

## Ultra-sound assisted nano Y- zeolite /Mn adsorbent to removed sulfur from crude oil

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**Abstract:** There are some types of crude oil that contains large quantities of various sulfur compounds that have great harm on the environment, oil economy, oil sector facilities such as fields and refineries. So developing ways to get rid of it is one of the most important goals of researchers in this sector. In this study, nanotechnology was used for environmentally friendly and available industrial materials (nano-zeolite Y), which can adsorb sulfur from crude oil, especially when it impregnated with manganese metals with ultrasound to increase the adsorption efficiency. The effect (temperature, adsorbent dose, Samples PH) was studied with ultrasound and without ultrasound. On the efficiency of removal had best results with ultrasound and it was found that this material is highly efficient in removing sulfur compounds, especially at a temperature of 100 C°, and at a dose of 13 g, and PH 7 it found the best adsorption efficiency about 99 %. The change in the properties of the adsorbent material is almost non-existent, with a change in the surface area and pore size.

**Keywords:** Ultra-sound, zeolite, sulfur, crude oil

### 1. Introduction

In many oil fields in the world oil extracted contains very high levels of sulfur with its various simple and complex compounds such as mercaptans, sulfates, and multiple sulfates which are the most complex and decomposing. Both these simple and complex compounds have a major impact on various fields. Therefore, it is of great importance to get rid of the various sulfur compounds (simple and complex) from crude oil and its derivatives (such as gasoline, diesel and LPG) because of the danger it poses to these fluids. Where sulfur compounds are burned in the fuel, toxic and sulfur oxide gases will be generated. Where when interacting with water in the atmosphere will be sulfate and acid rain that causes damage to buildings and the death of fish resources in lakes and rivers and acidification of the soil which in turn leads to great damage in nature in general and in plants in particular. The emission of sulfate gases has a major impact on human health as it causes respiratory diseases, heart diseases and asthma [1]. On the industrial level, the presence of sulfur in crude oil causes corrosion for tanks, pipes and pumps as well as refining columns in refineries [2]. On the economic level of crude oil, there is a big role for the percentage of sulfur it contains. When it decreases it leads to higher prices and vice versa [3]. Therefore, West Texas Intermediate and Brent Crude are the main international standard for crude oil in the world because they contain the least quantities of sulfur [4]. International regulations have determined the acceptable percentage of sulfur in crude oil varies from less than 0.05 wt.% to more than 14 wt.% depending on the source of crude oil [5]. And the sulfur content in transportation fuels such as gasoline and white oil should be less than 10 ppm according to environmental regulations [6]. For the reasons mentioned above, the processes of removing sulfur from crude oil is one of the most important issues for the petroleum sector. So there are many ways to remove sulfur compounds from crude oil including - Hydrosulfuration (HDS) method. It is a chemical process used to remove sulfur from crude oil and its derivatives using the hydrogenation method and applied to natural gas and refined oil derivatives such as kerosene and diesel fuel. It has many difficult requirements for use including the pressure should be about (60-100 bar) and the temperature around (250-350) C° [7]. Oxidative desulfurization (ODS) if the compounds containing the aromatic sulfur are oxidized to their analog sulfate and have been confirmed as one of the effective desulfurization processes. (Tahseen and Asaad 2019) they concluded that the use of ultrasound in the desulfurization process has proven successful and has produced a high desulfurization efficiency from crude oil [8]. Bio desulfurization (BDS) this technology is based on bacteria where bacteria remove organic sulfur from oily fractures without destroying the organic carbon structure of the compounds [9]. The efficiency of the process of removing sulfur by extracting with solvents has been studied with different solvents that were used such as acetonitrile, acetone and methanol. After 30 minutes' sulfur content was measured in the crude oil model where acetonitrile showed high efficiency in extracting sulfur compounds compared to acetone and methanol where the removal efficiency was 28.5% and by Mixing 3: 1 solvent/oil [10]. These methods are effective in removing alpha-sulfur compounds such as sulfates but they are ineffective in

removing aromatic sulfur compounds such as thiophene derivatives[11].Therefore,more effective methods must be devised to remove these compounds, and accordingly, some absorbing materials have been explored to remove sulfurspecifically zeolitewhich is environmentally friendly and also widely available and cheapas selectivity and good adsorption capacity. To enhance this selectivity, the zeolite material is supplied with the introduction of selective metals such as (Pd,Mn, Zn, Ni, Cu, Ce) it is reported that the process of removing sulfur from crude oil using zeolite and adsorbed minerals is carried out using an exchange or impregnation method. In this regard, Yanget al. (2003) Mentioned that the (AgY) zeolite obtained by ion exchange is able and with high selectivity to adsorb sulfur compounds at high pressureand temperature conditions [12]. While song et al. (2003)mentioned that (CeY)zeolite has proven its ability to remove complex sulfur compounds with high efficiency[13]. Chenet al. (2009) proved that zeolite impregnated with  $\text{Cu}^+$  was highly susceptible to removing thiophene sulfur compounds compared to zeolite impregnated with  $\text{Ag}^+$ . This study also demonstrated that the adsorbent  $\text{AgNo}_2 / \text{MCM}_41$  is highly efficient in removing sulfur compounds from JP\_5 Jet fuel (1172PPmws).[14]. We conclude from this that the presence of aromatic and alpha-sulfur substances in sulfur reduces the efficiency of the desulfurization process. In this regard, Sulfur adsorption was studied by Hua Song et al. (2015) for a sample of gasoline containing certain proportions of thermal sulfur compounds (thiophene and benzothiophene) by the intermediate material zeolite  $\text{Cu}(\text{II})\_Y$  and  $\text{Cu}(\text{IV})\_Y$  and the result of this study was that there is a high ability of these materials to remove sulfur compounds with high efficiency and high selectivity from gasoline [15]. Also, zeolite has good sulfur that contains capacitygood regeneration and stable structure.The adsorption process is the best separation process for sulfur from crude oil compared to other methods[16]. In our study, we usedNano zeolite type Y to extract sulfur from crude oil and by using Manganese ions to enhance the adsorption process for zeolite with using nanotechnologyand ultrasound as an alternative energy source.

## 2. Experimental Work

### 2.1-Material and Equipments

Fifteen samples of crude oil (100 ml / sample) was provided from Baba Gurgur oil field in the north of Iraq with it Properties in table 1, Synthetic Nano Zeolite (type Y) from CECA ARKEMA Group, Manganese (II)nitrate hydrate from the ALDRICH-United Kingdom, Ultrasound Device was purchased from Hans-Ulrich PetermannBeratungs, Germanywith power about 400watt and frequency about 24 kHz. Thermoshaker device from Heidolph with a speed of 1400 rpm and Temperature of 300 C°, Electrical oven with a temperature of 1000C, Magnetic stirrer –German with a speed of 1500 rpm.

Table(1). Properties of crude oil samples

Item	Measurement	Unit of
Measurement	Results	
1	Water	cut
	%Trace	
2	Salt	PPM13
3	Sulfur	%1.9
4	API@60F	35
5	Density @15 C°	Gm/cm <sup>3</sup> 0.849

### 2.2-Procedure

#### 2.2.1-Adsorbent Preparation.

Firstly, we got a Beaker with 1000 ml and we added 60 grams of Nano zeolite Y to it. After that, we added 666.36 ml of Manganese Nitrate Solution  $\text{Mn}(\text{NO}_3)_2$  [5M] for the impregnated percentage of 10%. After that, we shake the Solution in Beaker for 3 hours in Temperature of 70 C° until the Nano zeolite absorbed fully by using an ultrasound device. The next step we did was washed the Adsorbed Nano zeolite Y with distilled water to remove the impurities and ions that stuck to it. After the washing process, we dried the washed Nano zeolite in the oven in Temperature of 25 C° and increase it until 100 C° for 4 hours.After the

drying process finished we started in the Calcination Process which is a thermal treatment process for Nano zeolite Y with air or Oxygen to remove the volatile practicals from it. The process was done by putting the Nano zeolite in the oven in Temperature of 500 C° for 3 hours. After the Calcination Process has done Sample of Nano zeolite Y became ready for testing on crude oil sample by Batch Experiment Paragraph[17].

### 2.2.2-Characterization of adsorbents

Nanomaterials have a high relative area (area/volume), so its surface area was calculated using the BET method by Nitrogen impregnation at 77K and relative pressure ( $P / P_0$ ) about 0.95 and the results were about 630.31 m<sup>2</sup>/g surface area and 14.37 nm<sup>3</sup> pore volume and 2 nm pore radius. The samples were ground and each sample was placed on a silicon-carrying zero surface. Reflection data obtained using a diffractometer XRD\_7000 with copper K<sub>α</sub> as a radioactive source with operating conditions of 40 mA and 40 kV. The scanning speed was within 0.04 / 0.25 s Within (5°\_75°).

### 2.2.3-Batch Experiments

A fixed amount of the crude oil sample was mixed with an amount of about (100 ml) with different quantities of Nano zeolite Y saturated with manganese minerals as shown in the table (2) with changing working conditions (PH, Time, Temperature, Dose) each time and several attempts. Mixing was done by a mixer device. The mixture was stirred with heat using

the Thermostat shaker device and ultrasound device. After the mixing step and the homogeneity of the mixture by heat, we separated the adsorbents that must be sulfur-bearing after the adsorption process ends with Nanofiltration paper to be isolated from the crude oil that must be sulfur-free or contain a very small percentage of it. Measurement of sulfur content in the samples was made by SPECTROSCAN SW-D3 "WDX."

Run No.	Variables	Constants
1 2 3 4 5	<u>Dosage</u> 5 g 7 g 9 g 11 g 13 g	Temp.:90°C Time:3 hr. (2hr.with ultrasound+1hr. without ultrasound) PH:7
6 7 8 9 10	<u>PH</u> 5 6 7 8 10	Dosage:13 g Time:3 hr. (2hr. with ultrasound+1hr.without ultrasound) Temp.:90°C
11 12 13 14 15	<u>Temp. °C</u> 60 70 80 90 100	Dosage:13 g Time:3 hr. (2hr. with ultrasound+1hr.without ultrasound) PH:7

## 3. Result and discussion

### 3.1-Adsorbent characterization

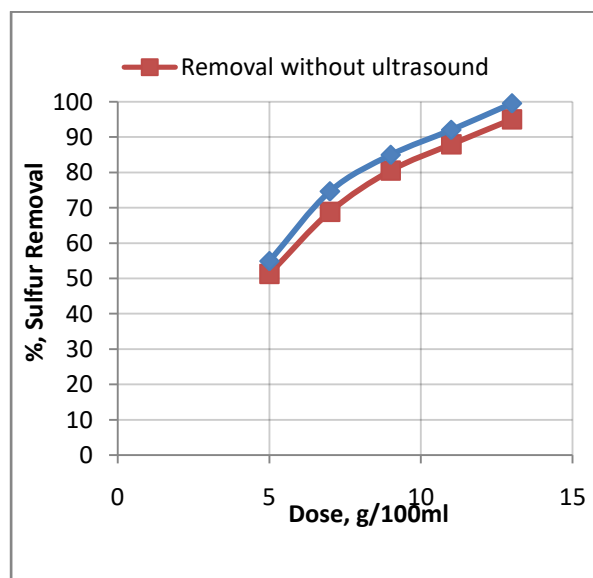
Through XDR tests, it was observed that the change in the structure of zeolite is almost non-existent and is only a very slight change caused by impregnation of chemical metals during the ion exchange process, which led to an increase in the ratio of (silicon/aluminum) in the composition of zeolite from 3.22 to 3.24 that mean increase of Silicon amount and it led to change catalytic active sites, this the aim of change (silicone/aluminum) ratio [18]. Multiple BET checks of adsorbent samples adsorbed by nitrogen adsorption N<sub>2</sub> and condensation inside pores showed that the surface area increased from its initial pre-adsorption value of 630.31 m<sup>2</sup>/g to its new value after adsorption of 681.42 m<sup>2</sup>/g and it was also found that the volume of pores after the adsorption process increased its value from 14.37 nm<sup>3</sup> to 16.84 nm<sup>3</sup>. The reason for the increase in both the surface area and the size of the pores is due to the impregnation it with metals [19], but after 950 C° as (Termal et al 2012) mentioned a decrease in pore volume and surface area when the temperature increase from 1176 C° to 1376 C° due to shattering walls of the pores due to the effect of increasing the temperature during the process [20].

### 3.2-Dose effect

The results showed that increasing the dose amount of the adsorbed materials in the crude oil sample increases the efficiency of adsorption and removing sulfur directly, as shown in Figure (1) without using ultrasound the best results at the high amount of dose 88% and 95.1% at 11 g and 13 g respectively. The best results with using ultrasound were 92.1 % and 99.6 % at 11 g and 13 g respectively. The reason for the increase in adsorption capacity and the decrease in sulfur amount when increasing the adsorbent dose is the decrease in concentration of sulfur, as the relationship between them and the adsorption dose is inverse, as shown in the following relationship.

$$\text{Adsorption amount} = (\text{initial Conc.} - \text{final Conc.}) \times (\text{volume} / \text{Adsorbent mass})$$

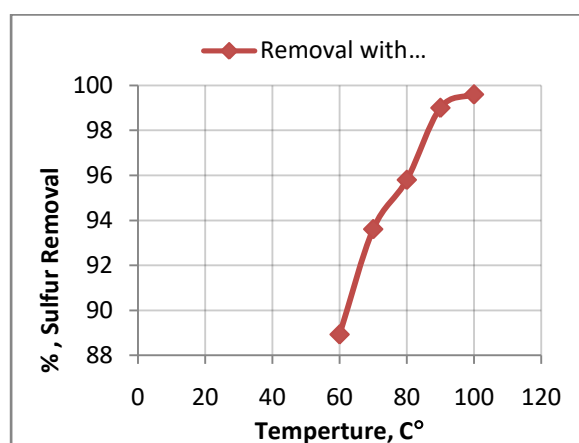
Furth more increased adsorption efficiency is increased accessibility to more surface binding sites when increasing the adsorption dose[21]. The reason for increase removal efficiency with using ultrasound as a thermal source is due to increase the temperature and pressure in a short duration compare with conventional thermal sources[22].Whereby doubling the dose amount by half of its initial value, the adsorption and desulfurization efficiency will increase by about 30%, in addition to the percentage of the initial removal. And experiments showed that the use of the ultrasound device in the process of mixing and homogenizing the samples has a noticeable effect in increasing the removal rate.



**Figure (1)** Effect of adsorbents dose on the Removal Efficiency of sulfur components (T:90 C° and PH:7)

### 3.3-Temperature effect

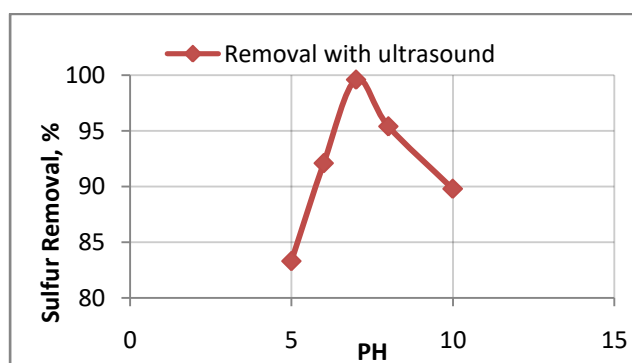
The results showed ,the increase in temperature has a direct effect on increasing the sulfur adsorption rate by adsorbents from crude oil. Best removal efficiency results we obtained it was 99.6 % and 99.64% at 90 C° and 100 C° respectively. This is due to the increased rate of the chemical reaction between the solute (zeolite) and the solvent (sulfur in oil) that will cause changes in the adsorption sites and enhances their activities. Furthermore, when the temperature increases the favorable intermolecular forces between the adsorbents are much stronger than those between adsorbent and solvent. As a result, the temperature increasing causes adsorbent to be easier to adsorb [23]. The higher the temperature the viscosity of crude oil decrease and sulfur rings will molecule into smaller rings then simple compounds were formed then these rings are easily broken, making the removal efficiency high[24].as (Basfar et al 2012) reported that DBT converted to H<sub>2</sub>S at high temperature [25].while(Yu Zhao et al 2013) reported the reason of increase removal efficiency when temperature increased due to decrease of sulfur solubility and that made its removal easy.Also at high-temperature crude oil viscosity decrease and its molecule's speed was increase and contact time between crude oil molecules and sulfur molecules was decrease too[26].



**Figure (2)**Effect of Temperature on the Removal of sulfur components (Dose:13g and PH:7)

### 3.4-PH effect

Through the results, it was found that the pH value of the crude oil samples below 7 affected directly by the removal and adsorption of sulfur compounds, where when the pH (from 1-7) increased, the removal rate increased significantly, as in Figure (3). The best result was 99.6 % at PH 7. The reason for this is that complex sulfur compounds break up into simple sulfur compounds such as sulfide [27]. Also for PH values above 7 (especially from 8-11) in crude oil showed good efficiency removal because crude oil has moderate alkalinity (PH from 9-11) this leads to a decrease in the concentration of sulfur in crude oil, thus increasing sulfur removal efficiency [28]. One of the reasons for increased adsorption efficiency in the PH incremental range of (1-7) is a change in active sites as the active sites increase in the acidic part and decrease as we get closer to the alkaline portion because the change in the PH value towards the alkaline portion affects the structure of the molecules and reduces their activity [29].



**Figure (3)**Effect of crude oil PH on the Removal Efficiency of sulfur components (T:90 C° and Dose:13g)

## 4. Conclusion

Depending on the experiments conducted on crude oil samples, the following can be concluded:

- When preparing adsorbents, it was found that when zeolites are kept for a long time and at high temperatures during the impregnation process, it can lead to a decrease in the pore volume in the material as a result of the shattering of their walls.
- The use of nanotechnology in the impregnation of particles of metallic materials with zeolite Y has increased the efficiency of saturation of zeolite with metallic materials compared to other techniques used in other studies.
- Increased temperature, adsorbent dose, adsorption time, and PH samples contributed significantly to adsorption and improved sulfur removal efficiency from crude oil.
- The high concentration of adsorbents improves sulfur adsorption efficiency. The use of an ultrasound source in the homogenization process increased sulfur adsorption and increased removal efficiency.
- Zeolite type Y has a higher sulfur removal efficiency than other types based on comparisons made with other studies.

The sulfur removal efficiency of crude oil increases when the adsorption time is increased at high temperatures.

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