

# Desulfurization of Gas Oil by Modified Clinoptilolite

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**ABSTRACT:** *The objective of this research is to find an economically attractive alternative method for hydrodesulfurization of petroleum fractions and to select a suitable adsorbent for this process. Deep desulfurization of transportation fuels (gasoline, diesel, and jet fuels) is being mandated by governments and is also needed for future fuel cell applications. However, it is extremely difficult and costly to achieve with current technology, which requires catalytic reactors operated at high pressure and temperature. Zeolites are a family of crystalline aluminosilicate minerals. About fifty natural zeolites are now known and more than one hundred and fifty have been synthesized. Clinoptilolite is a naturally occurring zeolite, formed by the diversification of volcanic ash in lake and marine waters millions of years ago. It is the most researched of all zeolites and is widely regarded as the most useful. It is an abundant natural zeolite. We show that  $Hg^{+2}$  and  $Ag^+$  clinoptilolite can adsorb sulfur compounds from commercial fuels selectively and with high capacities. The desulfurization of 83.60 % by  $Ag^+$  clinoptilolite at liquid to solid ratio of 50/100  $gr.ml^{-1}$ , 353 K, and flow rate of  $3.0 ml.min^{-1}$  was obtained*

**KEY WORDS:** *Zeolite, Ion exchange, Modification, Sulfur removal, Adsorption.*

## INTRODUCTION

The aim of this research is to investigate the capability of clinoptilolite and its ion exchange forms for reducing sulfur compounds in fuels. In common with other zeolites, clinoptilolite has a cage-like structure consisting of  $SiO_4$  and  $AlO_4$  tetrahedral joined by shared oxygen atoms. The negative charges of the  $AlO_4$  units are balanced by the presence of exchangeable cations -

notably calcium, magnesium, sodium, potassium and iron. These ions can be readily displaced by other substances, for example heavy metals and ammonium ions. This phenomenon is known as cation exchange, and it is the very high cation exchange capacity of clinoptilolite which provides many of its very useful properties [1].

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Clinoptilolite is also known to be a powerful adsorbent of certain gases, such as hydrogen sulfide and sulfur dioxide [2].

The presence of sulfur compounds in oil fractions is highly undesirable because they cause corrosion, catalyst poisoning and environmental problems. Sulfur compounds are also responsible for reducing the performance of engines. In conventional method of hydrodesulfurization (HDS) severe conditions such as high temperature and pressure is required. High consumptions of hydrogen and using expensive cobalt molybdenum catalysts are other disadvantages of the method. According to the limitation imposed by the International Fuel Quality Centre (IFQC), sulfur content of gas oil and gasoline must reduce to 10 ppm before 2010.

The new challenge is to use adsorption methods to selectively remove these sulfur compounds from transportation fuels. Because adsorption would be accomplished at ambient temperature and pressure, success in this development would lead to major advances in petroleum refining as well as for fuel cell applications. However, all of the commercially available sorbents that have been tested for desulfurization have proven ineffective. Studies of nonconventional sorbents have not yielded better results [3]. A class of highly sulfur-selective and high-sulfur-capacity sorbents has been discovered and is reported here. This class of sorbents binds thiophenic compounds selectively by  $\pi$ -complexation. These new sorbents are zeolites containing cuprous or silver cations and were prepared by ion exchange of zeolites using known ion-exchange procedures, [4].

Zeolite NaX used for the demercaptanization of natural gas [5]. Metal oxides supported on zeolites have been demonstrated to be effective regenerable desulfurization agents for high temperature removal of hydrogen sulfide from fossil fuels [6], *Mihaila* studied the adsorption of  $\text{SO}_2$  by thermally activated clinoptilolite [7]. Desulfurization of naphtha by adsorption was studied by *Baker* and *Salem* [8]. Thermal stability of zeolite NaCaA was investigated by *Lutz et al.*, [9] to evaluate its ability for desulfurization. *Wakita et al.*, [10] investigated the removal of sulfides and mercaptans by zeolite. Desulfurization of natural gas by modified Y zeolite was also studied by *Kobayashi* and *Satokawa* [11]. The aim of this work was to evaluate the capability of natural zeolite

clinoptilolite and its modified forms for removal of sulfur compounds from gas oil.

## EXPERIMENTAL

Natural clinoptilolite was obtained from deposits of Semnan in north-east of Iran. The sample was characterized by different methods including; wet chemical analysis, X-ray diffraction (XRD), thermogravimetry (TG), derivative thermogravimetry (DTG) and IR spectroscopy. In the XRD data of different samples several phases were observed. The sample No. 5 which contains highest amount of clinoptilolite was selected for experiments.

The sample was ground and screened, to particle size of 250 - 420  $\mu\text{m}$ . The ground material was purified. After removal of some impurities by a magnet bar, ultrasonic cleaning and refluxing with deionized water was used to remove soluble impurities. Carbonate impurities were dissolved in 1N sodium acetate buffer solution. The chemicals used were reagent grade and the solutions were prepared with deionized water. The clinoptilolite sample was modified through ion exchange process. The exchanged forms of Ag, Hg(II), Cu(II), Fe(II), Fe(III), Mn(II), Co(II), Cr(III), Ni, Pb and Zn were prepared under hydrothermal conditions by mechanical stirring of a mixture of 0.1N of desired cations with purified clinoptilolite. The volume to mass ratio was 10 and the equilibrium was achieved after 36 hours at 318 K [12]. The exchanged percent was estimated by the measurement of cations in the filtrate by a Varian Model Techtorn 1000 atomic absorption spectrometer.

Adsorption experiments were conducted in packed columns. Two glass columns with inner diameters of 2 cm and lengths of 50 cm were selected. The bottom of the first column was connected to the top of the second. 50 g of zeolite was packed into each column. Using a water jacket, the columns temperature was kept at 80 °C. Using a peristaltic pump 100 ml of gas oil was passed through the columns at a constant flow rate of 3.0  $\text{ml}\cdot\text{min}^{-1}$ , (Fig. 1). Sulfur content of the exist gas oil was measured spectrophotometrically using a Varian UV-VIS spectrophotometer model CARY-500.

The relationship between sulfur content of the samples and the reduction in peak area is linear, as reported by *Sharghi, Abedi* and *Massah* [13]. The method was based on the fact that chloroform-iodine complex

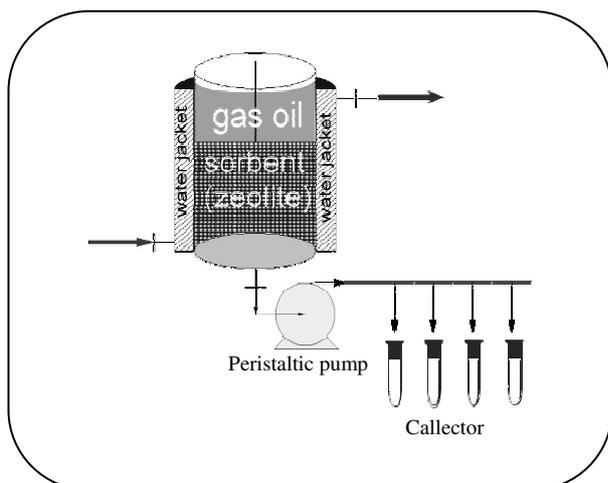


Fig. 1: Schematic representation of adsorption column.

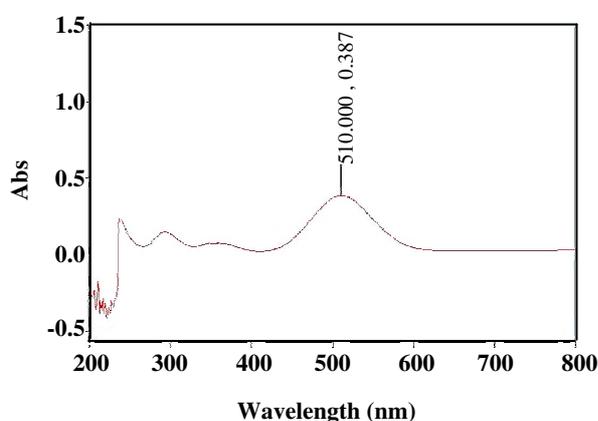


Fig. 2: UV-Visible spectra of chloroform-iodine complex.

gives a characteristic adsorption peak at 510 nm as illustrated in (Fig. 2). In the presence of sulfur compounds this complex will dissociate and its peak area observed at 510 nm will decrease, (Fig. 3).

Calibration curve was plotted using using dedecanethiol ( $C_{12}H_{26}S$ ) as standard reagent. Standard addition method was applied, (Fig. 4). DTG curves of the samples were prepared starting at room temperature to 973 K with heating rate of  $10 \text{ K}\cdot\text{min}^{-1}$  and in air atmosphere were used to estimate the amount of adsorbed sulfur. Efficient regeneration of the column was performed by three portions of 30 ml of chloroform. The initial experiments revealed that the adsorption capacity of silver and mercury forms toward sulfur compounds was very high, (Fig. 5). The breakthrough curves of the column filled with those exchange forms were constructed at three temperatures of 323, 343 and 363 K.

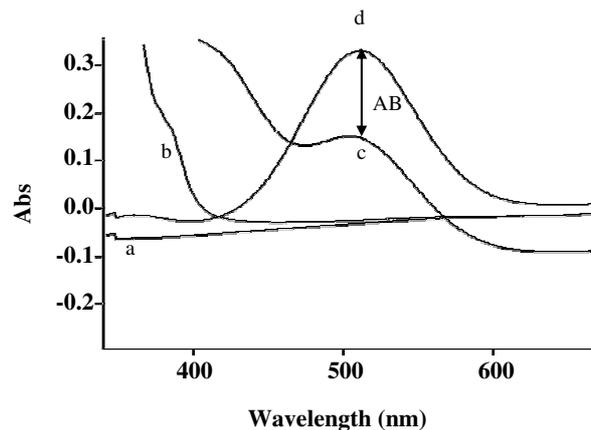


Fig. 3: UV-VIS spectra of: a-chloroform, b-gas oil and chloroform, c- gas oil, chloroform and iodine, d-chloroform and iodine.

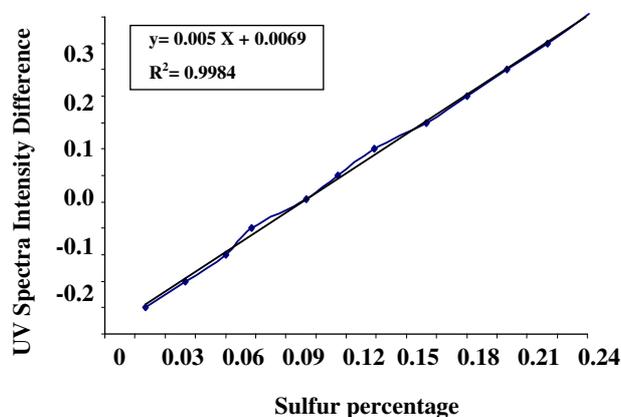


Fig. 4: Calibration curve prepared by dodecanthiol.

## RESULTS AND DISCUSSION

The XRD data of natural clinoptilolite is given in table 1. It was obvious that the major phase in the sample No.5 was clinoptilolite with some impurities. The clinoptilolite content of sample No.5 was highest between the studied samples. Therefore, this sample was selected for further experiments.

Chemical analysis of the sample was performed by the method proposed by Maxwell [14], and is represented in table 2. The TG and DTG curves of the samples showed a characteristic dehydration peak with 11.5 % weight loss, (Fig. 6). The weight loss peak which was observed, between 323-633K is attributed to the loss of water molecules from different hydration sites. The thermal curves of the exchanged forms showed the same general pattern, indicating that zeolite framework did not change during the course of exchange.

**Table 1: Information obtained from XRD data of the samples.**

Samples name's	Major Phases and recommended formula	Phases (%)
Sample No.1	Mordenite $(\text{Na}_2, \text{Ca}, \text{K}_2)\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 7\text{H}_2\text{O}$	45.7
	Clinoptilolite $(\text{Na}, \text{K}, \text{Ca})_6(\text{Si}, \text{Al})_{36}\text{O}_{72} \cdot 20\text{H}_2\text{O}$	39.5
	Quartz, syn $\text{SiO}_2$	3.3
	Orthoclase, barian $(\text{K}, \text{Ba}, \text{Na})(\text{Si}, \text{Al})_4\text{O}_8$	11.5
Sample No.2	Clinoptilolite $\text{KNa}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$	46.0
	Dolomite, ferroan $\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$	32.4
	Stilbite $\text{Ca}_{1.5}\text{Na}_{0.32}(\text{Si}, \text{Al})_9\text{O}_{18} \cdot 8.5\text{H}_2\text{O}$	8.4
	Potassium Magnesium Silicate $\text{K}_2\text{MgSi}_5\text{O}_{12}$	13.2
Sample No.3	Clinoptilolite $(\text{Na}, \text{K}, \text{Ca})_6(\text{Si}, \text{Al})_{36}\text{O}_{72} \cdot 20\text{H}_2\text{O}$	69.8
	Quartz, syn $\text{SiO}_2$	3.7
	Albite, calcian, ordered $(\text{Na}, \text{Ca})\text{Al}(\text{Si}, \text{Al})_3\text{O}_8$	26.5
Sample No.4	Clinoptilolite $\text{KNa}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$	72.1
	Stilbite $\text{Ca}_{1.5}\text{Na}_{0.32}(\text{Si}, \text{Al})_9\text{O}_{18} \cdot 8.5\text{H}_2\text{O}$	27.9
Sample No.5	Clinoptilolite $\text{KNa}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$	76.4
	Stilbite $\text{Ca}_{1.5}\text{Na}_{0.32}(\text{Si}, \text{Al})_9\text{O}_{18} \cdot 8.5\text{H}_2\text{O}$	23.6

**Table 2: Chemical analysis of the sample.**

Composition	Wight Percentage	Mol Percentage	$\frac{\text{Mol}}{\text{Mol Al}_2\text{O}_3}$	Elemental percentage	Atomic Ratio	Unite Cell
$\text{SiO}_2$	68.65±1.2	1.14	11.40	31.92	1.14	30.18
$\text{Al}_2\text{O}_3$	10.43±0.92	0.10	1.00	5.40	0.20	5.29
$\text{Na}_2\text{O}$	2.34±0.44	0.04	0.40	1.84	0.08	2.12
$\text{K}_2\text{O}$	1.72±0.29	0.02	0.20	1.56	0.04	1.06
$\text{CaO}$	1.78±0.46	0.03	0.30	1.20	0.03	0.79
$\text{MgO}$	1.21±0.31	0.03	0.30	0.72	0.03	0.79
$\text{Fe}_2\text{O}_3$	0.88±0.08	0.005	0.05	0.56	0.01	0.26
$\text{MnO}$	0.05±0.01	0.0007	0.007	0.04	0.0007	0.018
$\text{H}_2\text{O}$	12.94±0.06	0.72	7.20	-----	-----	19.06
O	-----	-----	-----	43.45	2.72	72

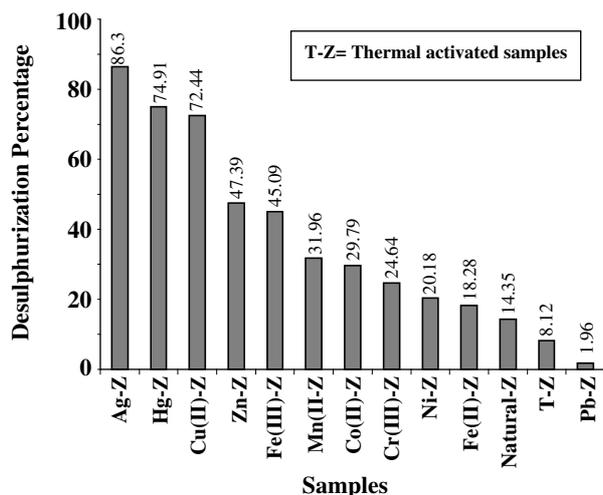


Fig. 5: Desulfurization percentage of different samples.

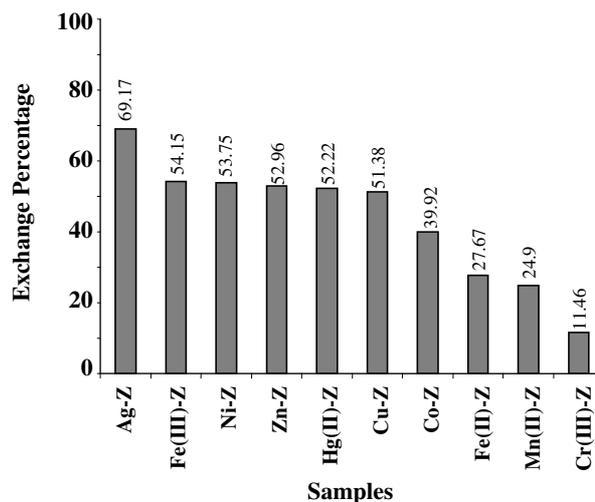


Fig. 7: Exchange percentage of modified samples.

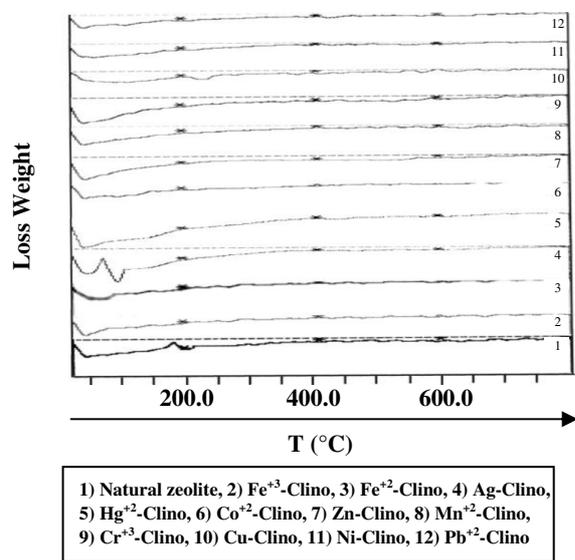


Fig. 6: DTG curves of natural zeolite and modified zeolites.

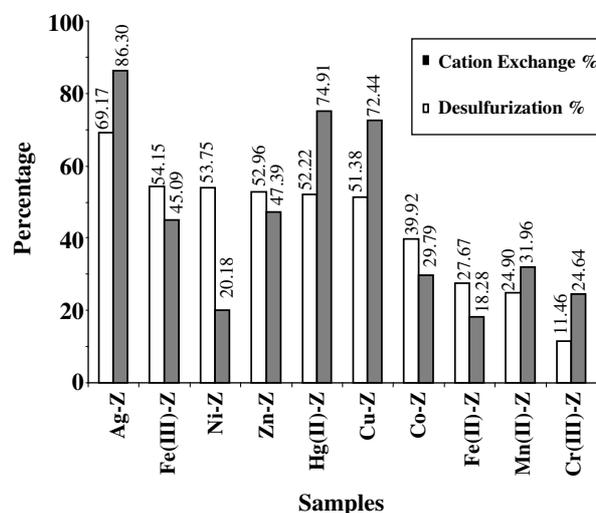


Fig. 8: Relationship between cation content and adsorption capacity of the modified samples.

Introduction of new cations into zeolite framework change both water content and dehydration temperature of the zeolite. This phenomenon is commonly seen in different exchanged forms of zeolites, [16].

Dehydration peak of Ag-exchanged form was split to two distinct peaks and appeared within the same dehydration range. This indicates that water molecules bonded to silver and sodium cations are not energetically similar. The exchange level varied for different cations, (Fig. 7). Under experimental condition the maximum exchange was always incomplete and less than 100 % of the theoretical capacity. The adsorption experiments were conducted under identical conditions for natural and the modified samples.

Desulfurization level of the samples is illustrated in Fig. 5. Silver exchanged form is of particular interest because of the demonstrated ability to reduce sulfur compound to the lowest concentration range, 86.30 % of the initial sulfur was removed by silver form. Sulfur removal by Cu (II), Hg (II) exchanged forms exceeded 74.91 and 72.44 % of the initial concentration, respectively. The difference in adsorption level of the exchanged forms can be related to the exchange percentage, cation charge, cation radius and water content of each sample.

Adsorption by thermally treated sample was less than the natural clinoptilolite. Heat treatment was carried out at 303 K. At this temperature, some of the water

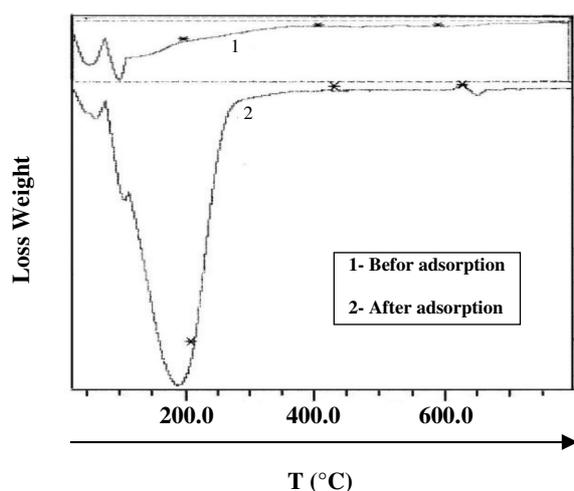


Fig. 9: DTG curves of Ag-Clinoptilolite.

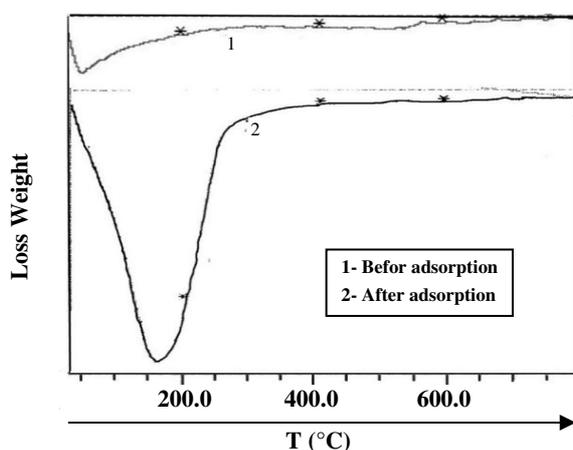


Fig. 10: DTG curves of Hg-clinoptilolite.

molecules escape and structure rearrangement may lead to the blockage or distortion of the channels, a process that could decrease the adsorption capacity of the samples. The adsorption level observed for Pb-exchanged form was negligible and much less than that obtained by natural clinoptilolite.

A linear relationship was generally observed between adsorption capacity of the modified samples and their cation contents, (Fig. 8). It is suggested that the sulfur removal can be enhanced by increasing cation content of the samples. This can be approached by applying more intensive experimental conditions i.e.; higher temperature and concentration. Comparison of DTG curves of Ag and Hg forms before and after sulfur removal, (Figs.9 and 10),

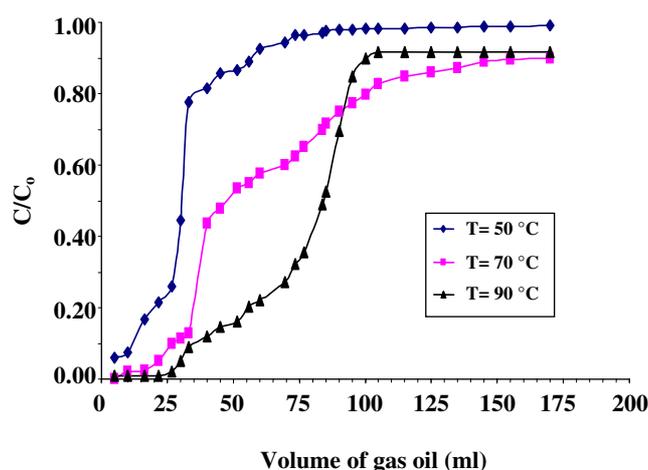


Fig. 11: Breakthrough curves of Mercury-clinoptilolite at different temperatures.

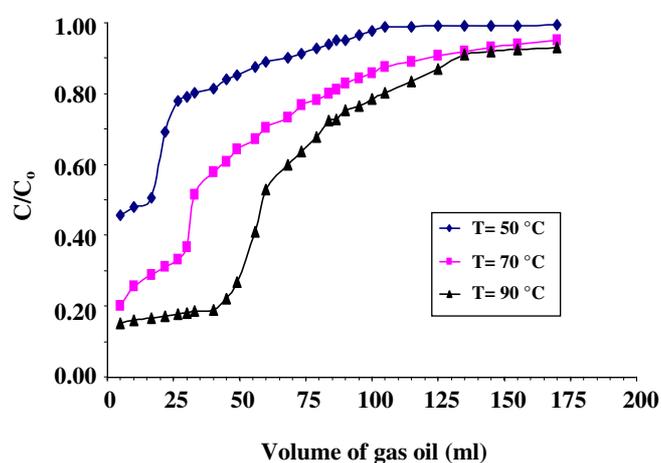


Fig. 12: Breakthrough curves of Silver-clinoptilolite at different temperatures.

473 K is due to decomposition of sulfur compound. The area of this peak increased as the sulfur removal intensified.

The adsorption theories to describe zeolite behavior are reported by Yang, R. T., [3] Hernandez-Maldonado, A. J., Yang, F. R., [4], Takahashi, F. H. and Yang, R. T. [16]. They used molecular orbital (MO) theory to search for sorbents that would bond thiophene more strongly than benzene. Here, Benzene was used as a model compound for aromatics, whereas thiophene represented the basic compound for sulfur. The adsorption bond energies were also measured from equilibrium adsorption isotherms at different temperatures. The agreement between the experimental and theoretical values was

excellent. The natural bond orbital analysis showed that the bonding followed the classical picture of  $\pi$  complexation.

There was some donation of electron charges from the  $\pi$  orbital of thiophene to the vacant s orbital of metals (known as  $\sigma$  donation) and, simultaneously, back-donation of electron charges from the d orbitals of metals to the  $\pi^*$  orbital (i.e., the antibonding  $\pi$  orbital) of thiophene (known as  $\pi$  back-donation). The results also showed that  $\sigma$  donation is more predominant for thiophene and the  $\pi$  back donation is more important for Benzene. The same argument can be applied for higher adsorption capacity observed for some cation exchanged form. The breakthrough curves of Ag-clinoptilolite and Hg-clinoptilolite were prepared at three different temperatures of 323, 343 and 363 K, (Figs. 11 and 12). In both samples, as temperature increases, the breakthrough point shifts to the lower volume of gas oil which may be attributed the reaction rate increase. The maximal value of  $C/C_0=1.00$  was obtained at 323 K where those measured at 343 and 363 K were 0.90 and 0.88, respectively.

## CONCLUSIONS

Adsorption of sulfur compounds by untreated clinoptilolite is negligible. The replacement of some cations such as Ag, Hg, and Cu sharply increases the adsorption capacity of the samples, whereas Pb replacement reduces the adsorption capacity. It is suggested that zeolite capacity still could be increased by preparation of Ag and Hg uniform under new experimental conditions.

The adsorption behavior of Ag-Z, Cu-Z and Hg-Z related to adsorption bond energies (in kcal/mol) from ab initio MO theory, was explained by *Takahashi, F. H.* and *Yang, R. T. Yang*, [16]. Ag-Z has the largest bonding energy, therefore, it is able to adsorb most sulfur organic compounds from gas oil.

On regeneration with solvents, total sulfur recovery was achieved at room temperature when chloroform was used as solvent. The solvent can be effectively removed by gentle heating. The abundant and cheapness of clinoptilolite in Iran, the simplicity of adsorption process, and ease of recovery is the most advantages of the method.

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