High Efficiency Desulfurization of Gas Condensate by Adsorption Method on Improved Zeolite

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RESUMEN

En la actualidad los compuestos de azufre de los combustibles contaminan seriamente el ambiente. Muchos gobiernos han aprobado leyes con el objetivo de reducir lo máximo posible el contenido de sulfuro de los distintos combustibles. Una gran cantidad del sulfuro producido por el condensado de los gases es liberado a la atmósfera. En este estudio, se han utilizado nuevos adsorbentes mejorados para prevenir la polución ambiental. Se ha seleccionado un adsorbente nuevo de alto rendimiento para la desulfuración (Ag impregnado en X-zeolita sintetizada) con el objetivo de eliminar los compuestos de azufre. También se ha estudiado el efecto de los compuestos aromáticos y acuosos en la eficacia del adsorbente. Los compuestos de azufre se eliminaban del condensado de gases sulfurosos y su contenido total en azufre se reducía del 0.26% a una cantidad inferior al 0.14%. La regeneración del adsorbente se investigaba en unas condiciones distintas de temperatura, velocidad de flujo del gas y tiempo de funcionamiento. Su capacidad se recuperaba hasta más del 96% después de la regeneración. Este adsorbente de elevada capacidad incluso después de varias regeneraciones presentaba el mejor rendimiento en desulfuración, sin sufrir cambios en sus estructuras durante los procesos de verdadera alimentación.

Palabras clave: Adsorción; desulfuración; zeolita; condensate

SUMMARY

Today fuels sulfur compounds pollute the environment seriously. Many governments have passed laws to decrease sulfur content of different fuels, as low as possible. A large amount of fuels sulfur that produced from gas condensate released into the atmosphere. In this study a new improved adsorbent are used for prevention of environmental pollution. A new high capacity optimized desulfurization adsorbent (impregnated Ag on X-zeolite synthesized) was selected to remove sulfur compounds. Also water and aromatic compounds effects on adsorbent efficiency were studied. Sulfur compounds were eliminated from the sour gas condensate and its total sulfur content reduced from 0.26% to less than 0.14%. Regeneration of the adsorbent is investigated in different temperatures, gas flow rate and operation time. Its capacity was recovered to more than 96%, after regeneration. This high capacity adsorbent even after regeneration for several times had the best desulfurization performance without any change in structure, amongst processes with actual feed.

Keywords: Adsorption; desulfurization; zeolite; condensate

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which is widely used in the world. This process is based on surface adsorption of sulfur compounds on appropriate metallic catalyst surfaces. Subsequently hydrogenation of the corresponding sulfur compounds takes place under high partial pressure of hydrogen and high temperature. Thus, the sulfur compounds are converted to corresponding hydrocarbon and hydrogen sulfide gas as a byproduct. Recent studies have revealed that the sulfur removal efficiency of the HDS process depends on the chemical structure and bulkiness of the sulfur compounds involved in hydrosulfurization. While HDS is successful in desulfurization of aliphatic thiols, mercaptans, thiocarbamates, sulfides and disulfides, this process is less effective in the removal of alkylated aromatic sulfur compounds, such as dibenzothiophene and its derivatives. In practice, the first sulfur compounds should be adsorbed on the metal catalyst surface in order to be hydrogenated. Evidently, steric hindrance of alkylated aromatic sulfur compounds restricts appropriate adsorption of these compounds on the catalytic surface. Although more severe operational conditions have been proposed to enhance the efficiency of the HDS process for these sterically hindered sulfur compounds, this attitude is usually rejected due to a sharp increase in both investment and operational costs. On the other hand, to achieve ultra low sulfur with the current hydrosulphurization (HDS) technology, applying higher temperature, higher pressure, larger reactor volume, and more active catalysts is very expensive, dangerous and leads to severe air pollution problems and acid rain falls.

Gas condensate is a special link fluid obtained from reservoirs within critical and cricondenthem temperatures. This is a liquid product condensed from the gaseous phase in surface separators during gas production. Gas condensate usually exists in gaseous state or in the initial reservoir conditions. However, in the course of production, the gaseous phase exchange to a two phase mixture consists of a gaseous phase and a liquid phase the liquid phase being named condensate. Gas condensate recovered from petroleum gas could be employed for mixing with the heavy crude oil and then distilled for producing transportation fuels. The removal of sulfur from transportation fuels has been mandated by governments around the world in order to reduce atmospheric pollution by sulfur compounds. More than 195 types of sulfur compounds are recognized in crude oil such as hydrogen sulfide, disulfides and organic sulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives. During the combustion, these compounds release sulfur oxides (SO) and sulfate particles into the atmosphere, which can lead to severe air pollution problems and acid rain falls. Due to the depletion of sweet oil and gas reservoirs, oil and gas producers around the globe are forced to utilize sour oil and gas wells. Some processes can lead to excessive release of sulfur compounds into the atmosphere. Growing concerns on environmental processes enforce the governments to pass restriction rules for permissible sulfur content thresholds. Legislation of 15 and 10 ppm as the acceptable standard levels of sulfur compounds for diesel fuels in the US and Europe, respectively, represents the efforts in pursuit of ultraclean fuels. Hence, desulfurization plants become an inseparable and essential part of refineries. At present, the hydro desulfurization (HDS) technique is almost the dominant desulfurization process, which is widely used in the world. This process is based on surface adsorption of sulfur compounds on appropriate metallic catalyst surfaces. Subsequently hydrogenation of the corresponding sulfur compounds takes place under high partial pressure of hydrogen and high temperature. Thus, the sulfur compounds are converted to corresponding hydrocarbon and hydrogen sulfide gas as a byproduct. Recent studies have revealed that the sulfur removal efficiency of the HDS process depends on the chemical structure and bulkiness of the sulfur compounds involved in hydrosulfurization. While HDS is successful in desulfurization of aliphatic thiols, mercaptans, thiocarbamates, sulfides and disulfides, this process is less effective in the removal of alkylated aromatic sulfur compounds, such as dibenzothiophene and its derivatives. In practice, the first sulfur compounds should be adsorbed on the metal catalyst surface in order to be hydrogenated. Evidently, steric hindrance of alkylated aromatic sulfur compounds restricts appropriate adsorption of these compounds on the catalytic surface. Although more severe operational conditions have been proposed to enhance the efficiency of the HDS process for these sterically hindered sulfur compounds, this attitude is usually rejected due to a sharp increase in both investment and operational costs. On the other hand, to achieve ultra low sulfur with the current hydrosulphurization (HDS) technology, applying higher temperature, higher pressure, larger reactor volume, and more active catalysts is very expensive, dangerous and leads to severe air pollution problems and acid rain falls.

The oxidative desulfurization (ODS) process can be considered as an alternative process for the HDS method. The ODS process consists of the two following consecutive steps:
(a) First, sulfur compounds are oxidized to their corresponding sulfoxides or sulfones by an oxidative agent.
(b) Then, highly polarized sulfoxides or sulfones are extracted by an appropriate polar solvent or adsorbed on high capacity sorbents.

Most of the reported oxidative desulfurization systems involve use of the oil insoluble oxidants, H2O2 or peroxides, which results in a biphasic oil-aqueous solution system. This biphasic system limits the mass transfer through the biphasic interface in the oxidation process, which leads to diminishing the oxidation rate. The liquid-liquid phase separation after the oxidation usually causes a loss of fuel oil in this step. The remaining sulfones in the oil phase need to be removed further by adsorption and abstraction, which also results in a loss of the fuel oil. Also in some studies, organic peroxide compounds with one phase process or fixed bed reactor with heterogeneous oxidative catalyst are used for oxidation step in ODS process. The water-soluble acid or base used as a catalyst in the biphasic system also corrodes the equipment. In order to avoid these problems, some researchers explored the systems using adsorbents to selectively remove the sulfur compounds in liquid hydrocarbon fuels which is one of the promising approaches, as this process can be conducted at ambient conditions without using costly material and a complementary process for HDS and ODS other desulfurization methods. As it is well known, the liquid hydrocarbon fuels contain not only sulfur compounds but also a large number of aromatic compounds that have aromatic skeleton structure similar to the coexisting sulfur compounds. This inherent problem makes a great challenge in the development of an effective adsorbent with high adsorptive selectivity for the sulfur compounds. The Si/Al molar ratio of zeolite plays important role in efficiency of applications, framework, crystals particulate properties and channels distribution that effect on adsorbent criteria. The higher Si/Al ratio in zeolites the lower Cation Exchange Capacity and Si/Al molar ratio reduction causes to increase desulfurization. The present study investigates the effect of water and aromatics and real feed on optimum sorbent that was synthesized and improved (4.5% Ag ion, 427 °C calcinations temperature and 74 °C operation temperature) in the previous study and gives adsorption isotherms and regeneration conditions.
MATERIALS AND METHODS

Materials
Sample of sour natural gas condensates was collected from south pars gas fields in Iran. All chemicals were directly used as received without any further purification. Toluene (98 wt%) and AgNO₃ (99.9 wt%) were purchased from Merck.

Theory and methods
Adsorbent was produced from X zeolite that was impregnated with Ag⁺-4.5% (Figure 1) The adsorbent was calcined in 436 °C and tests were performed in 74 °C. Zeolites were treated by Ag⁺ at 50 °C for 1 h. Ag⁺-impregnated zeolite was prepared by treating the NaX-zeolite with AgNO₃ solution (5.26 M, 5 mL) for 1 h. After the impregnation process, the samples were filtered, washed with deionized water, and dried at 100 °C overnight. The impregnation adsorbent samples were calcined at 436 °C for 4 h to dehydrate. The calcinations for the samples were carried out in air.

Analysis
The total sulfur content of the fuel was measured using an Analytikjena multi EA 5000 Total Sulfur Analyzer (TSA) by the pyrolysis method. The lower detection limit of TSA was measured to be 500 ppbw. To determine the sulfur content as well as sulfur speciation, fuel samples were analyzed in an Agilent GC-7890 unit equipped with an EC-5 capillary column (L) 30 m; (i.d.) 0.32 mm and a flame photometric detector. The column temperature program was set to increase from 50 °C to a set value at a 5 °C/min rate. For thiophene analysis, the column final temperature values were 230 °C. In addition, the injection port temperature was set to 70 °C and retention time for thiophene that diluted in sulfur-free n-octane to a known concentration was 7 min. The total elution time for thiophene for the GC condition described above was 10 min. The results are similar to those found in the literature for similar analysis conditions and setup. To establish the detection limit of the GC-FPD, solutions of thiophene in iso-octane, prepared by sequential dilution, were used. Detectable peaks were recorded at concentrations near 0.56 ppmw S (or 0.148 ppmw thiophene). For the 0.18 ppmw S solution, the peak was no longer visible and the intensity was comparable to that of the noise level. Thus, the detection limit was below 0.56 ppmw S.

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance

Isotherms equation
It is convenient to represent experimental equilibrium isotherms by analytical expressions. Many models have been proposed to describe the isotherms, for example, Langmuir, Freundlich, Sips and Toth. In this study, the Langmuir equation (2) was used to correlate the experimental data due to its adjustable parameters and good simulation behavior under liquid conditions. The sulfur uptake (q), expressed as sulfur removal per unit mass of adsorbent material (mg.g⁻¹), was calculated from the experimental data (C₀, V, m and Cᵣ) in each sample according to Equation(1).

$$ q = \frac{V(C₀-Cᵣ)}{m} $$

Where, V is the volume of the solute aqueous solution, Cᵣ corresponds to the initial solute concentration, C₀ the final solute concentration and m is the mass of adsorbent material [2]. The equilibrium data (isotherm) were fitted by Langmuir. Therefore, the experimental data fitted very well to the Langmuir model.

EXPERIMENTAL

Adsorption studies using improved zeolite
Adsorption studies of sulfur compounds onto AgX-zeolites were carried out in steel flasks containing 0.5 g of the adsorbent material and 10 mL of model solution and real condensate with constant concentrations of the solute. The studies of adsorption thiophene were performed using 10 mL from the model solution of thiophene (437 ppm) and condensate feed with 0.26% total sulfur and 1410 ppm mercaptane in a 50 mL steel tube as batch method. The systems were agitated (250 rpm) in an incubator shaker during 4 hours. After adsorption completion, the solution S was filtrated and analyzed (sulfur concentration).

Regeneration

The regenerability of silver adsorbent supported on X-zeolite was tested by heating the saturated adsorbent bed in flowing air. The temperature was slowly ramped to ensure appropriate evacuation of hydrocarbons and sulfur compounds from the adsorbent bed. After this, the bed was cooled down and tested again in breakthrough tests. The adsorbent was taken through five cycles of adsorption–regeneration using the model feed. Table 1 shows the breakthrough quantities of sulfur by fresh and regenerated AgX-zeolite adsorbents. The breakthrough performance was consistent for multiple cycles. To check the surface topography of the adsorbent after regeneration, the samples were studied via SEM. Figure 2(a),(b) shows the SEM images of fresh and regenerated AgX-zeolite adsorbent (five cycles).
present SEM images were not noticed here. However checking the surface topography of the adsorbents after regeneration demonstrated the crystalline size and morphology of the samples; these were surveyed and compared between the morphologies of fresh AgX zeolite and regenerated AgX zeolite. This demonstrates the homogenous morphology of the structure. In addition to this, it shows that the cubic morphology and crystalline size of AgX zeolite are almost retained after regeneration process that is indicated by SEM images in Figure 2(a),(b), although it can be seen that the crystal structure of regenerated AgX zeolite is slightly dark compared to AgX zeolite. The presence of some bigger particles in the regenerated AgX zeolite image is attributed to the aggregation of some small particles during regeneration process. In addition, SEM images obviously show that Ag has been dispersed and deposited uniformly on the external surface of X zeolite. Analysis (atomic absorption) shows that there are no Ag ions in product and therefore do not occur any Ag leaching from adsorbent in adsorption process. (Table 5)

Produce feed for survey water effect and aromatic effect

The adsorption of sulfur compounds was obtained by GC analysis (FPD detector) of the model feeds from a mixture of iso-octane and water by 400 to 40000, ppm deionized water (Table 2) and to compare the sulfur adsorption capacity of sorbents as aromatic compounds existed, in some cases, 5-30 wt % of toluene (Table 3) was also added into the first model feed, (iso-octane and 520 ppm sulfur as thiophene) as the representative of aromatics. The adsorption process occurred at 74 °C for 4h in a steel batch reactor. Table 1, 2 and 3 summarize the model feeds used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed S (ppmw)</th>
<th>Product S (ppmw)</th>
<th>S Uptake (mg S/g Sorbent)</th>
<th>S Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>437</td>
<td>50</td>
<td>5.3</td>
<td>89</td>
</tr>
<tr>
<td>regenerated</td>
<td>437</td>
<td>60</td>
<td>5.1</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 1. Sulfur Uptakes by Fresh and Regenerated AgX-zeolite Adsorbent

Table 2. Model feeds Used in the Experiments for Effect of water

<table>
<thead>
<tr>
<th>number</th>
<th>Sulfur compounds</th>
<th>Sulfur content (ppmw)</th>
<th>Water content(ppmw)</th>
<th>Aromatic content (wt %)</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thiophene</td>
<td>437</td>
<td>400</td>
<td>0</td>
<td>iso-octane</td>
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<tr>
<td>2</td>
<td>Thiophene</td>
<td>437</td>
<td>4000</td>
<td>0</td>
<td>iso-octane</td>
</tr>
<tr>
<td>3</td>
<td>Thiophene</td>
<td>437</td>
<td>6500</td>
<td>0</td>
<td>iso-octane</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>number</th>
<th>adsorbent</th>
<th>sulfur compounds</th>
<th>Sulfur content (ppmw)</th>
<th>aromatic compound</th>
<th>Aromatic content (wt %)</th>
<th>solvent</th>
<th>S uptake (mg/g Sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaX-zeolite</td>
<td>Thiophene</td>
<td>520</td>
<td>toluene</td>
<td>5</td>
<td>iso-octane</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>AgX-zeolite</td>
<td>Thiophene</td>
<td>520</td>
<td>---</td>
<td>0</td>
<td>iso-octane</td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>AgX-zeolite</td>
<td>Thiophene</td>
<td>520</td>
<td>toluene</td>
<td>5</td>
<td>iso-octane</td>
<td>1.46</td>
</tr>
<tr>
<td>4</td>
<td>AgX-zeolite</td>
<td>Thiophene</td>
<td>520</td>
<td>toluene</td>
<td>10</td>
<td>iso-octane</td>
<td>0.89</td>
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<tr>
<td>5</td>
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<td>Thiophene</td>
<td>520</td>
<td>toluene</td>
<td>20</td>
<td>iso-octane</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>AgX-zeolite</td>
<td>Thiophene</td>
<td>520</td>
<td>toluene</td>
<td>30</td>
<td>iso-octane</td>
<td>0.69</td>
</tr>
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</table>

Table 3. Model feeds Used in the Experiments for Effect of Toluene

Table 4. Chemical and physical properties of adsorbents

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal ion</th>
<th>Metal- impregnated/%</th>
<th>SBET /m2/g</th>
<th>Vt /cm3/g</th>
<th>L /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaX-zeolite</td>
<td>Na</td>
<td>0</td>
<td>691.52</td>
<td>0.3577</td>
<td>2.0688</td>
</tr>
<tr>
<td>AgX-zeolite</td>
<td>Ag</td>
<td>4.5</td>
<td>230.16</td>
<td>0.1826</td>
<td>3.1729</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Sorption Uptake

In the adsorption process of sulfur compounds on AgX-zeolite, the pore structure of the AgX-zeolite has been reported to affect the adsorption capacity of sulfur compounds [36]. Information about the pore structure of an adsorbent can be obtained through an adsorption BET. (Table 4)

Adsorption-Regeneration experiments

The first step in this study consisted of saturating the fresh AgX-zeolite sample by sulfur compounds under the conditions selected in our previous works: a temperature of 74 °C, initial S-concentration of 437 ppm for 120 h. Under these conditions, adsorption equilibrium is reached. For the adsorption of sulfur compounds on the fresh AgX-zeolite sample the amount of sulfur adsorbed at equilibrium is high and quite similar to that recorded in previous works [34]. The extent of sulfur compounds adsorption on this regenerated sample at 74 °C, following the same conditions as in the fresh sample, recorded an S-uptake of 5.1 mg S/g sorbent. The desorption process temperature at 100, 150, 200, 290 and 300 °C of sulfur compounds on the binder AgX zeolite in air flow for 1h are shown in Figure 3. They are reversible and do not display any hysteresis upon desorption of sulfur compounds. A fifth experiment was conducted on the same saturated sample, but this time regenerated at 200 °C, giving an adsorption capacity of 5.1 mg S/g adsorbent, which means a recovery of only 86% of the initial S-uptake. Above 200 °C, the minimum amount of sulfur compounds is extracted and the main bulk of sulfur compounds have been oxidized to SO2. Two factors may be responsible for this behavior: (i) some of the sulfur compounds molecules still remain retained within the porous structure of the zeolite sample and cannot be removed during the regeneration step; and (ii) reduction of the adsorption capacity of the sorbent due to the partial destruction of its crystalline structure.

To study the strength of sulfur adsorption sites, desorption has been performed at various temperatures. The amounts and proportions of the sulfur compounds in feed after desorption over sorbent impact on temperature level and regeneration time and gas flow. Regeneration time effects deso-
solution ratio of 0.5 g/10 ml for 4 h in model solutions, without aromatic compounds and water. The amounts of thiophene recovered were 50-89% at adsorption temperatures of 30-120 °C, and calcination temperature of 200-500 °C and metal percentage of 0.5-10%. In the second step, the effect of aromatic compounds and water content were studied in this paper under same conditions.

Thiophene uptake is advantageous for the effective recovery of sulfur compounds, and subsequent adsorption studies were performed at ambient conditions for time effect. Time dependences of Thiophene adsorptions on AgX zeolite at ambient condition is shown in Figure 6. The Thiophene adsorption was fast in first 15 min (1.25 mg s/g sorbent) and the thiophene uptake reached 22% after treatment for only 15 min and the adsorption equilibrium was achieved after treatment for 4 h. This shows that the adsorption processes are fast and most of the sulfur compounds are adsorbed within 240 min. This suggests that the best time for thiophene adsorption on AgX zeolite is 4 h (89%) but the sulfur compounds uptake reaches 47% after treatment for 1 h and the adsorption equilibrium is achieved after treatment for 4 h. Under this experimental condition, the sulfur adsorption capacity is above 5.3 mg s/g sorbent, and increases to 5.8 mg s/g sorbent when adsorption time reaches 440 min. However, the addition of time decreases the sulfur compounds uptake rate and the sulfur adsorption capacity to 5.3 mg s/g sorbent. Maximum sulfur compounds adsorbed to 96% after 1440 min (5.9 mg s/g sorbent).

In order to check the behavior of the prepared sorbent in a desulphurization process, the sulfur compounds adsorption-desorption cycles (five) were carried out on the original sorbent and prepared sorbent in different conditions (containing respectively temperature, gas flow) using the model feed in Table 5. Table 5 reports the amount of adsorbed sulfur compounds (five cycles) expressed, for practical reasons, as the actual amount of sulfur compounds adsorbed in the different operational conditions and the amount initially adsorbed during the first cycle. In particular, in Table 5, the initial sorbent shows a general decreasing trend in the quantity of sulfur compounds adsorbed during the adsorption-desorption cycles (in accordance with other studies [25]). This decrease appears to be more significant (86% after the 5th cycle) with the sulfur compounds. However, there is not a great difference between the general and regenerated sorbent.

From the above results, it can be deduced that the sorption characteristics of the sorbent are less sensitive to thermal degradation phenomena (due to the cyclic process of sulfur compounds sorption and desorption) when the sorbents are supported with suitable metallic derivatives and the sulfur adsorption.

**Effect of contact time**

In the first step, the effect of adsorption temperature and calcinations temperature and metal percentage were studied with AgX-zeolite under conditions of adsorbent-air mixture, adsorption time reaches 440 min. However, the addition of time decreases the sulfur compounds uptake rate and the sulfur adsorption capacity to 5.3 mg s/g sorbent. Maximum sulfur compounds adsorbed to 96% after 1440 min (5.9 mg s/g sorbent).

**Effect of water on Adsorptive Desulfurization**

The purpose of water addition was investigation of water effect in the adsorption process over an improved sorbent by Ag which was investigated by directly adding varying amounts of water(400, 4000, 6500, 8000, 13000, 23000 and 40000 ppm) into the model feeds. The impact of reaction temperature was also explored and the best temperature of 74 °C was observed (previous study). The effect of water on Adsorptive Desulfurization for improved sorbent carried out at 74 °C is shown in Figure 7 and the detailed composition of the model fuels is listed in Table 2. Water will always be present in varying quantities in real feeds during the process. Thus, a trend could be developed regarding the effect of varying amounts of water on the sorbent while at the same time the sorbent deactivation could also be monitored. The external addition of water caused a significant decrease in sulfur compounds adsorption. Moreover, adsorption did not recover when the water addition was above 4000 ppm. The effect of water was also evaluated at high levels for the same sorbent at similar conditions as used for tests. (Figure 7)
The presence of water in the liquid feed mixture decreases the sorption effect related to the presence of water (they show sulfur sorption values about 3.1 mg/g and 0.5 mg/g for quantities of 6500 ppm and 13000 ppm water in the feeds, respectively), while the other investigated quantities (400 and 4000 ppm) show less pronounced effects at sulfur compounds adsorption. An explanation of this behavior could be that the water may partly adsorb onto the pores and chock the input channels of the sorbents and/or occupy zones where the sulfur compounds want to connect to them. This condition causes a decrease in the total amount of sulfur compounds sorption. It is therefore evident that with certain water in the feed, the presence of humidity decreases the effect of desulfurization. This behavior is more enhanced for aromatics (as observed from data shown in the last section) which have higher activity in the process of the sulfur compounds adsorption.

**Effect of aromatics on Adsorptive Desulfurization.**

Toluene is chosen as an aromatic compound in this experiment. To clarify the influence of co-existing toluene on sulfur compounds adsorption, the adsorptive removal of sulfur compounds over zeolite under the conditions of the different amounts of toluene in 5, 10, 20 Vol %, and 30 Vol % have been carried out. The desulfurizationperformanc-es of AgX-zeolite were compared to those feeds. It can be seen from Figure 8 that the sulfur adsorption capacities are about 1.5, and 1 mg S/g sorbent, on AgX-zeolite for 5, 10 Vol % respectively, with toluene mix feeds. The detailed composition of the model feeds is listed in Table 3. However, when the toluene concentration increases to 10, 20, 30 Vol %, the sulfur adsorption capacity decreases to about 1, 0.9 and 0.7 mg S/g sorbent, respectively. The results demonstrate that the effect of toluene on the adsorbents decreases and the strong competitive adsorption of toluene takes place during sulfur adsorption by AgX-zeolite. Although the effect of toluene is not less on AgX-zeolite, AgX-zeolite shows the best adsorptive desulfurization performance for removing sulfur in the feed with different toluene concentrations. It is interesting to note that with the increase of the toluene concentration, the adsorptive removal of sulfur on NaX-zeolite decreases quickly, while the adsorptive removal of sulfur on AgX-zeolite decreases slowly. This result indicates that the interaction between sulfur and NaX-zeolite or AgX-zeolite is different. From the above results, it is clear that toluene had less effect on sulfur adsorption over AgX-zeolite than that over NaX-zeolite.26] also found that Ag-impregnated Z zeolites exhibited higher selectivity for sulfur compounds as compared to the selectivity of aromatics. They indicated that the sulfur compounds were adsorbed over Ag-impregnated Z zeolites via direct sulfur-adsorbent interaction rather than via π-complexation. On the basis of our results and their suggestions, we experimentally ascribe the selectivity of sulfur over AgX-zeolite to the presence of well-dispersed Ag species, removing sulfur compounds via direct sulfur-adsorbent interaction in the presence of toluene.
ents tested in the previous study, it is found that AgX-zeolite displays the highest adsorption capacity for the sulfur compounds. It also reveals that the adsorption selectivity trend of AgX-zeolite for the sulfur compounds increases. It can also be noted from the data displayed that AgX-zeolite displays a much higher sulfur adsorption capacity than others. This phenomenon can be ascribed to the fact that the impregnated Ag ion to sorbent increases the sulfur adsorbing sites. As mentioned above, the concentration of Ag is considerably enhanced during the existence of Ag on the zeolite surface and Ag is needed for n-complexation adsorption.

\[ Cs/q = 1/(Q_m b) + Cs/Q_m. \]  

Where \( q \) is the sulfur uptake (mg/g), \( C_s \) is the equilibrium sulfur concentration in solution (mg/ml), \( Q_m \) is the maximum adsorption capacity (mg/g), and \( b \) is the adsorption constant (dm\(^3\)/mg). From the fitting of the experimental data by plotting \( C_s/q \) against \( C_s \), the saturation capacity \( (Q_m) \) and the adsorption constant \( (b) \) for the sulfur compounds adsorption are evaluated as 0.150 mg/g and 0.517 ml/mg, respectively, with a correlation coefficient of 0.98.

A slightly smaller adsorption constant \( b \) value is observed in the Freundlich (Table 7) than in the Langmuir. Since the \( b \) value reflects the strength of adsorption; the smaller \( b \) value suggests that Freundlich interacts with zeolite more weakly than Langmuir in spite of the fact that the former has a larger \( Q_m \) value. In the case of the adsorption of organic sulfur compounds, weak Vander Waals interaction and steric interaction may slightly be involved, in addition to the strong interaction between the Ag ions and the organic sulfur compounds.

A very good agreement between the adsorption isotherm obtained on the Langmuir and those majored by 4.5% from Ag ion percentage for the AgX zeolite was observed indicating that the Freundlich does not modify the adsorption isotherm of the AgX zeolite for sulfur compounds. Therefore, the isotherms of AgX zeolite were well described by the Langmuir model and the fitting curve of the Langmuir isotherm of the AgX zeolite for sulfur compounds. Thereafter, the isotherms of AgX zeolite were well described by the Langmuir model and the fitting curve of the Langmuir isotherm of the AgX zeolite for sulfur compounds. Therefore, the isotherms of AgX zeolite were well described by the Langmuir model and the fitting curve of the Langmuir isotherm of the AgX zeolite for sulfur compounds. Therefore, the isotherms of AgX zeolite were well described by the Langmuir model and the fitting curve of the Langmuir isotherm of the AgX zeolite for sulfur compounds. Therefore, the isotherms of AgX zeolite were well described by the Langmuir model and the fitting curve of the Langmuir isotherm of the AgX zeolite for sulfur compounds. Therefore, the isotherms of AgX zeolite were well described by the Langmuir model and the fitting curve of the Langmuir isotherm of the AgX zeolite for sulfur compounds.

### Table 7. Langmuir and Freundlich isotherm information

<table>
<thead>
<tr>
<th>number</th>
<th>Isotherm Name</th>
<th>R2 (curve)</th>
<th>b (curve)</th>
<th>Qm (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Langmuir</td>
<td>0.98</td>
<td>0.150</td>
<td>0.517</td>
</tr>
<tr>
<td>2</td>
<td>Freundlich</td>
<td>0.94</td>
<td>0.599</td>
<td>0.300</td>
</tr>
</tbody>
</table>

### Adsorptive Desulfurization of Condensate

Desulfurization of condensate as real fuel containing about 0.24 % sulfur was studied over the best metal impregnated zeolites tested in the desulfurization of condensate and the results are presented in Table 8. As observed in the desulfurization of condensate, the AgX zeolite exhibited higher adsorption capacity around 5.8 mg S/g adsorbent. The sulfur content in the product after treatment is around 0.14 %. The adsorption capacity of X zeolite without Ag (3.1 mg S/g of adsorbent) is only about half of those containing Ag (5.8 mg S/g of adsorbent), indicating that the metal ions, particularly Ag impregnated in the X zeolite, contribute significantly to the removal of organic sulfur compounds. It is likely that the presence of various refractory sulfur compounds such as mercaptans, thiophenic acids, disulfides, etc. in the real feed (Table 8) require cations such as Ce or Ag for the adsorption and desulfurization. Thus, the amount of sulfur removed per cation impregnated is significantly high for AgX zeolite as compared to X zeolite. It can be expected that in X zeolites the cations present in the pores are accessible to organic sulfur compounds for adsorption and desulfurization. Thus, the higher adsorption capacity of AgX zeolite (per cation basis) could be due to the existence of Ag ions in the more accessible pores in the form of ligated Ag ions as reported earlier on the basis of other studies. On the other hand, Ag ions may exist in some small cages that are less accessible to organic sulfur compounds. Another factor that can also control the adsorption of organic sulfur compounds is the nature and extent of coordination between metal cation and sulfur compounds. It is known that metal ions such as Cu\(^{2+}\), Ce\(^{3+}\), Pd\(^{2+}\), etc. can form n-complexes with olefins and n-complexation with aromatics. Thus, the better performance of AgX zeolite (per cation basis) may also be due to the ease of n-complexation with thiophenics. It should be recalled that in the desulfurization of real feed, the AgX zeolite adsorbs thiophenic compounds completely along with other sulfur compounds, probably due to the involvement of n-complexation of Ag\(^+\) with thiophenics. The AgX zeolite exhibited the best performance in the desulfurization of real fuel and the sulfur content in the feed can be reduced to around 0.14 % by decreasing the fuel/adsorbent ratio to 1/20 feed/AgX zeolite. It is also interesting to note that the adsorption capacities of Ag impregnated zeolite is higher than that obtained over 4.7 wt % cerium.
and zinc (metal basis) impregnated on X zeolite under the same experimental conditions. The Ag ions in the metal impregnated samples are in sites while the well crystallized Ag₂O phase is formed in the impregnated sample and thus may be blocking the zeolite pores. The sulfur content in the model feed could be reduced to well below 50 ppm over the AgX zeolite adsorbent. However, in the desulfurization of real fuel the sulfur content has been reduced to around 0.14% under the same experimental conditions. This could be due to the presence of various refractory sulfur compounds and a high level of sulfur content. The FPD chromatogram of the treated real fuel showed (figure not shown) that the intensities of all peaks have decreased, and this suggested that under the present experimental conditions even other highly sulfur compounds have been removed significantly over AgX zeolites.

Table 8. The Real feed properties

<table>
<thead>
<tr>
<th>Name</th>
<th>Total sulfur(%)</th>
<th>Total Mercaptane (ppm)</th>
<th>Water content (ppm)</th>
<th>Aromatic content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate</td>
<td>0.26</td>
<td>1410</td>
<td>420</td>
<td>12.00</td>
</tr>
<tr>
<td>Treatment condensate</td>
<td>0.14</td>
<td>790</td>
<td>205</td>
<td>11.98</td>
</tr>
</tbody>
</table>

CONCLUSION

This study demonstrates that impregnated AgX zeolite is an excellent adsorbent for the removal of sulfur compounds. The introduction of Ag ions into X zeolite greatly improves the sulfur capacity in the model feed, containing thiophene and some amounts of toluene and water. These lead to a good desulfurization performance of AgX-zeolite. The presence of Ag ion in the X zeolite modifies the adsorption process. Thus, it follows that the AgX zeolite appears as a powerful microporous adsorbent of sulfur compound traces and an industrial sulfur adsorbent. The water effect on the AgX-zeolite activity has been investigated by adding various amounts of water to the feed. The addition of external water was found to decrease sulfur adsorption and in some cases deactivates it. This adsorbent can bear up to 4000 ppm water, in sulfur adsorption. The regeneration should be done, by desorption of SO₂ at 200 °C and 1.5 L/min air flow and during 1 hour period. This is true for a X zeolite being used as a support for 4.5% Ag ions content. The adsorbent desulfurization efficiency remains excellent, even after several adsorption-regeneration cycles.

REFERENCES