

Effects of Water Content on SO₂/N₂ Binary Adsorption Capacities of 13X and 5A Molecular Sieve, Experiment, Simulation, and Modeling

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ABSTRACT

In this work, SO₂ adsorption on 13X and 5A was explored at different concentrations, and the results were compared to molecular simulation and models. The adsorbent saturation tests were performed at four different concentrations of 250, 500, 750, and 1000 ppm, and it was observed that saturation would take more time for higher SO₂ concentrations. Grand Canonical Monte Carlo method was used for simulation. In addition, extra framework cations of Na were used 13X structure and Na and Ca Cations were used in 5A structure. The results of the simulation were compared to experiments. The effect of water molecule content on adsorption was determined by inserting a different number of water molecules. Also, the outcome of experiments and simulations were in good agreement. The results showed that 13X is a better adsorbent for SO₂ than 5A. 13X zeolite with 96 water molecules and 5A with 99 were provided the best prediction of experimental results. Yoon-Nelson and BDST models were also used to find the rate of adsorption capacity reduction related to breakthrough curve and loading amount. The results of the two model suggested that 13X has a higher loading capacity while 5A provided longer saturation time.

Keywords: Sulfur Dioxide, Adsorption, Molecular Simulation, Zeolite, 13X, 5A.

INTRODUCTION

The air quality in several countries has been troubled by ambient atmospheric concentrations of the main pollutants, predominantly, total suspended particles (TSP), sulfur dioxide (SO₂) [1–3], and nitrogen dioxide (NO₂). In addition, amongst the several atmospheric pollutants, the sulfur dioxide has been receiving an exceptional attention of the world government public organs due to the severity of its effects on the people,

animals or on the plants [4].

Iran latest energy balance sheet of 1394 (2015-2016) also shows that SO₂ emission in the energy section has increased by about 19% in a four-year period [5]. Moreover, this report also reveals that after CO and NO_x, SO₂ is the main pollutant; in addition, it encompasses 12.3% of the total hazardous gas pollutants. The amount of sulfur dioxide released from the country's industries is estimated to be 1075.6 thousand tons in 2015-

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2016. These facts demonstrate that it is necessary to do a vast research on finding better ways to remove SO₂ from the flue gas streams.

The use of the adsorption as an alternative process for the removal of gaseous pollutant emissions has attracted growing attention. Using the adsorption process in a solid adsorbent for the elimination of the SO₂ offers the great potential of the application [6,7]. Also, numerous investigations have been carried out on adsorbents [7–10], more specifically using zeolites, namely the adsorption of the pollutant gases (e.g. CO₂, SO₂, and organic solvent vapors, along with other gases).

The 13X and 5A type zeolites are molecular sieves with hydrophilic and porous characteristics. These zeolites have great stability to most of the mineral acids and also the necessary oxidizing conditions for its regeneration. The most advantage of adsorption by zeolite is the lower energy consumption for regeneration rather than solvent absorption. Moreover, the crystalline structure of these zeolites makes it possible to use them as an adsorbent in SO₂ removal from combustible gases. In addition, adsorption process can be performed in two forms of fixed and fluidized bed depending on the process condition in both which the mentioned zeolites can be applied.

In this work, zeolite 13X and 5A have been used as an adsorbent in SO₂ removal from a gaseous current. Nitrogen has been used as a carrier gas to dilute the pure SO₂ stream to the desired concentration. The employment of these molecular sieves is principally due to two main aspects: first, high porous volume, and second, the possibility of working at high temperatures because of high physical resistance, giving high process flexibility. The molecular simulation method is considered

as a reliable method for predicting properties and the performance of the material in different phenomena, provided that an appropriate model and a force field are chosen. This method makes it possible to reliably calculate the adsorption capacity of a porous adsorbent. Moreover, this method has been successfully used for numerous phenomena including colloidal stability [11], permeability [12], pyrolysis [13], force field parametrization [14], phase transition [15], NO/NH₃/N₂ adsorption [16], CO₂ adsorption on MWCNT [17], and water vapor or CO₂/CH₄ adsorption on different zeolites [18–21]. As an example, nitrogen adsorption on 12 different zeolite framework has been studied by Rahmati et al [22], and an acceptable agreement between the results and experiments has been found [22]. Also, water vapor adsorption by hydrophilic zeolite and by GCMC has been investigated by Khosravi et al [19], and the capability of this method in predicting adsorption phenomena has been reported by Khosravi et al [19]. The adsorption of CO, H₂S, and ethylbenzene by carbon nano tubes has been also investigated by Tasharrofi et al [23] by using Monte Carlo and molecular dynamics. Also, the reported results have shown the flexibility of molecular simulation method in the adsorption which has been processed. So it would be an interesting field of study to find an optimized model for predicting the adsorption behavior of these zeolites by means of a molecular simulation method. The results then may be compared with the experiments in order to generalize the model results to conditions where experimental data are either hard to collect or will be time-consuming and energy-consuming to be obtained. However, few simulation and modeling data are found in the literature for adsorption using zeolites. So, in this work, Grand Canonical Monte

Carlo results of SO₂/N₂ adsorption on 13X and 5A are presented and compared with experiments. The kinetic and equilibrium modelings of experimental data are also presented in understandable plots and tables.

Experimental Procedure

The experiments were carried out in a jacketed cell. SO₂ stream has been diluted using N₂ to obtain the desired inlet concentration. All experiments have been performed at 1 atm pressure. Moreover, breakthrough diagrams have been obtained by measuring the outlet stream at different times. Testo® detection device has been used to measure outlet temperature. At the beginning of each test, the outlet concentration has been low, but after the saturation of the adsorbent bed, the concentration has approached the inlet concentration. The time needed for saturation has been proportional to the inlet concentration of SO₂. Moreover, zeolite adsorbents of 13X and 5A have been purchased from Zarrineh Catalyst. In addition, the zeolites have been used without any preparations. Nitrogen adsorption/desorption of BET was performed to obtain the adsorption capacity of two adsorbents. Moreover, N₂ is used because it has the simplest structure and can be inferred as a standard for basic adsorption capacity of a porous structure. Pore volume distribution tests have been also carried out for both zeolites. This test gives the pore volume of each adsorbent in relation to its pore diameter. The results of this test can be used to understand which sizes of pores comprise the major pore volume of adsorbent. Another characterization test for the solid adsorbents has been X-ray diffraction analysis. Moreover, X-ray crystallography is a tool used for identifying the atomic and molecular structure of

a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron compactness, the mean locations of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder, and various other information. Characterization tests have been performed on 13X and 5A before being used as SO₂ adsorbents. The XRD graphs of 13X and 5A are given in Figures 1 and 2 respectively.

In these two figures, the peaks at 2θ values of 27 and 32 represent NaAlO₂ and α-SiO₂ groups respectively based on the standard charts of 38-0237 and 10-377. In addition, detected peaks include 6.108, 9.994, 11.737, 15.464, 23.360, 26.7, and 30.997 which show crystal surfaces of (111), (220), (331), (331), (533), (642), and (751) respectively. The XRD peak indexed at 2θ = 6.26° in Figure 1 corresponds to (111) plane of the 13X Zeolite. Crystal surfaces of (111), (533), (642), and (555) have been detected for zeolite 5A based on peaks at angles 8, 25, 27, and 32. The Zeolite which has been used in this study has not been a synthesized one. The natural zeolite has been tested as received. The existence of impurities can cause some minor shifts in the main peaks, and also emerging some undefined peaks which reflect other metals presented in the framework other than Na or Ca. The surface topology of 13X which has been obtained from scanning electron microscopy (SEM) image is displayed in Figure 3. The porous nature of 13X is obvious in this image. Also, the octahedral structure of the 13X crystal can be detected in this image.

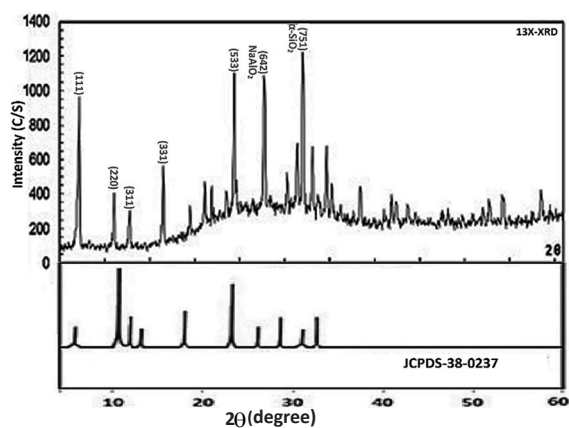


Figure 1: XRD graph of zeolite 13X.

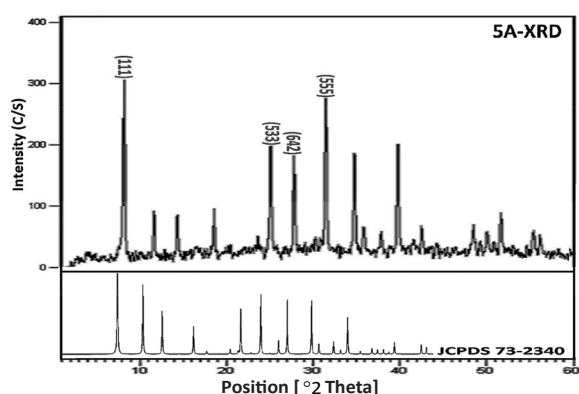


Figure 2: XRD graph of zeolite 5A.

ASAP (Active Surface Area and Porosity Analysis) analysis for pore size distribution and N₂ adsorption/desorption has been also performed for the adsorbents prior to SO₂ adsorption test. Both 13X and 5A showed good behavior for desorption, and low hysteresis effects were observed only at high relative pressures based on Figures 4 and 5. In addition, this would ensure the applicability of

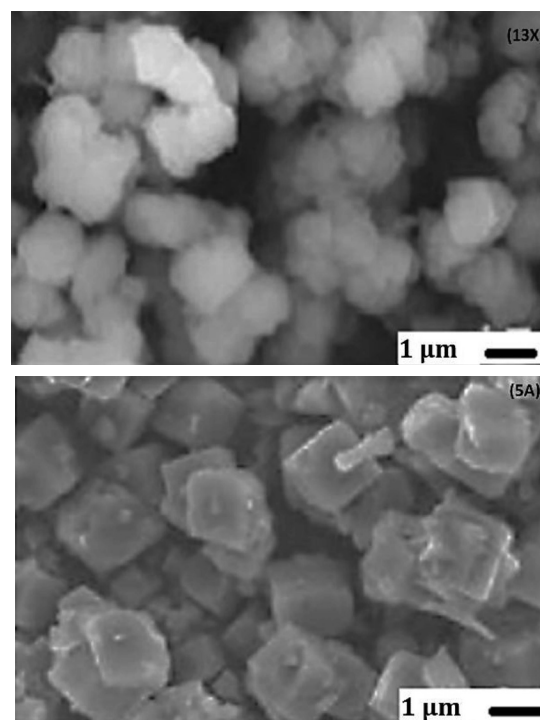
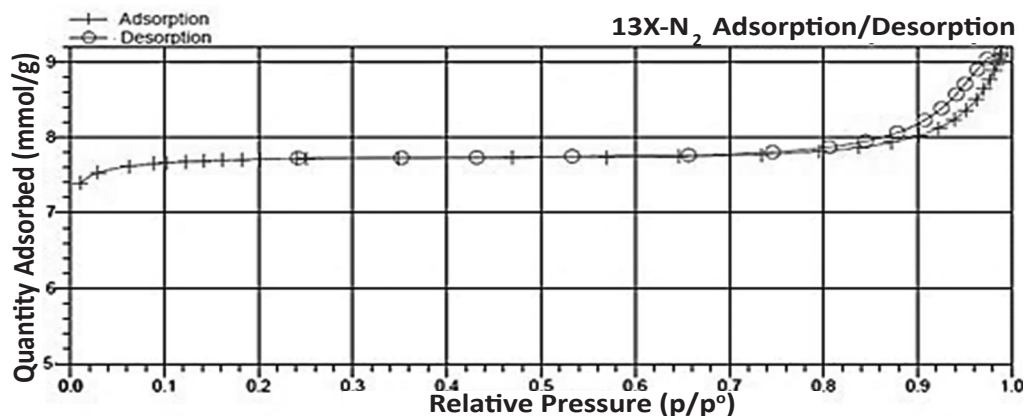


Figure 3: SEM image of zeolite 13X and 5A.

the adsorbents for industrial purposes where it is necessary for the adsorbents to remain active for a required adsorption/desorption circles. So 13X and 5A can be used with little concern about the adsorbate molecules to be captured during desorption or reactivation cycle.

Pore size distribution graphs for 13X and 5A are displayed in Figures 6 and 7. By considering these graphs, it can be seen that the pore size of 130 Å or 13 nm has the most population in 13X, while for 5A, the majority belongs to pores with 35 Å or 3.5 nm.

Figure 4: 13X-N₂ Adsorption/Desorption.

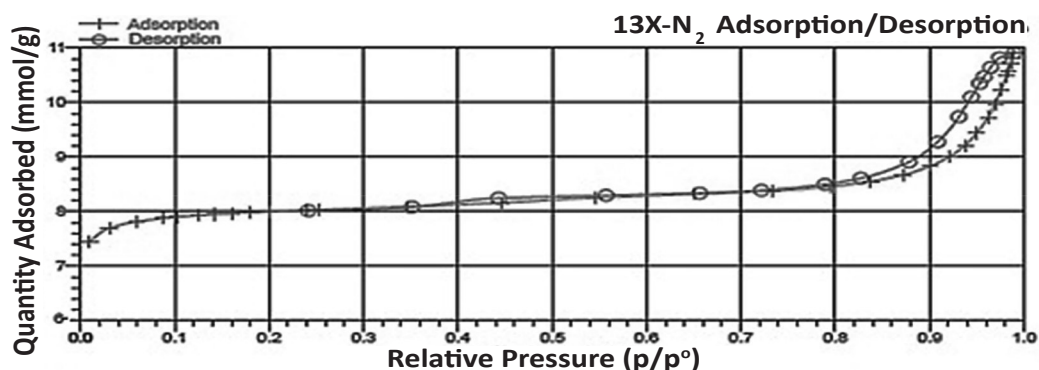


Figure 5: 5A-N₂ Adsorption/Desorption.

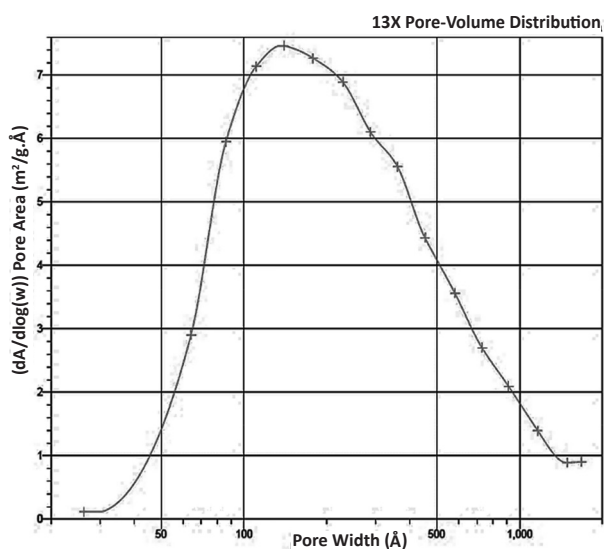


Figure 6: 13X-Pore Volume Distribution.

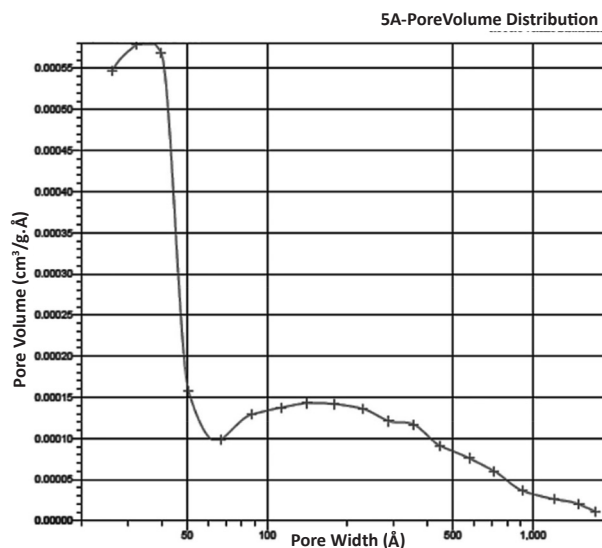


Figure 7: 5A-Pore Volume Distribution.

Simulation

Molecular simulation is used to predict the behavior of the molecules by means of intermolecular forces. There are two main molecular simulation techniques: Molecular Dynamics (MD) and Monte Carlo (MC).

In Molecular Dynamics, intermolecular forces are used to predict the next position of each molecule. Moreover, this process is repeated until the equilibrium state is found. In contrast,

in a typical Monte Carlo procedure, simulation of fluids, transitions between different states or configurations are achieved by: (a) generating a random trial position or configuration, (b) evaluating an acceptance criterion by calculating the change in energy and/or other properties in the trial configuration, and (c) comparing the acceptance criterion with a random number and either accepting or rejecting the trial configuration [24,25]. An isotherm for gas adsorption is

obtained by Grand Canonical Monte Carlo (GCMC) simulation in which adsorbate chemical potential (μ), volume (V), and temperature (T) are kept constant while a number of adsorbate molecules (N) is tolerated until the equilibrium numbers are found. In addition, the grand canonical ensemble is an open system in equilibrium with an infinite bulk fluid reservoir. The adsorption isotherm for a given porous adsorbent is then obtained by calculating the ensemble average number of adsorbed molecules (N). Also, in this work, SO₂ and N₂, as functions of pressure, are adsorbed molecules. The detailed procedure for the acceptance of these moves has been explained by Agnihotri et al [26]. All the simulation runs have been performed in the Materials Studio simulation package. In addition, simulation box has been constructed for 13X. Moreover, 5A zeolite and periodic boundary conditions have been applied in three dimensions in order to simulate an infinite system. Also, sorbate–zeolite and sorbate-sorbate interactions have been modeled using the Universal force field, in which the potential energy is expressed as a sum of valence (or bond), cross-term (intra-molecular), and non-bond (intermolecular) interactions. As an example, Al₃ structure which is considered for tetrahedral aluminum in both zeolites and O3z is considered for tetrahedral oxygen of zeolites. During the simulations, sorbate molecules have been translated, rotated, created, and deleted from the zeolite framework randomly with the probability of 0.2, 0.2, 0.3, and 0.3 respectively. The total 5×10⁷ steps have been considered for the equilibration stage, and the same number of steps has been used in the production stage. The simulations evaluated the average number of adsorbate molecules for

which the chemical potential of the gas in the bulk phase equals the chemical potential of the adsorbed gas at a given pressure and temperature. The partial pressure for the evaluation of the chemical potential was calculated using the Peng Robinson EOS which is exact enough in the pressure range of the experiments (1 bar).

The partial charges of atoms have been estimated by charge-equilibration, and electrostatic force has been obtained from Ewald summation method [27], which is highly accurate in calculating the long range forces. Moreover, the accuracy of Ewald has been 0.01 kcal/mol with a buffer width of 0.5 Å. The structure of SO₂ and N₂ molecules has been optimized by Discover module. The radius of SO₂ and N₂ molecules from Connolly surface and volume estimation has been roughly considered 2.094 Å and 1.756 Å respectively. The value of sulfur-oxygen bond length in SO₂ σ_{s-o} is 1.431 Å while the value of nitrogen is $\sigma_{N=N}$ =1.098. Lorentz-Berthelot mixing rule of the following form is applied for the calculation of van der Waals forces by means of Lennard-Jones potential, as seen in Equation 1:

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}, \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (1)$$

The Lennard–Jones potential has been used to calculate the interaction between adsorbate and Type zeolite framework atoms. Additionally, all the pair interactions have been truncated at a cutoff radius of 9.5 Å, as seen in Equation 2:

$$U_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

where σ_{ij} and ϵ_{ij} are the LJ potential parameters (adjustable parameters provided by Materials Studio software), and r_{ij} is the interatomic distance

between the i^{th} and j^{th} atoms.

The simulation of the adsorption isotherm has been performed using sorption module. The adsorption conditions (volume and temperature) have been constant the same as experiments. Extra framework cations of 13X-Na have been introduced in the zeolite framework of FUA by Sorption Locate module. For 5A zeolite, LTA frameworks have been used while Na and Ca have been introduced as extra framework cations. Moreover, P1 crystal symmetry has been used for the unit cell of zeolites. In addition, crystal symmetry parameters are given in Table 1.

Table 1: P1 crystal symmetry parameters used for the simulation of 13X and 5A unit cell.

Number of Symmetry Operators	1
Space Group Name	P1
Crystal System	TRICLINIC
Laue Class	-1
Point Group	1
Patterson Space Group	2
Lattice Type	P
symmetry	X,Y,Z
Asymm (or asymmetric)	$0 \leq x \leq 1$ $0 \leq y \leq 1$ $0 \leq z \leq 1$

The frameworks of FAU and Na-FAU (13X) are shown in Figure 8. The chemical formula of 13X is $\text{Na}_{86} \cdot [(\text{AlO}_2)_{2,86}(\text{SiO}_2)_{106}]$ with Si/Al ratio and molecular weight of 1.23 and 13444 g/gmol respectively. Also, unit cell volume and density for this framework are about $15677.6 \times 10^{-30} \text{ m}^3$ and 1421.77 kg/m^3 respectively.

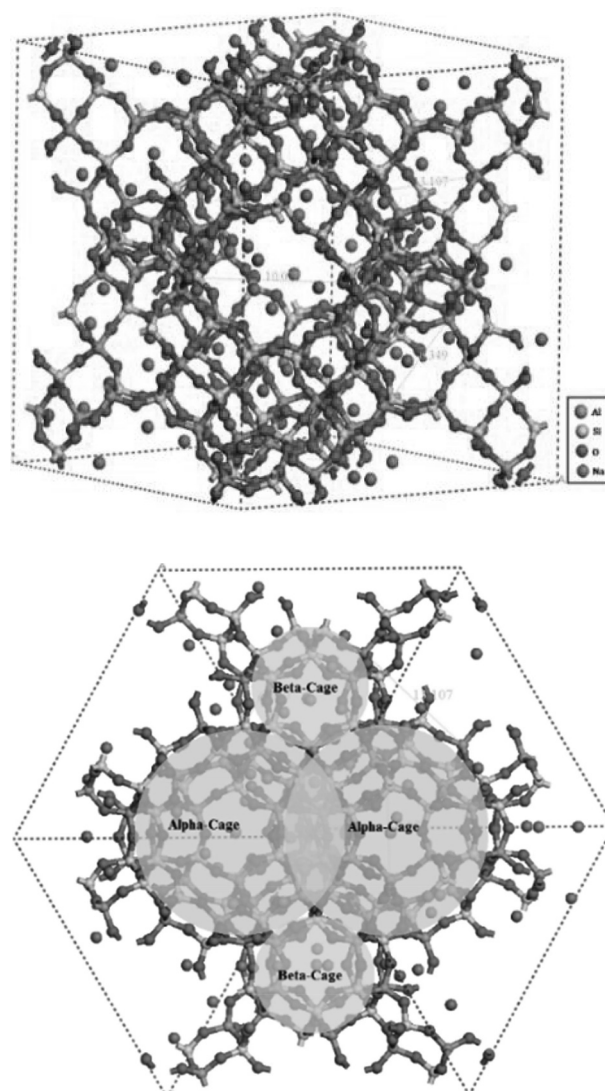


Figure 8: Zeolite 13X structure. (up) Schematic view of the FAU framework showing the connection between T-atom positions. super cage (α) and sodalite (β) cages are highlighted. (down) A view of the unit cell of 13X (NaX). The distances are displayed. The main channel has a diameter of 10 Å.

The structures of a unit cell of LTA and 5A zeolite are depicted in Figure 9. In addition, extra framework cations of Na and Ca are involved in this illustration. Each unit cell contains eight cages from which four frontiers one are highlighted. The opening channel of each cage has a diameter of about 7 Å which is measured by the distance tool of the Materials Studio software. The chemical formula of this

structure is $\text{Ca}_{32}\text{Na}_{32}[(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}]$ with Si/Al ratio and molecular weight of 1 and 13448.3 g/gmol respectively. Also, unit cell volume and density for LTA framework are about $1490.51 \times 10^{-30} \text{ m}^3$ and 1498.24 kg/m^3 respectively.

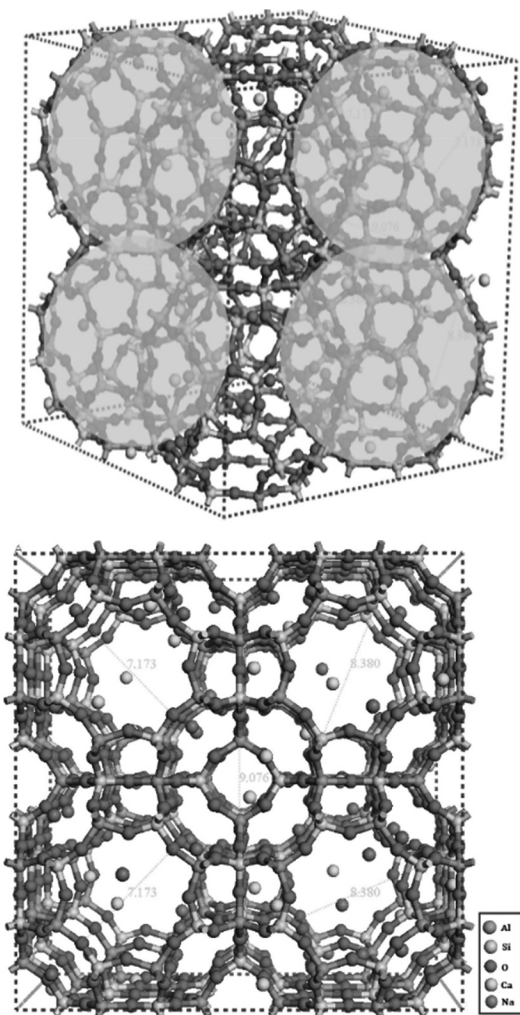


Figure 9: Schematic view of the LTA framework, eight frontier cages (up), Na cations are displayed in violet and Ca cations are displayed in green in a view onto the prospective display.

Metropolis method is used in the software to acquire adsorption equilibrium of each sorbate as well as gas mixtures. Framework structure and the place of cations have been intact during simulation while sorbate molecules have been displaced to find the relatively optimum position (minimum energy point).

Neighbor list is used in a simulation run to save computational time. In this procedure, only the interaction of each particle with its neighbors within the diameter of 2.5σ is counted, where σ is the covalent radius of the particle. The distance 2.5σ is selected since the short range dispersion forces of van der Waals are effective within this range. For long range forces, like that of electro static, a more complicated method of Ewald summation has been applied to ensure the effectiveness of these forces beyond the 2.5σ which is considered. The neighbor list has been updated periodically to account for any changes in the surrounding molecules.

Another feature of the Metropolis Monte Carlo simulation as mentioned before is the periodic boundary condition. This is necessary to extend the results of a simulation box to a macroscopic physical system. Moreover, in a typical periodic boundary condition, the exit of a molecule is considered equal to the entrance of the same molecule from the opposite side of the box from the same symmetrical point. Another important feature of this technique is that the interaction of corner molecules with each other is calculated by considering the molecules of the neighboring unit cell. A graphical representation of these concepts is given in Figure 10.

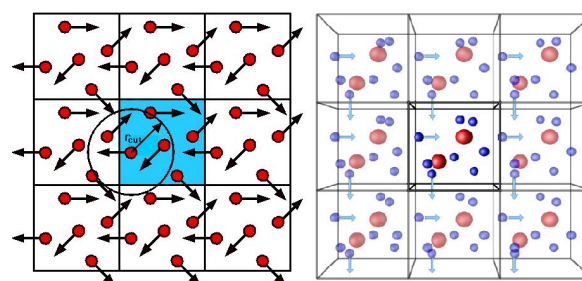


Figure 10: The graphical representation of neighbor list and cut-off distance (left) and periodic boundary condition (right).

The outcome of the software is expressed as the number of adsorbed SO₂ molecules/a unit cell (molecule/UC). Also, a unit conversion from molecule/UC to mol/kg and then mg/g is simply obtained by the following equation (Equation 3):

$$q\left(\frac{\text{mole}}{\text{kg}}\right) = \frac{q\left(\frac{\text{molecule}}{\text{UC}}\right)}{\rho V N_{\text{Av}}} \quad (3)$$

where $N_{\text{Av}} = 6.022 \times 10^{23}$ is the Avogadro constant. Density (ρ) and volume of the 13X and 5A unit cell are given in Table 2. Conversion from mol/kg to mg/g is then simply found from SO₂ molecular weight of 64.066 g/mol.

Table 2: Summary of adsorbent's properties.

Adsorbent	Density (kg/m ³)		Unit Cell Volume (Å ³)	Conversion Factor (Molecule/UC to mol/kg)
	Sim	Exp		
13X Na ₈₆ [(AlO ₂) ₈₆ (SiO ₂) ₁₀₆]	1421.77	1421.27	15677.6	0.074498
5A Ca ₃₂ Na ₃₂ [(AlO ₂) ₉₆ (SiO ₂) ₉₆]	1498.24	1508.37	14905.1	0.074358

Since experimental data is comparable with excess adsorption, and simulation data represent the absolute adsorption, equation 4 was used to relate (or connect) these two quantities to each other:

$$N_{\text{ex}} = N_{\text{abs}} - \rho_b V_{\text{free}} \quad (4)$$

where ρ_b is the bulk density obtained by solving the PR-EOS (Peng and Robinson equation of state), and V_{free} is the total available volume for fluid molecules in the simulation cell given in Table 3.

Table 3: The basic building of 13X, 5A zeolites.

Adsorbent	Free(V_{free})	Occupied Fraction	Void Fraction
13X	4795.45	0.69412	0.30588
5A	5880.83	0.60545	0.39455

The pore window size and shape of the window of the two frameworks are also given in Table 4.

Table 4: Pore structure and window diameter of 13X and 5A.

Framework	Pore (Å)	Window (Å)
FAU (13X)	10 Å	12 T-ring window of 7.4 Å size
LTA (5A)	7 Å	8 T-ring window of 5 Å size

The free volume size and surface area are very important parameters to understand the adsorption and the transport behaviors of the penetrated molecules in Nano porous materials. Moreover, the free volume is the total volume available in each structure, namely the summation of α and β cages volume in the 13X zeolite. Free volume and surface area characterization are performed by Connolly surface method and also atomic summation approach. The free volume is the unit cell volume given in Table 2 minus the total solid volume.

The simulation results were calculated at different water contents for adsorbents. First, the water molecules were inserted in the unit cell and then the adsorption runs were performed. NumberThe number of water molecules to find the best prediction of experimental results was 0, 64, 86, 96, 99, and 106 which were inserted like cation through Locate module.

RESULTS AND DISCUSSION

Breakthrough curves of SO₂ adsorption on 13X and 5A zeolites are displayed in Figures 11 and 12 respectively. Both adsorbents have been tested at the concentrations of 250, 500, 750, and 1000 ppm. In addition, the outlet concentration of SO₂ is displayed as a function of time in these curves. So this would be an indication of how long an adsorbent could be used for a specific concentration before being totally saturated.

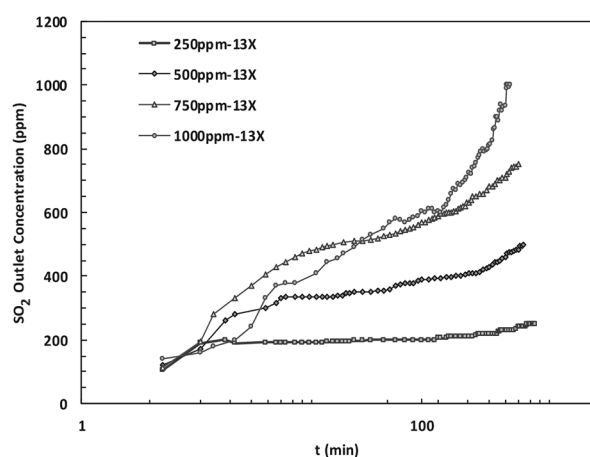


Figure 11: Breakthrough diagrams of SO₂ adsorption on 13X at concentrations of 250, 500, 750, and 1000 ppm.

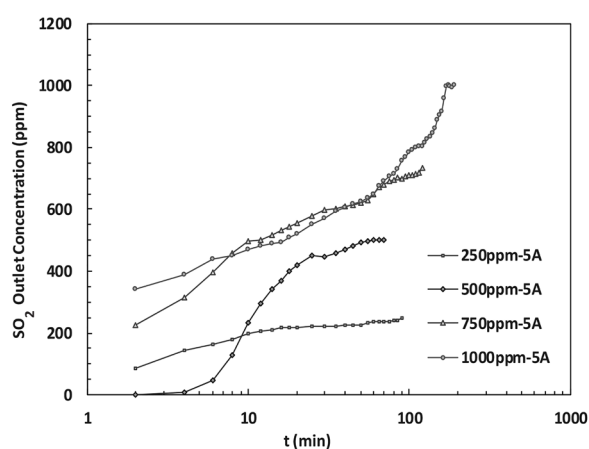


Figure 12: Breakthrough diagrams of SO₂ adsorption on 5A at concentrations of 250, 500, 750, and 1000 ppm.

As it could be perceived in Figure 11, at a concentration of 250 ppm, after 5 minutes nearly, the outlet concentration is about 200 ppm. At 500 ppm, this behavior is observed after about 10 minutes when the outlet concentration reaches a virtual steady state. For 750 and 1000 ppm, the stepwise concentration change is replaced by a gradual increase in concentration. For 750 ppm, a sudden increase in outlet concentration is observed before 12 minutes. After this moment a very long time was spared for the outlet concentration to become the same as the inlet stream. No stepwise curve-shape at the outlet stream was observed for 1000 ppm SO₂ inlet concentration.

of 250, 500, 750, and 1000 ppm are displayed in Figure 12. The breakthrough curves for the 5A are approximately the same as 13X for each corresponding concentration. Only 15 minutes are enough for an inlet stream with 250 ppm to reach a relative steady state concentration of 220 ppm. For 500 ppm, 5 minutes are needed to detect SO₂ in the outlet stream. A virtual steady state of outlet concentration is observed after about 30 minutes. In addition, like the case of 13X for 750 and 1000 ppm inlet concentration, no stepwise behavior is observed in outlet SO₂ concentration. For 750 ppm, an initial increase is observed after about 10 minutes. The total time for the concentration of the bed at 750 ppm is about 110 minutes. Moreover, for 1000 ppm, an initial sudden increase is observed at 7 minutes, and saturation time is about 170 minutes.

A comprehensive comparison of breakthrough curves of SO₂ outlet concentration on 13X and 5A is given in Figure 13.

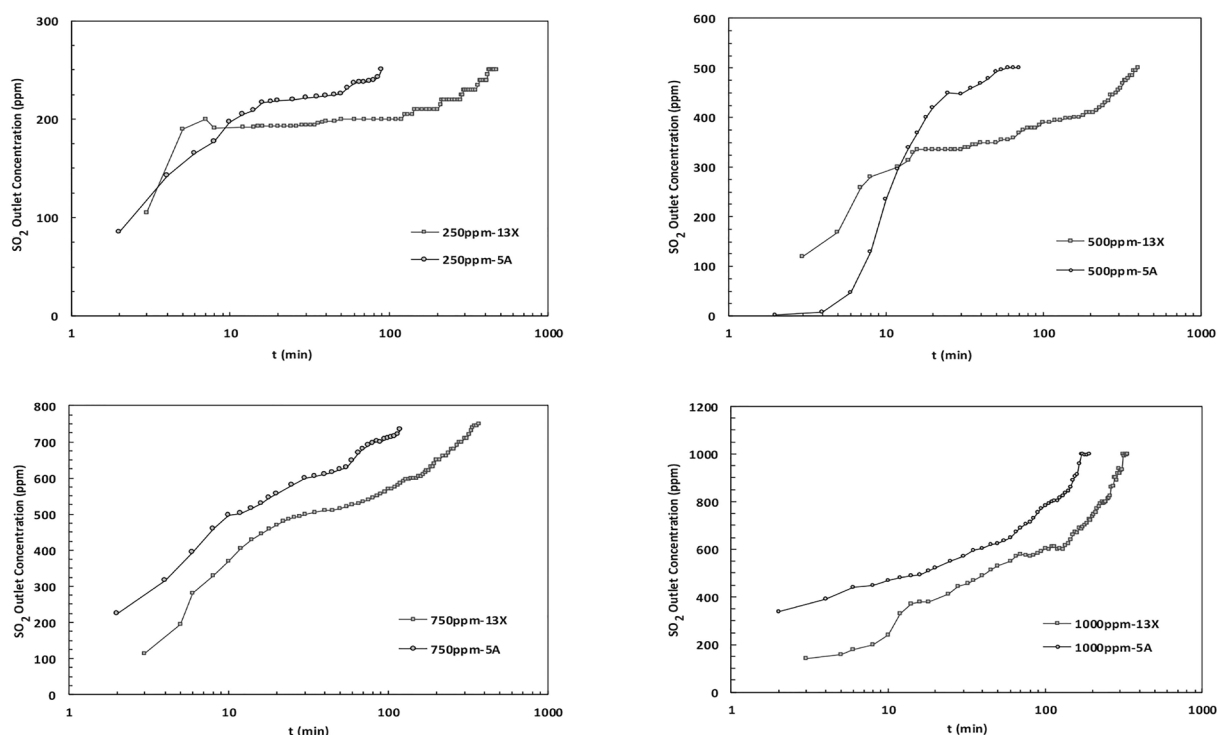


Figure 13: Comparison of breakthrough curves of SO₂ adsorption on 13X and 5A at concentrations of 250, 500, 750, and 1000 ppm; logarithmic (bottom) scale.

For the ease of judgement, at initial stages, a logarithmic scale is used. At 250 ppm, saturation time of 13X is greater than that of 5A by about one order of magnitude. The obvious contrast of the adsorbents at this concentration is the manner of saturation, i.e. 13X reaches its near saturation concentration at the initial stage while for 5A, saturation occurs gradually. In addition, the same behavior is observed at 500 ppm of SO₂ concentration. However, for 750 and 1000 ppm, 13X and 5A demonstrate similar behavior. Since the curve at 750 ppm has a downward curvature while this curvature is upward at 1000 ppm, it could be concluded that at higher concentration, both zeolite adsorbents reach their saturation level more gradually. Excluding the initial stages at 250 and 500 ppm, 13X always gives a lower outlet concentration; moreover, this could be the result of larger cavity and window sizes of 13X. Also, the

comparison of channel and window sizes of FAU (13X) and LTA (5A) frameworks are given in Table 7. Looking at the window (pore opening) and pore diameters and comparing it with free volume and void fraction parameters given in Table 3 gives the insight that pore opening diameter plays a more important role in adsorption behavior rather than free volume or void fraction.

A comparison of saturation time for SO₂ adsorption on 13X at three different temperatures of 25, 30, and 40 °C and pressures of 2 and 5 bar is illustrated in Figure 14.

As is apparent in this figure (i.e. Figure 14), at higher temperatures, 13X tends to adsorb fewer gas molecules in its porous media. This effect is more severe when the temperature is raised to 40 °C. This observation is reasonable since at higher temperatures, more kinetic movements of the gas molecules leads to less confinement

in the cages and pores of 13X. Pressure effect on the saturation time in this figure (Figure 14) shows that at higher pressure saturation occurs faster although the pressure effect is not intense.

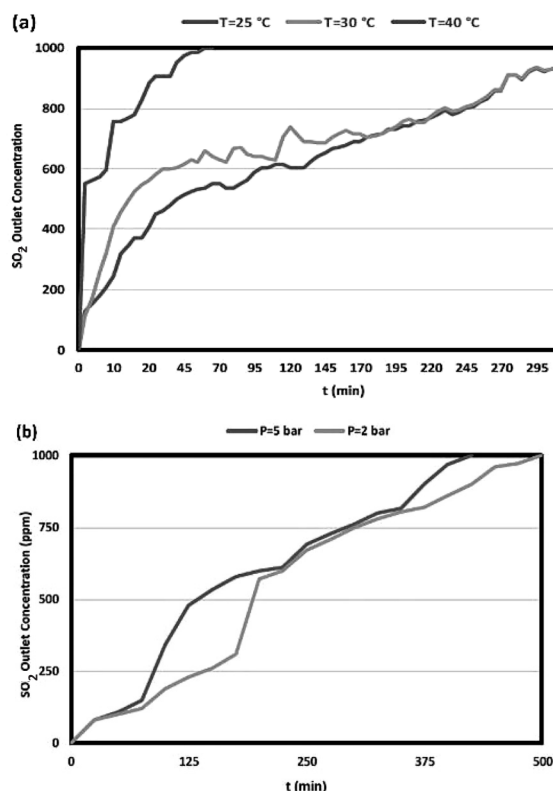


Figure 14: Effect of Temperature (a) and pressure (b) on the saturation time for SO₂ adsorption on 13X (inlet concentration 1000 ppm and volumetric flow of 200 ml/min).

Molecular Simulation

Quantities of SO₂ loading on 13X and 5A at different concentrations are displayed in Figures 15 and 16.

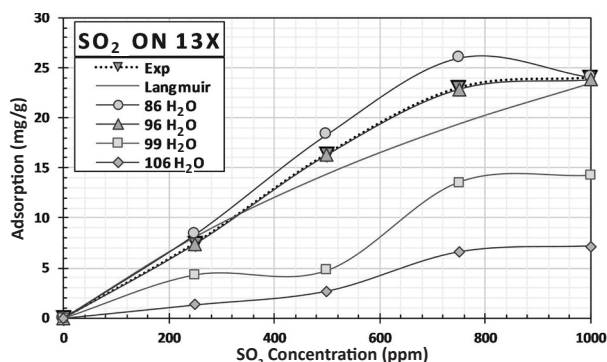


Figure 15: Simulation and experimental results of SO₂ loading on 13X versus concentration.

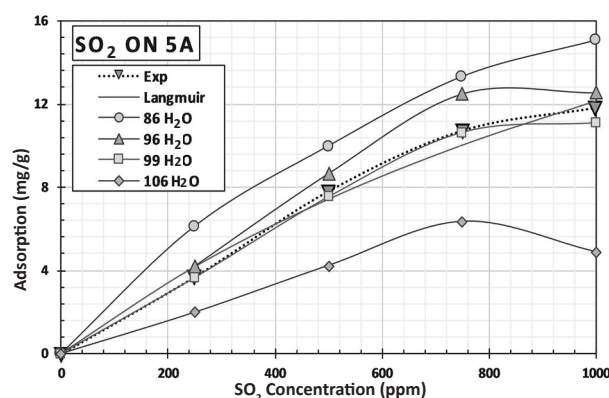


Figure 16: Simulation and experimental results of SO₂ loading on 5A versus concentration.

The molecular simulation results of Grand Canonical ensemble are also included to be compared with experimental results. With 96 water molecules, the results showed reasonable agreement between simulation and experiments for 13X, but for 5A, inconsistencies are substantial. For 5A instead of 99 H₂O in the structure gives the best fit of experimental data. Moreover, rare works on these concentrations and pressure. As the most similar investigation, the results at 1000 ppm on 13X are comparable to the reported amounts of SO₂ adsorption on 13X at 2000 ppm by Yi et al [28] where they have reported the adsorption to be about 0.4 mol/kg (25.6 mg/g) at a very low pressure of 5 kPa. But their results for 5A have been similar to 13X results and are not agree to our finding. Another example is the work of Deng et al [29]. They reported SO₂ adsorption on 13X and 5A at 323 K and low pressure to be 0.5 mol/kg (32 mg/g) and 0.2 mol/kg (12.81) respectively which shows acceptable agreement with the results of 5A. In addition, little discrepancies could be attributed to differences in materials and apparatus used in different works.

Modeling

Breakthrough curves at 1000 ppm have been modeled using Bed Depth Service Time (BDST) [30] and Yoon-Nelson models [31].

Usually, BDST model gives the simplest and fastest prediction for design and performance of the adsorption process. In this model, the bed size is related to time and it gives the highest adsorption capacity and constant of proportion. In this model, adsorption rate is related to the remained adsorption capacity and adsorbate's concentration with the following equation (Equation 5):

amounts of SO₂ adsorption on 13X at 2000 ppm by Yi et al [28] where they have reported the adsorption to be about 0.4 mol/kg (25.6 mg/g) at very low pressure of 5 kPa. But their results for 5A have been similar to 13X results and are not agree to our finding. As another example, the work of Deng et al [29] can be referred where they report SO₂ adsorption on 13X and 5A at 323 K and low pressure to be 0.5 mol/kg (32 mg/g) and 0.2 mol/kg (12.81) respectively which shows acceptable agreement with the results of 5A. In addition, little discrepancies could be attributed to differences in materials and apparatus used in different works.

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (5)$$

where C₀ is the initial inlet concentration (mg/L), C_b is the bed concentration at each time (mg/L), N₀ is the bed adsorption capacity at each inlet concentration (mg/g), Z is the bed height (cm), v is the linear velocity (cm/min), and K_a is a constant (1/(mg.min)). In order to obtain the parameters of this model (N₀ and K_a), a plot of $\ln \left(\frac{C_0}{C_b} - 1 \right)$ versus time is needed [32] as depicted in Figure 17.

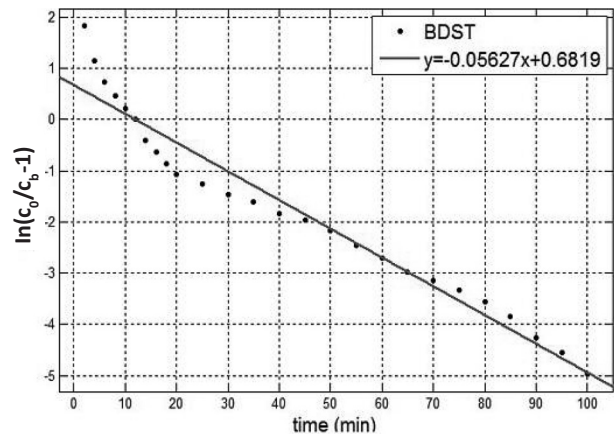


Figure 17: Fitting of adsorption data with the BDST Model (SO₂ on 13X at 1000 ppm).

The fitted parameters of BDST models are given in Table 5 for 13X and 5A along with fitting parameter R². The parameters indicate that for better adsorbent (13X), the equilibrium constant K_a is greater while N₀ is smaller than that of weaker adsorbent (5A).

Table 5: Parameters of the BDST model.

Adsorbent	K _a	N ₀	R ²
13X	0.00801306	15692.32976	0.94
5A	0.01464	7035.361	0.96

Based on the Yoon-Nelson model [33], the rate of adsorption capacity reduction is related to the breakthrough curve and the loading amount of each adsorbent with the following equation (Equation 6):

$$\ln \frac{C_t}{C_0 - C_t} = k_{YN} t - \tau k_{YN} \quad (6)$$

In this model, k_{YN} is the rate constant (L/min), and τ is the time (min) needed for the curve to reach 50% of its total value.

CONCLUSIONS

Plotting $\ln \left(\frac{C_t}{C_0 - C_t} \right)$ versus time gives the model constants. Also, the fitted parameters of this model are tabulated in Table 6 for 13X and 5A.

Table 6: Parameters of Yoon-Nelson model.

Adsorbent	k_{YN}	τ	R^2
13X	0.01018	22.879	0.93
5A	0.0212	23.5849	0.96

For better adsorbents, the equilibrium constant (k_{YN}) is smaller while the values of τ will be greater for better adsorbent. Langmuir isotherm in the following form (Equation 7) is used to fit the experimental data:

$$\frac{q_i}{q_s} = \frac{kx_i}{1 + kx_i} \quad (6)$$

where q_i is SO₂ adsorption value at each concentration in mg/g, x_i is the SO₂ concentration in ppm, and k and q_s are adjustable fitting parameters. The quantities of these two fitting parameters are given in Table 7.

Table 7: Fitting parameters of Langmuir isotherm.

Adsorbent	q_s (mg/g)	$k \left(\frac{1}{\text{ppm}} \right) \times 10^{-3}$
13X	63.38	0.5904
5A	33.54	0.5697

In this paper, SO₂ adsorption on 13X and 5A has been investigated. Monte Carlo molecular simulation has been performed beside experiments and the results have been compared. Breakthrough curves have shown that the saturation of 5A zeolite occurs faster than 13X. In addition, this might be interpreted as 13X provides more SO₂ adsorption capacity. This has been also observed in the isotherm of both experimental and molecular simulation results. Breakthrough curves at the industrial concentrations of 250, 500, 750, and 1000 ppm of SO₂ have proved that for both adsorbents, saturation time increases by an increase in the SO₂ concentration. Though few similar studies have been found on this range of concentration, our results are in reasonable agreement to similar studies which prove that both simulation and experimental

method are correct. Moreover, simulation of 13X and 5A has been successfully performed in grand canonical Monte Carlo ensemble using FAU and LTA framework respectively.

Different water contents have been tested for each adsorbent, and it has been concluded that 13X and 5A behaviors from simulation results are best modeled with 96 and 99 water molecules respectively. The simulation and experiment results have shown that both 13X and 5A are quite selective for SO₂ in presence of nitrogen gas. The overall outcome of our work and the comparison between 5A and 13X give the immediate conclusion that 13X is a better adsorbent for SO₂ based on adsorption capacity and saturation time.

Simultaneous use of experimental, modeling, and molecular simulation method for investigating the performance of nano porous zeolite with focus on their industrial, applications can be pointed out as the main novelty of this study. The molecular simulation results approved the water content of the zeolite with consistency in experiments and models. Further investigations in this field can approach other zeolite like 4A and 3A by these methods and find possible applications in adsorption for SO₂ or separation of a different mixture of gases.

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NOMENCLATURES

ASAP	: Active Surface Area and Porosity Analysis
BDST	: Bed Depth Service Time
GCMC	: Grand Canonical Monte Carlo
PR-EOS	: Peng and Robinson equation of state

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