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The Use of Locally Prepared Zeolite (Y) For the Removal of Hydrogen Sulfide from Iraqi Natural Gas.

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ABSTRACT

This work was conducted to study the ability of locally prepared Zeolite NaY for the reduction of sulfur compounds from Iraqi natural gas by a continuous mode adsorption unit. Zeolite Y was hydrothermally synthesized using abundant kaolin clay as aluminum precursor. Characterization was made using chemical analysis, XRD and BET surface area. Results of the adsorption experiments showed that zeolite Y is an active adsorbent for removal H_2S from natural gas and other gas streams. The effect of temperature was found inversely related to the removal efficiency. Increasing bed height was found to increase the removal efficiency at constant flow rate of natural gas. The adsorption capacity was evaluated and its maximum uptake was 5.345 mg H_2S/g zeolite.

Keywords: Natural gas sweetening, H_2S, Pressure swing Adsorption, Adsorption

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INTRODUCTION

Hydrogen sulfide gas and other sulfur compounds removal from natural gas and petroleum fractions is of crucial importance as being considered as highly pollutant materials having strong environmental impact. Hydrogen sulfide is a colorless, very poisonous, flammable gas with the smell of expired eggs. When combined with water it creates corrosive acid, causing holes corrosion and brittle cracking of metal due to hydrogen, which can cause the damage of the tanks or piping[1]. Many gas purification or, particularly desulfurization processes are adopted; chemical oxidation, catalytic combustion wet absorption and adsorption[2]. The latter technique is widely used at normal conditions and may be performed using different kinds of adsorbents, like activated carbon[3,4] alumina[5] and modified alumina[6,7] zinc oxide [8] zeolites[9,10], transition metal exchanged zeolites [11]modified bentonite [2] and magnetite- meso-porous silica composite [12] as adsorbents. Due to the low operating conditions and easy processibility, developments of ore efficient adsorbents are being actively pursued. However, high sulfur content in the natural gas stream from oil fields can be sweetened using the conventional Claus process [13].

Hydrogen sulfide is oxidized to SO_2which then reacts with two moles of Hydrogen sulfide to produce elemental sulfur. This process can work with multiple stages to reach the target. Also, a combination with a liquid redox process can improve sulfur recovery. One of the drawback of the process is the existence of SO_2 in the tail gas [14].

Zeolites , or the, Molecular sieves are porous solids with pores sizes of molecular dimensions, 0.3 – 2.0 nm in diameter. Structurally they are crystalline inorganic complex polymers based on an infinitely extending three dimensional, four – connected framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing oxygen ions. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by an extra - framework cation. The most common types are: the low silica type represented by zeolites A and X which are rich in aluminum (saturated), have the highest cation concentration and give optimum adsorption properties in terms of capacity, pore size and three - dimensional channel systems. They represent highly heterogeneous surfaces with a strongly water loving or hydrophilic surface selectivity. The intermediate type (Si/Al range 2-5) consists of the natural zeolites like, mordenite ,chabazite, and, clinoptilolite and the synthetic zeolite Y. Zeolites turn hydrophobic as Si/Al increases. The third type is the high silica to alumina ratio in the range of 10-100 like ZSM-5 and Beta. The latter group is characterized by high hydrophobicity. Therefore, the low and intermediate types can carry out separation processes on dry streams [15]. The feasibility of removing such gases from natural gas using the aforementioned adsorbents is widely investigated [1]. Cui et al [16] studied the removal of many sulfur compounds present in synthetic natural gas. They used commercial activated carbon modified by oxidation and impregnation for loading with some metals. It was concluded that copper and zinc loaded on activated carbon had the highest adsorption capacity for hydrogen sulfide removal. Wolff et al [17] used zeolite X and MOF's and concluded that they can be considered as excellent materials for sweetening and purification. The adsorption capacity was superior to commercial zeolite NaX. Cosoli et al [18[concluded that Zeolite NaY was the best adsorbent for this duty among NaX, dealumined MFI and LTA (Linde type A zeolite) using their simulation technique. Shawabkeh and Harahsheh [19] used local Jordanian oil shale ash to adsorb H_2S from untreated liquefied petroleum gas. They described the process as efficient, safe and economical. The adsorption of H_2S on zeolite X and Y was discussed by Gaillard et al [20] using combination of Infrared and NMR spectroscopy, a modification of the surface of zeolite Y is found. This is due to that a small amount of H_2S is adsorbed dissociatively and on increasing the amount in the pores, the adsorption became non-dissociative either by direct coordination to Na^+ or bridging with OH^{-1} group. By comparison with past studies on zeolite X, only dissociation adsorption of H_2S occurred. Earlier, Yasyerli et al [9] investigated the adsorption capacity on clinoptilolite using a gas mixture of H_2S 1.06% and at high temperature of 100-600 ^{o}C. They found that it was about 0.03 S/g at 600°C. Many gas purification processes can be done in a continuous manner as the use of pressure swing adsorption (PSA) where continuous adsorption/desorption mechanism occurs so that the adsorbent could be regenerated by reducing pressure after the breakthrough time. Zhou et al [1] proved that this process is feasible for removing H_2S from a simulated natural gas of 1340ppm H_2S using coated silica gel.

In this study, zeolite NaY is prepared using kaolin clay which contains basically of oxides of alumina and silica and is considered as a low cost silica -alumina source. The prepared zeolite is characterized using XRD, XRF, and surface area by nitrogen adsorption- Desorption Technique. The activity of the prepared zeolite

Y was investigated using gas purification unit which was constructed for this reason. H_2S content was tested in the outlet stream of natural gas using special gas detector.

Sweetening natural gas study is normally made using simulated gas by mixing pure methane gas with pure H_2S gas prepared from a certain chemical reaction. Also, found in literature a similar studies on biogas but this study is subjected on a real natural gas from Iraqi refineries having different sulfur compounds like sulfides and mercaptans in addition to H_2S, which can interfere the adsorption to some extent.

MATERIALS AND METHODS

Kaolin clay (SiO_2 50%, Al_2O_3 39%, Fe_2O_3 1.4%)was supplied by the Geological Research and Mining Company. Natural gas was supplied by the Al-Taji company. Na_2SiO_3 (99%) was purchased from local markets.

Preparation of Zeolite Y

Kaolin clay was sieved by 75 µm standard sieve, mixed with NaOH solution of 45wt% with weight ratio of kaolin/ NaOH 1/1.5, fused at 850 ^oC for 3h. 60 g of the treated kaolin was mixed with 72 g of sodium silicate and dispersed in 900ml of deionized water in a batch reactor. The mixture was heated to 60 ^oC for 1 h using controlled magnetic stirrer (type Labinco, Holland). Then the hot mixture was poured into sealed glass jar, and subjected to ageing at 50^oC for 24 h, in a programmed electrical furnace. Then the gel slurry was set for hydrothermal crystallization at 100^oC for 48 h. Two phase separation was obtained and precipitate was filtered, washed several times to pH of 11.5. The crystalline precipitate was dried at 100^oC for 16 h and calcined at 500^oC for one hour [21,22,23].

The prepared zeolite was characterized by XRD test (Shimadzu, Japan XRD-6000). Chemical composition was made using Atomic Absorption spectrophotometer (type GBC SensAA). Shaping of the powder into extrudates was made with diameter of 2mm and length of 4-8mm.

Laboratory continuous PSA Adsorption/Desorption unit

The activity experiments for the prepared Y- zeolite adsorbent were conducted in a laboratory continuous PSA unit. Figure (1) shows the schematic diagram of this unit. This unit consists of unsweetened natural gas (UNG) cylinder, N_2 cylinder zeolite 3A absorption beds, flow meters, H_2S gas detector, vacuum gauge, needle valve, vacuum pump and an appropriate heating system. PSA bed was heated and controlled automatically with PID controller using thermocouple (type k). The inlet and outlet temperatures of the bed were measured to ensure an isothermal operation. The needle valve was used to control the pressure inside the PSA unit and the vacuum pump was used to regenerate the activity of the adsorbent at the end of each experiment.

Activity Experiments

For each run, a specified amount of Y- zeolite adsorbent was charged in the PAS bed (2.54cm ID.) between two perforated layers of thermal Teflon (20 holes of 1mm ID). In the beginning, the bed was flashed with nitrogen 0.3 l/h for 1 h to purge the air from the system, then the adsorption/desorption (A/D) bed is heated to the desired temperature. The heater was place at the top of the A/D column. Two temperature sensors type K were place before and after the adsorbent bed in order insure isothermal operation. When A/D bed temperature is reached, the nitrogen valve is closed. A pre-specified flow rate of UNG was set on after removing the moisture in the zeolite 3A bed. UNG entered the reactor from the top, heated to the desired temperature and distributed uniformly on the adsorbent bed. The outlet SNG passed to the H_2S gas detector to measure the concentration of H_2S.

The activity tests conditions employed are temperature range 25 and 50^oC, bed height of 2,4,and 6 cm, adsorption time up to 10 hr, at a constant gas flow rate range of 1.5 lit/min and bed pressure of 6 bar.

At the end of each experiment the UNG gas stream was switched off and the vacuum line was set on to PSA column to regenerate the adsorbent bed by Desorption mechanism to remove the adsorbed H_2S. The vacuum pressure was adjusted by vacuum gauge and the desorption cycle continuous for (30) minutes.

RESULTS AND DISCUSSION

Zeolite Characterization

Zeolite NaY was synthesized through a custom hydrothermal method. It can be observed that the FAU type zeolite is obtained. The characteristic peaks of this type are distinguished as the values of the angle of Bragg, 2θ, 6.1, 10.148,15.6and 23.478. XRD results are given in Table (1). Htay and Mya Oo[24] concluded in their study of the factors affecting the preparation of zeolite Y that the aging time is close related to the SiO_2 / Al_2O_3 ratio in the range studied of 2.64-3.3 and a time beyond 2 days could decrease this ratio in the product zeolite. Also the presence of zeolite P was dominated in all the samples even at those having high ratio of 3.3. In this study, the chemical analysis of the prepared zeolite revealed that the SiO_2 / Al_2O_3 ratio is 2.7. This value could be considered low comparing to the zeolite produced from pure precursors. Also, the participation of zeolite P and/or X in the crystallization step could decrease the yield of zeolite Y [25]. Dubey et al[26] used zeolite Y, which had a silica to alumina of 2.5 as a support in the design of certain photocatalyst and was successful.
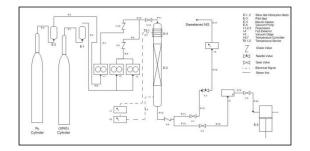

Fig. 1 Laboratory PSA Gas Purification Unit

Table (1) XRD standard Peaks

Peak no.	2theta(deg) Standard	2theta (deg)Prepared	Intensity
1	6.1	6.29	100
2	10.148	10.109	34
3	15.518	15.545	32
4	23.478	23.412	46

The BET and Langmuir surface area were 157 and 228 m^2/g respectively while the measured pore volume was 0.15cm^3/g and pore size was 38.3381A^o implying that a micro/meso- porous material had been synthesized.

Desulfurization Experiments

Effluent concentration

The ability of the prepared zeolite Y to adsorb H_2S from natural gas can be observed in Fig (2) and Fig (3). The concentration of the effluent gas is plotted against the time duration of the cycle. It can be seen from Fig (2) that the concentration is decreasing until reaching C/C_0=0 (i.e.100% removal efficiency) at the end of the cycle. Investigation at different bed heights of 2,4 and 6 cm had the same rate of decreasing in the concentration. The time needed for complete removal using bed height of 6 , 4, and 2cm was 4,2,and 1 h which reveals that as the bed height is increased, the time for reaching complete removal of H_2S and purification of the feed natural gas is increased. This decrease can be explained by that the increase of bed height implies the increase of the zeolite loading. Therefore, the increase of the adsorbent offers extra empty sites for guest molecules. Also, the bed of the lowest height possesses fast bed saturation.
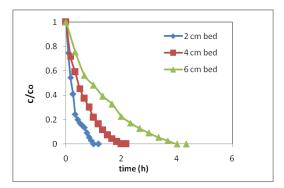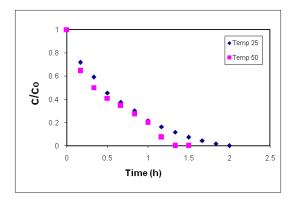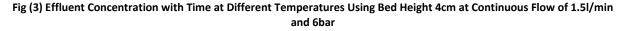
Fig (2) Effluent Concentration with Time for Different Bed Heights at 25°C at Continuous Flow of 1.5l/min and 6 bar

The effect of temperature on the adsorption of H_2S on zeolite NaY using two different temperatures (25 and 50°C) was studied. The results are in Fig (3). In this figure, it is obvious that at both temperatures, there is quick uptake of the pollutant gas but at 25°C it is faster reaching the point of zero effluent concentration after 1.5h, whereas at 50°C, the concentration drops to zero after 2 h. This can be explained by that the adsorption processes are best performed at low temperature when the physical adsorption is taking place. This can be true when considering that many studies are found in literature which use the pressure swing adsorption so that there is continuous adsorption- adsorption cycles for regeneration the adsorbent in a simple strategy adopted for gas purification technologies as done by Zhou et al[1]. Seol-Hee Lim et al [12] studied a simulated gas of methylmercaptan/methane gas and got the same conclusion for temperatures of 25, 50,100 °C.

In fact regeneration depends on the concentration of the pollutant as well as the interactions and the affinity of the adsorbent to adsorbate.

In the PSA, a reduction in pressure is subjected to the adsorber or the bed of adsorbent and as the molecular weight gets higher, an inert gas is introduced to the bed to release the adsorbed species and empties the pores so that to accept new guest molecules in a new cycle[27].

Fig (3) Effluent Concentration with Time at Different Temperatures Using Bed Height 4cm at Continuous Flow of 1.5l/min and 6bar

Breakthrough curves

Effect of Bed height

Breakthrough curves are plotted at the three bed height using a constant flow rate of the natural gas, and are shown in Fig(4). These curves also, are known as pilot testing. Break though time can be defined as the time when H_2S is appeared in the effluent gas. This time can be designed according to maximum allowable concentration of the pollutant and means that the saturation of the bed starts, and the regeneration cycle should be switched on in an industrial scale. The idealized breakthrough curve is shown in Fig(5) and the movement of the mass transfer zone (MTZ) through the bed is shown in Fig(6).

Fig (4) shows that the bed has breakthrough point of higher than 1,3,5 h using bed height of 2,4 and 6cm respectively. These times reflect the ability of zeolite Y to maintain continues clean effluent flow of natural gas.
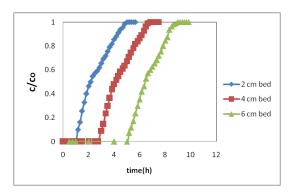

Fig (4) Breakthrough Curves Using Different Bed Heights at Temperature 25ºC at Continuous Flow of 1.5l/min and 6Bar.
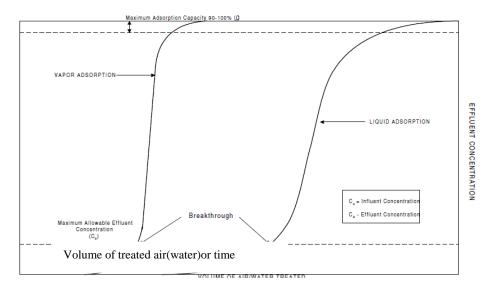

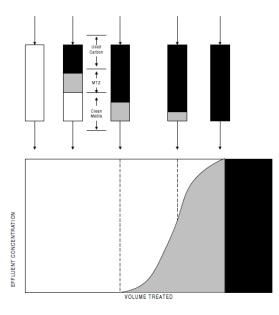**Fig (5) The Idealized Breakthrough Curve[27]**
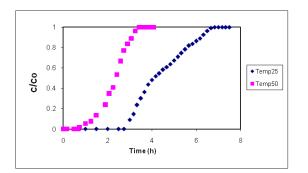

Fig (6) Mass Transfer Zone.

Fig (7) Breakthrough Curves Using Bed Height 4cm and Different Temperatures at Continuous Flow of 1.5 lit/min and 6Bar.

Effect of temperature

Breakthrough curves at temperature of 50°C reveal a faster saturation of the bed It can be seen from Fig (7) that the bed stayed 45 min before the pollutant appeared again in the effluent gas. While working with the same bed height of 4cm but at 25°C the bed maintains 3 h with zero ppm. Therefore, it is concluded that the breakthrough point was higher using lower temperature.

Zeolite Capacity (ZC)

The Zeolite capacity for H_2S uptake (ZC) can be evaluated using Eq.1.[16] Results can be found in Table(2).

$$ZC = ((Q_v)(t)(C_o)(34)/(22.4(m_z)x1000) \qquad \textbf{...(1)}$$

If the complete cycle of operation(5,7,9h) is considered in calculation then ZC is found 2.969, 4.157, and 5.345 mg/g zeolite, using bed height of 2, 4, and 6cm at 25°C. The aforementioned bed heights correspond to 8.9, 25.3 and 40.5 g of the prepared zeolite. On considering the bed breakthrough points(1,3,5,h), these values of the adsorption capacities are 0.594, 1.782 and, 2.969 mg/g zeolite.

Referring these values to the work of Cui et al [16] for the ZC for H_2S for comparison; they concluded that modified activated carbon is better that virgin AC, where ZC using $CuSO_4$ modified activated carbon was for H_2S 0.17mg/g and was 4.8mg/g using HNO_3 modified activated carbon for total sulfur compounds including tetra hydro-thiophene which was added as odorant.
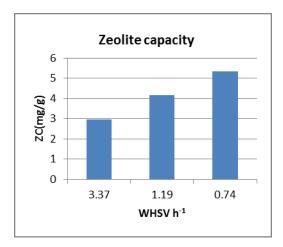
Table (2) Zeolite Adsorption Capacity for the Full Cycle

wt g	WHSV h^{-1}	ZC(mg/g)
8.9	3.37	2.9697
25.3	1.19	4.157
40.5	0.74	5.345

These results are in good agreement with the information in literature for zeolites have higher affinity for H_2S gas and considered as selective adsorbents and as concluded in the example above that the higher surface area of activated carbon did not enhance the function of the adsorbent unless modified by coating or impregnation methods.

Therefore, and referring to Fig(8),zeolite adsorption capacity toward H_2S is found to increase as the WHSV is decreased. As high is the catalyst loading or less is the mass flow rate will the reasons behind increasing the uptake of the pollutant gas offering extra host sites and higher residence time of the guest gas.

Fig(8) Zeolite adsorption capacity at different WHSV

Gas sweetening by adsorption is studied on different adsorbents. Some of these studies are listed in Table (3) for comparison.

Table (3) Comparison with Previous Studies

Feed	Adsorbent	Capacity g/g sorbent	Reference
H_2S 1.06%in Helium 100-600°C	Clinoptilolite	0.083 g/g sorbent	Yasyerli et al. 2002[9]
1340ppm +pure CH_4	NMP coated silica gel	0.175mg/g	Zhou et al 2004[1]
LPG, H_2S 467ppm syringe injection	Oil shale	30mg/L(LPG).g sorbent	Shawabkeh and Harahsheh 2007[19]
Exp. and Simulation study	NaY	5 kg/mol	Cosoli et al 2008a[31]
Synthetic NG (9.9ppm max sulfur compounds)	AC-$CuSO_4$	0.17mg/g sorbent	Cui et al 2009[16]
Mixture (H_2S+N_2)	Bentonite Fe-Bentonite Cu-Bentonite	12.7mg/g sorbent 39.2 mg/g 15.1 mg/g	Stepova et al 2009[2]
Simulated gas(200ppm)	Activated coke	0.03g/g sorbent	Yoshinori et al (2009)[32]
H_2S 20ppm(Batch mode) 100-600°C	Zsm5 Zeolite A	300 μL/sorbent 450μL/sorbent	Kishida et al 2011[33]
Mixture (10% H_2S+CO_2)	Red mud	8.3mg/g	Huynh et al 2012[34]
Real NG(115ppm)	Prepared NaY	5.345mg/g	Present study

The adsorption capacity in the study can be considered of acceptable value compared to the past studies whereas working on a real fuel gas from oil fields is quite different than synthetic mixture of gases. A real natural gas contains extra sulfur compounds of mercaptanes and sulfides and similar compounds which can poison the adsorbent surface. Also, the presence of higher hydrocarbons can definitely interfere the adsorption of H_2S. Competitive adsorption on the surface of zeolite is expected between sulfur compounds from a side and between methane and H_2S from other side. H_2S is superior having the smallest molecular weight between all. Traces of water vapor (if present) after the drying step with zeolite 3A could reduce the uptake of H_2S to some extent.

Pressure drop

Packed bed pressure drop due to the resistance found by the narrow paths through the adsorbent bed is related to the permeability or the porosity of the bed. In the case presented by this study, the pressure drop is calculated using Eq. (2)[28]:

$$\Delta p = \frac{150\mu\ L\ vs(1-\varepsilon)2}{Dp\ \varepsilon^3} + \frac{1.75\ L\ \rho\ vs^2\ (1-\varepsilon)}{D_p\ \varepsilon^3} - - \qquad ---(2)$$

Where the superficial velocity was 0.05m/s, D_p was 3.3 mm and ε=0.35. Therefore, Δp/L was calculated and found equal to 254Pa or (12700-4233Pa/m). By comparing these findings with past studies, it was concluded that only the bed height of 6cm was in good agreement to typical acceptable values (2470-4490Pa/m)[29]. Pressure drop could be affected by many parameters like, particle size distribution, shape, ratio of bed diameter to particle diameter (D/Dp) and bed height.

Ribeiro et al [30] stated that (D/Dp) ranges between 2-17 and is inversely proportional to the average bed porosity. So, in the present study, the ratio of D/D_p was 7.7 revealing good distribution and moderate wall contribution as it falls within the range.

CONCLUSIONS

The removal of hydrogen sulfide is investigated using zeolite Y, prepared from locally available kaolin clay and was converted successfully to synthetic zeolite by careful adjustment of silica to alumina ratio and thermal treatment.

Gas purification setup was constructed for this purpose with a continuous flow of natural gas. Zeolite Y proved to function quite well as found to produce clean effluent of natural gas using bed heights of 2, 4, 6cm and at 25 and 50°C at continuous flow of 1.5 lit/min and 6 bar.

The highest duration for complete gas purification cycle was 5 hours using 6cm at 25°C. At the same operating conditions, the maximum adsorption capacity was 5.345mg/g of the synthetic zeolite. Sweetening of real natural gas by PSA process is considered efficient for promising prospects.

ACKNOWLEDGMENT

Nomenclature

C_o initial concentration (ppm)
D   Column diameter
D_p Particle diameter
L   Bed height
LPG Liquefied petroleum gas
m_z mass of zeolite (g)
Qv   volumetric flow rate of natural gas
t   time (min)
v_s Superficial velocity
ZC   Capacity of zeolite mg/g
Greek
μ Viscosity
Δp Pressure drop
ε Bed voidage
ρ Density

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