Sulfur dioxide adsorption by iron oxide nanoparticles@clinoptilolite/HCl

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ABSTRACT:

Introduction: The purpose of this study was to investigate and compare the effect of iron oxide nanoparticles on the adsorption of sulfur dioxide by modified zeolite with hydrochloric acid. In this investigation was used modified zeolite with HCl with and without iron oxide nanoparticles (Iron Oxide Nanoparticles@Clinoptilolite/HCl) as adsorbent.

Materials and methods: Structural characteristics, chemical composition and specific surface area of adsorbent were determined using the FTIR, FE-SEM, EDX, Mapping, XRD, XRF and BET techniques. Glass cylinder filled with zeolite seeds and SO_2 cylinder balanced with N_2 gas was used for experiments. It was evaluated factors affecting SO_2 uptake process including temperature and contact time, also thermodynamics and kinetics of adsorption. Sulfur dioxide adsorption of real sample was taken with both adsorbents.

Results: Adsorption efficiency of SO_2 in the synthetic and actual sample were %82.8±5.5 and %67.2±7.21 respectively, by modified zeolite with HCl and iron oxide nanoparticles in the optimum conditions of temperature of 25 °C and duration 28.5 min. As well as, removal percentage average was obtained in the synthetic and actual sample %46.1±4.34 and %35.8±5.85 respectively, by modified zeolite with HCl without nanoparticles in optimum condition of temperature of 25 °C and contact time of 20.5 min.The results showed that SO_2 adsorption is an exothermic and spontaneous process and adsorption kinetics of sulfur dioxide by both adsorbent is more consistent Pseudo-second order kinetics model.

Conclusion: The use of iron oxide nanoparticles on the zeolite can increase SO_2 removal efficiency from the gas phase.

Introduction

Sulfur dioxide is a nonflammable, nonexplosive and colorless gas that cause taste in concentrations of 0.3 to 1 mg/L in the air. It has a strong, irritating odor in high concentrations of 3 mg/L [1]. SO_2 is converted in the atmosphere to more stable end products [2]. Sulfur dioxide is formed from sulfur containing fossil fuels combustion and industrial activities such as the iron and steel industry [3].

SO_2 emissions have harmful effects on human health such as respiratory difficulties and lung

illnesses [4]. Epidemiological studies show that exposure to elevated SO_2 concentrations can lead to respiratory illness and cardiovascular diseases mortality [5]. In addition, after oxidation and reaction with water in the atmosphere, SO_2 is responsible for acid rain that increases acidity of lakes, rivers and soils, damages to tree foliage and agricultural crops, corrodes buildings and monuments [6].

Different technologies as wet scrubbing or dry sorption methods have been developed for the sulfur dioxide removal [7, 8]. One of the wet methods that is used for SO_2 removal, is washing process with water and lime, although the aforementioned method is ability to remove SO_2 large amounts, but a large volume of wastes is produced during process [9]. Because of their simplicity and relatively low cost, dry sorption methods are more economical than wet technologies [7].

Dry processes such as physical adsorption process can be a promising approach to remove SO_2 due to its unique advantages including it requires to minimum energy for the adsorbent regeneration, gas adsorbent design is relatively simple compared to the design of a chemical reactor and there is less problems in waste disposal [10]. The adsorptive purification of flue gases from SO_2 has several advantages such as adsorbents have a high resistance at multi-cycle exploitation, are stable at high temperature and treatment with acid, selectivity of SO_2 in the presence of gas mixture other compounds [11].

Various studies are done for SO_2 adsorptions by activated carbon, alumina, graphite, rice husk ash, metal surfaces and natural and synthetic zeolites [12-18]. In a research, it was reviewed surface modification of activated carbon for adsorption

of SO_2 and NO_X [19]. Many reserachers studied SO_2 adsorption and desorption on Pt/Pd catalysts [20]. Some researchers studied zeolites for the removal of SO_2 and NOx from flue gases [21]. Due to the abundance and low cost, has been many used of clinoptilolite to adsorb and environmental applications [22]. In a study, natural clinoptilolite was used for CO_2/N_2 gas separation, they found that clinoptilolite could be used as an efficient adsorbent [23].

Natural zeolites treatment using the acidic solutions can improve the structural properties and adsorption ability of natural zeolites [24].

Studies in the field of nanotechnology indicate various properties of materials on the nanoscale for different ingredients. For instance, it can be noted increase in oxidation, reduction and catalysis property of various compounds through transition metals elements on the nanoscale [25]. Iron is one of transition elements which is common in the desulfurization process due economic considerations and optimum dynamic properties [26]. The use of nanosized iron increases SO_2 uptake efficiency because of the increasing ratio of surface area to volume and to achieve properties that these properties do not exist in macroscopic size [27]. In a study, researchers studied SO_2 adsorption on clinoptilolite/nano iron oxide and natural clinoptilolite [28].

In previous studies iron sulfate $Fe_2(SO_4)_3$ is suggested as the main product of surface reactions between SO_2 and iron. Formation of iron sulfate is related to surface pH reduction after exposure of sample to SO_2 in wet conditions and as well as a decrease in the number of OH groups associated with the iron hydroxide [29].

Numerous studies have been done in order to SO_2 adsorption investigation by modified with Hy-

drochloric Acid clinoptilolite, but no study has been conducted yet in the field of SO_2 adsorption by clinoptilolite of functionalized with iron oxide nanoparticles. The purpose of the current research is comparative study of iron oxide nanoparticles effects on sulfur dioxide adsorption by modified with hydrochloric acid zeolite.

Materials and methods

Study is experimental that was conducted in Environmental Health Engineering Research Center of Kerman University of Medical Sciences, Kerman, Iran.

Preparation of the adsorbent

In the investigation was used granulating natural clinoptilolite with an average diameter of 1-2 mm. Clinoptilolite zeolite was purchased from Afrazand company. To improve efficiency, zeolite seeds were washed with 1 N hydrochloric acid during two stages of 6 h, then washed with deionized water, and dried at 180 ºC in an oven [30]. Subsequently, 10 g of iron oxide nanoparticles (Fe_2O_3) (purity 99.5%) was added to 1 L of distilled water and suspended by ultrasonic device. Iron oxide nanoparticle suspension was added to 200 g of modified with HCl granulated zeolite, and placed in a shaker for 2 h, then slowly dried in an oven at 80 ºC for 10 h. Finally for activation of nanoparticles, composite of iron oxide nanoparticles supported on modified clinoptilolite with HCl was heated in the oven at 300 ºC for 2 h [31, 32].

Characterization of the adsorbent

The FT-IR of the samples was obtained using a FT-IR 6300 Brucker, and XRD of the Iron Oxide Nanoparticles@Clinoptilolite/HCl was recorded in the diffraction angle range of $2\theta = 10\text{-}80°$ by an X'Pert PRO MPD P Analytical using Ni-FILTERED Cu $K\alpha$ radiation. The microstructure, morphology, and chemical composition of adsorbent was investigated by FESEM-EDS (MIRA-3TESCAN-XMU). EDS mapping was employed to further confirm the components and element distribution (MIRA3TESCAN-XMU) [33]. The BET (Brunauer-Emmet-Teller) method using a BELSORP-max (Bel Japan, Inc.) instrument [34].

Adsorption evaluation of SO_2

Glass cylinder with 19.5 mm diameter and 500 mm length was used for experimental. 100 g of zeolite grains with nanoparticles and without nanoparticles was placed in the glass cylinder, separately. Schematic diagram of the experimental setup is shown in Fig. 1. The sulfur dioxide gas was provided in a high-pressure cylinder which contained 2700 ppm (purity 99.98%) of SO_2 balanced with N_2. The gas cylinder was equipped with a pressure regulator. By passing gas containing SO_2, its removal rate was measured by determining the of output concentration.

The gas flow rate was 1200 mL/min. Sampling was conducted during current to flow at 17, 20.5, 28.5 and 40 min and at 25, 35, 60 and 80 °C. The required temperature was supplied using a 250 W electric heating elements which had wrapped around the chamber covering cylinder. In order to setting the exact temperature, chamber's temperature was continuously controlled by a sensor, which was placed inside of the chamber. Sensor acted quickly when temperature was changed. If the chamber temperature was reduced from the desired temperature, the electronic thermostat was quickly turned the heater on and if it was increased from considered temperature, thermostat was turned the heater off.
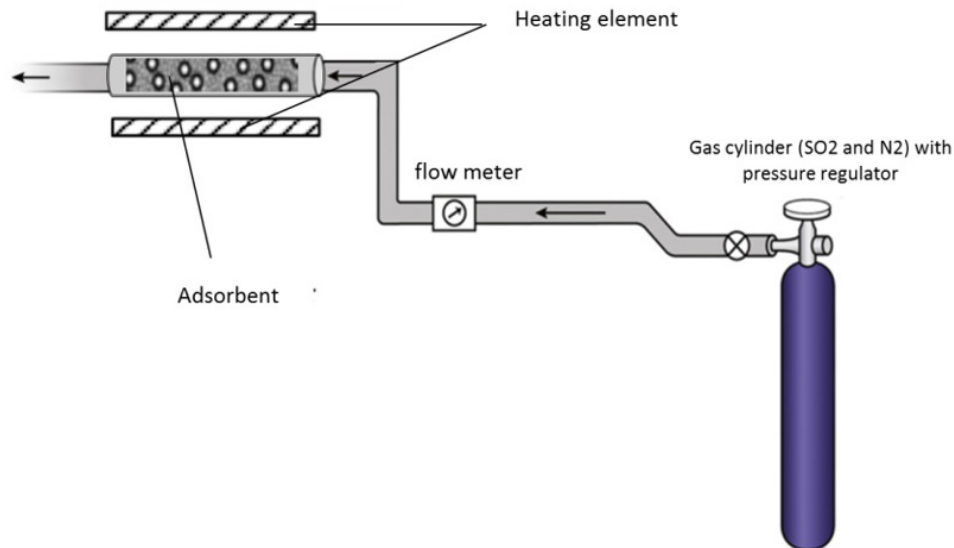
Fig. 1. Schematic diagram of the experimental system

Gas after passing through the adsorbent was entered in Midget Impinger Gas outlet was passed through a solution containing H_2O_2 (3 vol.%) , for the determination the amount of sulfur dioxide in the effluent. Then, formed H_2SO_4 was measured by titrating with NaOH (0.01 mol/L) solution and bromcresol green and methyl red as indicator to determine titration endpoint. The amount of H_2SO_4 was applied to calculate the total sulfur amount on adsorbent [35].

The amount of sulfur dioxide in output current was determined according to the mentioned methods in the book of Standard Methods for the Examination of Water and Wastewater (APHA) [36].

Each experiment was performed three times. Diesel automobile the exhaust outlet was used as real sample.

Instrumentation

In this study, used instruments were including HR200 analytical sensitive scale (A & D Japan) with precision of 0.0001 g for weighing chemicals, ultrasonic device TI-H5 model (Elma Germany) for separating Nanoparticles, Taiwanese vacuum pump model of VC-701 and Iranian oven. Chemicals that were used for laboratory work are Merck Germany with high purity.

Data analysis was performed by descriptive statistics using the SPSS (version 21).

Thermodynamic properties and kinetics of SO_2 adsorption

Kinetic equations of pseudo-first order and pseudo-second-order respectively, were calculated using linear Eqs. 1 and 2 [37, 38]:

$$\ln(q_e - q_t) = lnq_e - K_1 \times t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} \times t \tag{2}$$

Where q_e is the amounts of SO_2 adsorbed at equilibrium (mg/g), q_t amounts of SO_2 adsorbed at time *t (mg/g)*, k_1 and k_2 are rate constants of these two equations [39]. Diagram of *Log (q_e-q_t)* against time and diagram of *t/q_t* versus time was plotted in order to test pseudo-first order and pseudo-second-order respectively, for modified zeolite with HCl with and without the nanoparticle in 25 ° C.

Values of K_1, K_2 and q_e were obtained for both models by determination of slope and intercept. To determine the thermodynamic parameters such as changes in standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), were employed Eqs. 3 and 4 [40, 41]:

$$Ln\,K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

So that a straight line achieved from plotting changes of *LnK* against *1/T*. ΔH° and ΔS° obtained from the slope and intercept, respectively, of the linear plot.

Results and discussion

To characterize Iron Oxide Nanoparticles@Clinoptilolite/HCl various techniques were employed. FTIR spectrums of modified zeolite with hydrochloric acid and iron oxide nanoparticles are shown in Fig. 2.

In the FT-IR spectra of the amended zeolite with nanoparticles, vibrations of the hydroxyl functional group bands at 3612 cm^{-1}, can be seen. The peaks at 667 cm^{-1} and 788 cm^{-1} are due to Fe-O bands that appeared after the functionalization that it indicate the iron nanoparticles are well placed on the surface of the clinoptilolite [42, 43]. The surface morphology of the adsorption material was assessed by FE-SEM. Morphological results of Iron Oxide Nanoparticles@Clinoptilolite/HCl is illustrated in Fig. 3. As can be seen in the FE-SEM figures, the particles are uniform, spherical in shape, and non-clumped in nanometer dimensions.
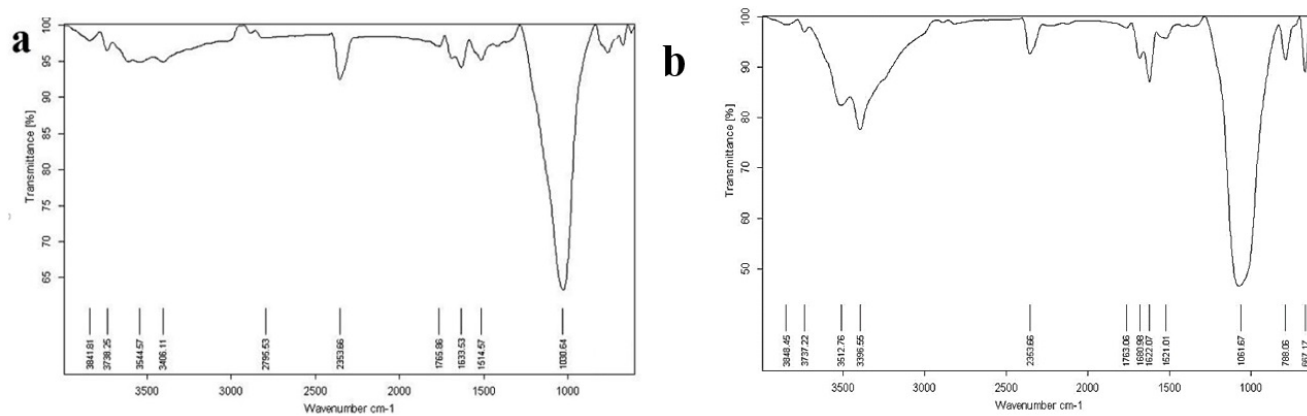

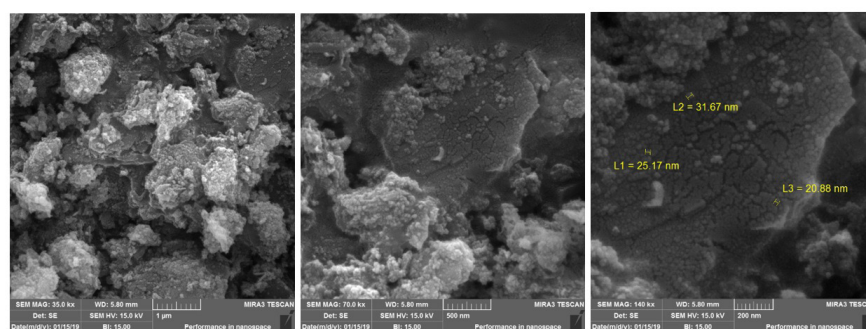Fig. 2. FTIR spectrums of Clinoptilolite/HCl and Iron Oxide Nanoparticles@Clinoptilolite/HCl

Fig. 3. The FESEM images of Iron Oxide Nanoparticles@Clinoptilolite/HCl

The figures show that the nanoparticles are located on the surface of the zeolite.

To check the chemical composition of the adsorbent, EDS was analyzed. The results revealed 29.91% O, 24.70% C, 20.95% Fe, 17.19% Si, 2.87% Al, 1.98 % Cl, 1.24 % K, 0.18 % Mg, 0.40 % Ca, 0.49 % Na and 0.09 % Y in accordance with the expected values for confirming the chemical structure of Iron Oxide Nanoparticles@Clinoptilolite/HCl (Fig. 4).

EDS mapping was used to determine the element distribution of as-prepared Iron Oxide Nanoparticles@Clinoptilolite/HCl (Fig. 5). According to Fig. 4, all elements, and Iron Oxide Nanoparticles had a homogeneous distribution, indicating
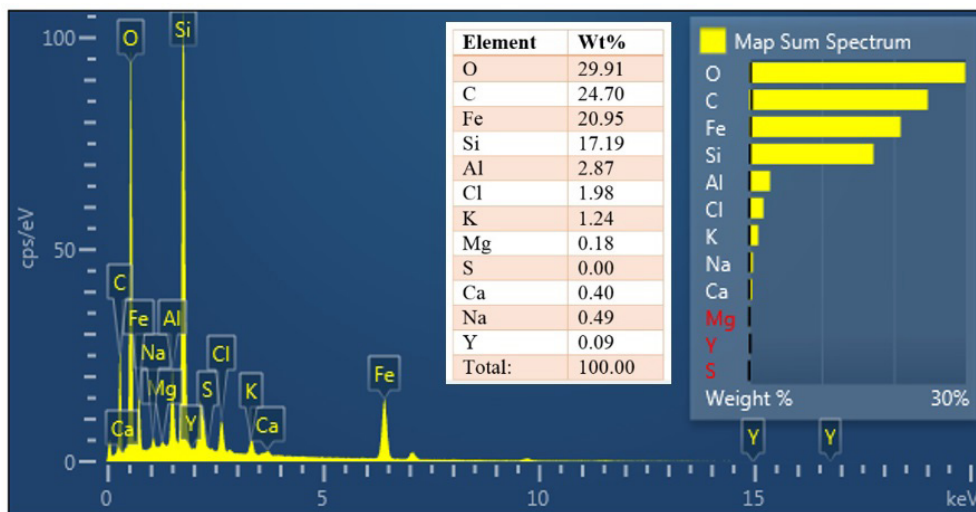

Fig. 4. EDS patterns of the as-prepared Iron Oxide Nanoparticles@Clinoptilolite/HCl
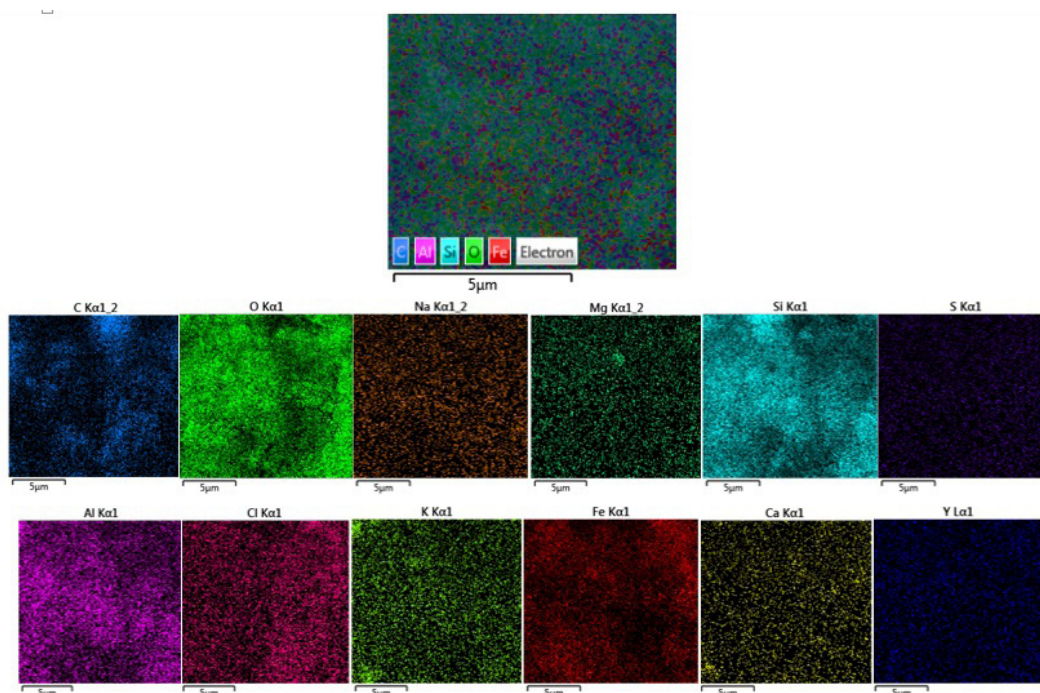

Fig. 5. The elemental mapping images of the as-prepared Iron Oxide Nanoparticles@Clinoptilolite/HCl

the high uniformity of the prepared adsorbent. Clinoptilolite used in this study has a light yellow color where silica and alumina are the main compounds (Table 1). Potassium is the most metal element found in clinoptilolite samples followed by calcium, magnesium and iron. Natural clinoptilolite has a high Si/Al mole ratio.

The results of XRD of adsorbent befor (Fig. 6a) and after (Fig. 6b) modified with iron oxide nanoparticles in the range of 10 to 80 degrees (2θ = 10°- 80°) are showed in Fig. 6. The presence of sharp and strong peaks in regions 2θ = 35.62°, 58.84° and 62.88° in Fig. 6b and comparison of peak locations with reference data indicate the iron nanoparticles are well placed on the surface of the clinoptilolite.

Table 1. XRF analysis result of used clinoptilolite

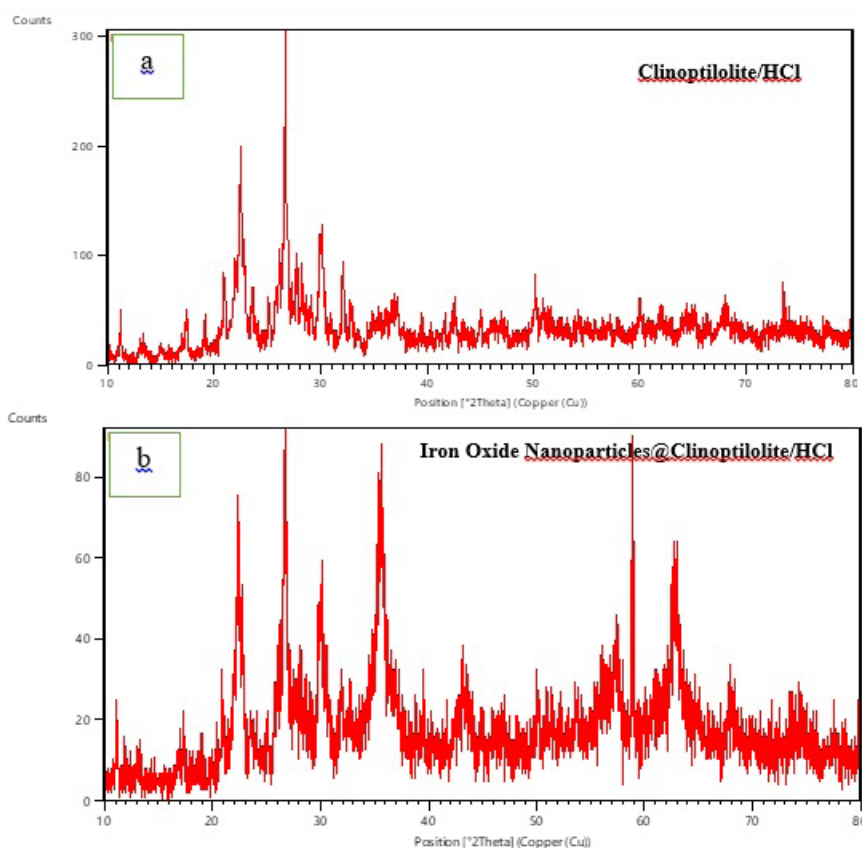| Na (%)	Mg (%)	Al (%)	Si (%)	K (%)	S (%)	Cl (%)	P (%)	Ca (%)	Ti (%)	V (%)	Cr (%)	Mn (%)
0.8	0.17	4.43	29.75	3.17	0.12	0.18	0.02	0.45	0.12	<0.01	<0.01	0.01
Fe (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Ga (%)	Ge (%)	As (%)	Se (%)	Br (%)	Rb (%)	Sr (%)	Y (%)
0.67	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01
Zr (%)	Nb (%)	Mo (%)	Ag (%)	Cd (%)	Sn (%)	Sb (%)	Te (%)	I (%)	Cs (%)	Ba (%)	La (%)	Ce (%)
0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	0.01
Pr (%)	Nd (%)	Hf (%)	Ta (%)	W (%)	Hg (%)	Tl (%)	Pb (%)	Bi (%)	Th (%)	U (%)	-	-
<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	-

Fig. 6. The XRD patterns of Clinoptilolite/HCl and Iron Oxide Nanoparticles@Clinoptilolite/HCl

The BET surface area of clinoptilolite/HCl and modified zeolite with iron oxide nanoparticles were obtained at 42.2 m²/g and 60.7 m²/g, respectively. Adding nanoparticles of iron oxide as the active phase on the clinoptilolite zeolite has increased the specific surface area. The contact surface increases due to the small size of nanoparticles.

Effect of temperature on the removal of sulfur dioxide

The effect results of temperature on the removal of sulfur dioxide in modified zeolite with HCl and modified zeolite with HCl and iron oxide nanoparticles is presented in Fig. 7.

Maximum value of SO₂ removal efficiency is at temperature of 25 ° C by modified zeolite with HCl and modified zeolite with HCl and iron oxide nanoparticles 46.1±4.34 and 82.8±5.50 per-

cent, respectively.

The results of the investigation of temperature show the removal efficiency of sulfur dioxide is reduced with increasing temperature, this indicates gas adsorption process is exothermic on zeolite and iron oxide nanoparticles. Researchers in Romania studied sulfur dioxide adsorption on zeolite Y. They reported that with increasing temperature, the adsorption capacity is reduced [12]. Some researchers studied sulfur dioxide adsorption on activated carbon. They reported that the adsorption decreases with increasing temperature and ΔH° is a negative value, which complies with the result of this study [44].

Effect of contact time on the removal of sulfur dioxide

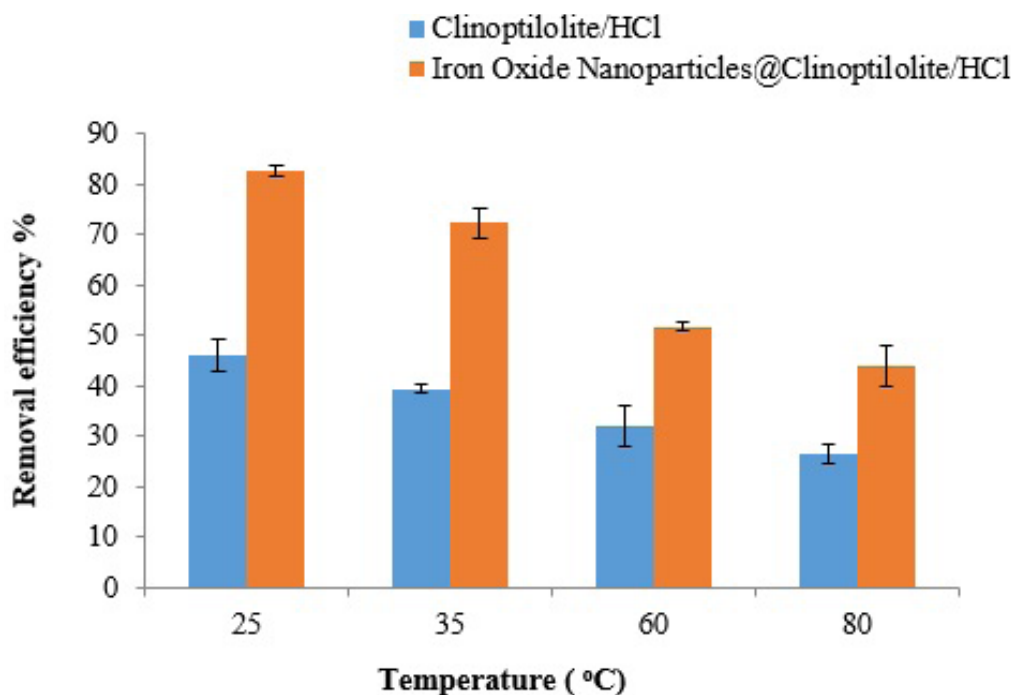The influence of contact time on the SO₂ removal efficiency investigated and the results is provided in Fig. 8.

Fig.7. The influence of temperature on the removal efficiency sulfur dioxide

Maximum removal efficiency of SO_2 obtained in the contact time of 20.5 min by modified zeolite with HCl 46.1±4.34 percent.

Also, maximum removal capacity of SO_2 obtained in the contact time of 28.5 min for modified zeolite with HCl and iron oxide nanoparticles 82.8±5.50 percent.

The results of the investigation of the contact time demonstrate the most of SO_2 adsorption occurs in the contact time of 20.5 and 28.5 initial minutes at 25 ° C for zeolite without nanoparticle and with nanoparticle respectively. This phenomenon reflects that all sites of adsorbent are empty and gas concentration gradient is high in primary minutes, as a result of this, speed of sulfur dioxide adsorption process is high. Then increasing the contact time leads to differences in adsorption efficiency due to being restricted surface area available for adsorption, and ultimately decreases adsorption efficiency. Some researchers found that with increasing contact time, the SO_2 removal efficiency by CaO as desulfurizers decreased; this is similar to the results of the current study [45]. The addition of iron oxide nanoparticles as the active phase on the structure of the zeolite has resulted in significant improvement at activity of adsorbent. This positive effect on the removal of sulfur dioxide may be due to strong catalytic properties of iron oxide and particle size uniformity.

Adsorption kinetics

Kinetic constants are presented in Table 2 along with the corresponding correlation coefficients for modified zeolite with HCl with and without the nanoparticle in 25 ° C.
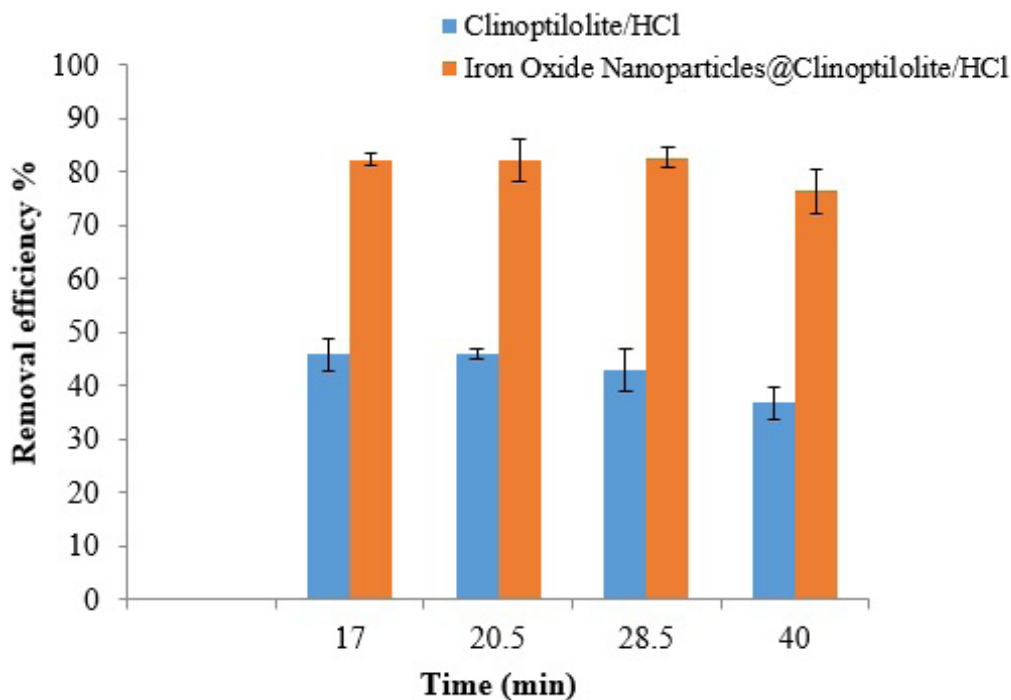

Fig. 8. The influence of contact time on the removal efficiency sulfur dioxide

It can be seen from Table 2 that adsorption of SO_2 follows Pseudo-second-order kinetic model because linearity Percent of this equation is more than other equation.

Adsorption of sulfur dioxide on both adsorbent followed Pseudo-second-order kinetic model. Researchers investigated the adsorption performance of γ-Fe_2O_3 nanoparticles for sulfide, sulfite, and thiosulfate from aqueous solutions. They reported that the adsorption process followed pseudo-second-order kinetics, which is similar with results of this study [46].

Thermodynamic of adsorption

Fig. 8 shows plot of LnK versus *1/T* for the heat of adsorption for SO_2 at different temperatures.

ΔH^o and ΔS^o obtained from the slope and intercept, respectively, of the linear plot. Table 3 displays results of thermodynamic parameters.

According to obtained results in Table 2, ΔH^o is negative value in this process which confirms adsorption of SO_2 is exothermic. It is well understood that physical adsorption decreases with increasing temperature according to Le Chatelier's Principle. In a research in China, sulfur dioxide adsorption was studied on zeolite. They reported that the adsorption decreases with increasing temperature and ΔH^o is negative value [47]. Therefore, reduction in sulfur dioxide adsorption efficiency is justifiable in actual sample due to the high temperature of exhaust outlet.

Table 2. The kinetic parameters for removal of SO_2 by modified zeolite with HCl and
modified zeolite with HCl and nanoparticles at 25 ° C

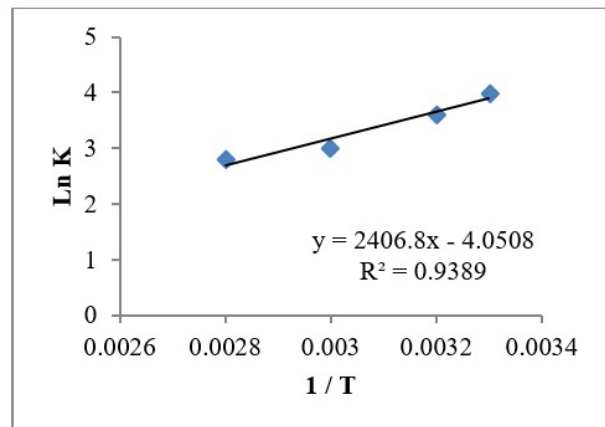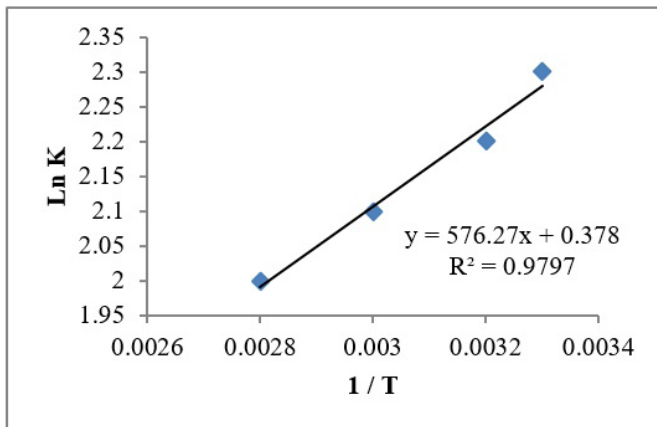| Adsorbent	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	K_1	q_e (mg/g)	R^2	K_2	q_e (mg/g)	R^2
Clinoptilolite/HCl	0.1328	49.4	0.6601	0.016	10.45	0.9977
Iron Oxide Nanoparticles@Clinoptilolite/HCl	0.1309	73.7	0.9261	0.021	23.87	0.9994

Fig. 9. plot for the heat of adsorption a) Clinoptilolite/HCl and b)
Iron Oxide Nanoparticles@Clinoptilolite/HCl

Table 3. Thermodynamic parameters of the adsorption process for SO_2 at different temperatures

Temperature (K)	Clinoptilolite/HCl			Iron Oxide Nanoparticles@Clinoptilolite/HCl		
	ΔG° (J)	ΔS° (J/mol)	ΔH° (J/mol)	ΔG° (J)	ΔS° (J/mol)	ΔH° (J/mol)
298	-5726	3.14	-4791	-9967	-33.7	-20010
308	-5758			-9630		
333	-5836			-8788		
353	-5899			-8114		

Negative value of Gibbs free energy shows the adsorption process of SO_2 is spontaneous. The value of ΔS° is 3.14 J/mol for modified zeolite with HCl that positive sign shows an increasing degree of irregularity during the adsorption process and adsorption is irreversible. Vice versa the value of ΔS° is -33.7 for modified zeolite with HCl and iron oxide nanoparticles, negative sign demonstrates decreasing degree of disorderliness during the adsorption of SO_2 [48, 49].

The obtained results from deposition of iron oxide nanoparticles on modified zeolite with HCl , suggests that process of nanoparticle deposition on modified zeolite with HCl has had appropriately function with this procedure and can also be acceptable economically.

Modified zeolite with HCl and containing iron oxide nanoparticles showed more power to adsorb sulfur dioxide than modified zeolite with HCl. The presence of iron oxide nanoparticles can have an effective role in the catalysis of pollutants in carry out the process of redox [31]. Iron can cause reducing pollutants by electron transfer them [50]. Electron transfer to pollutants can make the production free radicals of hydroxyl (OH•) and hydrogen (H) in the presence of water vapor and high temperature. The radicals cause decomposition of pollutants by reaction with them. A study in America showed that iron nanoparticles are used to decompose organic compounds in water and they convert to positively charged double iron with giving electrons [51]. This result confirms the above comment about the release of electron through the iron nanoparticles. In a study in Australia, nanoparticles of titanium dioxide (TiO_2) was applied on porous silicon dioxide (SiO_2) order to remove volatile organic compounds. They reported that toluene as an indicator of VOCs eliminates with mechanism of adsorption and catalysis [52]. In the present study the mechanisms of adsorption and catalysis can affect the efficiency of removal of SO_2, adsorbing properties of zeolite and strong catalytic activity of iron oxide nanoparticles. Iron oxide nanoparticles reaction depends on the area, thus the smaller nanoparticles increase the contact area and the rises reactivity of the nanoparticles.

Conclusion

According to obtained results, modified zeolite with HCl and iron oxide nanoparticles has a better efficiency in adsorbing of sulfur dioxide compared to zeolite without nanoparticles due to

containing abundant uptake sites and iron oxide nanoparticles as catalyst. It can be considered as a practical, reliable and efficient method for the removal of sulfur dioxide from the air.

Competing Interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Ethical considerations

Ethical considerations (including plagiarism, informed consent, misconduct, data fabrication or falsification, double publication and submission) have been completely observed by the authors.

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