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Adsorption Desulfurization Of Iraqi Heavy Naphtha Using Zeolite 13x

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Abstract— This work was conducted to study the effect of selective adsorption on removal of sulfur compounds from Iraqi heavy naphtha from Al-Dura refinery by using molecular sieve (13X) in a fixed-bed column and it was be run out at 1.5–6.0h-1 LHSV, 15–30 gr weight of molecular sieve (13X), 600–1650ppm sulfur concentration in the feedstock , the adsorption temperature was 25°C and 40°C. The best operating conditions for removing sulfur compounds was 3.0 h-1 LHSV, 20 gr molecular sieve bed weight and 25°C temperature, where the sulfur content in heavy naphtha was reduced from nearly 600 ppm to less than 1 ppm (by weight). Regeneration steps was thermally took place by hot air flow in a range from 16.66 – 25 liter / min and temperature range from 200–350°C, the best desorption conditions for (85.8%) weight percent removing was at 16.66 liter / min air flow and 350 °C.

Keywords— Adsorption, heavy naphtha, molecular sieve 13X; fixed bed, regeneration.

1. Introduction

In Iraq, Sulfur is the most important contamination present in petroleum fractions where it take place in amount from thousands parts per million to about near to hundred, the most concentrated petroleum treatment research work currently being led in hydrocarbon processing is directed to the removal of sulfur compounds from various petroleum fractions(6) . Sulfur might be present in inorganic forms like elemental sulfur, H2S and COS, or positioned within organic molecules like Sulfides (CH3-CH2-CH2-S-(CH2)4-CH3 (propyl pentyl sulfide)) , Disulfides having the general formula R-S-S-R' presents in light fractions, Thiols or mercaptans(CnH2n+lSH) found in low boiling fractions, and Thiophenes with their derivatives often present in fractions boiling over 250oC(8) . In the naphtha boiling range thiophenes, nanocyclic mercaptans and sulfides are the major group(3). In fact, reduce of sulfur level emission to nearly zero was named of global in coming 5–10 years(6). Environmental regulations have been introduced in many countries everywhere the world to decrease the sulfur content in distillate fuels to ultra-low levels (10 ppm), lead to take down the transportation fuel machine’s harmful expend emissions and improving air quality (2) .

Naphtha which is used mainly in gasoline production in the petroleum industry (12) , is a limited sulfur compounds content that most generally removed or changed to a inoffensive form by physical method through adsorption on different adsorbent or by chemical treatment with lye, Doctor solution, copper chloride, or similar treating like agents, Hydrorefining ,Extractive Desulfurization , Oxydesulfurization , and Biodesulfurization processes also frequently used in place of chemical handling (7) .

Zeolite (molecular sieves) A and X, the most public commercial adsorbents are crystalline, extremely porous materials, which belong to the type of aluminosilicates, and these crystals are categorized by a three-dimensional pore system, and Due to the attendance of alumina, zeolites show a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface , and these cations can be exchanged to fine-tune the pore size or the adsorption characteristics, also Zeolite molecular sieves offer a range of pore openings, cavity and channel sizes, and framework of Si/Al ratio , and they are also available in various cation-exchanged (partial or complete) forms (11) .

The sodium form of zeolite X (13X) have pore slot around 8 Ångstrom (11). The type X framework is also made with a lower Si/Al ratio(1.0 compared to 1.25 for normal X type), which can provide a higher concentration of cations in the crystal than the normal X type. This type is called low- silica X (LSX) zeolite (13).

Yang et al. (16) presented that at ambient temperature and pressure Cu+ and Ag+ zeolite Y can adsorb sulfur compounds (by complexation) from marketable fuels selectively with high sulfur capacities. Thus, the sulfur content was reduced from 430 to less than 0.2 ppm by weight in a commercial diesel at a sorbent Assimilation of 34 cubic centimeters of clean diesel produced per gram of sorbent . In another work, Yang et al. (1) conclude that it can be get 19 cm3 of diesel fuel per gram of adsorbent with a weighted average content of 0.22 ppm sulfur from the desulfurization of a commercial diesel fuel (297.2 ppm Sulfur) with the best adsorbent sequence , Selexsorb CDX (alumina)/Ni(II)-Y (SSIE-500) [layered bed of 25 wt % activated alumina followed by Ni(II)-Y] by different nickel (II)-exchanged faujasite zeolites in a fixed-bed adsorber ran at same conditions .

Ng et. al. (10) showed that zeolites, and more specifically sodium-Y type zeolite (NaY) can be used for the elimination of thiophenic sulfur compounds from both n-octane and n-hexadecane under flow conditions.

Zeng et al.(17) studied removal of mercaptan from model gasoline fuel with average sulphur concentration of ethanethiol for the petroleum was stated to be 500 and 800 ppmw in Jinling, China, respectively, by adsorption on 13X loaded with Zn+2 in a batch adsorber. The desulfurizing capacity growths due to the Zn+2 impregnated.

Herna´ndez (a) et al. (4)found that the exclusion of thiophene molecules from liquid hydrocarbon assortments can be done by using zeolites like copper and silver exchanged faujasite type (Ag-Y and Cu(I)-Y) which they concluded that can be an efficient adsorbents; also Herna´ndez (b) et al. (5) presented that the sulfur content can be desulfurize (decreased) less than 0.28 of ppmw for both commercial gasoline and diesel fuels by using Cu(I)-Y zeolite together with an activated carbon guard bed layer . For the item of diesel fuel, the guard bed / Cu(I)-Y combination adsorbed 1.08 and 1.85 wt % total sulfur at breakthrough point and saturation, respectively .

Muzic et al.(9) studied the use of commercial activated carbon and 13X type zeolite for removing sulfur contaminants from diesel fuel by adsorption in a batch adsorbed.

The aim of this research was to study the efficiency of sulfur compound removal from Iraqi heavy naphtha by using molecular sieve 13X at different operating conditions in a fixed bed, like liquid hourly space velocity, bed weight, concentration and temperature.

2. EXPERIMENTAL WORK

2.1 *Materials*

Heavy naphtha with sulfur content nearly 600 ppm supplied by Al-Dura refinery (Company of Middle Refineries) was used in this research. Granulated material 3.2 mm cylindrical(pellet) shape 13X Zeolite Molecular sieve supplied by (Sigma-Aldrich Science and High Technology company) was used as adsorbent , had an XRD analysis taken by XRD-6000 Shimadzu X-ray Diffractometer device, as shown in Fig.1. Carbon disulfide (CS2) in its pure form have a colorless, sweet aromatic odor ,the technical product is a yellowish liquid with a disagreeable odor , was used to change the total sulfur content in heavy naphtha

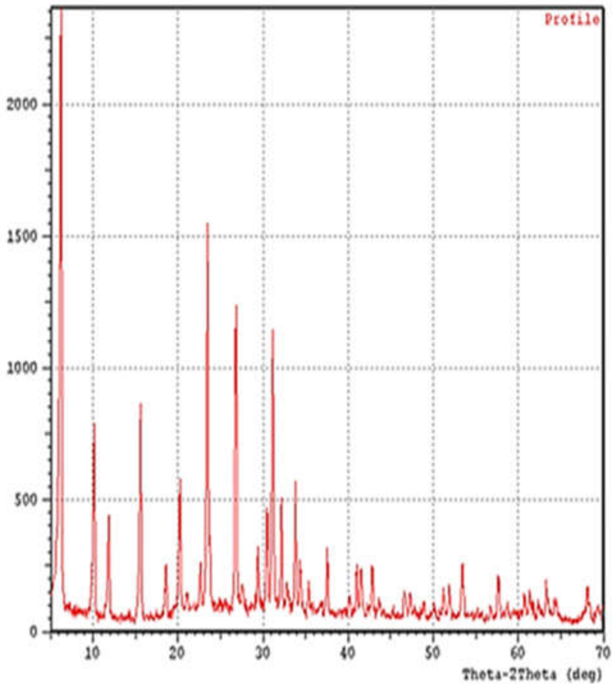

Figure 1: XRD analysis of 13X zeolite by XRD-6000 Shimadzu X-ray Diffractometer

2.2 *Fixed Bed Adsorption*

A schematic flow diagram of the experimental equipment, fixed bed adsorption unit, as shown in Fig. 2. It is consist of a glass column with jacket having an internal diameter 1.5 and 2.7 cm respectively with a length of 50 cm, it was packed with molecular sieve 13X adsorbent in the middle space of the column, surrounded from top and bottom with a small piece of glass wool and aplenty of 7 mm length 4mm inside diameter cylindrical glass tubes to support the bed and reduce the channeling and mal distribution of feed through the bed, also to protect (particles) of the adsorption bed from the mechanical force and attrition. The upper aperture of the column is suitable for packing or replacing the zeolite, also for temperature reading of effluent stream and the bottom end was connected with dosing pump for charging the fluid feed at a desired flow rate. 1 liter Separating funnel was used as naphtha storage. 250 ml conical flask receiver, many 10, 20, 50 ml of volumetric flasks for collecting treated naphtha samples. The standard method ISO 20884 (wave dispersive X-ray fluorescent spectrometer) was used to identified the total sulfur concentration

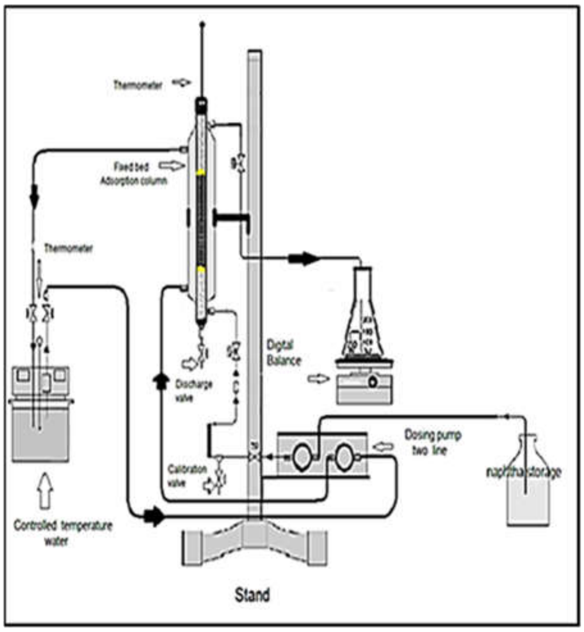

Figure 2: Schematic flow diagram of laboratory fixed bed adsorption unit

2.3 *Adsorption Procedure*

The behavior of molecular sieve type 13X in a fixed bed adsorber at different flow rates, bed weights, initial concentrations of sulfur compound and two temperatures was investigated to estimate the breakthrough curves. A known quantity of molecular sieve was activated by heating in electronic control furnace (Nabertherm) at 120 oC for two hours in order to remove the water of hydration, then must be cooled in a desiccator to avoid the humidity from the environmental during the storage.

The granules of Zeolite (13X) was packed by gentle tapping through adsorption column length to avoid or reduce the channeling and voidage, which affect the adsorption capacity of molecular sieves. The feed is pumped through adsorption bed at desired flow rate then the product was collected continuously at certain intervals of time and the concentration of adsorbate at each time interval was determined. The process was continued until the concentration of adsorbate in effluent stream reaches the concentration of influent, this means that the adsorbent is saturated

2.4 *Regeneration Procedure*

Regeneration took place at high temperature and air flow , inside a manufactured desorption tool had 20 gr spent catalyst (saturated catalyst) maximum capacity which was fixed inside the furnace .

3. RESULTS AND DISCUSION

Fixed bed column experiments was achieved in order to engender the data for gaining the breakthrough curves. The breakthrough time and the shape of the breakthrough curve are very significant characteristics for the determination of dynamic response of the adsorption column. The breakpoint is definite as the time of adsorption when the outlet concentration from the column was about 1-5% of the inlet concentration (14) . The effects of some important parameters was studied like 1.5–6 h-1 LHSV, 15–30 gr bed weight, 600–1650 ppm sulfur compounds initial concentration and temperature conditions at 25oC and 40oC, in a fixed bed column was studied . Also studying thermal regeneration with 200–350oC temperature,16.66 and 25 liter /min air in a simple tool designed for this purpose .

3.1 *Effect of LHSV*

The effect of liquid hourly space velocity on adsorption of sulfur compounds was investigated in the range of 1.5–6.0 h -1 as shown in Fig. 3, with 20 gr bed weight , 600 ppm initial sulfur concentration ,and 25oC temperature, the Figure shows increase in gradient of breakthrough curve with increasing the LHSV from (1.5 to 6.0 h-1),and it was explained by the fact that when the residence time of adsorbate in the fixed-bed is not long enough for the adsorption equilibrium to be reached at high flow rate, the contact time between the adsorbate and zeolite 13X bed was very short, results in a decrease in the removal efficiency. Another reason for the faster saturation of the bed at higher flow rates could be that with an increase in the flow rate, mixing increases and the thickness of the liquid film surrounding the zeolite particle decreases, which reduces the film transfer resistance and hence an increase in the mass transfer rate

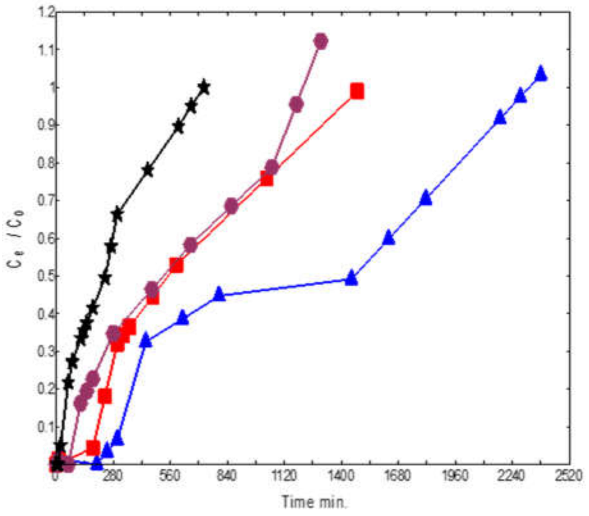

Figure 3 : Effect of LHSV on breakthrough curve for sulfur removal by using 20 gr 13X sorbent , 600 ppm (Co) initial sulfur content in naphtha and at 25o C, (▲)1.5 h-1 (■) 3.0 h-1 (⬢) 4.0 h-1 , (★) 6.0 h-^{1}

3.2 Effect of Bed Weight

The effect of bed weight on adsorption of sulfur compounds was investigated in the range from 15–30 gr as shown in Figure 4. The LHSV was fixed at 3.0 h-1, 600 ppm initial sulfur concentration and 25oC temperature. From Fig. 4, it can be observed that, when the bed weight increase, breakthrough time increase. The increase in bed weight leads to increase adsorption sites, which cause increasing in contact time between the adsorbate and adsorbent and lead to increase in the surface area available for adsorption and achieve complete saturation. So, the adsorption capacity increases by bed weight increase at constant flow rate

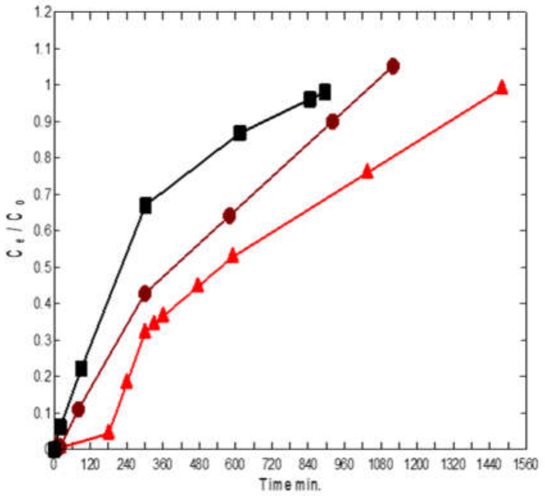

Figure 4: Effect of bed dosage (13X sorbent) on breakthrough curve for sulfur contaminate removal at 3.0 h-1 LHSV, 600 ppm initial concentration (Co) and 25o C, (▲) 20gr ,(■) 15 gr (⬢) 30 gr

This figure show that the shorter bed length leads to shorten the contact time, and is generally responsible for earlier breakpoint, because the bed depth is shorter than the required MTZ, which renders the system ineffective The best breakthrough time results that gotten was approximately 183.6 min at 20gr bed weight , 3.0 h-1 LHSV , 600 ppm sulfur compounds initial concentration and the same temperature 25oC.

3.3 *Effect of Initial Concentration*

The effect of inlet initial concentration on adsorption of sulfur compounds was investigated in the range of 600 – 1650 ppm. Fig. 5 shows the effect of inlet initial concentration on breakthrough time. The adsorbent bed weight was fixed at 20 g, 3.0 h -1 LHSV and 25 oC temperature

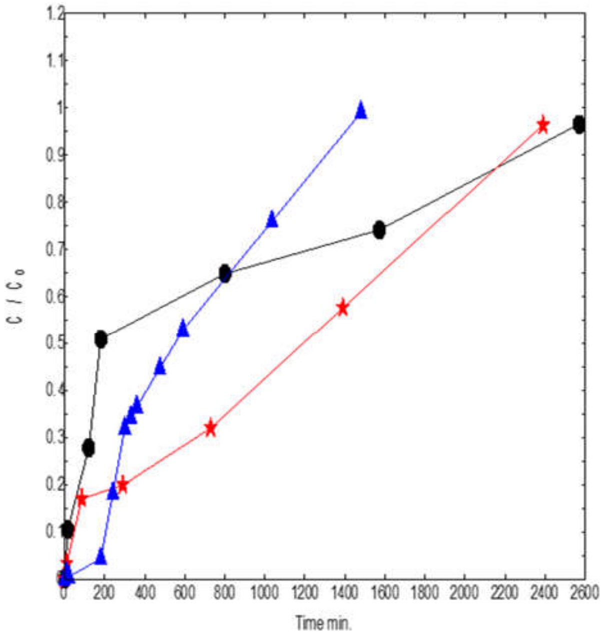

Figure 5: Effect of different initial concentration on breakthrough curve for sulfur contaminate removal at 3.0 h^{-1} LHSV , 20 gr 13X sorbent and 25^{o} C,(▲) 600 ppm ,(●) 1080 ppm, (★) 1650 ppm

Fig.5 shows that the increase in initial concentration causes a decrease in the breakthrough time and makes the breakthrough curves steeper. This is due to increase of driving force for mass transfer across the liquid film, and the adsorbent sites are quickly filled with the increase of adsorbate concentration. Hence increasing the adsorption rate leads to quick saturation of the adsorbent thereby decreasing the breakthrough time. Hence, the equilibrium is quickly attained. The initial concentration 600 ppm and 1650 ppm have breakthrough time 184 and 20 min, respectively , Also it shows that the bed replace point (operating limit point) for high sulfur concentration take time longer than the low concentration .

3.4 Effect of Temperature

The effect of temperature on adsorption of sulfur compounds was investigated at two different values 25 and 40oC. Fig.6 below shows the effect of temperature on breakthrough time with 20 gr bed weight , 600 ppm initial sulfur concentration in and 3.0 h-1 LHSV.

From Fig. 6 it was concluded that with an increase in temperature happen the rate of adsorption decreases, it is attributed to the exothermic nature of the process which is hampered with the rise in temperature. For this reason the decline in desulfurization has been observed, because the optimum temperature for Adsorptive desulfurization is room temperature 25 oC. It was clear from the breakthrough curves , the breakthrough time value in 25 and 40oC were 183.6 and 0.9 min , respectively .

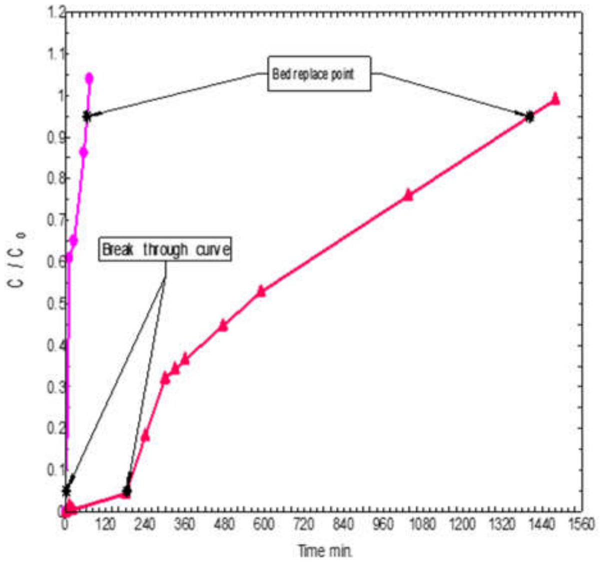

Figure 6 : Breakthrough curves of sulfur compounds in fixed-bed adsorber at 20 gr 13X sorbent ,3.0 h^{-1} LHSV, 600 ppm(C_o) sulfur content in naphtha, (▲) 25 °C, (●)40°C.

3.5 Oxidative Regeneration

Fig.7 shows the effect of temperature in the range from 200 – 350 oC and air flow rate of 16.66 and 25 liter /min on regeneration of 13X zeolite .

From Fig.7, desorbing had been accomplished through temperature swing. According to the kinetic theory of matter, the molecules gain kinetic energy when heated, and this allows a heated molecule to “fly” out of the well. This regeneration of the adsorbent should be done when the adsorbent has become unable to hold more, and must be done before the adsorbent can be used again (15).

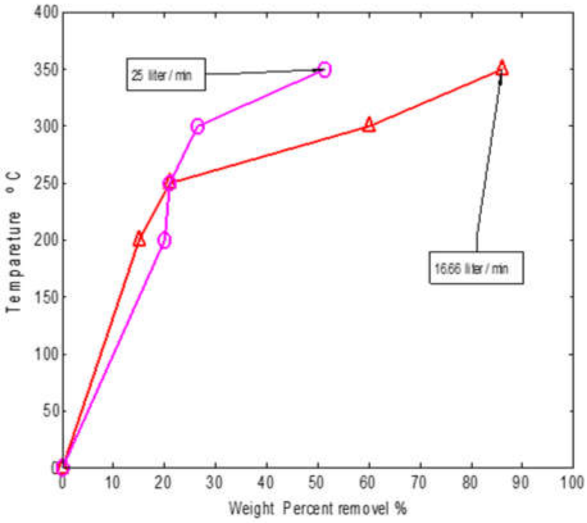

Figure 7 : Weight percent removal of different compounds from 13X adsorbent at different air flow and temperature

4. CONCULOSIONS

The breakthrough curves become steeper as the LHSV increases from 1.5 to 6.0 h -1 at constant bed weight, while the breakthrough time decreases from 274.29 to 21.73 min respectively. The breakthrough time was increased with the bed weight increase, while breakthrough curves become steeper and the breakthrough time decreased when the adsorbate inlet concentration increases. The breakthrough time and the mass transfer rate decreased with temperature increases. The maximum weight percentage of adsorbent removal in the regeneration process was obtained at 1 m3 /hr air flow and 350 oC.

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إزالة الكبريت بالامتزاز من النفثا العراقية الثقيلة بواسطة زيولايت X 13

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الخلاصة – أجري هذا العمل لدراسة تأثير الامتزاز الانتقائي على إزالة مركبات الكبريت من النفثا العراقية الثقيلة من مصفاة الدورة باستخدام المنخل الجزيئي (X13) في عمود ثابت ، تم تشغيله عند (1.5–6.0 h-1 LHSV)، 30-15 غم من المنخل الجزيئي (13X)، (1650-600) جزء بالمليون تركيز الكبريت في المواد الخام و درجة حرارة الامتزاز 25 و 40 درجة مئوية .

كانت أفضل ظروف التشغيل لإزالة مركبات الكبريت هي (3.0 LHSV h-1) و 20 غرام من وزن المنخل الجزيئي و 25 درجة مئوية، حيث تم تقليل محتوى الكبريت في النفثا الثقيلة من حوالي 600 جزء في المليون إلى أقل من 1 جزء في المليون (بالوزن). تم إجراء خطوات التجديد حراريا عن طريق تدفق الهواء الساخن في نطاق من 66,16 - 25 لتر / دقيقة ودرجة الحرارة تتراوح بين 200-350 درجة مئوية ، وكانت أفضل ظروف الامتزاز لإزالة (8,85٪) وزنا في المئة عند 66,16 لتر / دقيقة تدفق الهواء و 350 درجة مئوية.

الكلمات الرئيسية – الامتزاز، نافثا الثقيلة، منخل جزيئي 13, Xالحشوة الثابتة ، اعادة الفعالية.