Chapter IV

Results and discussions

The simultaneous removal of SO_2 and NO from simulated gas stream was carried out under semi-batch and continuous mode of operation. For semi-batch operation bubble column and magnetic stirrer vessel were used. The spray column was used for continuous mode of operation regarding simultaneous removal of SO_2 and NO from the gas stream. The entire data for simultaneous removal of SO_2 and NO by various absorbents is given in Appendices A1-A34. Among various absorbents like NaClO, $Ca(OCl)_2$, etc., the NaClO and NaClO/NH_3 blend showed excellent removal efficiencies of SO_2 and NO during simultaneous absorption of SO_2 and NO. Therefore, the theory on absorption of SO_2 and NO into NaClO is provided instead of all absorbents used.

4.1. Theory of absorption of SO_2 and NO into NaClO

4.1.1. Process chemistry

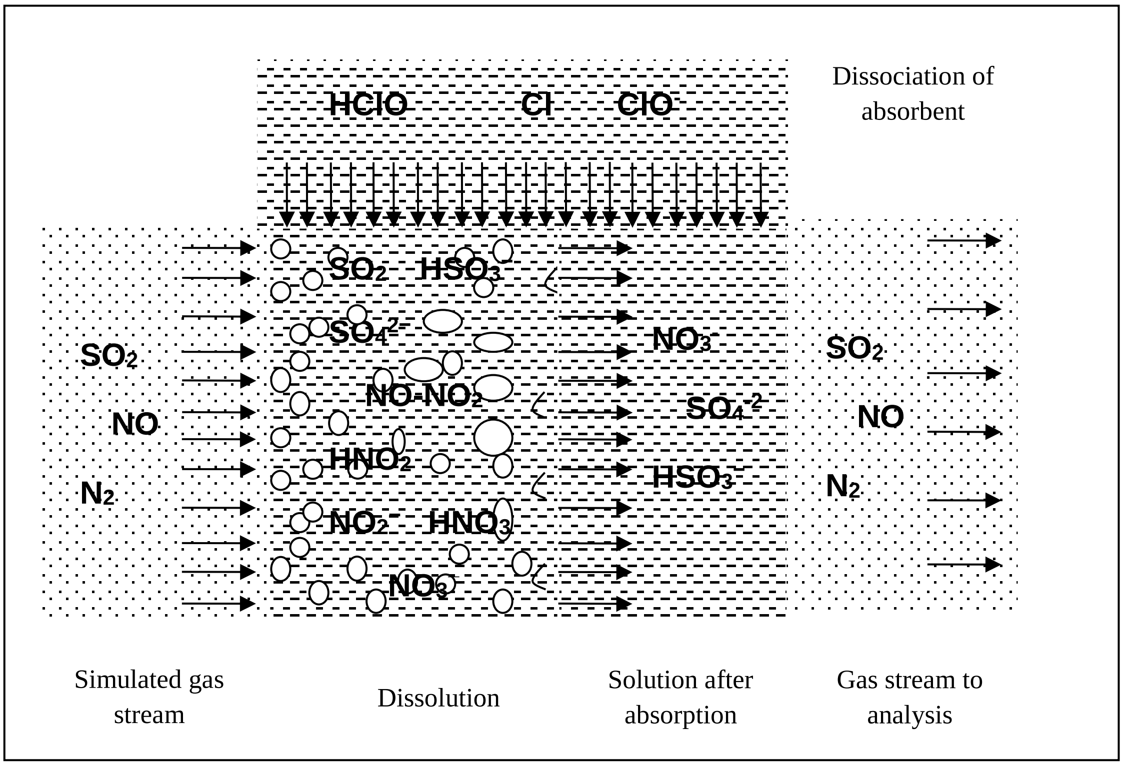


Figure 4.1. Flow pattern of species during absorption of SO_2 and NO using NaClO solution

For better understanding the process of simultaneous removal of SO_2 and NO using NaClO, the reaction mechanism of simultaneous desulfurization and denitrification can be considered step by step. Detailed process chemistry with reaction mechanism including initiation, propagation and termination for simultaneous removal of SO_2 and NO using NaClO was explained. The process chemistry includes dissociation of absorbent NaClO into water to HClO, Cl^-, ClO^- ions in aqueous phase. Further absorbed of SO_2 and NO in the liquid are in the form of dissolved SO_2, HSO_3^-, SO_3^{2-}, SO_4^{2-}, NO-

NO_2, HNO_2, $NO_2^−$, HNO_3 and $NO_3^−$ where $HSO_3^−$, $SO_4^{2−}$, $NO_3^−$ are the major sulphur and nitrogen species present in the liquid phase.

Schematic diagram of process chemistry for simultaneous absorption of SO_2 and NO in the present study was represented in Figure 4.1 which explains the details of dissolution, dissociation and flow pattern of the dissolved species in the process. The chemistry of the process can be visualized as diffusion of SO_2 and NO from gas to the liquid phase, dissociation of chlorine species in liquid phase, absorption of SO_2 by HClO and then the NO absorption augmentation by HClO. Dissociation of chlorine species lead to formation of Cl^-, HClO, ClO^- ions in the liquid phase. Chlorine dissociation can be summarized as follows (Chen et al., 2005):

$$Cl_2\,(g) \rightarrow Cl_2\,(l) \tag{4.1}$$

$$Cl_2\,(g) + H_2O\,(aq.) \rightarrow HClO\,(aq.) + H^+\,(aq.) + Cl^-\,(aq.) \tag{4.2}$$

$$HClO\,(aq.) \leftrightarrow + H^+\,(aq.) + ClO^-\,(aq.) \tag{4.3}$$

$$Cl_2\,(aq.) + Cl^-\,(aq.) \leftrightarrow Cl_3^-\,(aq.) \tag{4.4}$$

Regarding the SO_2 absorption in liquid phase, the following reactions (equations (4.5-4.9)) can be presumed:

$$SO_2\,(g) \rightarrow SO_2\,(aq.) \tag{4.5}$$

$$SO_2\,(aq.) + H_2O\,(l) \rightarrow H^+\,(l) + HSO_3^-\,(aq.) \tag{4.6}$$

$$SO_2\,(aq.) + 2OH^-\,(aq.) \rightarrow H_2O\,(l) + SO_3^{2-}\,(aq.) \tag{4.7}$$

$$HClO\,(aq.) + HSO_3^-\,(aq.) \rightarrow SO_4^{2-}\,(aq.) + 2H^+(aq.) + Cl^-\,(aq.) \tag{4.8}$$

$$ClO^-\,(aq.) + HSO_3^-\,(aq.) \rightarrow SO_4^{2-}\,(aq.) + H^+\,(aq.) + Cl^-\,(aq.) \tag{4.9}$$

The total SO_2 absorbed by the absorbent are in the form of dissolved SO_2, HSO_3^{-}, SO_3^{2-}, and SO_4^{2-} where HSO_3^{-} and SO_4^{2-} are present in appreciable amount in liquid phase (Zhao et al., 2010; Yoon et al., 2004). In the process of NO absorption, the total NO consumed in the liquid phase can be written by the following reaction scheme as equations (4.10-4.14):

$$NO\ (g) \leftrightarrow NO\ (l) \tag{4.10}$$

$$NO\ (l) + HClO\ (aq.) \leftrightarrow NO_2\ (aq.) + HCl\ (aq.) \tag{4.11}$$

$$3NO_2\ (aq.) + H_2O\ (l) \leftrightarrow 2HNO_3\ (q.) + NO\ (aq.) \tag{4.12}$$

$$2NO_2\ (aq.) + H_2O\ (l) \leftrightarrow HNO_3\ (aq.) + HNO_2\ (aq.) \tag{4.13}$$

$$3HNO_2\ (aq.) \leftrightarrow HNO_3\ (aq.) + 2NO\ (aq.) + H_2O\ (l) \tag{4.14}$$

The total NO absorbed are in the form of dissolved NO-NO_2, HNO_2, NO_2^{-}, HNO_3 and NO_3^{-} where NO_3^{-} is the major nitrogen species present in the liquid phase.

4.1.2. Kinetic expressions

Instantaneous absorption of SO_2 and NO by the oxidative absorbent NaClO includes mass transfer with chemical reaction. The temperature, time, initial concentration of solute and absorbent are the important parameters to transfer SO_2 and NO from gas phase to the liquid phase which is controlled by the dissolution and ionization behavior of the intermediate species in the liquid phase. The process was concerned about oxidizing sparingly soluble NO to soluble NO_2. Hence, the NO absorption was the dominant reaction in the process of simultaneous removal of SO_2 and NO. The total NO absorbed in the liquid phase can be written in the following scheme based on intermediates of reactions in equations (4.10-4.14). The reaction between NO and

NaClO can be taken as a pseudo mth order reaction with respect to NO interface concentration (C_{NOi}). Thus, the reaction rate can be expressed as following:

$$r = k_{r\,NO} C_{NO_i}^{m} \tag{4.15}$$

Here $k_{r\,NO}$, is pseudo mth order rate constant.

According to Whitman Two-film theory, under steady state, the absorption flux of NO is given by the following equation (Danckwerts, 1970; Zhang, 1985):

$$N_{NO} = k_{NO_g}\left(p_{NO_b} - p_{NO_i}\right) = E.k_{NO_l}\left(C_{NO_i} - C_{NO_b}\right) \tag{4.16}$$

Where N_{NO} is molar absorption flux of NO in kmol/m^{2}s, k_{NO_g}, is gas phase mass transfer coefficient in kmol/m^{2}s.Pa, k_{NO_l}, is liquid phase mass transfer coefficient m/s, p_{NO_b} is partial pressure of NO in the bulk of the gas phase in Pa, p_{NO_i} is partial pressure of NO in gas at gas-liquid interface in Pa, C_{NO_l}, is concentration of NO in bulk of the liquid phase kmol/m^3, C_{NO_i}, is concentration of NO in liquid at gas-liquid interface in kmol/m^3 and E is the enhancement factor which is defined as degree of enhancement in mass transfer due to chemical reaction.

The interfacial concentrations can be obtained from the equilibrium relationship governed by Henry's law:

$$p_{NO_i} = HC_{NO_i} \tag{4.17}$$

Where H is Henry's law constant in Pa.m^3/kmol

The overall mass transfer coefficient based on the gas phase K_{NO_g} can be expressed as:

$$N_{NO} = K_{NO_g}\left(p_{NO_b} - HC_{NO_i}\right) \tag{4.18}$$

By combining equations (4.16), (4.17) and (4.18), the following expression is obtained and can be used to calculate N_{NO}, in terms of individual phase mass transfer coefficients as:

$$\mathrm{N}_{NO} = \left(\mathrm{p}_{NO_b} - \mathrm{HC}_{NO_b}\right)\left(\frac{1}{\mathrm{k}_{NO_g}} + \frac{H}{E.\mathrm{k}_{NO_l}}\right)^{-1} \tag{4.19}$$

A significant parameter, the Hatta coefficient (Ha), which denotes the ratio between the rate of chemical reaction and the rate of physical absorption in liquid film, is given by the following expression (Danckwerts, 1970; Zhang, 1985):

$$\left(\mathrm{Ha}.k_{NO_l}\right)^2 = \frac{2}{\mathrm{m}+1}\mathrm{k}_{r.NO}\mathrm{D}_{NO_l}\mathrm{C}_{NO_i}^{m-1} \tag{4.20}$$

Where D_{NO_l} is diffusion constant of NO in liquid. The Hatta number explains about the rate at which NO is absorbed in NaClO solution. According to two-film theory, if Ha >3 reaction can be considered as a fast reaction with E = Ha (Danckwerts, 1970; Zhang, 1985). To calculate the reaction order and reaction rate constant, it was assumed that reaction accompanying mass transfer of gases is fast. Chemical reaction in the liquid film actually enhances the rate of mass transfer of gases from bulk of the gas phase to the interface. As the reaction is very fast, the concentration of NO in the bulk of the liquid phase is almost zero. The results from this calculation were used to calculate Ha and it was found that the assumption was true, which was done in later stage.

By using $E.\mathrm{k}_{NO_l} = Ha.\mathrm{k}_{NO_l}$ and $\mathrm{C}_{NO_l} = 0$, the equation for absorption rate becomes,

$$\mathrm{N}_{NO} = \mathrm{p}_{NO_b}\left(\frac{1}{\mathrm{k}_{NO_g}} + \frac{\mathrm{H}}{\left(\frac{2}{\mathrm{m}+1}\mathrm{k}_{r.NO}\mathrm{D}_{NO_l}\mathrm{C}_{NO_i}^{m-1}\right)^{1/2}}\right)^{-1} \tag{4.21}$$

The above equation is rearranged into the following expression:

$$\frac{H\,\mathrm{N}_{NO}.\mathrm{k}_{NO_g}}{(\mathrm{p}_{NO_b}.\mathrm{k}_{NO_g}-\mathrm{N}_{NO})}=\left(\frac{2}{\mathrm{m}+1}\mathrm{k}_{r.NO}\mathrm{D}_{NO_l}\mathrm{C}_{NO_i}^{m-1}\right)^{1/2} \tag{4.22}$$

The expression of NO interfacial concentration can be taken from equations (4.16) and (4.17) as:

$$\mathrm{C}_{NO_i}=\frac{1}{H}\left(\mathrm{p}_{NO_b}-\frac{\mathrm{N}_{NO}}{\mathrm{k}_{NO_g}}\right) \tag{4.23}$$

Eliminating p_{NO_b} , from equations (4.22) and (4.23), we get

$$\mathrm{N}_{NO}=\sqrt{\frac{2}{\mathrm{m}+1}.\mathrm{k}_{r.NO}.\mathrm{D}_{NO_l}.\mathrm{C}}_{NO_i}^{\frac{m+1}{2}} \tag{4.24}$$

Taking log on both sides, the above equation (4.24) becomes:

$$\log \mathrm{N}_{NO}=\frac{1}{2}\left\{\log\left(\frac{2}{\mathrm{m}+1}.\mathrm{k}_{r.NO}.\mathrm{D}_{NO_l}\right)+(m+1)\log \mathrm{C}_{NO_i}\right\} \tag{4.25}$$

The reaction rate ($\mathrm{k}_{r.NO}$), and order (m) can be found from the slope $\frac{\mathrm{m}+1}{2}$, and intercept $\frac{1}{2}\left(\log\frac{2}{\mathrm{m}+1}.\mathrm{k}_{\mathrm{r.NO}}.\mathrm{D}_{\mathrm{NO_l}}\right)$ of the plot between $\log \mathrm{N}_{NO}$, and $\log \mathrm{C}_{NO_i}$, according to equation (4.25).

The molar absorption flux of SO_2 can be expressed in accordance to two-film theory:

$$\mathrm{N}_{SO_{2g}}=\mathrm{k}_{SO_{2g}}\left(\mathrm{p}_{SO_{2b}}-\mathrm{p}_{SO_{2i}}\right)=E.\mathrm{k}_{SO_{2l}}\left(\mathrm{C}_{SO_{2b}}-\mathrm{C}_{SO_{2i}}\right) \tag{4.26}$$

For a completely gas phase controlled process, $\mathrm{p}_{SO_{2i}}=0$, simplifying the absorption equation to the following:

$$\mathrm{N}_{SO_2}=\mathrm{k}_{SO_{2g}}.\mathrm{p}_{SO_{2b}} \tag{4.27}$$

4.1.3. Data analysis

4.1.3.1. Removal efficiency (η)

The concentration of the outlet gases was measured at an interval of every 20 min and the removal efficiency was calculated as

$$\eta = \frac{\mathrm{p_{in}} - \mathrm{p_{out}}}{\mathrm{p_{in}}} \times 100 \tag{4.28}$$

Where, $\mathrm{p_{in}}$, and $\mathrm{p_{out}}$, are inlet and outlet concentration of the gas in ppm, respectively.

4.1.3.2. Molar absorption flux

The molar absorption flux for SO_2 is given as

$$\mathrm{N}_{SO_2} = \frac{\eta_{SO_2}.\mathrm{p}_{SO_{2in}}.Q_g.\rho_{SO_2}}{\mathrm{M}_{SO_2}.\mathrm{a}_g.\mathrm{V}_l} \times 10^{-8} \tag{4.29}$$

Where N_{SO_2} is the absorption flux of SO_2 in kmol/m^2.s, Q_g, is the gas flow rate in m^3/s, ρ_{SO_2}, is the density in kg/m^3, M_{SO_2}, is the molecular weight of SO_2 in kg/kmol, a_g, is gas-liquid specific interfacial area (m^{-1}), V_l, is the volume of absorbent in m^3.

Similarly, the molar absorption flux for NO is given as

$$\mathrm{N}_{NO} = \frac{\eta_{NO}.\mathrm{p}_{NO_{in}}.Q_g.\rho_{NO}}{\mathrm{M}_{NO}.\mathrm{a}_g.\mathrm{V}_l} \times 10^{-8} \tag{4.30}$$

Where ρ_{NO}, is the density of NO in kg/m^3 and M_{NO}, is the molecular weight of NO in kg/kmol.

4.1.3.3. Interfacial concentration and pressure

The partial pressure of NO in gas at gas-liquid interface can be determined from equation (4.16):

$$\mathrm{p}_{NO_i} = \mathrm{p}_{NO_b} - \frac{N_{NO}}{K_{NO_g}} \tag{4.31}$$

The interfacial concentration for NO in liquid at gas-liquid interface C_{NO_i} can be determined by the application of Henry's law (Danckwerts, 1970; Zhang, 1985) according to equation (4.17).

The interfacial concentration of NO in ionic solutions is dependent on the ionic strength of the species (Onda et al. (1970a, 1970b)). It was first observed by Krevelen and Hoftijzer as given by the following equation:

$$\log\left(\frac{\mathrm{C}_{NO_i}}{\mathrm{C}_{NO_{iw}}}\right) = -\mathrm{K}_{NaClO}.\,\mathrm{I}_{NaClO} \tag{4.32}$$

Where K_{NaClO} is salting out parameter for NaClO. It depends on the concentration of anions, cations and dissolved gas in the liquid and is given by the equation:

$$\mathrm{K}_{NaClO} = \mathrm{X}_{S_1} + \mathrm{X}_{S_2} + \mathrm{X}_g \tag{4.33}$$

Where X_{S_1}, X_{S_2} and X_g are contributions to K, by Na^+, ClO^- and dissolved NO, respectively. These values are assumed to be constant and do not vary with temperature and can be taken from the data of Sada et al. (1986) and Onda et al. (1970a, 1970b):

$$\mathrm{X}_{S1} = -0.0183;\ \mathrm{X}_g = -0.01825 \tag{4.34}$$

However, X_{S_2} from ClO^- is not available in the literature so far, thus its value is assumed to be same as the data available for $ClO_2{}^-$ (Chu et al. 2001):

$$\mathrm{X}_{S_2} = 0.3497 \tag{4.35}$$

4.1.3.4. Physical and mass transfer parameters

The Diffusion coefficients D_{NO-H_2O}, $\mathrm{D}_{SO_2-H_2O}$, D_{NO-N_2} and $\mathrm{D}_{SO_2-N_2}$ are taken from obtained results of experimentation with NaClO solution. The values of diffusion coefficients in liquid phase can be obtained by the following relationship (Ebrahimi et al. 2003):

$$D_{NO-l} \, \alpha \, T \tag{4.36}$$

$$D_{SO_2-l} \, \alpha \, T \tag{4.37}$$

Where, T is the desired temperature in 'K'.

For diffusion constant in gas phase, following equations (Welty et al. 1984; Bird et al. 1960) were used:

$$D_{NO-N_2} \alpha \, T^{3/2} \tag{4.38}$$

$$D_{SO_2-N_2} \, \alpha \, T^{3/2} \tag{4.39}$$

Where, T is the temperature and D is the diffusion coefficient.

The value of $k_{SO_{2g}}$, can be obtained from the slope of the graph between $N_{SO_{2g}}$ and $p_{SO_{2b}}$ as expressed in equation (4.26). Sada et al. (1978) indicated that the value of k_{NO_g} can be calculated by the following relationship:

$$k_{NO_g} = k_{SO_{2g}} \left(\frac{D_{NO-N_2}}{D_{SO_2-N_2}} \right)^{2/3} \tag{4.40}$$

The specific interfacial area a_g, was assumed to be temperature independent and their values were taken from Liu et al. (2013). The Henry's law coefficient (526.32 Pa.m^3/kmol) for NO in pure water at 298.15 K was taken from Sander (1999). The effective coefficient at 313 K was calculated from following equation:

$$\frac{H_2}{H_1} = e^{K\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{4.41}$$

Where H_2 and H_1 are the Henry's law coefficients at respective temperatures T_2 (313 K) and T_1 (298.15 K), and the value of K was taken as 1500 K calculated by Sander (1999). The Henry's law coefficient must be calculated at 313 K, this operating temperature was chosen from the experimental results of absorption with NaClO solution.

4.1.4. Thermodynamics of the process for SO_2 and NO absorption

The calculation of thermodynamic parameters explains the feasibility of the process. It also helps to understand the absorption mechanism and even the influenced behaviour of the components during simultaneous removal of SO_2 and NO. The evaluation thermodynamic parameters such as enthalpy change, Gibbs free energy change, equilibrium constant and the equilibrium partial pressure of the components were evaluated for simultaneous removal of SO_2 and NO using NaClO absorbent and NaClO with additive.

4.2. Absorption in semi batch bubble column with NaClO

The reagent sodium hypo chlorite (NaClO) is of low cost and readily available. In this work NaClO, therefore, was used to scrutinize simultaneous removal of SO_2 and NO from simulated gas stream. Here SO_2 and NO were absorbed using NaClO solution as absorbent in laboratory scale bubble column. The major concern in this process is to convert insoluble NO to NO_2 using aqueous NaClO. Several operating parameters have been studied in this process keeping remaining parameters as frozen. The major operation parameters were temperature, pH, initial SO_2 concentration, initial NO concentration and initial absorbent concentration. Effective removal efficiency of 91% NO and 99% of SO_2 was obtained in this process.

NaClO has shown gigantic removal efficiency for both SO_2 and NO during the absorption in laboratory scale bubble column. The optimum conditions for removal of SO_2 and NO with use of NaClO in bubble column were formed as process temperature 305 K, 0.032 M NaClO absorbent concentration and pH of 5.6. Maximum removal efficiencies of 99 % for SO_2 and 91 % for NO were obtained under optimal experimental conditions. The saturation time for the process was determined as 260 min for NO and 350 min for SO_2 with initial SO_2 concentration 6348 ppm, NO concentration 1804 ppm and other optimized conditions stated above.

4.2.1. Effect of contact time using NaClO in bubble column

The variation of removal efficiency with time was determined in this process by measuring the absorbed gas stream within regular time interval of 10 min maintaining temperature, NaClO concentration, initial SO_2 concentration, NO concentration and pH of the solution as constant. The change in removal efficiency of NO and SO_2 with respect to time is shown in Figure 4.2. This provides efficiency of absorbent in SO_2 and NO absorption for an essential contact time. Till 2 h the removal efficiency of both SO_2 and NO was maintained constant and then the graph tends to decrease.

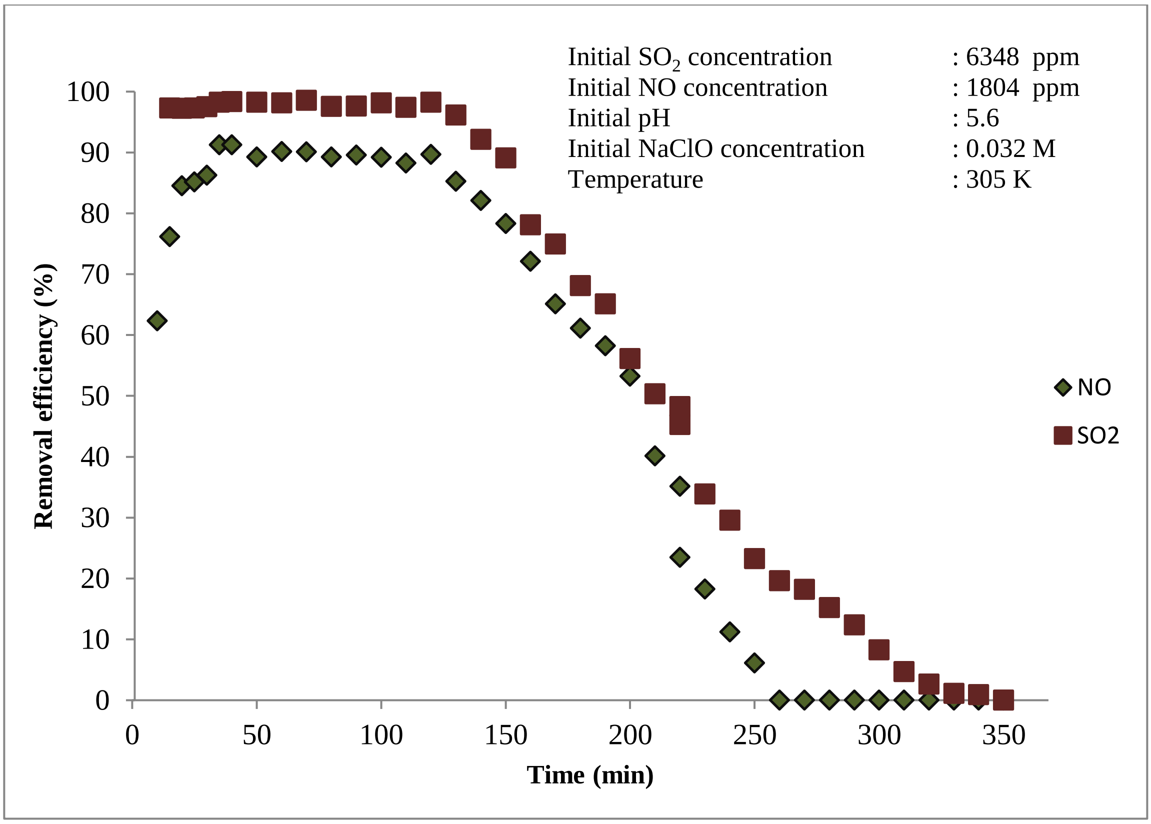


Figure 4.2. Effect of time on removal of NO and SO_2 in bubble column using NaClO

From the results, it was shown that the optimum time in the process for a 0.032 M NaClO was 2 h with SO_2 concentration 6348 ppm, NO concentration 1804 ppm, pH of 5.6 and temperature of 305 K. The saturation time at these conditions was determined as 260 min for NO and 350 min for SO_2. The time lag between saturation of both gases was due to dissolution of SO_2 in water, it indicated SO_2 was further soluble in water even though hypochlorite species in liquid solution were saturated. The initial variation between SO_2 and NO removal efficiency was observed in the graph, which explained the preliminary reaction step to covert NO to NO_2.

4.2.2. Effect of initial SO_2 concentration using NaClO in bubble column

The initial concentration variation of SO_2 was studied under the constant parameters such as flow rate of the gas stream, absorbent temperature, absorbent concentration, contact time, initial NO concentration and initial pH of the solution (the results are shown in Table C1 of appendix C). This study examined the reactive tendency of absorbent on NO with variation in SO_2 concentration. There was a minute increase in a NO removal with increase in SO_2 concentration. This is because SO_2 acts as oxidant for NO in NaClO absorption. The constant operating parameters in this process were 0.032 M NaClO with reaction time 2 h, as initial NO concentration was 1804 ppm, initial pH of 5.6 and temperature of 305 K.

4.2.3. Effect of initial NO concentration using NaClO in bubble column

The change in initial concentration of NO was studied under the constant parameters such as absorbent temperature, flow rate of the gas stream, absorbent concentration, contact time, initial pH of the solution and initial SO_2 concentration (the results are shown in Table C2 of appendix C). This study showed the reaction capability of NaClO on SO_2 with variation in NO concentration. It was shown similar trend as that of the effect of initial SO_2 concentration for SO_2 but there was a slight decrease in NO removal with increase in NO concentration. This is due to consumption of absorbent for removal of both SO_2 and NO. The constant operating parameters in this process were 0.032 M absorbent with contact time 2 h, SO_2 concentration of 6348 ppm, initial pH of absorbent 5.6 and absorbent temperature of 305 K.

4.2.4. Effect of NaClO concentration in bubble column

The change in SO_2 and NO removal with respect to absorbent concentration was studied with constant parameters such as contact time 2 h, SO_2 concentration 6348 ppm, NO concentration 804 ppm, pH of 5.6 and temperature of 305 K to study effectiveness and expectant requirement of absorbent for the process. The range of NaClO during the process was 0.004-0.04 M. The change in removal efficiency with respect to concentration range is shown in Figure 4.3.

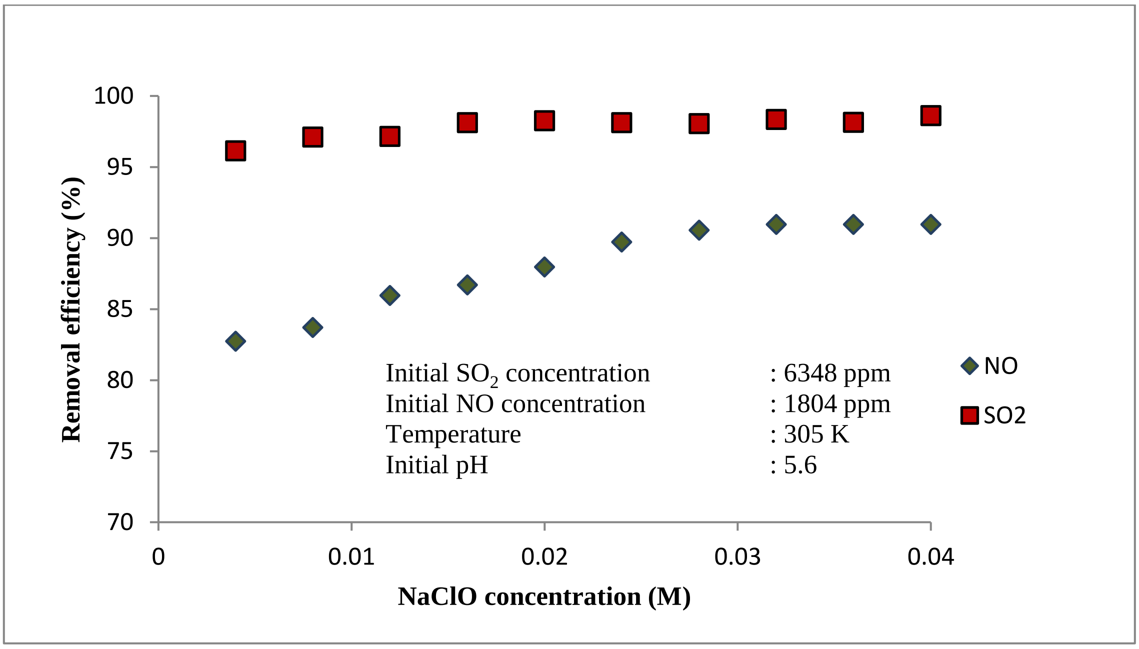


Figure 4.3. Effect of NaClO concentration on removal of NO and SO_2 in bubble column

From the data, the optimistic absorbent concentration for the process was obtained as 0.032 M. The supreme removal efficiency 91% was acquired for NO and 99% for SO_2 in this process. Standard oxidation of SO_2 and NO in the liquid stream to produce acidic intermediates such as HNO_3, HNO_2 and H_2SO_4 was the major operation carried out in the process. The presence of hypochlorite ions helps in conversion of NO to NO_2.

4.2.5. Effect of absorbent temperature using NaClO in bubble column

The required temperature of absorbent was maintained to study the effect of temperature for simultaneous removal of SO_2 and NO using NaClO solution. The change in temperature with constant parameters such as reaction time 2 h, SO_2 concentration 6348 ppm, NO concentration 1804 ppm, pH of 5.6 and absorbent concentration 0.032 M is shown in Figure 4.4. The change in removal efficiency of SO_2 and NO for the temperature range of 283-325 K was illustrated in this process. Initially the removal was increased with rising temperature till 305 K and then decreased; hence 305 K was considered as optimum temperature for maximum removal efficiency in this process. Initial increase is due to presence of unused hypochlorite ions present in the solution and decrease is due to dissolution of absorbent in liquid phase.

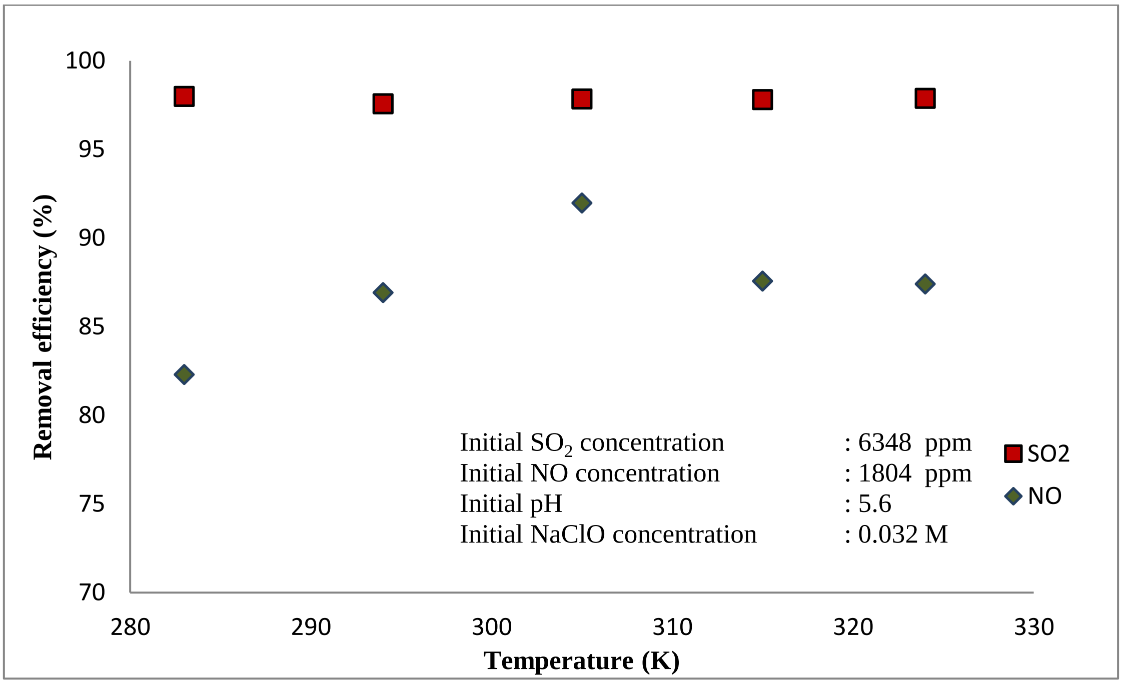


Figure 4.4. Effect of absorbent temperature on removal of NO and SO_2 in bubble column using NaClO

4.2.6. Effect of initial pH of NaClO in bubble column

The effect of initial pH of NaClO was examined keeping flow rate of the gas stream, temperature, concentration, time, initial SO_2 concentration and initial NO concentration as constant (the results are shown in Table C3 of appendix C). The operating parameters were contact time 2 h, SO_2 concentration 6348 ppm, NO concentration 1804 ppm, temperature 305 K and absorbent concentration 0.032 M. This study accomplished the optimum pH of the solution containing NaClO for simultaneous removal of SO_2 and NO. The Optimum pH obtained in the process was given as 5.6.

4.3. Absorption in semi batch magnetic stirrer vessel with NaClO

The experimental results obtained from absorption of SO_2 and NO using NaClO in bubble column influences the process to conduct in semi batch agitation. Since the bubble column has only axial mixing, to understand complete feasibility of absorbent and to improvise the contact between gas and liquid, the experimentation was carried out in semi batch magnetic stirrer vessel where both axial and radial mixing took place. An amalgamated SO_2/NO removal system were tested with absorbent in a magnetic stirrer vessel. Based on gigantic SO_2 removal efficiency, the NO removal efficiencies under various experimental conditions were emphatically measured. The various operating parameters such as initial NaClO concentration, initial NO and SO_2 concentration, and temperature were tested to find the maximum removal of SO_2 and NO.

A detailed study was carried out to check the effects of various parameters on simultaneous NO and SO_2 removal using NaClO solution in stirred vessel. Results showed that there was no appreciable change in SO_2 removal efficiency showing a value of almost 100% but the removal efficiency of NO depicted an increasing trend with the rise of operating conditions like NaClO concentration, initial SO_2 concentration and NO concentration. Removal efficiency of SO_2 remained almost 100% but NO removal efficiency significantly decreased with increase in time. Regarding the effect of temperature removal efficiency of SO_2 was independent on temperature, but removal efficiency of NO initially increased up to a maximum value and then decreased with increase in temperature. The maximum removal efficiency of SO_2 and NO was found as 100 % and 92 %, respectively at 0.01 M NaClO concentration and 313 K. The experimental findings showed that NaClO solution can be used as efficient low-cost absorbent for simultaneous removal of NO and SO_2 from simulated gas stream related to coal-fired thermal power plant stack gas.

4.3.1. Effect of contact time using NaClO in stirred vessel

The effect of contact time on simultaneous removal of SO_2 and NO for constant SO_2 and NO initial concentration at 313 K at fixed 0.01 M NaClO concentration is shown in Figure 4.5. It was seen from Figure 4.5 that for a fixed concentration of NaClO, the NO removal efficiency decreased with time and SO_2 removal efficiency almost independent on time indicating that absorption of NO and SO_2 took place from gas to liquid phase. The results indicated that the removal efficiency of NO decreased appreciably as compared to SO_2 with respect to time. The NO removal efficiency decreased significantly with increase in time due to batch variation in NaClO concentration in the liquid phase.

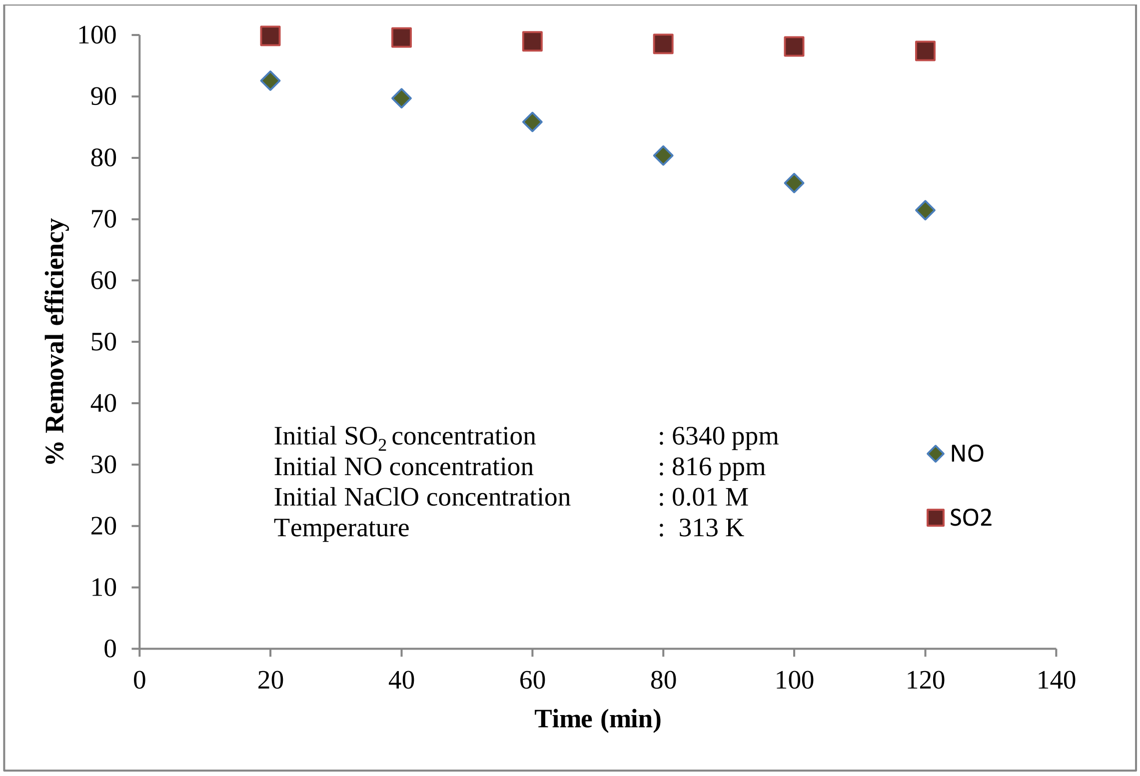


Figure 4.5. Effect of time on removal of NO and SO_2 in stirred vessel using NaClO

4.3.2. Effect of NaClO concentration using NaClO in stirred vessel

The NaClO concentration was one of the important influencing factors for simultaneous SO_2 and NO absorption. The effect of various concentrations of absorbent on simultaneous removal of SO_2 and NO for constant SO_2 initial concentration of 6340 ppm and 816 ppm NO initial concentration at 313 K is shown in Figure 4.6. It was found from Figure 4.6 that increase in NaClO concentration tentatively lead to increase the NO and SO_2 removal efficiencies.

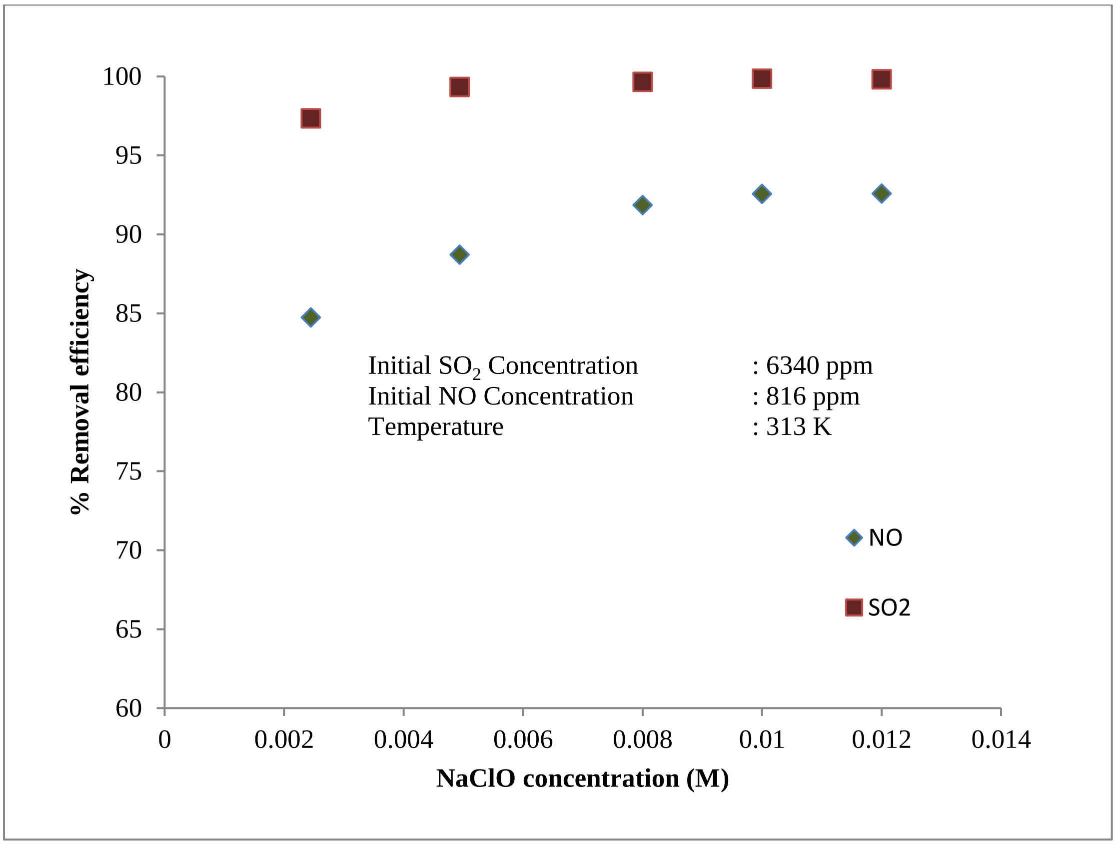


Figure 4.6. Effect of NaClO concentration on removal of NO and SO_2 in stirred vessel

The removal efficiency of SO_2 was observed approximately 100% irrespective of NaClO concentration and maximum removal efficiency of NO of 92% was obtained at

0.01 M NaClO concentration. It was also seen from Figure 4.6 that the NO absorption efficiency increased more rapidly from 82% to about 91% as the NaClO concentration is increased from 0.002 to 0.008 M. But when the NaClO concentration exceeded 0.08 M, NO removal efficiency increases very minutely and reached maximum removal efficiency of 92%. This was because chemical reaction and the physical properties were the two important aspects in the process of absorption. The reaction rate may accelerate the absorption process which is responsible to enhance the rate of diffusion of dissolved species in the liquid phase.

4.3.3. Effect of absorbent temperature using NaClO in stirred vessel

Simultaneous absorption of SO_2 and NO by the absorbent involves mass transfer with gas–liquid reactions. The temperature of absorbent has an important role on the transfer of SO_2 and NO from bulk of the gas phase to the bulk of the liquid phase governed by the diffusion, dissolution and ionization behavior of the species in the liquid phase. The effect of temperature on simultaneous removal of SO_2 and NO was studied experimentally by varying temperature from 293 to 323 K as shown in Figure 4.7. From Figure 4.7, the removal efficiency of SO_2 was same almost 100% irrespective of absorbent temperature. On the other hand, removal efficiency of NO initially increased and then reached maximum and finally decreased with increase in temperature. Thus, at early stage of the absorption, removal efficiency of NO is increased with increase in temperature, which may be due to the increase of both the ionization of NaClO and diffusion of NO and related dissolved species in the liquid phase. In the latter stage, the decrease of absorption of NO may be due to the decrease of NO solubility with temperature. Some intermediate reactions as represented by equations (4.12) and (4.14) are also responsible for desorption of NO at higher temperatures.

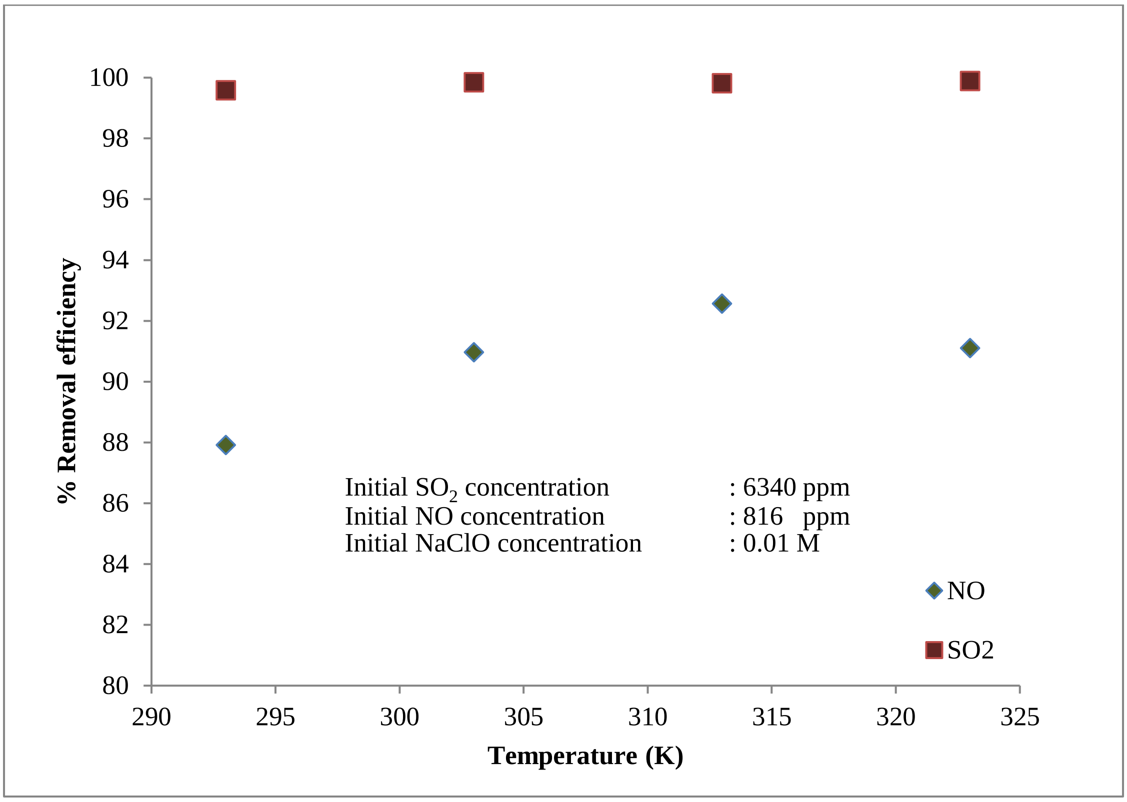


Figure 4.7. Effect of absorbent temperature on removal of NO and SO_2 in stirred vessel using NaClO

4.3.4. Effect of initial SO_2 concentration using NaClO in stirred vessel

The effect of various initial SO_2 concentrations on simultaneous removal of NO and SO_2 for constant NO initial concentration of 816 ppm is shown in Figure 4.8 at 313 K and 0.01 M NaClO concentration. From Figure 4.8 it was observed that for fixed initial concentration of NO, the removal efficiency of NO increased with increase in initial SO_2 concentration from 4170 to 7135 ppm and there was no appreciable change in SO_2 removal efficiency. The removal efficiency of SO_2 was almost 100% showing that SO_2 absorption was independent on initial SO_2 concentrations. Initially rapid enhancement of

NO absorption with increase of SO_2 initial concentration is due to the transfer of NO from bulk of the gas phase to the liquid and oxidation of NO into NO_2 in the liquid phase. In the latter stage, slow absorption of NO may be due to the fact that almost all NaClO is consumed in the liquid.

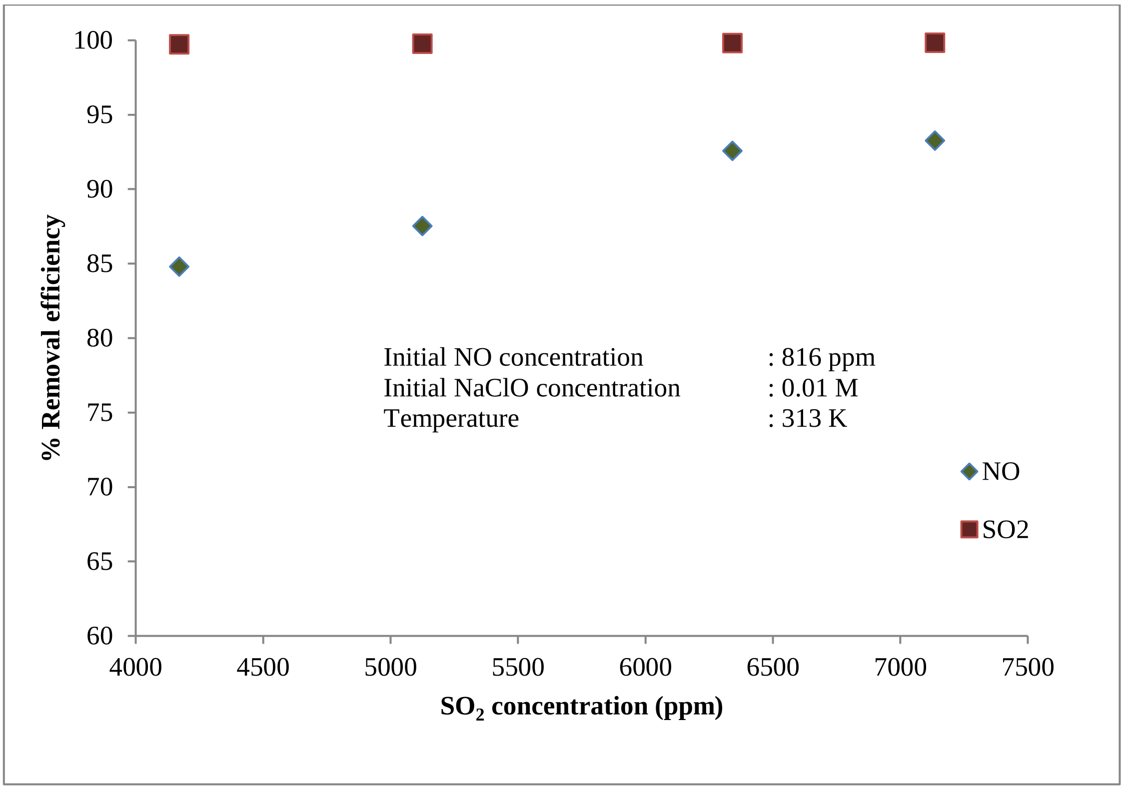


Figure 4.8. Effect of initial SO_2 concentration on removal of NO and SO_2 in stirred vessel using NaClO

4.3.5. Effect of initial NO concentration using NaClO in stirred vessel

The result of experiments conducted to test the removal efficiency of NO in simultaneous removal of NO and SO_2 by using 0.01 M NaClO solution for fixed SO_2 concentration of 6340 ppm was illustrated in Figure 4.9 at 313 K. From Figure 4.9 it was observed that for fixed initial concentration of SO_2, the removal efficiency of NO increased with increase in initial NO concentration and the removal efficiency of SO_2 remained 100% irrespective of initial NO concentration from 508 to 816 ppm. The interphase mass transfer may result the increase of NO absorption with increasing initial NO concentration due to the increase in the concentration driving force from bulk of the gas phase to the gas-liquid interface.

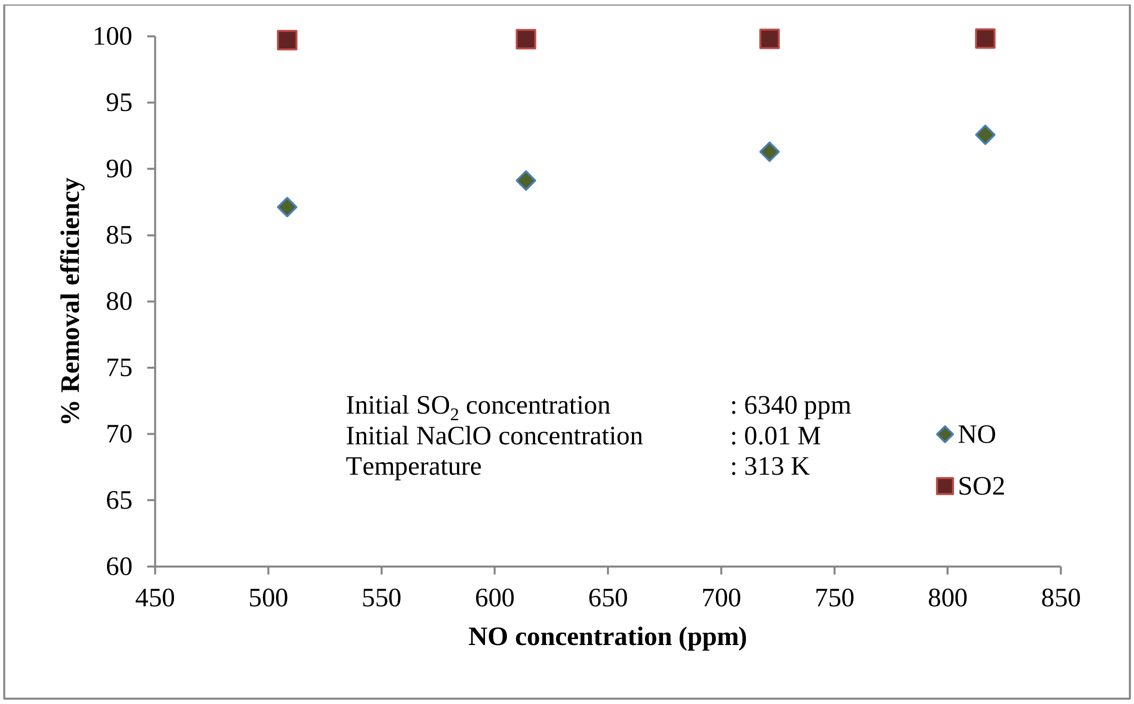


Figure 4.9. Effect of initial NO concentration on removal of NO and SO_2 in stirred vessel using NaClO

4.3.6. Effect of initial pH of NaClO in stirred vessel

The pH of the solution has great influence on equilibrium at gas–liquid interface for simultaneous absorption of SO_2 and NO. To study the effect of initial pH of NaClO solution on simultaneous removal of NO and SO_2, experiments were carried out by changing NaClO solution pH from 4.0 to 9.0. Figure 4.10 showed the effect of solution pH on simultaneous removal of SO_2 and NO. From Figure 4.10 it was found that SO_2 removal efficiency remained almost 100% indicating negligible effect of solution pH on SO_2 removal efficiency.

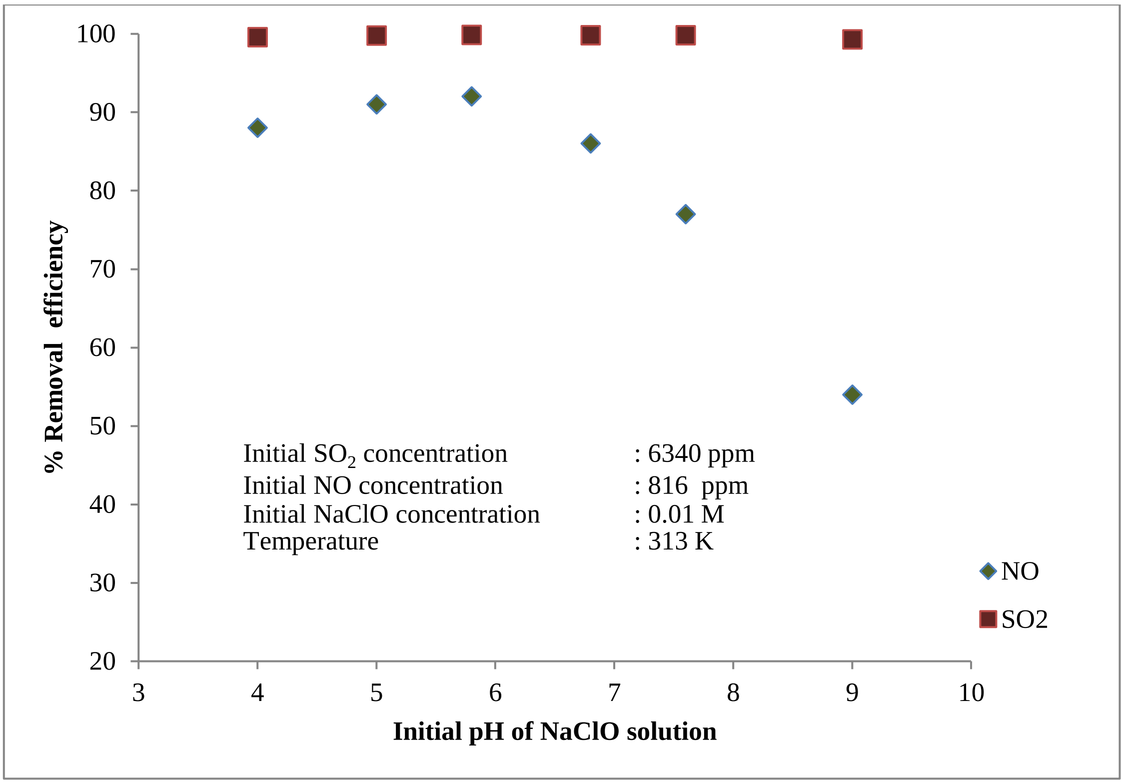


Figure 4.10. Effect of initial pH of NaClO on removal of NO and SO_2 in stirred vessel

The solution pH showed significant impact on NO removal efficiency. Initially there was a slight increase in NO removal efficiency and it was peaked maximum at NaClO solution pH 5.8. After that it decreased continuously with increase in solution pH up to 9.0. The results for having high SO_2 removal efficiency and negligible effect of pH on

SO_2 removal may be attributed to high solubility of SO_2 in liquid whereas dependence of NO removal efficiency as function of solution pH may be attributed to the fact that NO is sparingly soluble in liquid until it is successively oxidized to NO_2 and nitrate in the liquid phase according to the reactions.

4.4. Absorption in semi-batch magnetic stirrer vessel with $Ca(OCl)_2$

This process was concerned about the instantaneous removal of SO_2 and NO with a complex absorbent calcium hypochlorite ($Ca(OCl)_2$) using magnetic stirrer vessel. Use of $Ca(OCl)_2$ improvised the oxidation rate to convert NO to NO_2 and further reactions led to absorption of SO_2 and NO. In this process concentrations of SO_2 and NO were taken as similar to the desired concentrations of SO_2 and NO in stack gas emission of coal-fired thermal power plant. A simulated gas blend was prepared during the process. This gas blend was subjected to absorption and the effective parameters such as absorbent concentration, operating temperature, initial pH, initial SO_2 concentration and initial NO concentration were varied to study the feasibility of $Ca(OCl)_2$ as absorbent for integrative absorption of SO_2 and NO parameters in stirred vessel.

Complex absorbent $Ca(OCl)_2$ showed an effective removal efficiency of both SO_2 and NO of this integrative process. The optimum conditions for simultaneous removal were obtained at a process temperature of 313 K. Absorbent concentration was 5 gram/100 ml and pH of 5.6 in the simulated gas absorption. Removal efficiencies of 99% for SO_2 and 85% for NO were accomplished, respectively under optimal experimental conditions.

4.4.1. Effect of contact time using $Ca(OCl)_2$ in stirred vessel

The change in absorption efficiency with respect to time was determined in this process by analysing the absorbed gas stream at a regular time interval of 10 min keeping other parameters frozen. This provided effectiveness of absorbent over SO_2 and NO absorption for a required contact time in the process. From the results, it was observed that the optimum time for the absorption process for a 5 g/100 ml $Ca(OCl)_2$ was 120 min at initial SO_2 concentration of 6126 ppm, initial NO concentration 876 ppm, initial pH of 5.6 and temperature of 313 K.

4.4.2. Effect of $Ca(OCl)_2$ concentration in stirred vessel

The effect of absorbent concentration provides the capability and optimistic requirement of absorbent for simultaneous SO_2 and NO removal at required time. The effect of $Ca(OCl)_2$ at different concentration range of 1-7 g/100 ml on simultaneous SO_2 and NO removal was illustrated in **Figure 4.11**. From the figure, it was observed that the removal efficiency increased with increase in absorbent concentration till 5 g/100 ml of $Ca(OCl)_2$ and tended to constant with increase in concentration. The maximum removal efficiency 85% was obtained for NO and 99% for SO_2 in this process. Form the data it was concluded that the optimal concentration was given as 5 g/100 ml of $Ca(OCl)_2$. Initial dissolution of absorbent in water has been taken place and which leads to accumulate in terms of hypochlorite ions; these hypochlorite ions react with NO and convert it to NO_2 which proceed to formation of HNO_3, HNO_2 and simultaneously to H_2SO_4 due to dissolution of SO_2 in liquid phase. The efficiency of this process was effective and the absorbent may be considered in large scale operation.

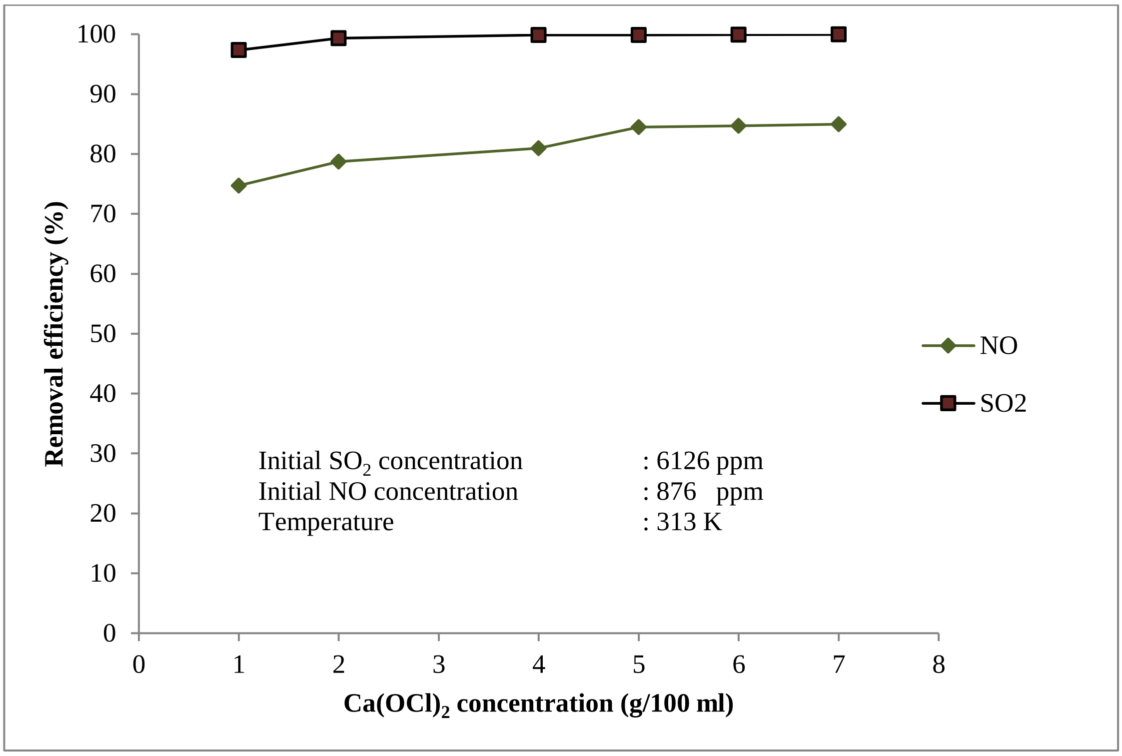


Figure 4.11. Effect of Ca(OCl)$_2$ concentration on removal of NO and SO$_2$ in stirred vessel

4.4.3. Effect of absorbent temperature using Ca(OCl)$_2$ in stirred vessel

Effect of absorbent temperature on the process is a potential approach to study the change in removal efficiency with respect to the temperature of the absorbent. In this process, the detailed illustration was given in Figure 4.12 regarding the temperature change at a range of 293-323 K with respect to the removal efficiency of SO$_2$ and NO. The dissolved species of the absorbent in water react with simulated gas stream of SO$_2$ and NO in which operating temperature plays an effective role on gas-liquid reactions. The removal efficiency was steadily increased with increase in temperature from 293 to 313 K and then decreased. At the later stage, the decrease was due to the solubility of gas decreased with increase in temperature and the initial increase in removal efficiency was due to the reactive affinity of hypochlorite with NO in liquid phase. This was due to increase in presence vacant hypochlorite ions with increase in temperature due to solubility factor. The major intermediates formed during the absorption process initially were HClO, Cl^-, ClO^- ions in aqueous phase due to aqueous dissociation of $Ca(OCl)_2$ and additional absorption of SO_2 and NO by the agitation of solution were in the form of dissolved SO_3^{2-}, SO_4^{2-}, NO_2^- and NO_3^- the main sulphur and nitrogen species in the liquid phase. From the data, the optimal temperature feasible for this process was 313 K.

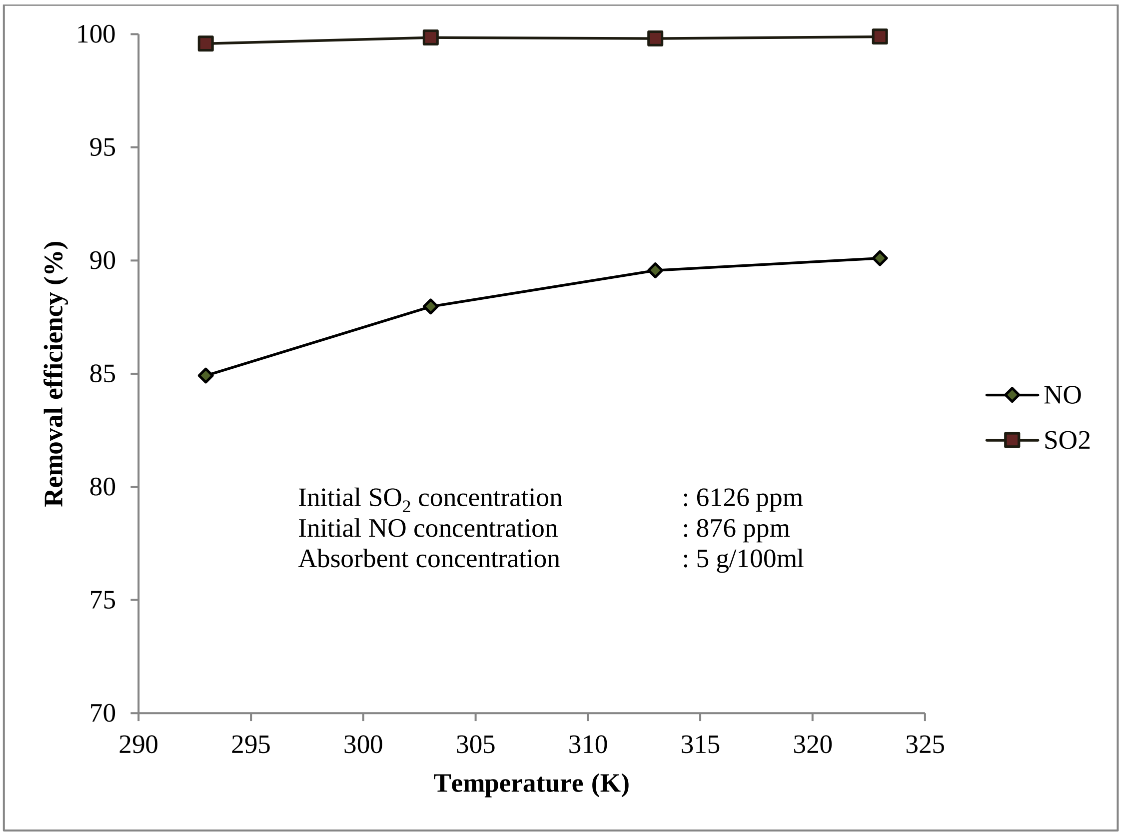


Figure 4.12. Effect of absorbent temperature on removal of NO and SO_2 in stirred vessel using $Ca(OCl)_2$

4.4.4. Effect of initial pH of $Ca(OCl)_2$ in stirred vessel

The effect of initial pH of $Ca(OCl)_2$ on simultaneous removal of SO_2 and NO was examined by keeping 5 g/100 ml absorbent with reaction time 2 h, SO_2 concentration 6126 ppm, initial NO concentration 876 ppm and reaction temperature of 313 K. This study concludes the required optimum pH of the liquid containing $Ca(OCl)_2$ for simultaneous removal of SO_2 and NO. The Optimum pH of the process was obtained as 5.6.

4.4.5. Effect of initial SO_2 concentration using $Ca(OCl)_2$ in stirred vessel

The initial SO_2 concentration was varied to study its effect on removal efficiency of SO_2 and NO with constant parameters of temperature, absorbent concentration, contact time, initial NO concentration and initial pH of the liquid. With increase in SO_2 concentration the removal efficiency of both SO_2 and NO increased slightly till certain time and then tended to maintain constant. The removal efficiency with variation of SO_2 concentration showed same trend as depicted for NaClO in Figure 4.8. As far as $Ca(OCl)_2$ concern, the increase in SO_2 species in liquid phase had less impact in simultaneous removal of SO_2 and NO gas. Because of SO_2 is a promoting agent for NO oxidation and soluble in water. The constant operating parameters in this process were 5 g/100 ml $Ca(OCl)_2$ concentration, contact time 2 h, initial NO concentration 876 ppm, initial pH of 5.6 and temperature of 313 K.

4.4.6. Effect of initial NO concentration using $Ca(OCl)_2$ in stirred vessel

The NO concentration effect on simultaneous removal of SO_2 and NO using $Ca(OCl)_2$ as absorbent in magnetic stirrer vessel at constant parameters like contact time, initial SO_2 concentration, initial pH of the liquid, absorbent concentration and temperature explained the requirement of absorbent to oxidize NO. Because NO is slightly soluble in water as compared to highly soluble SO_2. The increase in NO concentration resembled more consumption of absorbent. Hence, slight decrease in NO removal efficiency was observed with increase in its concentration under batch condition of absorbent. The obtained trend was similar to the trend for NaClO shown in Figure 4.9. The constant operating parameters in this process were 5 g/100 ml $Ca(OCl)_2$ concentration with time 2 h, initial SO_2 concentration 6126 ppm, initial pH of 5.6 and temperature of 313 K.

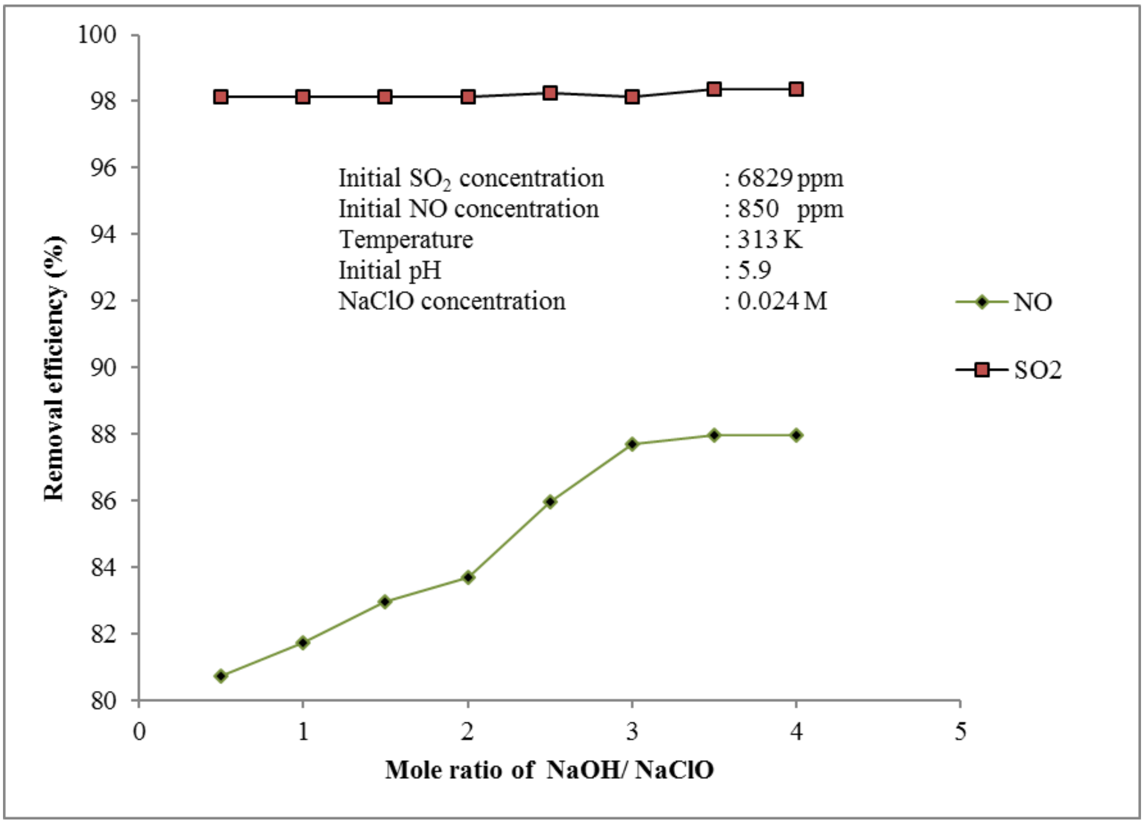


Figure 4.13. Effect of mole ratio of absorbent blend NaOH/NaClO in stirred vessel

4.5. Absorption in semi batch magnetic stirrer vessel with NaOH/NaClO

This study was concerned about the removal of SO_2 and NO simultaneously with use of a complex absorbent NaOH/NaClO. It was prepared from blending of NaClO and sodium hydroxide (NaOH) to increase the removal efficiency of the nitrogen dioxide (NO_2) whereas present of NaClO was used in conversion of NO to NO_2. A simulated SO_2/NO gas steam were tested with use of this complex absorbent in the stirrer vessel. The operating parameters like temperature, initial concentration of complex absorbent as mole ratio, initial SO_2 and NO concentration, absorbent pH was changed to find out the combined SO_2 and NO removal using complex absorbent blend during experimentation.

Complex absorbent had shown an increase in removal efficiency of both SO_2 and NO_x. Addition of NaOH led to increase in NO_2 and thereby conversion of NO into NO_2 absorption. Experimental aspects were accessed in a laboratory scale agitated column for simultaneous removal of SO_2 and NO using complex absorbent NaOH/NaClO. The optimum conditions for simultaneous removal of SO_2 and NO were obtained at a process temperature of 313 K, absorbent concentration about 3 mole ratio of NaOH to NaClO and pH of 5.9 in the simulated gas absorption. Removal efficiencies of 98% for SO_2 and 87% for NO were accomplished, respectively under optimal experimental conditions.

4.5.1. Effect of mole ratio of NaOH/NaClO in stirred vessel

To study the effect of molar ratio of complex absorbent on removal efficiencies of SO_2 and NO, molar ratio of NaOH to NaClO was varied from 0.5 to 4.0 and the results were shown in Figure 4.13.

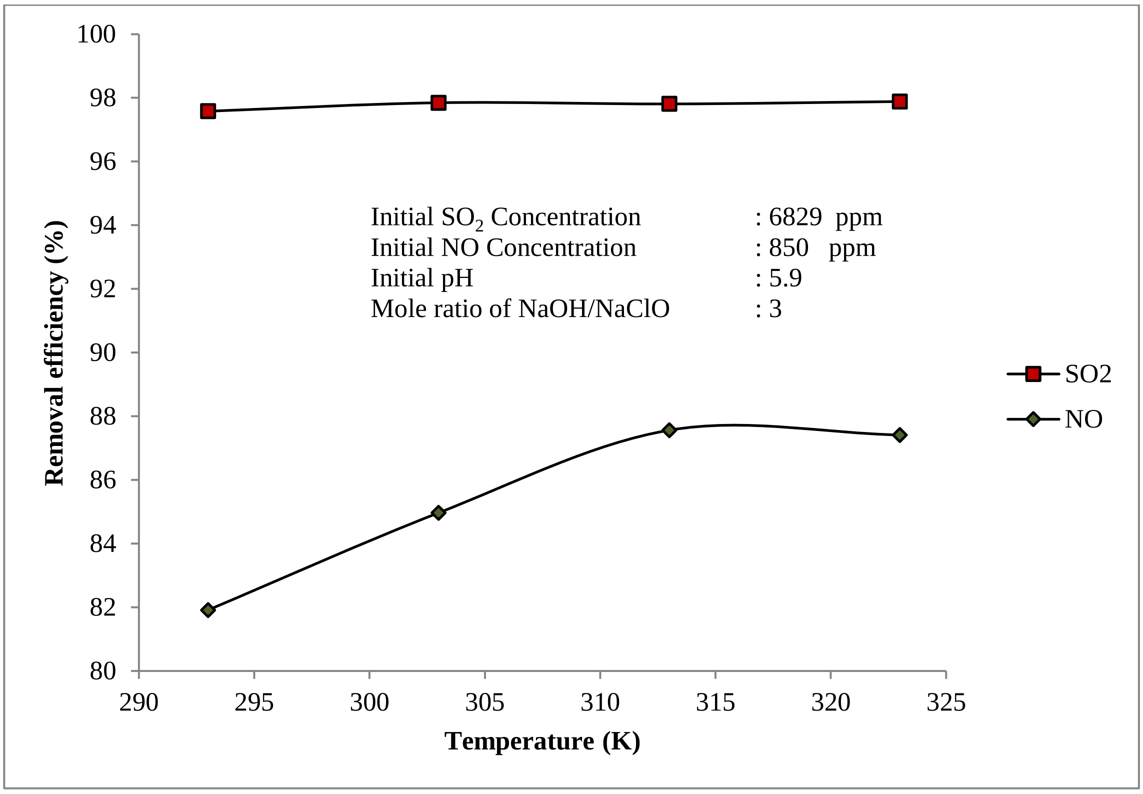


Figure 4.14. Effect of absorbent temperature in stirred vessel using NaOH/NaClO blend

From Figure 4.13, the molar ratio of NaOH to NaClO had a slight effect on desulfurization but remarkable effect on NO removal. The SO_2 removal efficiency was observed nearly 98% and NO removal efficiency was about 87%.

4.5.2. Effect of absorbent temperature in stirred vessel with NaOH/NaClO

Since reactions between SO_2 and absorbent, and NO and absorbent blend belonging to dissolved gas–liquid absorbent reactions, the absorbent temperature plays an important role on simultaneous removal of SO_2 and NO. The removal efficiencies of SO_2 and NO change with absorbent temperature were investigated experimentally and the results were shown in Figure 4.14. It can be seen from Figure 4.14 that the removal efficiency of SO_2 was slightly affected by reaction temperature and almost retained at 98%, but the removal efficiency of NO was shown increasing at early stage of absorption and then maintained nearly constant with the rise of absorbent temperature. The maximum removal efficiency of NO was achieved at 313 K.

4.6. Comparison of the results in semi-batch column with some published works

Table 4.1 Comparison of maximum removal efficiency of SO_2 and NO_x in semi-batch column

S. No.	Reactors/column	Process	Absorbent	Removal efficiency (%)	Reference
1.	Bubble column	Absorption	aqueous ClO_2	SO_2:100, NO_x: 72	Jin et al., 2006
2.	Bubble column	Absorption	M/$NaClO_2$ complex	SO_2:100, NO: 85	Zhao et al., 2010
3.	Bubble column	Absorption	$NaClO_2$	SO_2:100, NO_x: 85	Yi et al., 2009
4.	Bubble Column	Absorption	NaClO	SO_2:99, NO: 91	Present study
5.	Magnetic stirrer vessel	Absorption	NaClO/NaOH	SO_2:98, NO: 87	Present study
6.	Magnetic stirrer vessel	Absorption	$Ca(ClO)_2$	SO_2:99, NO: 85	Present study
7.	Magnetic stirrer vessel	Absorption	NaClO	SO_2:100, NO: 92	Present study
8.	Bubble column	Absorption	Fe^{II} EDTA with Na_2SO_3	SO_2:95, NO: 90.2	Wang et al., 2007

The comparison of the results of present work with some most studied absorbents in literature regarding simultaneous removal of NO_x and SO_2 using semi-batch column is given in Table 4.1. Comparisons of the removal efficiencies of SO_2 and NO by various absorbents are difficult because of dissimilarities in absorption conditions used by various researchers. The experimental results of the present work had enhanced value of both SO_2 and NO removal as compared to the earlier related research findings available in literature. Therefore, NaClO can be used as an innovative low-cost absorbent in the pool of other absorbents used for simultaneous removal of NO and SO_2 from SO_2 and NO_x contaminated gas streams.

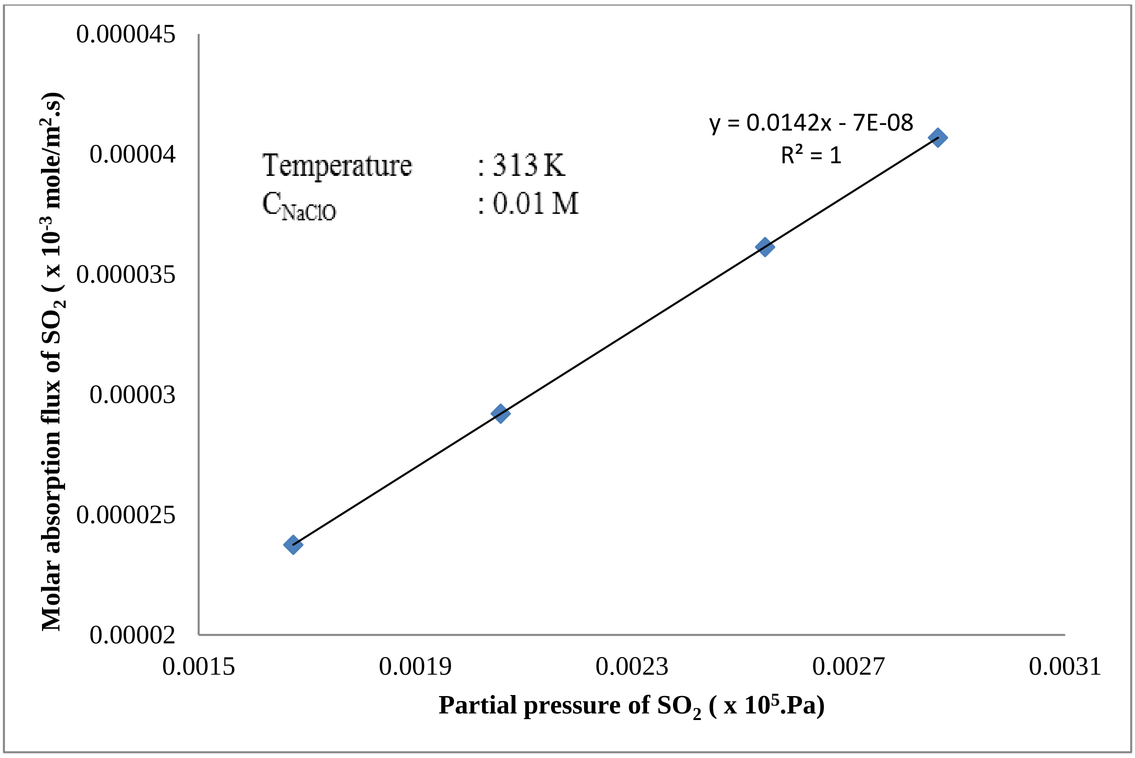


Figure 4.15. The N_{SO_2} vs. $p_{SO_{2g}}$ for estimation of $k_{SO_{2g}}$ with NaClO

4.7. Estimation of reaction kinetics of SO_2 and NO with NaClO

The mass transfer mechanism and kinetics of the reaction involved in the simultaneous absorption of SO_2 and NO in NaClO solution was done. The data from the earlier experiments regarding combined SO_2 and NO removal from simulated gas stream by NaClO as low-cost absorbent in semi batch magnetic stirrer vessel was used. The reaction order and reaction rate constant for NO absorption in the absorbent NaClO was calculated along with the mass transfer co-efficient for the absorption of SO_2 in NaClO. For the calculation purposes, reaction was assumed to be pseudo m^{th} order reaction and this assumption was successfully verified.

The mass transfer-reaction process for the simultaneous absorption of NO and SO_2 in NaClO was analysed. It is well known that mass transfer and reaction kinetics parameters of gas absorption are the essential theoretical basis for industrial design of the process. The effects of various operating parameters were analysed and some important reaction parameters were determined. Rate equations for absorption of NO and SO_2 were also established. The results are essential for numerical simulations for the process.

4.7.1 Estimation of $k_{SO_{2_g}}$ with NaClO

As per consideration of gas phase controlling system for SO_2 reaction in simultaneous absorption, the estimation of $k_{SO_{2_g}}$ was found from equation (4.27). The graph between N_{SO_2} and $p_{SO_{2_b}}$ was plotted in Figure 4.15 at C_{NaClO} of 0.01 M and temperature of 313 K.

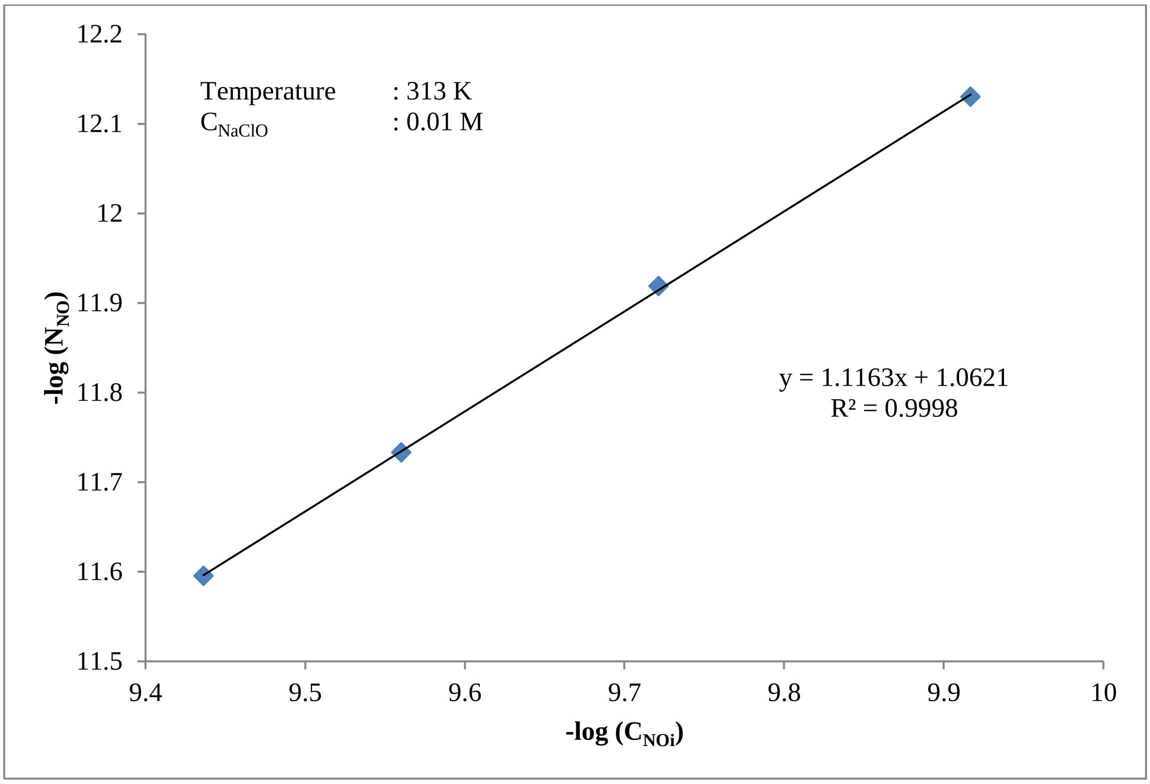


Figure 4.16. $\log \mathrm{N}_{NO}$ vs. $\log \mathrm{C}_{NO_i}$ for estimation of reaction order of NO with NaClO

From Figure 4.15 a linear behaviour of SO_2 was observed between the changes in absorption flux $\left(\mathrm{N}_{SO_2}\right)$ to the change in partial pressure$\left(\mathrm{p}_{SO_{2_b}}\right)$. The value of $\mathrm{k}_{SO_{2_g}}$was found to be equal to 0.0142 kmol/m^2.s. Pa and it was obtained from the slope of the linear equation fitted to the experimental data with R^2 value almost equal to 1.

4.7.2. Estimation of reaction order for NO with NaClO

Considering equation (4.25), the reaction order was calculated by plotting $\log \mathrm{N}_{NO}$ vs. $\log \mathrm{C}_{NO_i}$ at C_{NaClO} at 0.01 kmol/m^3 and temperature 313 K as shown in Figure 4.16. From the figure, it was seen a linear change between $\log \mathrm{N}_{NO}$ and $\log \mathrm{C}_{NO_i}$. The linear equation was fitted with the data to get observed R^2 value equal to 0.9998. The slope of the line was 1.1323, which was equal to (m+1)/2. This value was almost equal to 1 and thus the order of the reaction with respect to NO was approximately 1. Then, the rate constant of the reaction was calculated from the value of the intercept of the line as shown in Figure 4.16 and from equation (4.24). Its value was found to be $3.98\times10^7 s^{-1}$.

4.7.3. Calculation of Hatta number with NaClO

To check whether assumption of the present study for reaction between NO and NaClO to be a fast reaction, Hatta number was also calculated from the equation (4.17). Its value came out to be 15.87. As this value was considerably greater than 3 (Ondo et al. 1970a, 1970b), our assumption of fast reaction between NO and NaClO was correct.

4.8. Thermodynamic parameters of SO_2 and NO absorption with NaClO

The properties of NaClO, NO, SO_2, and available literature suggests the final chemical equation for instantaneous removal of SO_2 and NO by using NaClO solution which is as follows:

$$2NO + 2SO_2 + 8NaClO + H_2O \leftrightarrow 2Na_2SO_4 + 2NaNO_3 + 2NaCl + H_2O + 3Cl_2 \quad (4.42)$$

4.8.1. Enthalpy change for absorption of SO_2 and NO in NaClO

Since the optimum process temperature was 313 K using NaClO for simultaneous removal of SO_2 and NO, the enthalpy change was calculated in the temperature range 283-353 K. This range was also selected to include the wet-bulb temperature (i.e., 323 K) of coal-fired power plant stack gases.

The desired enthalpy change of the process at constant pressure was calculated from the formula:

$$\Delta H = \Delta H^{\circ} + \int_{298}^{T} \Delta C_P \, dT \tag{4.43}$$

$$\text{Where } \Delta C_P = \sum v_i C_{Pi} \tag{4.44}$$

Here v_i refers to the molar volume of component i. Table B1 in appendix B reports standard molar enthalpy and specific heat of the reactants at isobaric condition taken from the work of Dean, 1970. The specific heat of NaClO at constant pressure was not found in literature, so it was replaced by that of HClO. The reaction enthalpy change with respect to temperature is shown in Figure 4.17.

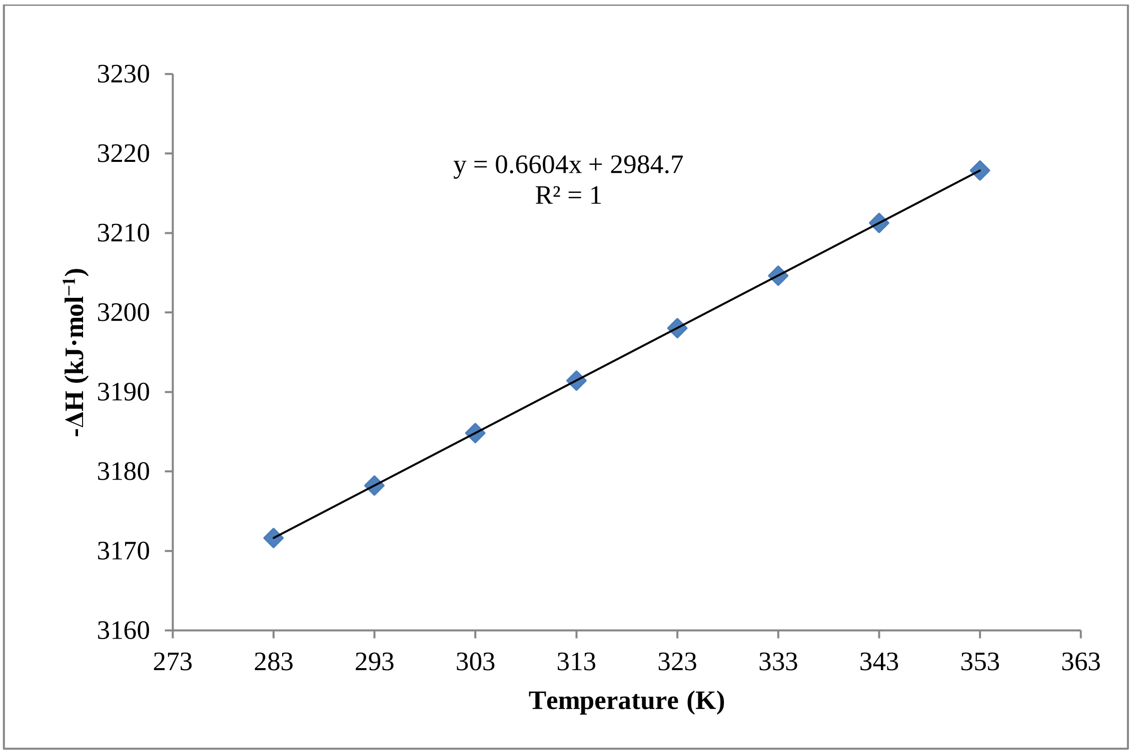


Figure 4.17. Effect of temperature on enthalpy change with NaClO

The heat of reaction as shown in equation (4.42) was found to be negative indicating the exothermic nature of the process. The data summarized that increasing temperature was not the individual parameter that favoured the absorption.

4.8.2. Gibbs free energy change for absorption of SO_2 and NO in NaClO

The change in Gibbs free energy for the process was calculated from the formula as given below:

$$\Delta G = \Delta H - T\Delta S = \Delta H - T\Delta S^{\circ} - T\int_{298}^{T} \frac{\Delta C_P}{T} dT \tag{4.45}$$

Figure 4.18 showed that the change of Gibbs free energy values as function of temperature were less than zero, indicating spontaneity of the reaction and suggesting that other parameters were also promoted the rate of absorption including temperature.

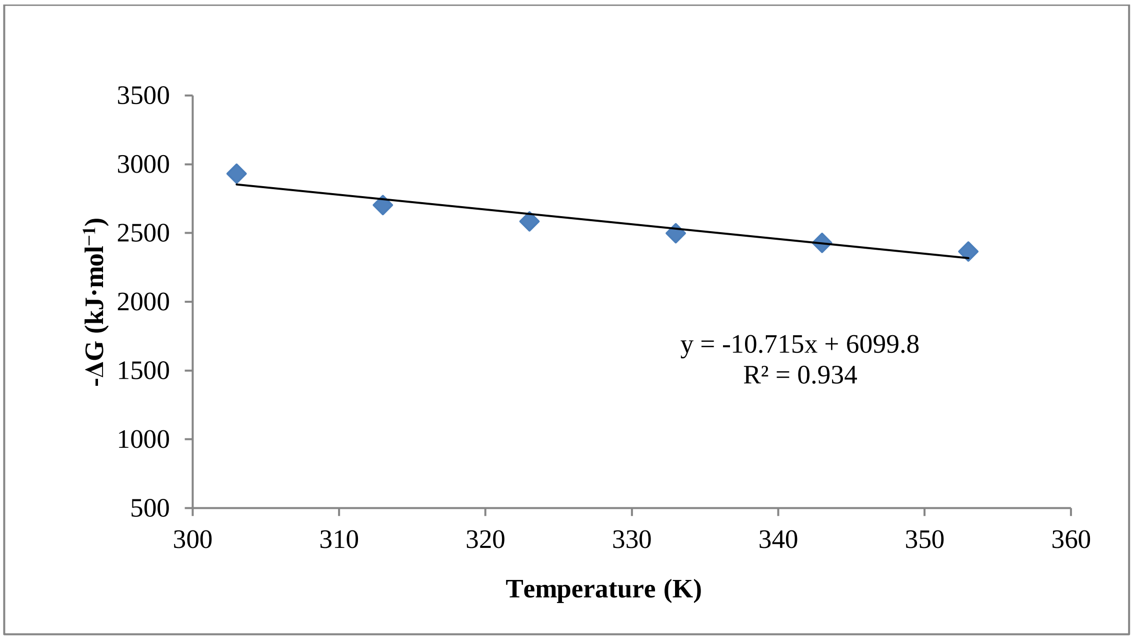


Figure 4.18. Effect of temperature on Gibbs free energy change with NaClO

Table 4.2. Equilibrium constant at different temperatures with NaClO

T (K)	303	313	323	333	343	353
K	e^{1166}	e^{1041}	e^{964}	e^{904}	e^{852}	e^{807}

4.8.3. Equilibrium constant for absorption of SO_2 and NO in NaClO

The equilibrium constant for the process at any temperature was calculated from the following formula:

$$\ln K_{12} = -\frac{\Delta G}{RT} \tag{4.46}$$

The equilibrium constant K_{12} of the process governed by equation (4.44) at different temperatures was shown in Table 4.2. The data obtained conveys large reaction limit due to its high equilibrium constant.

4.8.4. Equilibrium partial pressure for absorption of SO_2 and NO in NaClO

Gibbs free energy change becomes zero for the system to attain equilibrium. The equilibrium partial pressure of the components at any temperature T was calculated by the formula as given below:

$$\ln\left(\frac{p_{p_i}^{\gamma_p}}{p_{R_i}^{\gamma_R}}\right) = -\frac{\Delta G}{RT} \tag{4.47}$$

$$\text{and } \Delta G = \sum v_i \Delta G_i \tag{4.48}$$

Where, p_{p_i} and p_{R_i} are equilibrium partial pressures of the product and reactant, respectively. γ_p and γ_p are the stoichiometric coefficients of product and reactant, respectively. ΔG_i is the individual Gibbs free energy change of the component. The equilibrium partial pressures of SO_2 and NO were reported in Table 4.3. The equilibrium partial pressure of both components increased with an increase in temperature, indicating that the high temperate did not favour the reaction. The equilibrium partial pressure of SO_2 and NO is very small even at maximum temperature of 353 K which indicates the feasibility of simultaneous absorption of SO_2 and NO by using NaClO as absorbent.

Table 4.3. The equilibrium partial pressure under different conditions with NaClO

T (K)	303	313	323	333	343	353
***p_{SO2}* (MPa)**	1.1308×10^{-284}	1.334×10^{-275}	4.3172×10^{-267}	4.3172×10^{-267}	1.4678×10^{-251}	1.8726×10^{-244}
***p_{NO}* (MPa)**	2.3586×10^{-127}	2.6197×10^{-123}	1.6344×10^{-119}	6.0328×10^{-116}	1.3794×10^{-112}	2.0349×10^{-109}

4.9. Absorption in continuous spray column with NaClO

In earlier investigation, NaClO showed gigantic removal of both SO_2 and NO from gas stream. Being low cost, readily available and efficient reagent, NaClO was used for removal of SO_2 and NO from simulated gas stream using continuous spray column. The experimental results were reported with effect of various operating parameters such as initial NaClO concentration, initial NO and SO_2 concentration, and temperature on removal of SO_2 and NO from the gas stream.

Under experimental optimum condition for simultaneous removal of SO_2 and NO of 313 K, pH 5.4, 0.024 M NaClO concentration, gas flow rate 600 mL/min and liquid flow rate 1500 mL/min, SO_2 could achieve maximum of 97% removal and that of 82% for NO removal in spray column. The effective removal efficiency of SO_2 and NO was achieved due to excellent oxidizing property of NaClO. With increase of NaClO concentration, NO initial concentration, initial SO_2 concentration and temperature, the NO removal efficiency was steadily stabilized; whereas SO_2 removal efficiency was stick to maximum. Addition of CO_2 had a minimal effect on removal efficiency of SO_2 and NO; and showed maximum of 40% removal efficiency of CO_2 itself under optimum experimental condition of simultaneous absorption of SO_2 and NO. The dissolved SO_2, HSO_3^-, SO_3^{2-}, SO_4^{2-}, NO-NO_2, HNO_2, NO_2^-, HNO_3 and NO_3^- free radicals played a leading role in removal of NO and SO_2 by spray scrubbing using NaClO. These continuous mode experimental results would be helpful for prediction or modeling the process suited for large scale operation. In the spray column, continuous simulated gas stream is contacted with the disperse phase of aqueous NaClO solution counter-currently, the NO and SO_2 react with the absorbent and thereby removed from gas stream. Higher gas flow rate is accountable for coalescence of sprayed liquid droplets which decreases the gas-liquid interfacial area resulting low mass transfer from gas to liquid phase. The gas and liquid flow rate were kept constant as 600 and 1500 mL/min, respectively to keep the pressure drop minimum within the provision of spray column dimension used in the experimentation. In addition to this, gas flow rate of 600 ml/min and liquid flow rate of 1500 ml/min were fixed to ensure proper mixing between sprayed liquid and gas stream is effective zone of spray column. Each of the experimental parameters such as time, absorbent concentration, temperature, initial SO_2 concentration, initial NO concentration and initial pH was varied individually keeping other parameters constant and removal efficiency of NO and SO_2 was calculated with all parameters experimented. The removal efficiency of NO and SO_2 was denoted by $E_{f\,(NO)}$ and $E_{f\,(SO_2)}$, respectively. $p_{NO\,(f)}$ is the final concentration of NO, $p_{NO\,(i)}$ the initial concentration of NO. $p_{SO_2\,(f)}$ is the final concentration of SO_2 and $C_{SO_2\,(i)}$ the initial concentration of SO_2. Finally, $E_{f\,(NO)}$ and $E_{f\,(SO_2)}$were calculated using following equation (4.49) - (4.50):

$$E_{f\,(NO)} = \frac{p_{NO\,(i)} - p_{NO\,(f)}}{p_{NO\,(i)}} \tag{4.49}$$

$$E_{f\,(SO_2)} = \frac{p_{SO_2\,(i)} - p_{SO_2\,(f)}}{p_{SO_2\,(i)}} \tag{4.50}$$

4.9.1. Effect of time using NaClO in spray column

The effect of time on simultaneous removal of SO_2 and NO for inlet gas flow rate of 600 mL/min and liquid flow rate of 1500 mL/min with spray distributor having outlets of diameter 1 mm each was reported in Figure 4.19 at 313 K and 0.024 M NaClO concentration. Time optimization plays an important role in the absorption process with chemical reaction. The optimum time for the process was estimated to be 120 min and since then there was a sharp continuous decrease in removal efficiencies of both SO_2 and NO. Because of the process of absorption was done with continuous recirculation of fixed concentration of NaClO. Absorption of NO and SO_2 was taken place from gas to liquid phase and it was gas phase controlling operation. It was also observed that compared to NO, the SO_2 removal efficiency was more effective with respect to time as 98% SO_2 removal persisted for long period of time and thereby a significant decrease in removal was found with increase in time due to variation in NaClO concentration for recirculation.

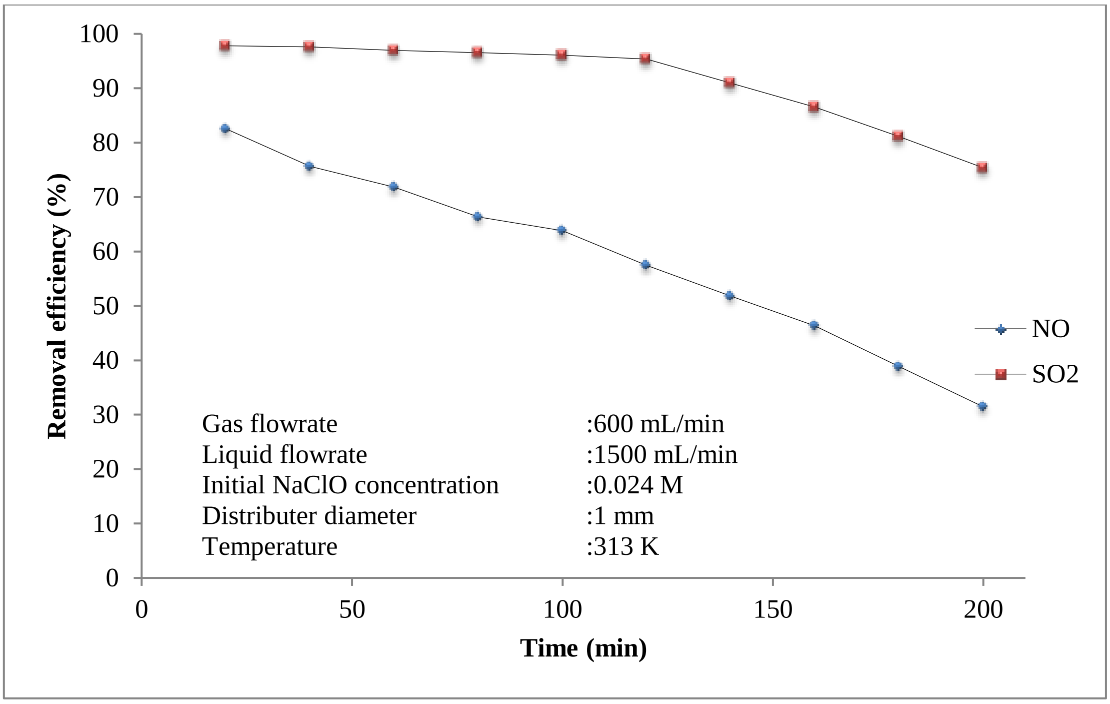


Figure 4.19. Effect of time on removal of SO_2 and NO using NaClO in spray column

4.9.2. Effect of NaClO concentration in spray column

Optimizing the absorbent concentration leads to find the desired concentration of NaClO for simultaneous removal of SO_2 and NO from fixed inlet composition of simulated gas stream which resembles the industrial stack emission regarding SO_2 and NO. The effect of absorbent concentration on simultaneous removal of SO_2 and NO for inlet gas flow rate of 600 mL/min and liquid flow rate of 1500 mL/min with spray distributor outlets of diameter 1 mm each was shown in Figure 4.20 at fixed temperature of 313 K. The removal efficiency of SO_2 was stick to 98% and maximum removal efficiency of NO of 82% was obtained at 0.032 M NaClO concentration. Slight increase in removal efficiencies of NO was observed from 0.004 to 0.032 M NaClO concentration and the NaClO concentration was 0.024 M for further study. From Figure 4.20 it was observed that NO removal efficiency increased sharply up to 78 % as of NaClO concentration was 0.024 M and then increased steadily till it attains maximum removal efficiency of 82 %. This encompasses the increase rate of dissolution of gases in the liquid phase at higher absorbent concentrations. And it proves that the liquid phase concentration affects the overall resistance in gas phase controlling operation.

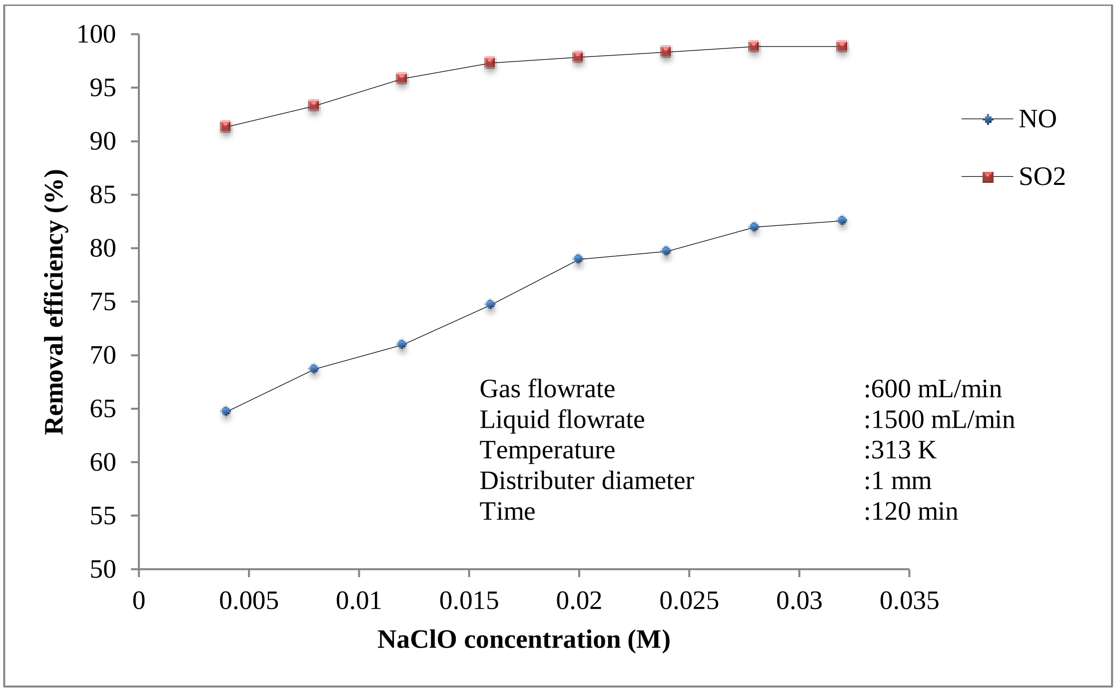


Figure 4.20. Effect of NaClO concentration on removal of SO_2 and NO in spray column

4.9.3. Effect of temperature using NaClO in spray column

During the study of temperature effect on simultaneous removal of SO_2 and NO, constant temperature water bath was used in association with the column to maintain the temperature of the spray column. Temperature variation is a key parameter in mass transfer process as it provides the compatibility for gas phase molecules to diffuse in to the liquid phase in gas-liquid mass transfer operation.

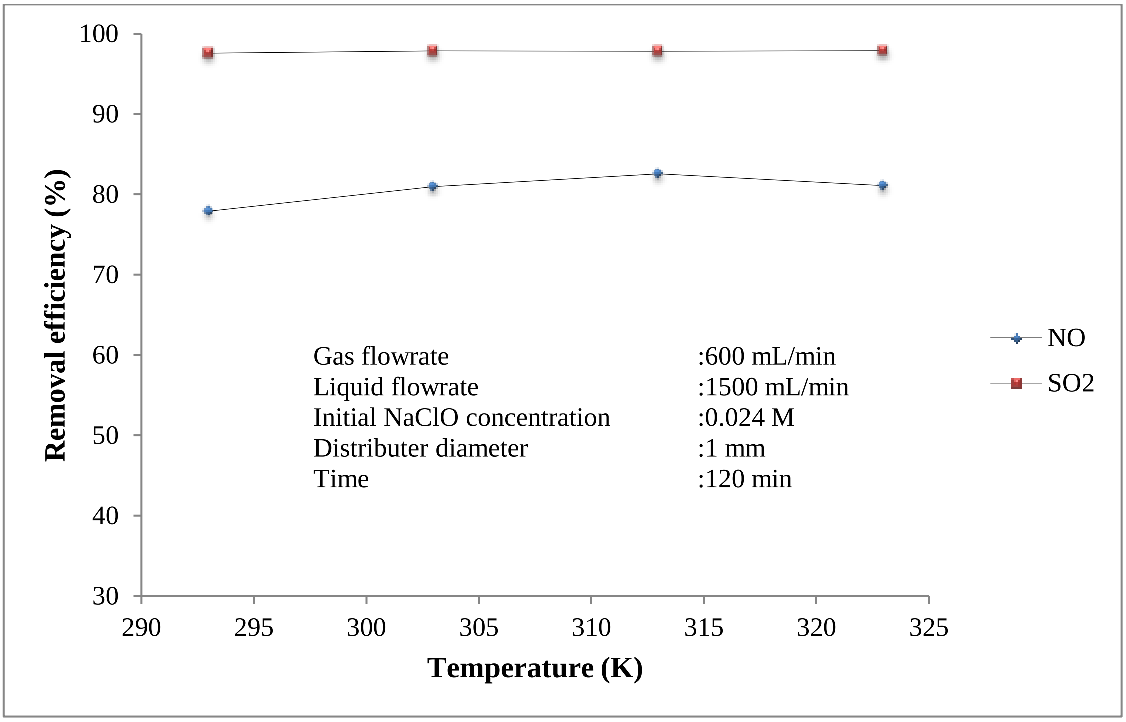


Figure 4.21. Effect of temperature on removal of SO_2 and NO using NaClO in spray column

The effect of temperature on simultaneous removal of SO_2 and NO for constant inlet gas flow rate of 600 mL/min and liquid flow rate of 1500 mL/min was investigated experimentally and shown in Figure 4.21 at 0.024 M NaClO concentration. Experiments were performed at several temperatures of 293, 303, 313 and 323 K. The Figure 4.21 depicted that the removal efficiency of SO_2 was minutely affected by the temperature and almost retained at 98%, but the removal efficiency of NO was shown increasing at first and then dropped with the rise of temperature. The highest removal efficiency of NO was achieved at temperature range of 313 – 323 K. That is why temperature effect has shown its prophecy for simultaneous removal of SO_2 and NO at or near the wet-bulb temperature of stack gas emission.

4.9.4. Effect of initial SO_2 concentration using NaClO in spray column

The effect of initial SO_2 concentration explains the change in removal efficiency of SO_2 and NO in (SO_2 + NO + NaClO) system. For simultaneous removal of SO_2 and NO, the variation of initial SO_2 concentration was investigated experimentally for inlet gas flow rate of 600 mL/min, liquid flow rate of 1500 mL/min at 313 K, NO initial concentration of 816 ppm and fixed NaClO (0.024 M) concentration and shown in Figure 4.22. From Figure 4.22 it was observed that the removal efficiency of NO increased with increase in initial SO_2 concentration from 2431 to 6815 ppm and for SO_2 removal efficiency the change was very minute. Increase in concentration of SO_2 promotes the absorption of NO, so it might act as oxidant which accelerates in the diffusion rate of NO from gas to the liquid phase.

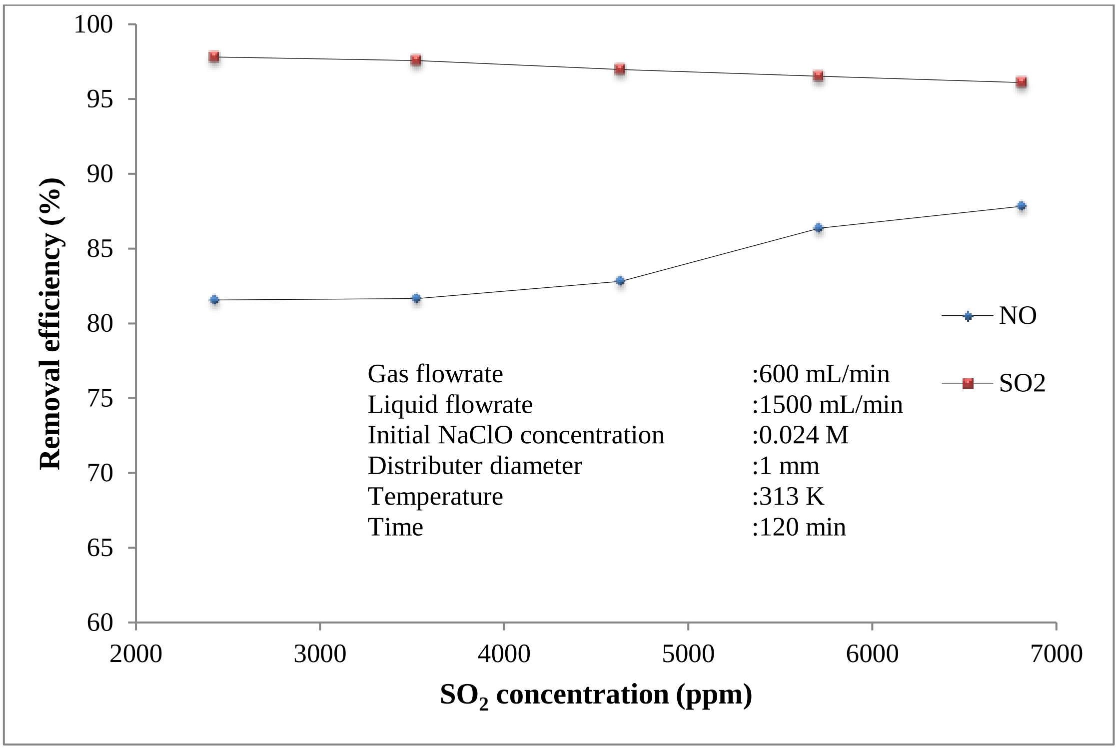


Figure 4.22. Effect of initial SO_2 concentration on removal of NO and SO_2 using NaClO in spray column

4.9.5. Effect of initial NO concentration using NaClO in spray column

The experimental results to see the effect of various initial concentrations of NO on simultaneous removal of NO and SO_2 for inlet gas flow rate of 600 mL/min and constant liquid flow rate of 1500 mL/min with spray distributor outlets of diameter 1mm each were illustrated in Figure 4.23 at 0.024 M NaClO concentration and 313 K. From Figure 4.23 it was observed that for fixed initial SO_2concentration, the removal efficiency of NO increased with increase in NO initial concentration and SO_2 removal efficiency retained at 98%. The NO absorption rate is dependent on the concentration driving force of NO from the bulk of the gas phase to the surface of liquid droplets in which gas liquid mass transfer takes place in accordance to Film theory. Therefore, the enhancement of gas phase partial pressure of NO makes the concentration driving force between gas and liquid phase larger so that mass transfer rate of NO by absorption with chemical reaction from gas to liquid is enhanced.

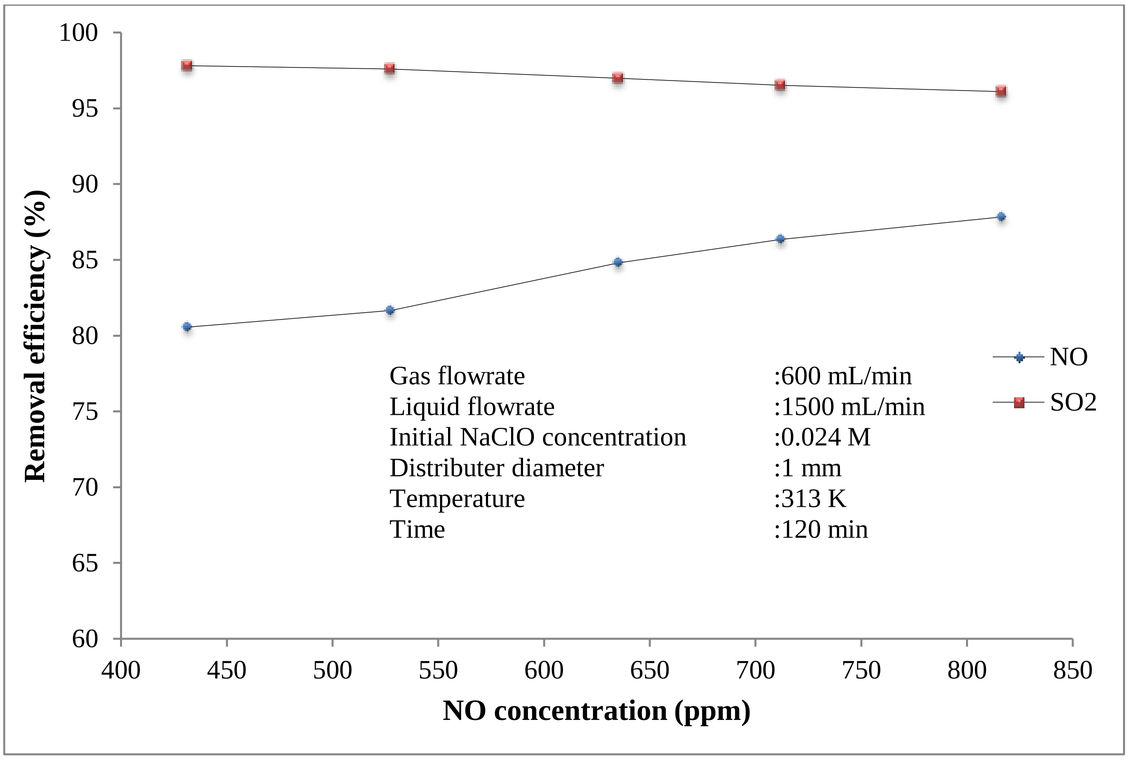


Figure 4.23. Effect of initial NO concentration on removal of SO_2 and NO using NaClO in spray column

4.9.6. Effect of various initial pH of absorbent using NaClO in spray column

The initial pH of the absorbent plays an important role for simultaneous absorption of SO_2 and NO in liquid phase. The change in absorption of SO_2 and NO with initial pH was illustrated in Figure 4.24. The inlet gas flow rate of 600 mL/min and liquid flow rate of 1500 mL/min with spray distributor outlets of diameter 1mm each, NaClO concentration of 0.024 M and temperature 313 K were maintained for studying the effect of initial pH on simultaneous removal of SO_2 and NO. The Figure 4.24 concluded the gigantic absorption of SO_2 and the maximum removal of NO was observed at a pH of 5.6. Here maximum removal efficiencies of SO_2 and NO were stick to 98 and 82%, respectively. The acidic pH is responsible for decomposition of NaClO and it promotes the oxidation of NO into soluble NO_2 and hence accelerates the dissolution of NO in the liquid phase.

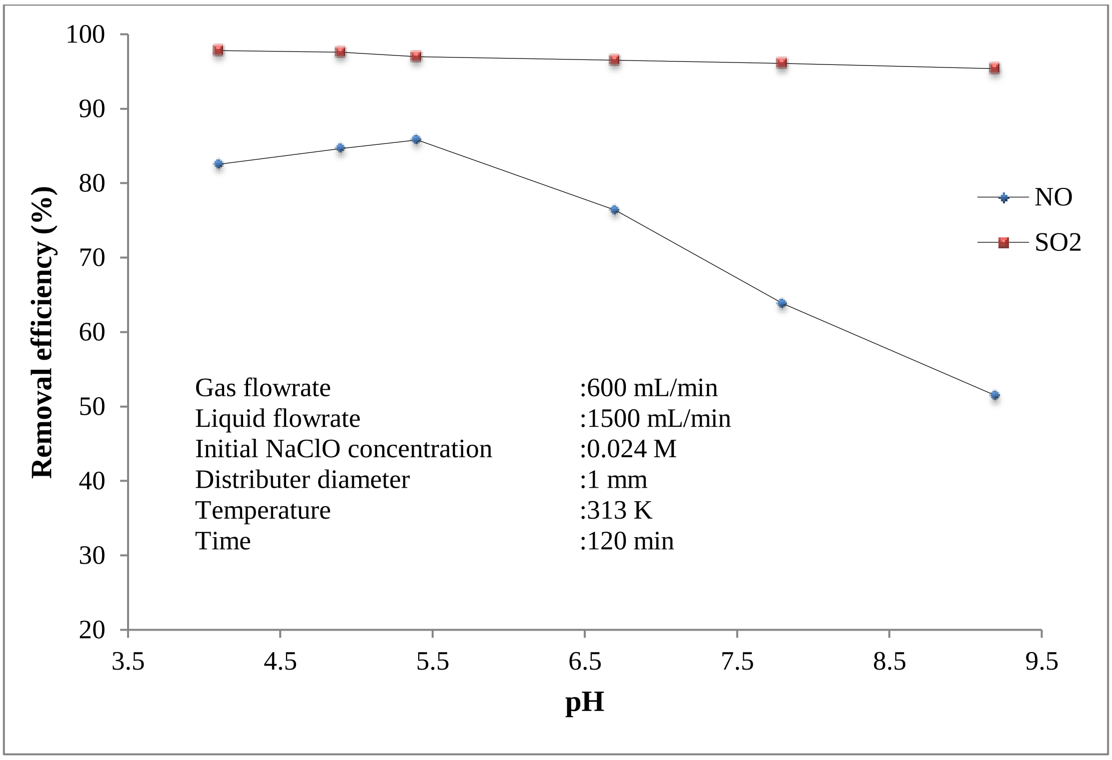


Figure 4.24. Effect of initial pH of absorbent on removal of SO_2 and NO using NaClO in spray column

4.9.7. Effect of addition of CO_2 to simulated gas stream using NaClO in spray column

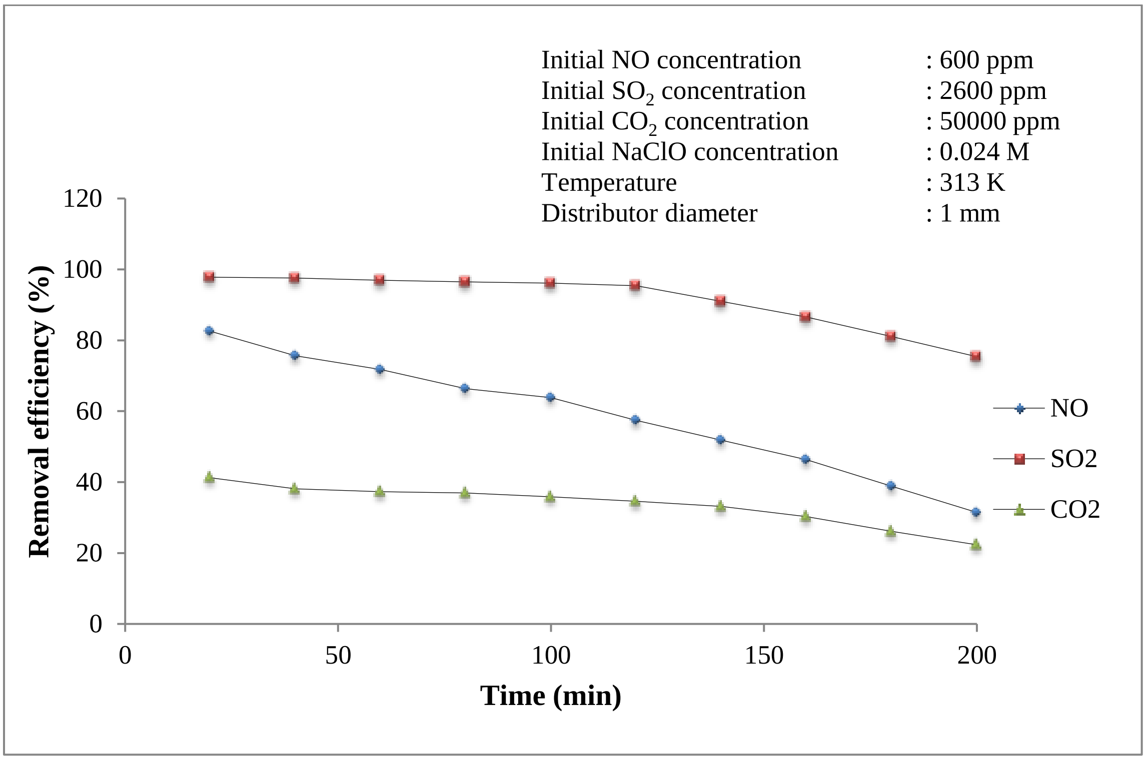


Figure 4.25. Effect of addition of CO_2 on removal of SO_2 and NO using NaClO in spray column

The experimental results with inlet gas flow rate of 600 mL/min and liquid flow rate of 1500 mL/min with spray distributor outlets of diameter 1 mm each at 0.024 M NaClO concentration to study the effect of CO_2 addition to simulated gas stream on simultaneous removal of NO and SO_2 were illustrated in Figure 4.25. The NO initial concentration of 600 ppm, SO_2 initial concentration of 2600 ppm and CO_2 initial concentration of 50000 ppm were maintained at 313 K under total pressure of 101.3 kPa. From Figure 4.25 it was observed that the addition of CO_2 did not affect the removal efficiency of SO_2 but it showed very little enhancement of NO removal efficiency. Besides simultaneous SO_2 and NO absorption, removal of CO_2 was also taken place due to solubility phenomenon and removal efficiency was around 40%.

4.9.8. Comparison of SO_2 and NO removal efficiencies for continuous absorption column

Table 4.4. Comparison of results in continuous absorption column with some published works

S. No.	Reactors/column	Process	Absorbent	Removal efficiency (%)	Reference
1.	Packed column	Absorption	Urea	SO_2:100, NO_x: 40	Fang et al., 2011
2.	Spray column	Absorption	NaClO	SO_2:98, NO: 82	Present study
3.	Spray sieve tray	Absorption	$NaClO_2$/NaOH	SO_2:100, NO_x:71.9	Chien et al., 2000
4.	Twin-fluid atomizers	Absorption	Calcium magnesium acetate	SO_2:>80, NO_x: 80	Nimmo et al., 2004
5.	Wetted-wall Column	Absorption	$NaClO_2$	SO_2:100, NO_x: 67	Pillai et al., 2009

The comparison of maximum removal efficiency of SO_2 and NO for present work and also the works by using various absorbents available in literature was done by using continuous column for simultaneous removal of SO_2 and NO from gas stream (Table

4.4). The results of present work using NaClO as absorbent was showed superior absorption efficiency for both SO_2 and NO as compared to the various absorbents used in the proof of similar type of literature.

4.10. Effect of additive NH_3 solution with NaClO

Based on the available literature and our previous experiments for simultaneous removal of SO_2 and NO, this study was aimed to utilize the spent absorbent after absorption. This is the reason to prepare the blend of NH_3/NaClO and committed for simultaneous absorption of SO_2 and NO from simulated gas stream. Here, NH_3 solution was used as additive with most suitable absorbent NaClO. The results were shown the end products such as ammonium nitrate and ammonium sulphate, which are effective fertilizers used in agricultural field. This helps in gaining useful end products in treatment of stack gases. As ammonia solution is successful absorbent for CO_2 capture this blend can applicable for flue gas clean-up and hence to produce carbonate, sulphate and nitrate. Initially the semi batch process has shown effective results from the feasibility of the process and then the optimal results were found out for simultaneous absorption of SO_2 and NO with various operating parameters. The thermodynamic analysis for the process of SO_2 and NO removal using NH_3/NaClO blend was also done.

4.10.1 Thermodynamic parameters for absorption of SO_2 and NO in NaClO/NH_3

The mass transfer of SO_2 and NO from bulk of the gas phase to the aqueous NaClO/NH_3 is influenced by diffusion rate and reactive potential of SO_2 and NO with absorbent. The properties of NaClO, NH_3, NO and SO_2 propose the major steps involved for simultaneous removal of SO_2 and NO by using NaClO/NH_3 as given in equations (4.51) and (4.52). The blend should be taken care in such a way that it should be committed immediately for absorption to avoid the chain reaction between bleach and ammonia solution resulting chloramine, dichloramine and nitrogen tri chloride with increase in time.

$$NO + 2HClO^{-} + 2NH_4OH \rightarrow NO_3^{-} + 2NH_4^{+} + 2H_2O + 2Cl^{-} \quad (4.51)$$

$$SO_2 + 2HClO^{-} + 2NH_4OH \rightarrow SO_4^{-} + 2NH_4^{+} + 2H_2O + 2Cl^{-} \quad (4.52)$$

Here $HClO^-$ and NH_4OH were formed during the initial dissociation of NaClO and NH_3 in water. The product species NO_3^-, NH_4^+, SO_4^-, Cl^- and H_2O in the proposed reactions suggest the formation of NH_4NO_3 and NH_4SO_4.

4.10.1.1. Enthalpy change for absorption of SO_2 and NO in NaClO/NH_3

The obtained optimum temperature from the experimental data in simultaneous removal of SO_2 and NO using NaClO/NH_3 blend was 323 K**.** Based on this value the enthalpy change was calculated at a temperature range of 303-353 K to fit for the coal-fired power plant stack gas wet-bulb temperature of 323 K. The enthalpy change in an isobaric process at any temperature T was evaluated by the formula given in equation (4.43) using the data of standard molar enthalpy and specific heat of the reactants from Table B1 in appendix B. The enthalpy change with respect to temperature was shown in Figure 4.26. The heat of reaction for the both reactions as shown in equations (4.51) and (4.52) was less than zero indicating the exothermic nature of the process. The results showed that increasing temperature was not alone which favoured the absorption process.

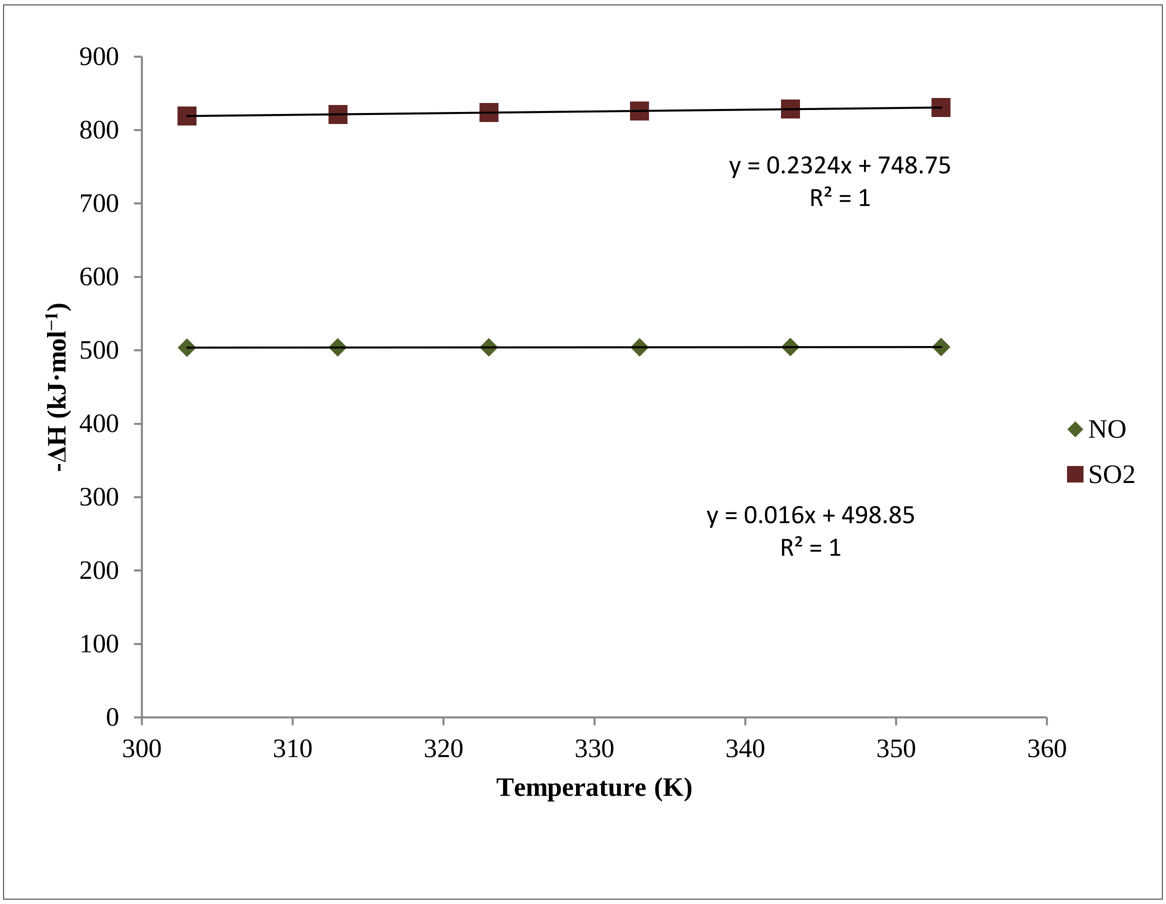


Figure 4.26. Effect of temperature on enthalpy change with NaClO/NH_3

4.10.1.2. Gibbs free energy change for absorption of SO_2 and NO in NaClO/NH_3

The Gibbs free energy change for the process was calculated by the equation (4.45). Figure 4.27 showed Gibbs free energy change as a function of temperature. The results of negative value of Gibbs free energy change concluded that other parameters also responsible to promote the rate of absorption including temperature.

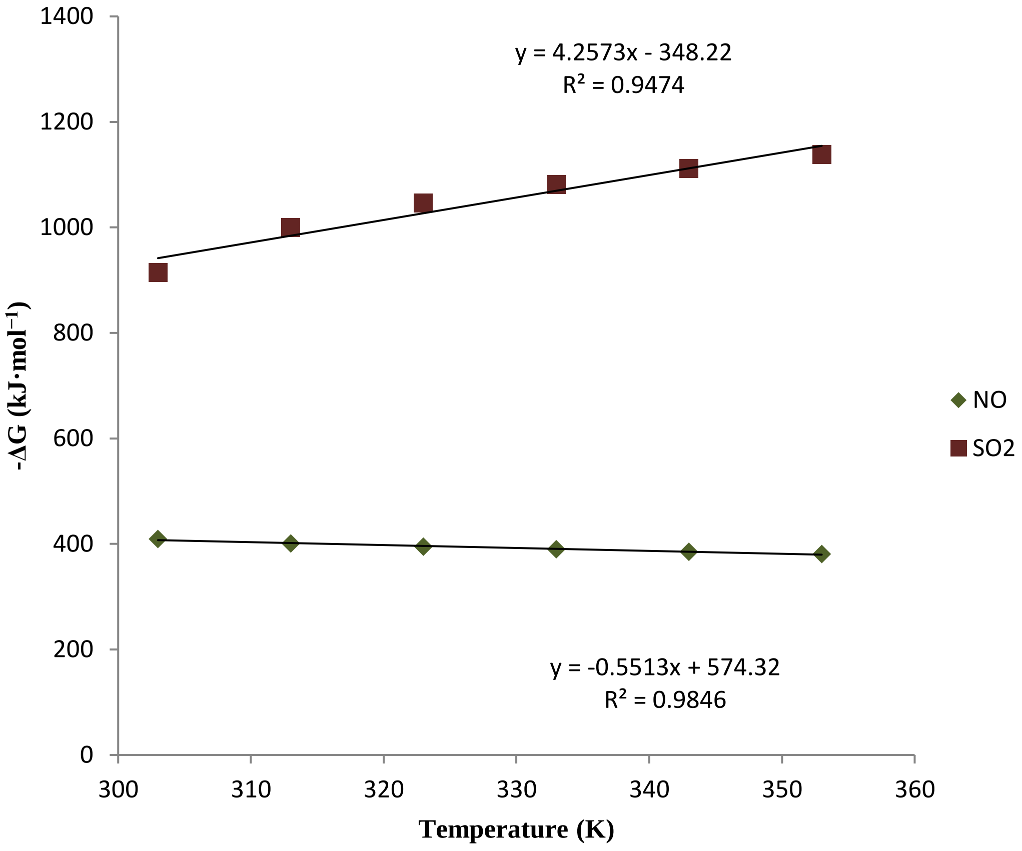


Figure 4.27. Effect of temperature on Gibbs free energy change with NaClO/NH_3

4.10.1.3 Equilibrium constant for absorption of SO_2 and NO in NaClO/NH_3

For absorption of SO_2 and NO in NaClO/NH_3, the equilibrium constant at any temperature was calculated by the equation (4.46). The equilibrium constant K for the process at different temperatures were shown in Table 4.5. Here K_1 and K_2 are different equilibrium constants for equation (4.51) and equation (4.52), respectively. The data obtained insists large reaction limit due to the high equilibrium constants.

Table 4.5. Equilibrium constant at different temperatures with NaClO/NH_3

T(K)	303	313	323	333	343	353
K_1	e^{363}	e^{384}	e^{390}	e^{391}	e^{390}	e^{388}
K_2	e^{162}	e^{154}	e^{147}	e^{141}	e^{135}	e^{129}

4.10.1.4. Equilibrium partial pressure for absorption of SO_2 and NO in NaClO/NH_3

The Equilibrium partial pressure of the components for process at any temperature T was calculated using equation (4.47-4.48). The equilibrium partial pressure of SO_2 and NO were given in Table 4.6. The equilibrium partial pressure of both components increased with increase in temperature, indicating that the high temperate did not favour the absorption process. The partial pressure of SO_2 and NO at equilibrium is not appreciated even at maximum temperature of 353 K which shows the feasibility of simultaneous absorption of SO_2 and NO in NaClO/NH_3 blend.

Table 4.6. The equilibrium partial pressure value under different conditions with NaClO/NH_3

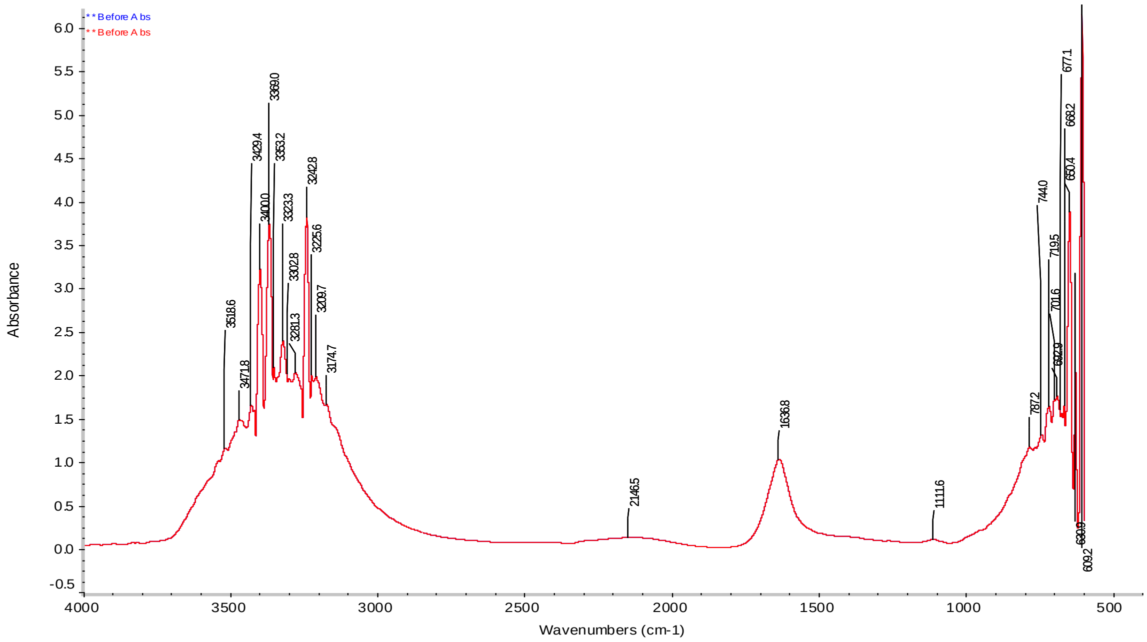
T(K)	303	313	323	333	343	353
$\boldsymbol{p_{SO_2}(MPa)}$	1.153	1.148	1.143	1.138	1.134	1.130
$\boldsymbol{p_{NO}\ (MPa)}$	1.729	1.699	1.671	1.645	1.622	1.6

4.10.2. Feasibility of NaClO/NH_3 blend for SO_2 and NO absorption

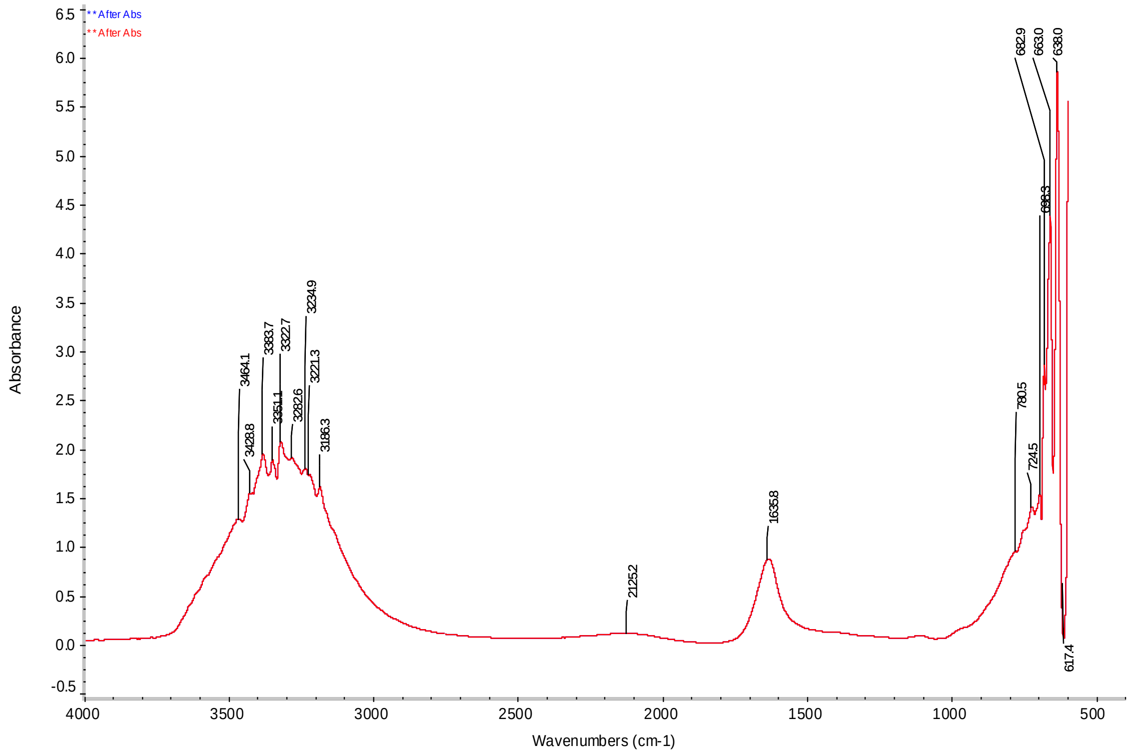
Initial feasibility of the process was investigated with use of absorbent on simultaneous removal of SO_2 and NO by varying the fundamental parameters such as process temperature, initial absorbent concentration, initial pH, change in initial SO_2 concentration and initial NO concentration. Another important parameter concerned to this experiment was blend ratio in NH_3-NaClO solution. These feasibility operations were studied initially with exact mole ratio and then implemented to semi batch operation to determine the saturated concentrations. The Fourier-transform infrared spectroscopy (FTIR) of fresh and used absorbent were analysed to identify the important functional groups which would confirm the absorption of SO_2 and NO into NaClO/NH_3 blend.

4.10.3. Fourier-transform infrared spectroscopy analysis

Initial feasibility of absorption was tested by passing the simulated gas stream in the magnetic stirrer vessel containing 100 ml of absorbent for three hours. This used absorbent was subjected to FTIR analysis to observe the changes in initial and final absorbent after absorption of SO_2 and NO. The observations were done in Thermo electron Nicolet 5700 FT-IR spectrophotometer and the results were reported in Figure 4.28. The change in initial and final composition with respect to addition of NH_3 to the oxidant NaClO was reported. Figure 4.28 (a) provides the FTIR analysis for initial NaClO/NH_3 blend and Figure 4.28 (b) gives FTIR analysis for the absorbed solution after experimentation.



(a)



(b)

Figure 4.28. FTIR-spectra analysis of NaClO/NH_3 blend **(a)** before and **(b)** after absorption of SO_2 and NO

From the Figure 4.28 (a), the peaks at a range of 3174.7-3518.6 cm^{-1} were due to presence of water molecules in the solution, minute peak was observed at 2146.5 cm^{-1}, 1636.8 cm^{-1}, 1111.6 cm^{-1} and again huge spectral range was found between 609.2-787.2 cm^{-1} due to presence of sodium/ammonium compounds in the solution. Figure 4.28 (b) showed that as the initial range was changed to 3186.3–3464.1 cm^{-1}, the accumulation was shifted to the range of 617.4-780.7 cm^{-1} and the huge accumulation was observed at 617.4-682.5 cm^{-1}. The literature even supports the presence of at a spectra range of 600-700 cm^{-1} for SO_4^{2-} and NO_3^- ions, 3200-3500 cm^{-1} for O-H groups, 3400-3420 cm^{-1}, 450-700 cm^{-1} and 1000-1220 cm^{-1} for sodium and ammonium based compounds (Yang et al., 2016; Lim et al., 2015; Liu et al., 2013; Periasamy er al., 2009; Zhao et al., 2015). This FTIR data provides the information about SO_2 and NO accumulation in spent absorbent which results to carry on the further study of the process.

4.10.4. Absorption in semi batch magnetic stirrer vessel with $NaClO/NH_3$

In this process, a feasible method was explained for simultaneous removal of SO_2 and NO_x by $NaClO/NH_3$ scrubbing with the final product of ammonium sulphite, ammonium nitrite, ammonium sulphate and ammonium nitrate which can utilized as fertilizers for plants in agricultural field. The products are small quantities of $(NH_4)_2SO_4$, $NaSO_4$, NH_4Cl and NH_4NO_3, which are all good for soil health to yield crops. $NaClO/NH_3$ blend was an efficient and economic absorbent for SO_2 and NO capture. The reactions between $NaClO/NH_3$ blend and SO_2/NO were fast, and the SO_2 removal efficiency was more than 99% and for NO it was more than 93% indicating that the heat of evolution for SO_2 and NO absorption by aqueous $NaClO/NH_3$ solution. But the illustrated procedure for this process had not been provided before by any researcher. Therefore, a valuable process has to be developed particularly suitable for coal fired thermal power plants. Aqueous $NaClO/NH_3$ solution can also absorb CO_2 in presence of SO_2 and NO.

4.10.4.1. Saturation time estimation in stirred vessel with $NaClO/NH_3$

The removal efficiency of SO_2 and NO were analysed for every 10 min throughout the process keeping other feasibility parameters such as absorbent temperature, pH, initial SO_2 concentration, initial NO concentration, absorbent mole ratio, etc. frozen. This lead to the estimation of optimal time for the process with fixed feasibility parameters. After the optimum time, the saturation concentration required for the solution was determined. The data was interpreted in Figure 4.29 with initial SO_2 concentration 1807 ppm, initial NO concentration 1020 ppm, pH of 5.3 and temperature of 313 K. It was shown from Figure 4.29, the effective removal efficiency was maintained till to reach 180 min and then decreased continuously till it reached zero removal efficiency and hence showed the optimum time for the absorbent. The optimum time required for this process was obtained as 180 min. The removal efficiency at optimum time was 90.1% for NO and 97.02% for SO_2. The saturation time observed for this operating condition was 290 min for NO and 420 min for SO_2. The delay in attainment of saturation time for SO_2 compared to NO was due to its dissolution capability in aqueous phase. This implies that SO_2 is additionally soluble in water even though the reactive species in liquid solution were consumed.

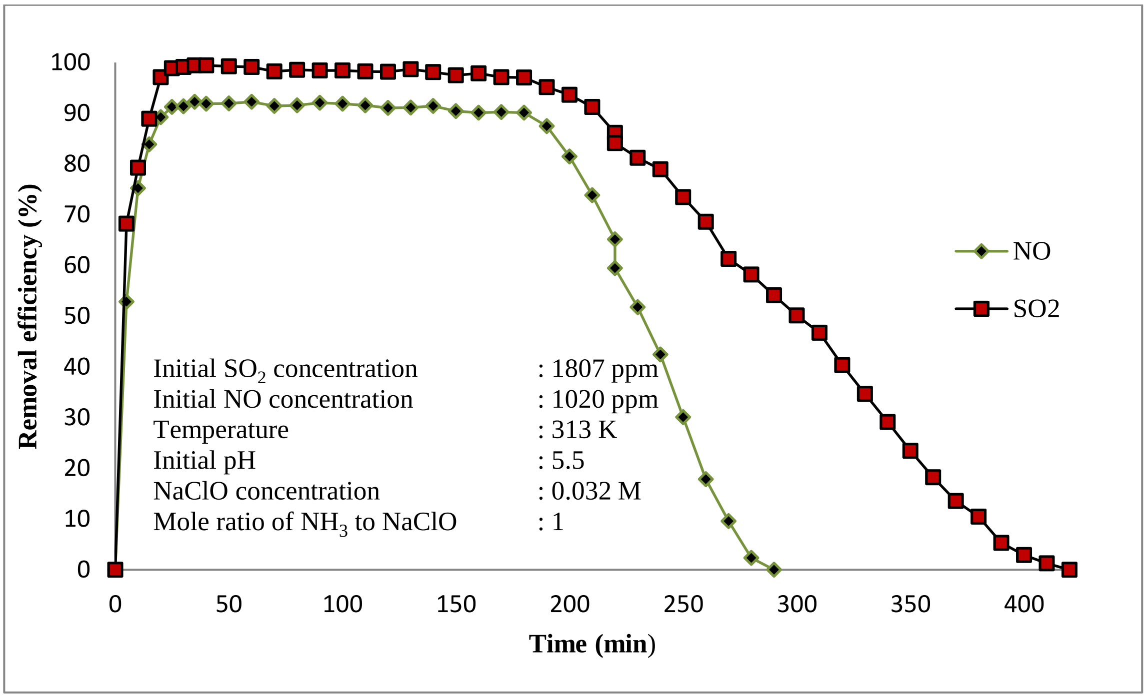


Figure 4.29. Estimation of equilibrium time for removal of SO_2 and NO in stirred vessel with NaClO/NH_3

4.10.4.2. Effect of molar ratio in using NaClO/NH_3 in stirred vessel

While keeping the concentration of NaClO constant, the effect of molar ratio of NH_3 to NaClO on removal of SO_2 and NO was examined experimentally and the results were shown in Figure 4.30. During the experimentation for simultaneous absorption of SO_2 and NO, the removal efficiency of NO significantly increased with an increase in mole ratio of NH_3 to NaClO between 0.08 - 0.68 (moles of NH_3/ moles of NaClO), attained maximum at 0.99 (moles of NH_3/ moles of NaClO) subsequently remained stable till 1.06 (moles of NH_3/ moles of NaClO) and then tends decreased with mole ratio. Similar trend was observed for SO_2 removal efficiency where increasing range was 0.08 - 0.38 (moles of NH_3/ moles of NaClO), stable range was 0.38 – 1.14 (moles of NH_3/ moles of NaClO) and reached maximum at 0.99-1.06 (moles of NH_3/ moles of NaClO).

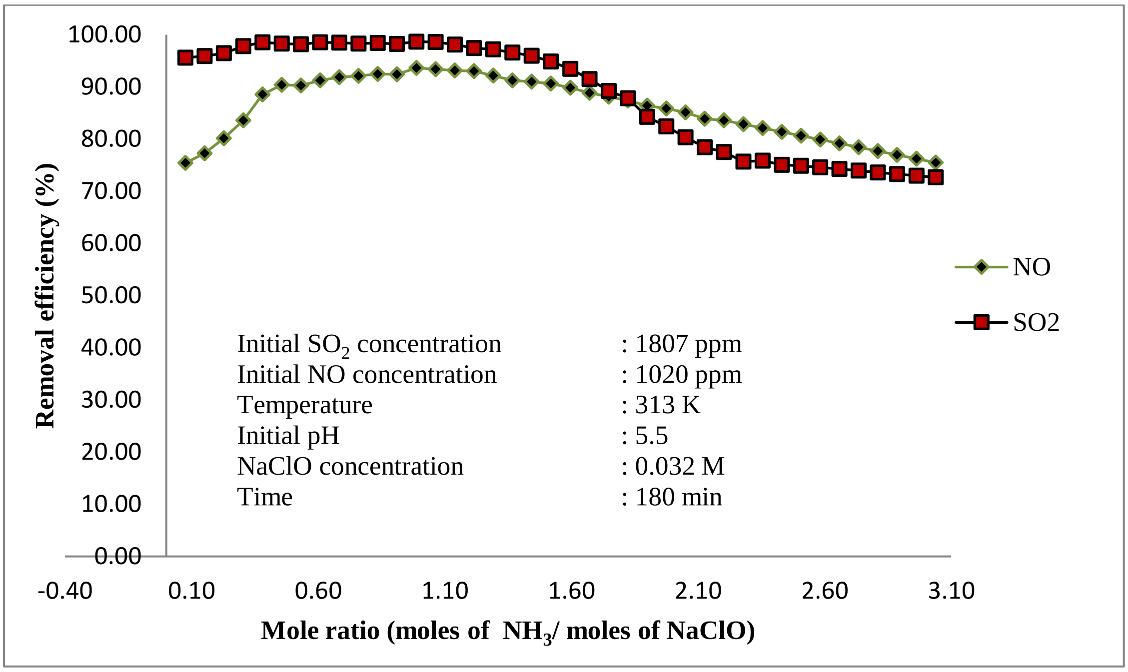


Figure 4.30. Estimation of optimal molar ratio for removal of SO_2 and NO in stirred vessel with $NaClO/NH_3$

From the Figure 4.30 it was observed that the removal efficiency range of SO_2 was higher than NO removal efficiency at lower molar ratio and decreased after molar ratio of 1.90 (moles of NH_3/ moles of NaClO). This is due to increase in NaOH concentration in absorbent blend due to addition of NH_3 in NaClO solution. From basic chemistry, it is known that when NaClO is mixed with NH_3 it forms NaOH and chloramine (NH_2Cl). The NH_2Cl further reacts with NaClO to form NaOH and dichloramine ($NHCl_2$). Finally, $NHCl_2$ reacts with NaClO to form NaOH and nitrogen tri chloride (NCl_3). But in this process the NaOH formed is useful for NO absorption and hence then removal efficiency is increased with increase in molar ratio of NH_3 to NaClO. But for considering effective removal efficiency for simultaneous absorption of SO_2 and NO, molar ratio of 1 (moles of NH_3/ moles of NaClO) was the optimal molar ratio.

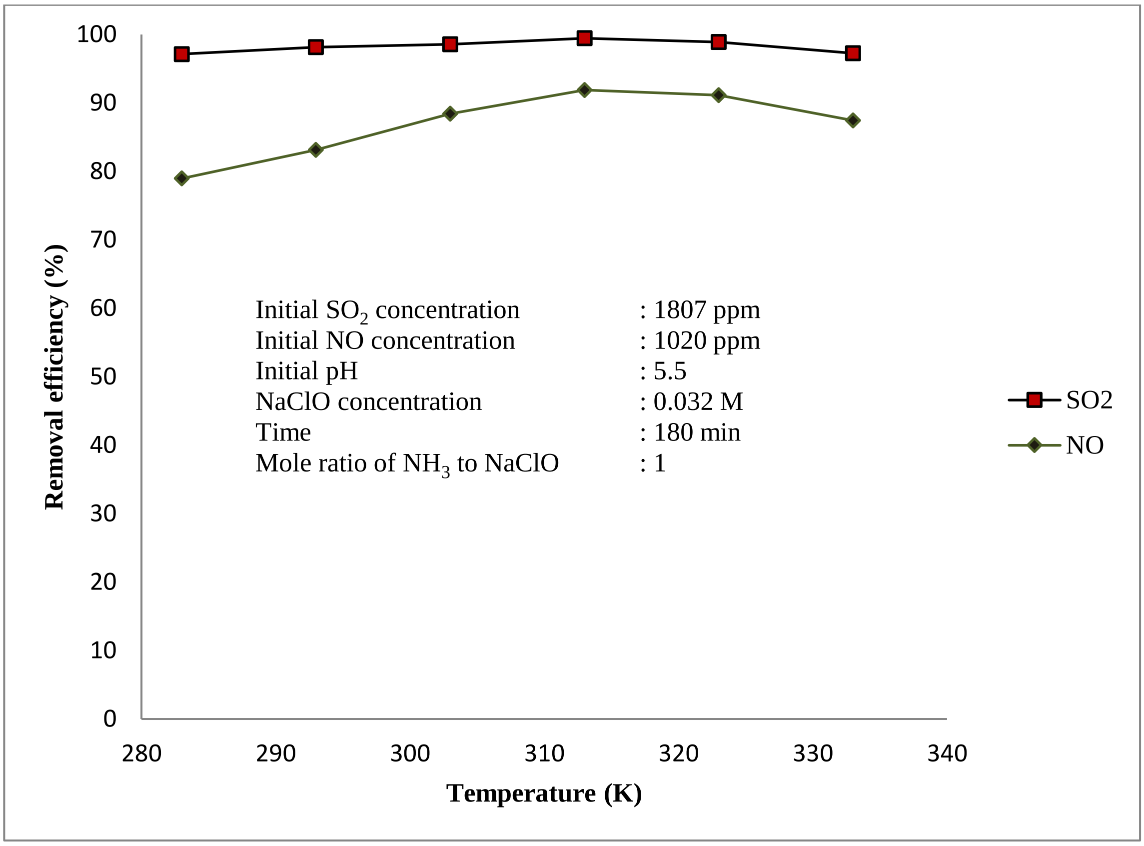


Figure 4.31. Estimation of optimal temperature for removal of SO_2 and NO in stirred vessel with NaClO/NH_3

4.10.4.3. Effect of temperature in magnetic stirrer vessel with NaClO/NH_3

The temperature change with respect to steady operating conditions in terms of removal efficiency for simultaneous absorption of SO_2 and NO was shown in Figure 4.31. The frozen experimental parameters were initial SO_2 concentration (1807 ppm), initial NO concentration (1020 ppm), initial NaClO concentration (0.032 M), reaction time (180 min) and molar ratio of NaClO-NH_3 blend (1 moles of NH_3/ moles of NaClO). From the Figure 4.31, it was observed that the removal efficiency of SO_2 remained at maximum with slight difference at a temperature range (283-333 K). But for NO removal the trend increased from 283 to 313 K and then decreased slightly. Maximum removal attained at 313 K and hence optimal temperature range was found to be 313-323 K. Initial increase in removal efficiency at temperature range 283-313 K against the traditional solubility phenomena was due to promotion of reaction between gas phase and liquid phase with increase in temperature. After 323 K the removal efficiency decreased due to dissolution drop in gas phase with increase in temperature. The feasible temperature range can provide best results during flue gas desulfurization and de nitrification.

4.10.4.4. Effect of NaClO-NH_3 blend pH in magnetic stirrer vessel

Solution pH has an active effect on performance of NaClO-NH_3 blend, and influenced the SO_2/NO removal efficiency during simultaneous absorption of SO_2 and NO. Hence the impact of NaClO-NH_3 blend solution pH on the instantaneous removal was investigated, and the change in removal efficiency with respect to solution pH was shown in Figure 4.32. From the figure, it was observed that the variation of solution pH had a negligible effect on the SO_2 removal, but the influence of pH had a great campaign on the NO_x removal, as the efficiencies were significantly increased from 70 to 82 % for NO in the pH range of 3–5, attained stable range of 82 to 85% for NO when the pH was between 5 and 7, and finally tended to decrease from 82 to 70% for NO in the range of 6.5 to 10. Hence from the experimental data the optimal pH range of 5-7 was recommended as the maximum pH was obtained at 5.5. Even though the removal efficiency of NO decreased during alkaline conditions, for the large-scale operations maintaining the solution in alkaline range can be useful for efficient removal because this operation is concerned not only for NO removal but for SO_2 removal also. Since SO_2 is an acidic gas, maintaining the absorbent at alkaline range can help to improve in oxidation capacity of absorbent. NaClO-NH_3 is a blend containing oxidative compounds such as ClO^-, HClO, and OH^- with large surface area. This determines NaClO-NH_3 blend as a strong base and weak acid, as well as contains complicated equilibrium conditions. These conditions may help to improvise reactive tendency of NaClO-NH_3 blend towards oxidizing SO_2 and NO. In acidic conditions the functional groups OH^-, ClO^- and NH_2^- would react with H^+ to produce the NH_3 residue, causing in shrinkage of inter surface area which may result in great loss of removal efficiency as well increase in reactive time to reach stability.

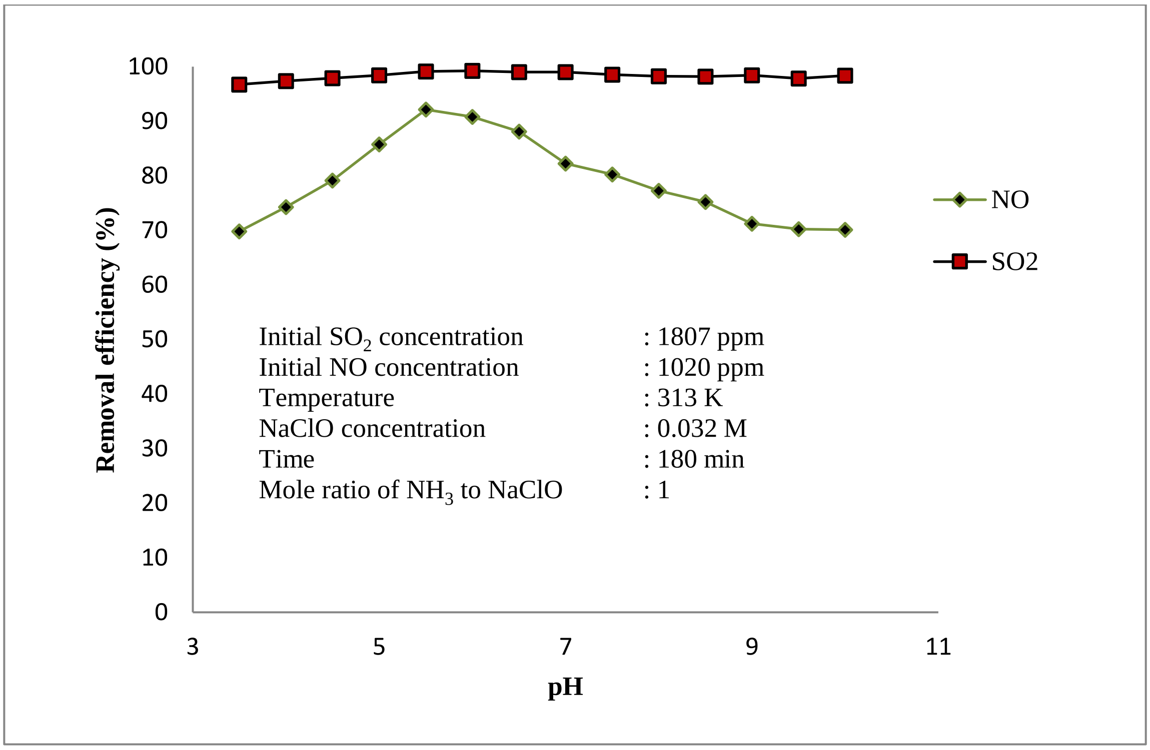


Figure 4.32. Estimation of optimal pH for removal of SO_2 and NO in stirred vessel with NaClO/NH_3

4.10.4.5. Effect of initial SO_2 concentration using $NaClO/NH_3$ in stirred vessel

Experimentation was carried out to study the change in removal efficiency of SO_2 and NO for simultaneous absorption with respect to initial SO_2 concentration by keeping the remaining operating parameters constant such as initial NO concentration (1020 ppm), initial NaClO concentration (0.032 M), reaction time (180 min) and molar ratio of $NaClO-NH_3$ blend of 1 (moles of NH_3/ moles of NaClO) and reaction temperature (313 K) (Figure 4.33).

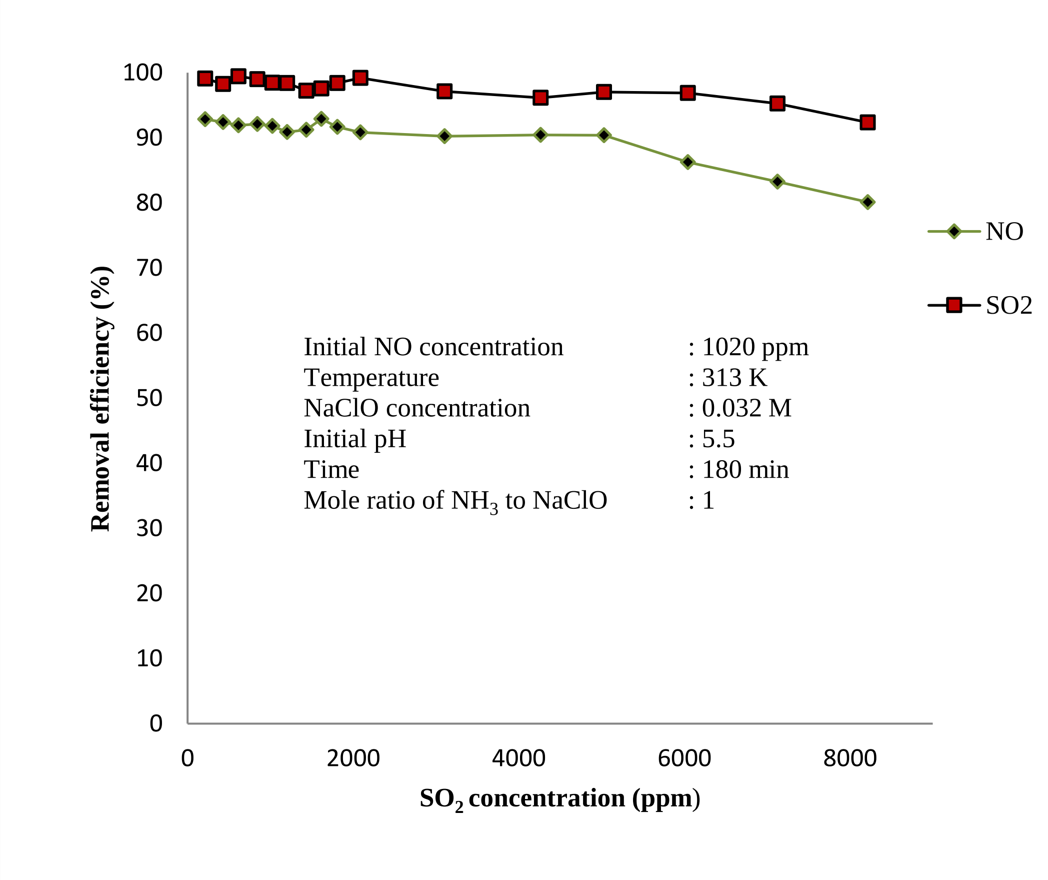


Figure 4.33. Effect of initial SO_2 concentration for removal of SO_2 and NO in stirred vessel with $NaClO/NH_3$

To check the influence of SO_2 on the reaction between NO and absorbent blend, the experiments were performed by considering two types of concentration changes where the initial range was 214 to 1807 ppm and next range was 2086 to 8216 ppm. The reason for considering two ranges is that minute range helps for feasibility consideration and major range is considered for industrial stack concentration resemblance. In the minute range of SO_2 (214 to 1807 ppm) concentration, the removal efficiency of NO sticked to maximum removal and it was almost steady with minimum fluctuation. Where as in major range (2086 to 8216 ppm), the removal efficiency maintained nearly constant till from 2086 to 5028 ppm and then tended to decrease. The removal efficiency drop is about 10% from 5028 to 8216 ppm this is due to availability of more SO_2 particles in comparison to NO which promotes the reaction of SO_2 with absorbent, even though the removal efficiency of SO_2 was dropped by 5% with increase in SO_2 concentration from 5028 to 8216 ppm. From the data, the optimal SO_2 concentration zone feasible for this process was 214 to 5028 ppm.

4.10.4.6. Effect of initial NO concentration in magnetic stirrer vessel with NaClO/NH_3

Effect of various initial concentration of NO on simultaneous removal of SO_2 and NO to select an optimal range feasible for the process was carried out by varying NO concentration from 220.21 to 1845 ppm and the results were shown in Figure 4.34 with constant operating parameters like temperature (313 K), molar ratio of NaClO-NH_3 blend (1 moles of NH_3/ moles of NaClO), initial SO_2 concentration (1807 ppm), initial NaClO concentration (0.032 M) and contact time (180 min).

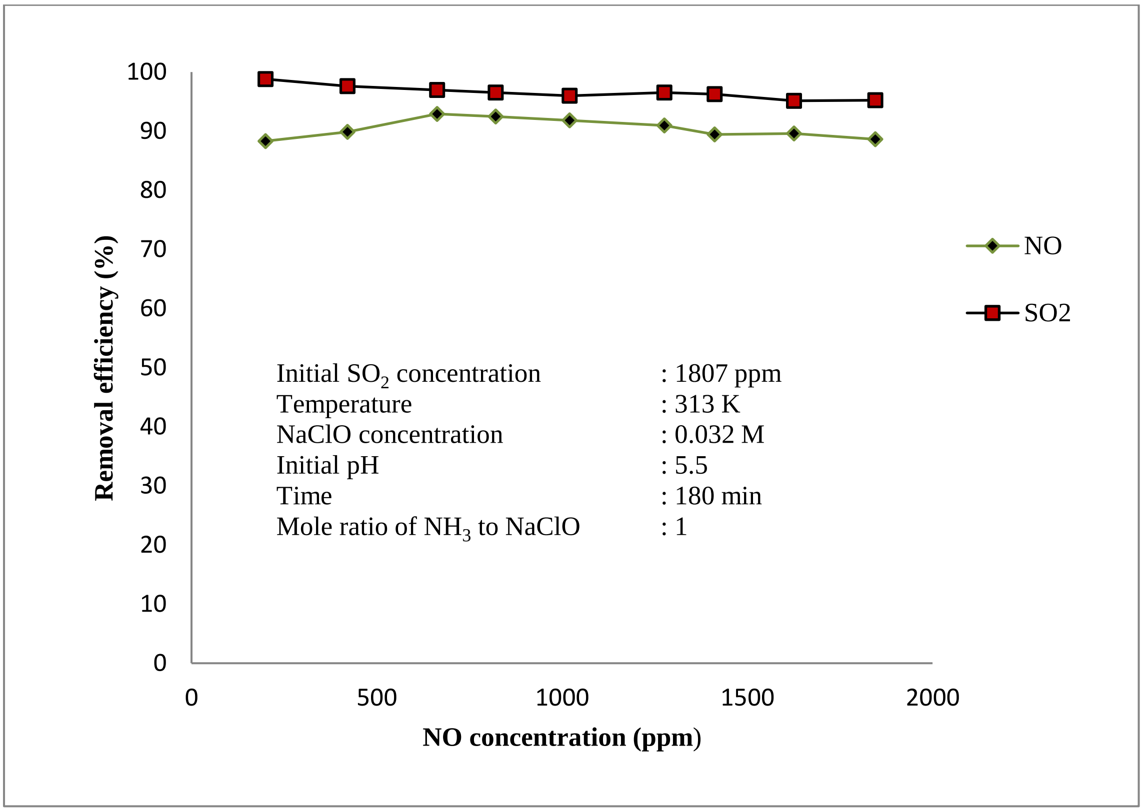


Figure 4.34. Effect of initial NO concentration for removal of SO_2 and NO in stirred vessel with NaClO/NH_3

From the figure, it was seen that the SO_2 removal decreased slightly with increase in NO concentration. The reason for this trend might be NO removal increased with increase in NO concentration till attained maximum removal due to the decrease in dissolution of SO_2 in absorbent. Then maximum removal attained for NO at a range of 663 to 1276 ppm which could be treated as the optimum removal zone. After attaining maximum NO removal, the graph tended to decrease till 1845.26 ppm. As for SO_2, the removal efficiency decreased steadily with increase in NO concentration. This is due to inter reactivate collision frequency between NO and absorbent to convert it in to NO_2.

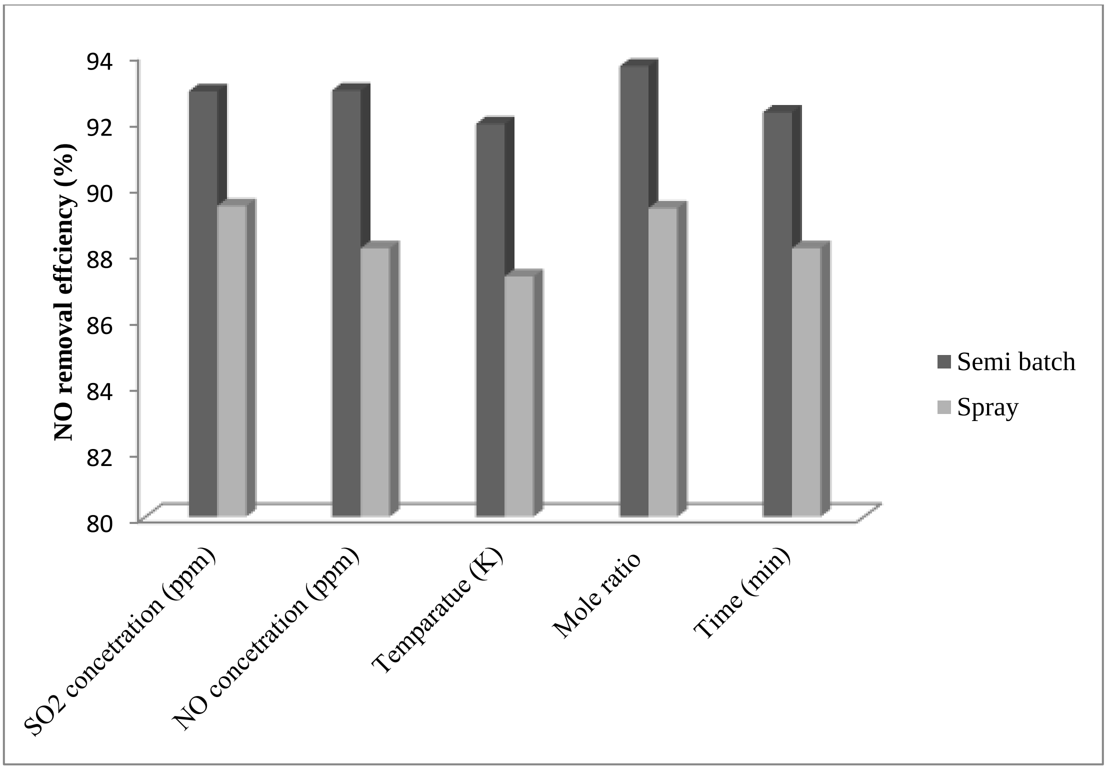


Figure 4.35. Comparison of NO maximum removal efficiency with respect to operating parameters in semi batch and spray column with NaClO

4.10.5. Simultaneous absorption in continuous spray column with NaClO/NH_3

The maximum removal comparison was shown in Figure 4.35 for different operating parameters in case of NO removal efficiency. From the figure, it was clearly observed that the contact zone provided by semi batch operation was quite effective than spray contact zone due to decrease in inter molecular collision between NO and NaClO/NH_3 blend. It was seen from Figure 4.35 that the average maximum removal percentage drop was about 4.6 % lower in spray column compared to semi batch process. From the experimental data done, the similar removal efficiency decrease was observed in all trends with different operating parameters.

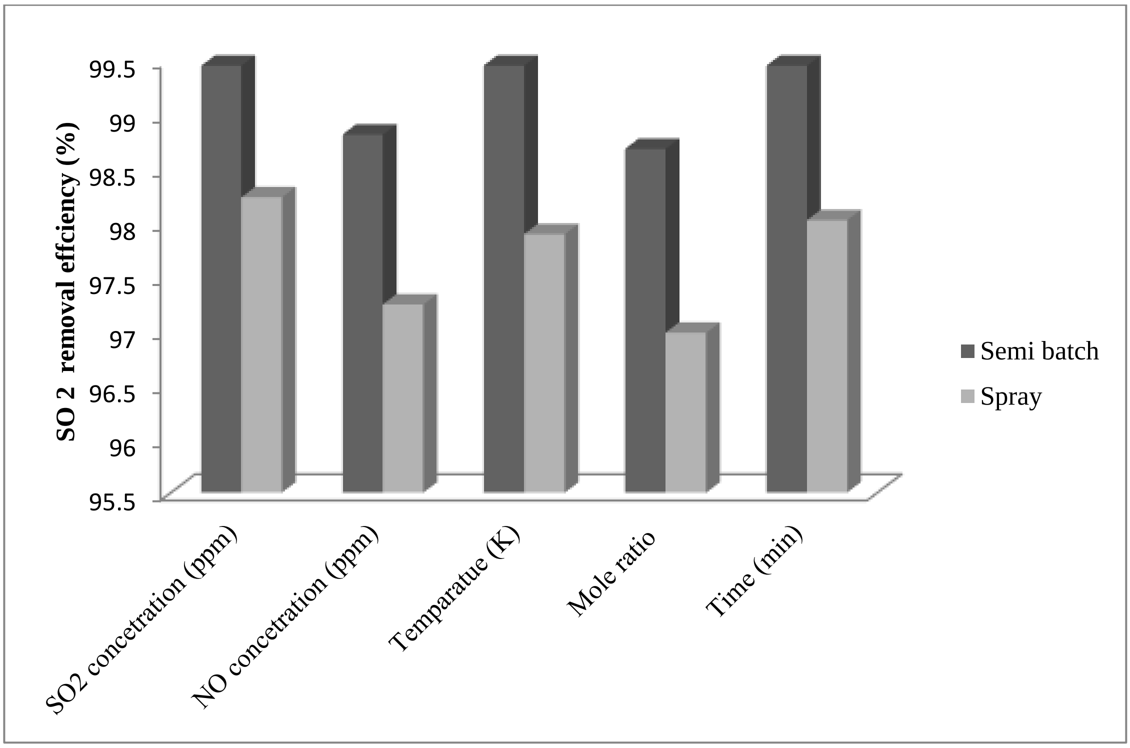


Figure 4.36. Comparison of SO_2 maximum removal efficiency with respect to operating parameters in semi batch and spray column

In case of SO_2 removal, the comparison for maximum removal efficiency with different operating parameters in semi batch and spray column were plotted in Figure 4.36. It was seen from the figure that the removal efficiency drop was less in comparison with NO removal efficiency. The average maximum removal efficiency drop was observed as 1.5% in continuous process as compared to semi batch operation. This is due to reactive tendency of SO_2 with water, even the low availability of absorbent SO_2 has capability to be solubilized in liquid phase.