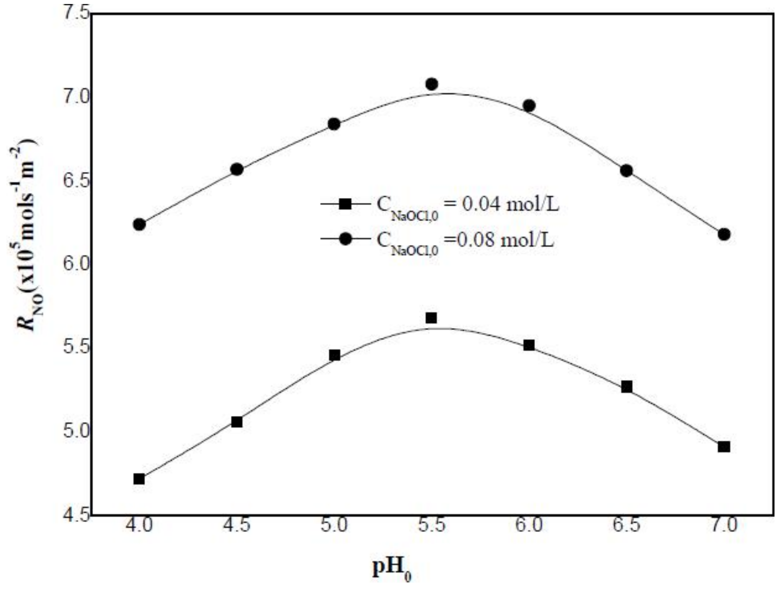

Figure 4 : Effect of initial pH value on NO absorption rate at 328K, and $C_{NO,0}$ = 800 ppm

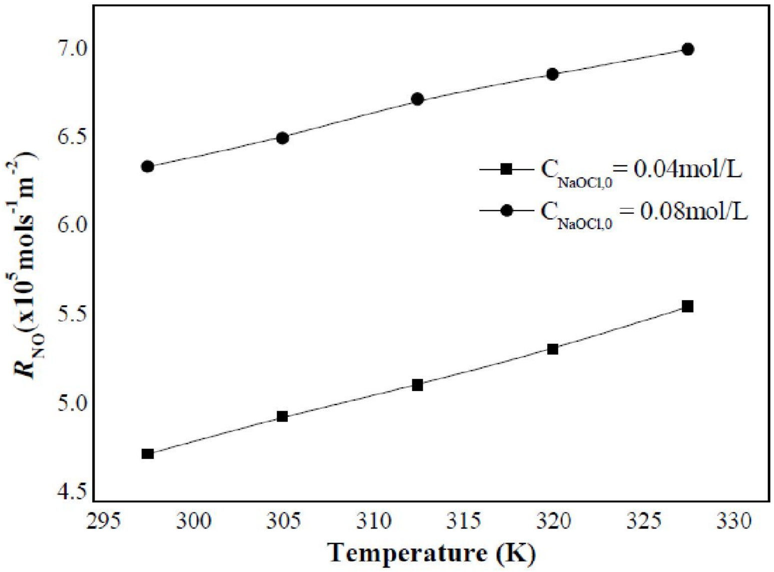

Figure 5 : Effect of temperature on NO absorption rate at $C_{NO,0}$ = 800ppm and initial pH of 6.0

lationship between $\log R_{NO}$ and $\log C_{NaOCl,i}$. The slope of this line is about 0.5, i.e. = 0.5, so the reaction follows 1st order kinetics with respect to NaOCl.

Putting the value of order of reaction of NO and NaOCl, the absorption rate under the fast-reaction regime can be expressed by:

$$R_{NO}=\sqrt{k_2 \times D_{NO} \times C_{NOi}^2 \times C_{NaOCl}} \quad \textbf{(12)}$$

Effect of initial pH

Experiments were performed to investigate the effect of initial pH value on NO absorption rate at T = 328K, $C_{NO,0}$ = 800 ppm and $C_{NaOCl,0}$ of 0.04 M and 0.08 M. Figure 4 shows the effect of initial pH on NO absorption rate. Initial pH of the solution was varied from 4 to 7. NO absorption rate increased with the increasing pH value and reached to maximum value at pH 5.5, thereafter NO absorption rate decreased with increasing pH value. The low pH value is unfavorable to NO_2 absorption, which eventually hinders NO absorption rate.

The reduction half-reaction of HOCl in acidic medium may be written as:

$$\mathbf{HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O} \quad E^{Ů} = 1.482\ V^{[29]} \quad \textbf{(13)}$$

The reduction potential of above reaction may be calculated by Nernst equation:

$$E = E^{o} - \frac{2.303RT}{nF}\log\frac{[Cl^-]}{[HOCl][H^+]} \quad \textbf{(14)}$$

$$\because \ pH = \log\frac{1}{[H^+]} \quad \textbf{(15)}$$

So Eq. (14) may be written as:

$$E = E^{o} - \frac{2.303RT}{nF}\left[\log\frac{[Cl^-]}{[HOCl]} + pH\right] \quad \textbf{(16)}$$

It is evident from the Eq. (16) that the reduction potential will decrease with the increasing pH value, thereby decreasing the oxidizing ability of the scrubbing solution. As a result of reduced oxidizing power at higher pH, the absorption rate of NO decreased too.

Effect of temperature on NO absorption rate

Effect of temperature on NO absorption rate was examined at $C_{NO,0}$ = 800 ppm, initial pH of 6.0, $C_{NaOCl,0}$ of 0.04 M and 0.08 M by varying the temperature from 298 K to 328 K. It is obvious from Figure 5 that NO absorption rate increased with increasing temperature. Though higher temperature will certainly decrease the solubility of NO in the scrubbing solution, but the diffusion coefficient of NO and moreover the rate constant increased with temperature. The latter effect seems to play significant role on NO absorption process.

Activation Energy and Pre-exponential Frequency factor

It is well known that rate constant is markedly affected by the temperature. The value of rate constants were obtained at various temperatures ranging from 298K to 328K and then graph was plotted between *log k* vs. 1/T. The activation energy 'E_a' and pre-exponential frequency factor 'A' were obtained from slope and intercept of the Arrhenius plot using logarithm form as follows:

$$\log k = \log A - \frac{E_A}{2.303RT} \qquad (17)$$

The activation energy 'E_a' and frequency factor 'A' were found to 7.2×10^8 $m^3/(mol\ s)$ and 2.44×10^4 J/mol, respectively.

CONCLUSION

The kinetic study on scrubbing of NO into NaOCl solution was performed in a lab scale bubbling reactor. The operating variables included 200-1000 ppm NO, 0.02-0.1 mol/L NaOCl solution, pH of 4-7, and temperature of 25-55$^{\text{Ú}}$C respectively. The reaction was found to be first-order with respect to both NO and NaOCl. NO absorption reached to maximum value when the initial pH value of NaOCl solution is taken 5.5. The pre-exponential frequency factor (A) and the activation energy (E_a) were found 7.2×10^8 $m^3/(mol\ s)$ and 2.44×10^4 J/mol respectively. It is obvious from the experimental study that sodium hypochlorite is an efficient oxidative absorbent for controlling the NO_x emission of the exhaust gases.

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REFERENCES

[1] K.K.Baveja, D.Subba Rao, M.K.Sarkar; *J.Chem.Eng.Jpn.*, **12**, 322-325 **(1979)**.

[2] D.Littlejohn, S.Chang; *J.Ind.Eng.Chem.Res.*, **29**, 420-1424 **(1990)**.

[3] H.Perlmutter, H.Ao, H.Shaw; *J.Environ.Sci.Technol.*, **27**, 128-133 **(1993)**.

[4] E.Sada, H.Kumazawa, I.Kudo, T.Kondo; *Chem.Eng.Sci.*, **33**, 315-318 **(1978)**.

[5] E.Sada, H.Kumazawa, I.Kudo, T.Kondo; *Ind.Eng. Chem.Proc.Des.Dev.*, **18**, 275-278 **(1979)**.

[6] C.Brogen, H.T.Karlsson, I.Bjerle; *J.Chem. Eng.Technol.*, **21**, 61-70 **(1998)**.

[7] H.Chu, T.W.Chien, B.W.Twu; *J.Hazard.Mater.*, **B84**, 241-252 **(2001)**.

[8] H.K.Lee, B.R.Deshwal, K.S.Yoo; *Korean J.Chem.Eng.*, **22-2**, 208-213 **(2005)**.

[9] C.Brogen, H.T.Karlsson, I.Bjerle; *J.Chem.Eng. Technol.*, **20**, 396-402 **(1997)**.

[10] H.Chu, S.Y.Li, T.W.Chien; *J.Environ.Sci.Health*, **A33**, 801-827 **(1998)**.

[11] D.S.Jin, B.R.Deshwal, Y.S.Park, H.K.Lee; *J.Hazard.Mater.*, **B135**, 412-417 **(2006)**.

[12] B.R.Deshwal, D.S.Jin, S.H.Lee, S.H.Moon, J.H.Jung, H.K.Lee; *J.Hazard.Mater.*, **150**, 649-655 **(2008)**.

[13] K.Kustin, I.ATaub, E.Weinstock; *Inog.Chem.*, **5**, 1079-1082 **(1966)**.

[14] E.Sada, H.Kumazawa, N.Hayakawa, I.Kudo, T.Kondo; *Chem.Eng.Sci.*, **32**, 1171-1175 **(1977)**.

[15] S.Uchida, T.Kobayashi, S.Kageyama; *Ind.Eng. Chem.Proc.Des.Dev.*, **22**, 323-329 **(1983)**.

[16] H.Takeuchi, M.Ando, N.Kizawa; *Ind.Eng.Chem. Proc.Des.Dev.*, **16**, 303-308 **(1977)**.

[17] M.Teramoto, S.Hiramine, Y.Shimada, Y.Sugimoto, H.Teranishi; *J.Chem.Eng.Jpn.*, **11**, 450-457 **(1978)**.

[18] A.Warshaw; *Removal of nitrogen oxides from a gas stream, US Patent*, 3565575, **(1971)**.

[19] N.E.Khan, Y.G.Adewuyi; *Ind.Eng.Chem.Res.*, **49-18,** 8749-8760 **(2010)**.

[20] R.Guo, W.Pan, X.Zhang, J.Ren, Q.Jin, H.Xu, Wu; J.*Fuel,* **90-11**, 3295-3298 **(2011)**.

[21] Y.Shi, H.Wang, S.Chang; *Environ.Prog.*, **16-4**, 301-306 **(1997)**.

[22] M.K.Mondal, V.R.Chelluboyana; *Chem.Eng.J.*, **217**, 48–53 **(2013)**.

[23] L.Chen, C.Hsu, C.Yang; *Environ.Prog.*, **24-3**, 279-288 **(2005)**.

[24] J.A.Dean; *Lange's Handbook of Chemistry*, 15th Edition, McGraw-Hill, New York, **(1999)**.

[25] B.R.Deshwal, H.K.Lee; *J.Environ.Sci.*, **21**, 155–161 **(2009)**.

[26] K.Onda, E.Sada, T.Kobayashi, S.Kito, K.Ito; *J.Chem.Eng.Jpn.*, **3-1**, 18-24 **(1970)**.

[27] P.V.Danckwerts; *Gas-Liquid Reactions*, McGraw-Hill, New York, USA, Chapter **1**, 18-20 **(1970)**.

[28] R.B.Bird, W.E.Stewart, E.N.Lightfoot; *Transport phenomena*, New York, Wiley, 510-515 **(1960)**.

[29] D.R.Lide; *CRC Handbook of Chemistry and Physics*, 87th Edition, Boca Raton, Fl, ISBN 0-8493-0487-3, **(2006)**.