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# REMOVAL OF SULFUR COMPOUNDS FROM IRAQI CRUDE OIL USING γ-$Al_2O_3$ NANOPARTICLES

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**ABSTRACT**. γ-$Al_2O_3$ nanoparticles have been synthesized using aluminium(III) sulfate as a source of metal. *Ceratonia silique* leaves extract was used as a reducing agent and sodium hydroxide solution as a precipitating. XRD, BET, FE-SEM, EDX, and DLS Techniques were used to characterize the prepared alumina. The desulfurization process was applied by adsorption of sulfur compounds from Iraqi crude oil using the prepared γ-$Al_2O_3$ nanoparticles. The efficiency of aluminium oxide nanoparticles as an adsorbent was studied for different factors such as adsorbent quantity, contact time, pH, and temperature. The average size of γ-$Al_2O_3$ nanoparticles is 12.44 nm, with a size distribution of particles from 90 nm to 900 nm. The mixture was drained at 80 ºC, and then calcined at 600 ºC, BET analysis shows a high surface area (72.03 $m^2 g^{-1}$) and uniform pore sizes of $Al_2O_3$ NPs. The FE-SEM images showed that the nanoparticles appeared smooth and cylinder-shaped within the average size of 100.53 nm. The obtained results of removal of the sulfur compounds from crude oil using γ-$Al_2O_3$ nanoparticles showed a high desulfurization and were achieved with adsorbent at specific conditions: 150 min, 0.5 g of adsorbent, temperature at 25 ºC and acidic medium pH = 2.

**KEY WORDS**: Crude oil, γ-$Al_2O_3$ nanoparticles, *Ceratonia siliqua* leaves extract

## INTRODUCTION

Adsorption is a very important industrial process; many research has reported uses of the adsorption process as an adsorbent of heavy metals and dyes from wastewater [1-3]. $Al_2O_3$, generally referred to as corundum, has many phases such as gamma (γ), delta (δ), theta (θ), eta (η) and kappa (κ), a $Al_2O_3$ can also exist in numerous crystal forms [4]. The two alumina, γ and δ, are the main focus. Because of its high surface area and stability across a wide temperature range as a catalyst for most reactions, gamma alumina (γ-$Al_2O_3$) is of the highest interest [5, 6]. Due to its unique qualities, such as high mechanical strength, and wide surface area relative to the volume, high hardness, and strong chemical stability, nanosized aluminium oxide (γ-$Al_2O_3$) has been discovered to be employed in numerous industries [7].

In particular, aluminium oxide nanoparticles have been proposed as adsorbents of heavy metals [8]. A wide variety of techniques, including co-precipitation [9, 10], micro-emulsion [11], sol-gel [12], wet-chemical [13], solvothermal [14], laser ablation [15], and biosynthesis employing *Hibiscus rosa-sinensis* leaf extract, are utilized to prepare alumina oxide nanoparticles. The metal salt is converted into metal oxide thanks to the presence of many phytochemicals (carbohydrates, thymol, steroids, flavonoids, terpenoids, saponins, anthraquinone, and phenols) [16]. More than 80% of the world's energy needs are fulfilled from fossil fuels, mostly crude oils, and as society has progressed, so too has the awareness of the challenges posed by exhaust emissions. As a result, the worldwide supply of crude oils still feels the effects of the ever-increasing demand from the automotive, aviation, and maritime industries. Since the combustion

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or processing of crude oils can result in emissions of considerable amounts of harmful gases like sulfur dioxide ($SO_2$) and hazardous compounds, this trend toward using crude oils as the principal energy source has a direct impact on the environment. The sulfur content of fuels in many nations is now capped at 10 ppm due to stricter environmental restrictions. Sulfur levels and API gravity are the most important factors in determining crude oil quality [17, 18]. Incorporating heavier and more sour (high-sulfur) feedstocks into the market is necessary to meet the world's energy needs. The sulfur level of crude oil can reach up to 14 wt%, making it the heteroelement with the highest average abundance [19, 20].

The elemental sulfur content in crude oil is typically between 0.16 and 14.2 weight percent, while this number may be greater for specific crude oils and asphalts. Mercaptans, thiophenes, benzothiophenes, dibenzothiophenes, benzonaphthothiophenes, and dinaphthothiophenes are all examples of aromatic ring-structured molecules that can be found in organic forms [21].

Bentonite treated with metal oxides has been the subject of extensive research towards removing sulfur compounds from petroleum products [22]. In various sulfur compounds adsorption processes, including activated alumina is used as an adsorbent because of its crystalline structure and high porosity [23]. Alumina's primary use as a catalyst is in the Claus reaction, which converts $H_2S$ into sulfur, which removes $H_2S$ from gas streams in refineries [24]. Due to its high surface area, huge numbers of active sites, excellent stability, corner defect sites, unique lattice planes, and high surface to volume ratio, nano-adsorbents have recently attracted significant scientific interest for their usage in the treatment of sulfur compounds [25].

In this work, synthesis and characterization of $\gamma$-$Al_2O_3$ nanoparticles are used in the removal of sulfur compounds from Iraqi crude oil, which is considered to be one of the most important oil product problems.

## EXPERIMENTAL

The aluminium sulfate ($Al_2(SO_4)_3$) which was used as a source of $\gamma$-$Al_2O_3$ was purchased from Sigma-Aldrich. *Ceratonia siliqua* extract was obtained from the local garden in Baguba City - Iraq. Crude oil was used from Midland Oil Company Reservoir in Baghdad - Iraq with a content sulfur compounds ratio of 2.7%. Deionized water was used from the Department of Chemistry, College of Education for Pure Science, University of Diyala, Iraq.

### *Preparation of $\gamma$-$Al_2O_3$ using Ceratonia siliqua leaves extract*

$Al_2(SO_4)_3$ (0.5 g, 0.00146 mol) was dissolved in 50 mL of deionized water and 10 mL of *Ceratonia siliqua* extract solution (20 g of *Ceratonia siliqua* leaves powder was added to 100 mL of deionized water and boiled for 30 min until the solution color was changed and then the mixture was cooled to room temperature and filtered, followed by centrifugation of the obtained liquid at 1200 rpm for 4 min to remove biomaterials) was added gradually at room temperature then the mixture was heated to 80 °C. Sodium hydroxide solution (0.1 M) about 20-30 mL was added to obtain pH 12. The precipitate was filtered and washed with deionized water and 100% ethanol five times. The product was calcined in a muffle furnace at (600 °C) for 6 hours to obtain the $\gamma$-$Al_2O_3$ NPs.

### *Studying the factors affecting the adsorption method*

In order to determine how various factors, such as adsorbent quantity of sulfur compounds, contact time, pH, and temperature, affect the amount of sulfur compounds adsorbed at equilibrium, qe (mg/g), a batch technique was employed. A sample solution was taken at predetermined intervals and analyzed with a fluorescence X-ray sulfur dispersive analyzer (ASE-2, ED-XRF) to analyse sulfur compounds. Adsorption equilibrium is determined by the equation [26, 27]:

$$qe = \frac{(Co - Ct)\ V}{w} \tag{1}$$

where $C_o$ and $C_e$ (mg/L) are the initial and equilibrium sulfur concentrations, respectively, $q_e$ (mg/g) is the amount of adsorbed sulfur compounds. The volume of crude oil is V. W is the adsorbent weight (g).

Adsorption efficiency was determined using the following formula.

$$\%\ \text{removal} = \frac{(Co - Ce)}{Co} \times 100 \tag{2}$$

where $C_o$ and $C_e$ (mg/L) are the initial and equilibrium sulfur concentrations, respectively.

*Effect of contact time on sulfur compounds adsorption*

An adsorbent amount of (0.5) g of $\gamma$-$Al_2O_3$ NPs was added into each flask containing 100 mL of crude oil with an initial ratio of sulfur contents (2.7%wt) and sealed them with glass stoppers before shaking them at 200 revolutions per minute in a water bath at a constant temperature of 298 K at various time intervals (30, 60, 90, 120, 150 min). Then, the solutions were filtered, and finally, the sulfur contents in the crude oil solutions were measured using a sulfur analyzer in the Baiji Refinery - Salah Al-Din Province.

*Effect of quantity of $\gamma$-$Al_2O_3$ nanoparticles adsorbent*

Using a constant volume (100 mL) of crude oil (with a sulfur content of 2.7%wt), temperature (298 K), and stirring speed (200 rpm) for 90 min, the effect of adsorbent quantity on the removal of sulfur compounds from crude oil was investigated.

*Effect of temperature*

Adsorption experiments were carried out at different temperatures (273, 298, 323, 348, and 373 K), contact time (90) min, and adsorbent quantity (0.5) g to remove sulfur compounds from crude oil to investigate the effect of temperature on adsorption.

*Effect of pH*

Experiments were conducted to determine the effect of pH on adsorption by removing sulfur compounds from crude oil at varying pH values (2, 4, 6, 8 and 10), contact times of 90 min, and adsorbent quantities of 0.5 g at a temperature of 298 K.

## RESULTS AND DISCUSSION

*XRD analysis*

The obtained peaks were compared to those in the standards database (JCPDS Card No: 00-029-0063) [28] and were determined to be in good agreement. The production of the $\gamma$-$Al_2O_3$ species with an average nanoparticle size of 12.44 nm is revealed by the four typical reflections at 2 theta = 32.05, 37. 94, 46.29, and 66.99, with corresponding reflection planes of 220, 311, 400, and 440.

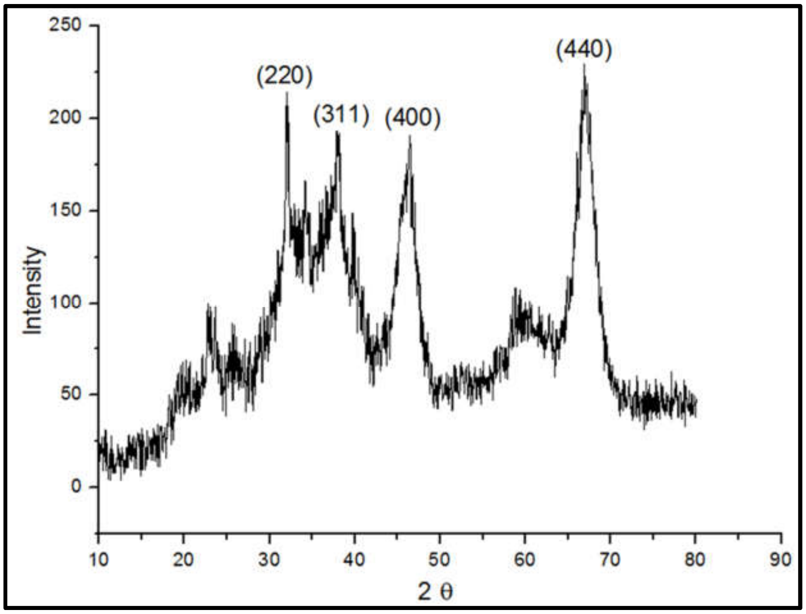


Figure 1. XRD diffraction pattern of γ-$Al_2O_3$ NPs.

*FE-SEM image*

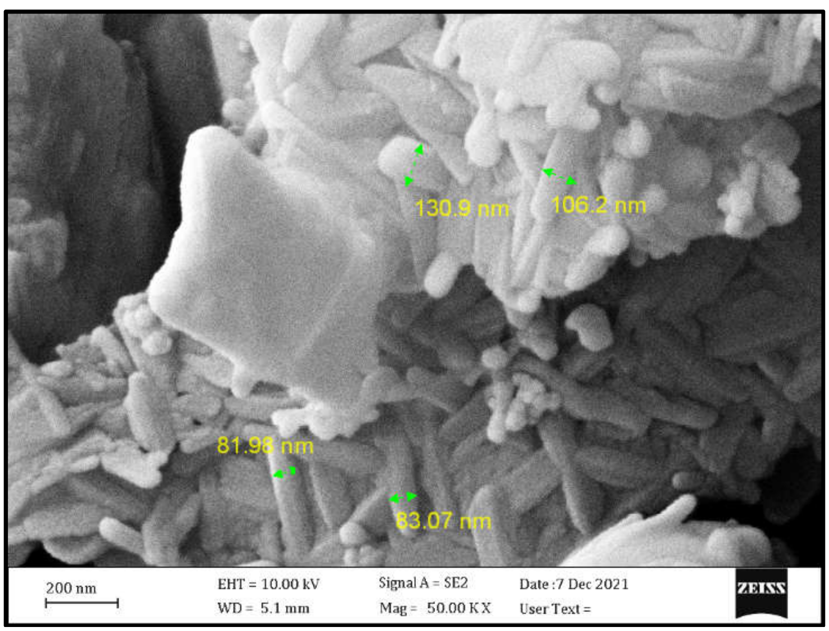


Figure 2. FE-SEM image of γ-$Al_2O_3$ NPs.

Figure 2 shows FE-SEM images used to study the surface morphology of γ-$Al_2O_3$ NPs. The FE-SEM microscopy also confirmed the nanoparticles' existence in the nanoscale. Weak van der Waal forces were revealed to be the driving mechanism for the aggregation of nanoparticles. The nanoparticles had a cylindrical shape and an average size of 100.53 nm, which suggested that they were smooth

*DLS analysis*

The particle size distribution of the $Al_2O_3$ powder was evaluated by dynamic light scattering (DLS). Figure 3 illustrates the mean particle diameter which obtained from DLS measurement and found to be 511 nm with area percentages about 32%.

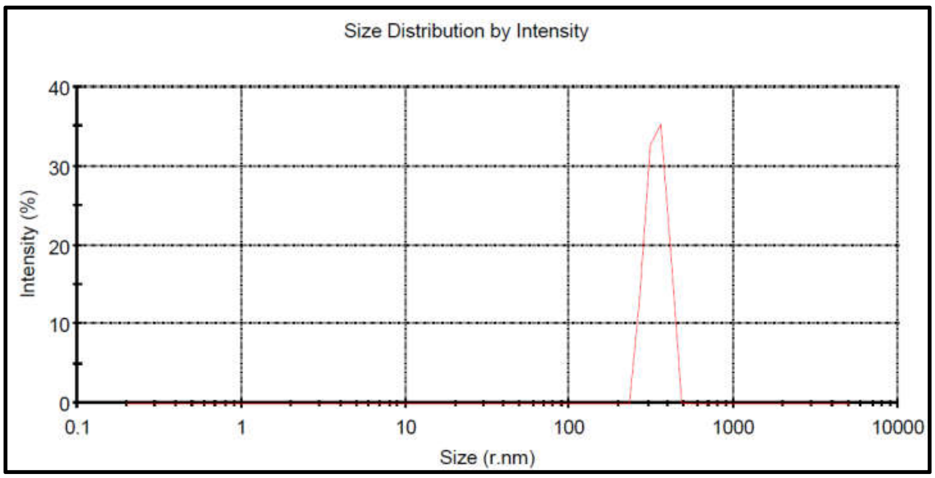


Figure 3. Dynamic light scattering (DLS) spectrum showing the γ-$Al_2O_3$ NPs size distribution.

*BET analysis*

The textural qualities of the resultant sample were evaluated using $N_2$ sorption studies. The hysteresis loop of type H1 in Figure 4 is characteristic of a type IV isotherm, indicating that mesoporous structures are present in the adsorbent [29]. According to the Brunauer-Emmett-Teller (BET) equation, the specific surface area is 72.03 $m^2$/g. The pore diameters were calculated using the BJH pore size distribution curve analysis. Figure 4 shows mesoporous pores (with dimensions between 2 and 10 nm) make up most of the pores, with microporous pores (with diameters between 1 and 100 nm) accounting for the remaining 20%. The adsorbent's average pore size and pore volume were 27.248 nm and 0.4907 $cm^3g^{-1}$, respectively. Hence, this provides an ideal environment for the removal and adsorption of sulfur compounds from crude oil.

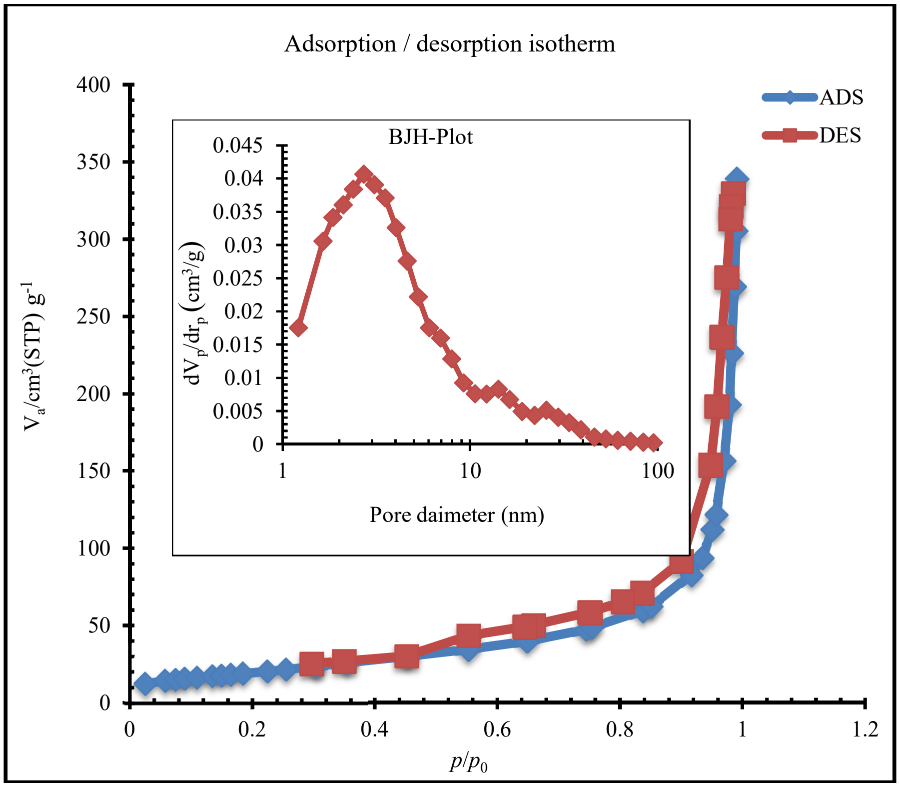


Figure 4. γ-$Al_2O_3$ nanoparticles $N_2$ adsorption-desorption isotherm (Inset: Pore size distribution curves).

*The optimum condition for adsorption*

*Effect of contact time on sulfur compounds adsorption*

At Co = 2.7%, the removal % of sulfur compounds was studied (Figure 5). Adsorption of sulfur compounds was rapid in the first 30 min and subsequently increased steadily until equilibrium was reached 90 min later. The removal efficiency increased by 22% when the contact time was 150 min. The sorption readings at 90 and 150 min were so close that it was expected that the equilibrium condition would be reached in 20 min. All batch studies were performed at pH = 2, because in a sulfur compounds solution at acidic conditions the dissolution of sulfur compounds can be possible, therefore assessment of sulfur compounds adsorption and its removal by γ-$Al_2O_3$ NPs can be clear, with a 30-minute contact period and a 200 rpm shaking velocity. After a certain point in the sorption process, the repulsive forces between the solute molecules and the solid adsorbent make it difficult for the remaining vacant surface positions to be filled. As can be shown in Table 1, the contact time has a significant role in the elimination of sulfur compounds [30].

*Effect of the adsorbent quantity on sulfur compounds adsorption*

Figure 5 and Table 1 depict the experimental findings showing a considerable increase in the adsorption efficiency from 22.96% at low quantity to 45.92% at high quantity when using γ-$Al_2O_3$

NPs as the adsorbent. A higher ratio of active adsorption sites of the adsorbent is likely available at higher adsorbent quantity than at lower adsorbent quantity, which could account for such a result [31].

*Effect of the temperature on sulfur compounds adsorption*

Adsorption's rate is affected by temperature, which makes it a crucial process parameter. Adsorption rates are thought to rise with temperature because sulfur compounds can diffuse more quickly through adsorbent pores and overcome the activation energy barrier at higher temperatures. Whether an increase or decrease in temperature results in a greater or lesser adsorption capability [32]. Figure 5 displays the outcomes of an investigation into how temperature affects the removal of sulfur compounds by **γ**-$Al_2O_3$ nanoparticles. At 0 °C, adsorbent efficiency in removing sulfur compounds is at its highest (41.48%), whereas at 100 °C, it is at its lowest (31.48%).

*Effect of pH on sulfur compounds adsorption using γ-$Al_2O_3$*

Since the pH of the solution controls the surface charge of both the adsorbent and the adsorbate, pH is a crucial parameter in regulating the sorption process [33]. The effect of pH using alkaline solution 1 M NaOH solution and acidic solution conc. HCl on the removal of sulfur compounds utilizing alumina nanoparticles was investigated over a range of pH from 2 to 10, and the results are given in Figure 5. The results show that at acidic pH 2.0, there was a marked increase in adsorption due to the dissociation of the sulfur compounds in the acidic media. While, at higher pH, the number of negatively charged sites on aluminium oxide particles increased, which reduced the sulfur compounds adsorption on the adsorbents due to the electrostatic repulsion and the competition between hydroxyl and sulfur compound ions for the adsorption sites, whereas with increasing pH, percentage of removed sulfur decreased from 51.48 to 36.29% .

Table 1. Effect of contact time, temperature and adsorbent quantity on the adsorption of sulfur compounds by γ-$Al_2O_3$ NPs.

| γ-$Al_2O_3$ (at 298 K) | | | | γ-$Al_2O_3$ (298 K and 30 min) | | | |
|---|---|---|---|---|---|---|---|
| Time, min | %$S_{(initial)}$ | %$S_t$ | R% | Wt, g | %$S_{(initial)}$ | %St | R% |
| 30 | | 2.01 | 25.5555 | 0.1 | | 2.08 | 22.9629 |
| 60 | | 1.83 | 32.2222 | 0.2 | | 1.97 | 27.0370 |
| 90 | 2.7 | 1.45 | 46.2963 | 0.3 | 2.7 | 1.73 | 35.9259 |
| 120 | | 1.43 | 47.0370 | 0.4 | | 1.46 | 45.9259 |
| 150 | | 1.42 | 47.4074 | 0.5 | | 1.45 | 46.2963 |
| γ-$Al_2O_3$ (30 min and 0.5 g) | | | | γ-$Al_2O_3$ (30 min, 298 K and 0.5 g) | | | |
| T, K | %$S_{(initial)}$ | %$S_t$ | R% | pH | %$S_{(initial)}$ | %$S_t$ | R% |
| 273 | | 1.58 | 41.4818 | 2 | | 1.31 | 51.4818 |
| 298 | | 1.67 | 38.1485 | 4 | | 1.35 | 50 |
| 323 | 2.7 | 1.81 | 32.9626 | 6 | 2.7 | 1.48 | 45.1859 |
| 348 | | 1.83 | 32.2222 | 8 | | 1.61 | 40.3707 |
| 373 | | 1.85 | 31.4818 | 10 | | 1.72 | 36.2963 |

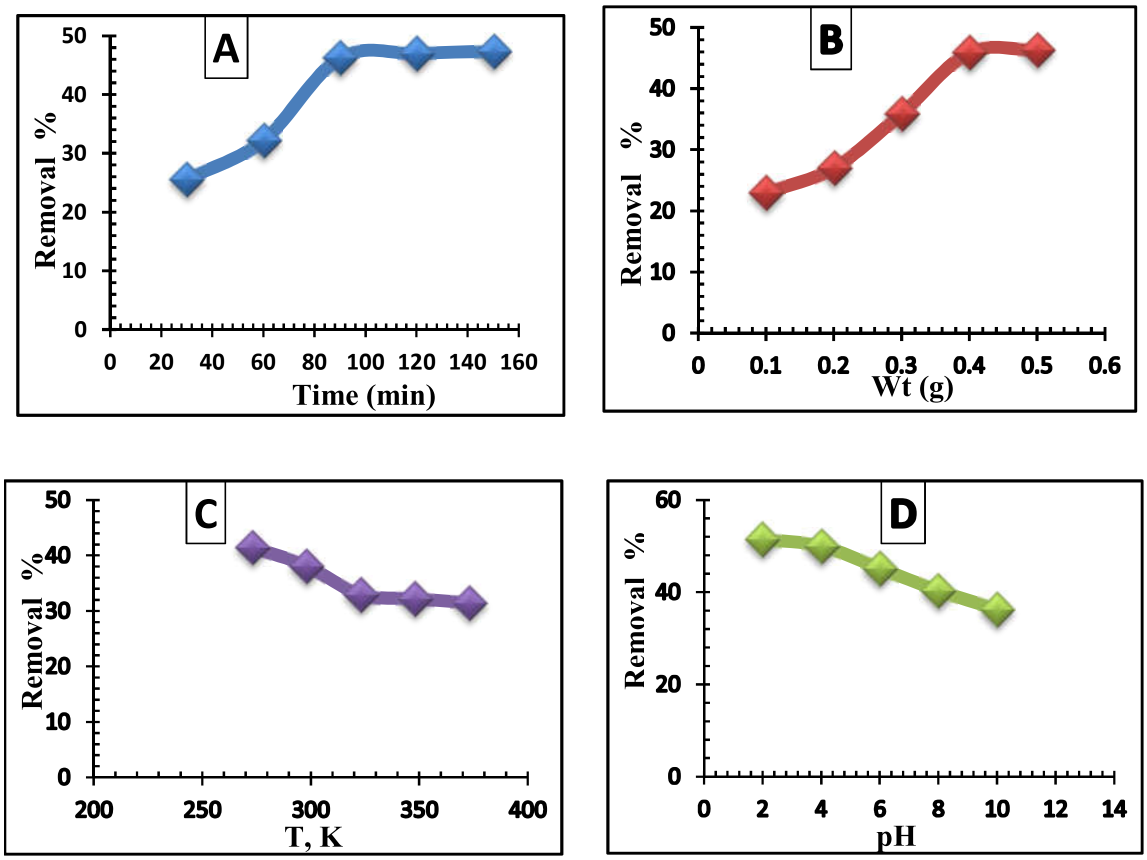


Figure 5. Shows the removal % of sulfur compounds versus (A) contact time, (B) weight of γ-$Al_2O_3$, (C) temperature and (D) pH.

## CONCLUSION

The biosynthesis method in terms of green chemistry was used successfully to prepare γ-$Al_2O_3$ nanoparticles. The obtained nanoparticles have cylindrical shapes with an average particle size of 12.44, 100.53 and 511 nm which were measured using XRD, FE-SEM and DLS, respectively. The results indicate that the efficiency of sulfur compounds adsorption is reduced in alkaline conditions (pH > 7), which is believed to be due to the interplay between the pH value of sulfur compounds in the Iraqi crude oil and the pH value of the prepared γ-$Al_2O_3$ NPs. The evaluation study of the reaction conditions indicates that the increasing of adsorbent quantity (from 0.1 to 0.5 g) and contact time (from 30 to 150 min) increased the adsorption efficiency. In contrast, increasing temperature (from 273 to 373 K) and pH (from 2 to 10) had a negative effect on the efficiency of the adsorption. Hence, better adsorption was obtained for sulfur compounds which were at 273 K temperature and in the acidic medium (pH = 2).

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## REFERENCES


1. Belete, T.; Gebeyehu, D.; Temesgen, A. Efficient removal of methylene blue dye from aqueous solution using a new biosorbent derived from *Ensete ventricosum* (Enset). *Bull. Chem. Soc. Ethiop.* **2024**, 38, 69-84.
2. Asmamaw, T.; Solomon, M.; Shimelis, A. Adsorption of lead(II) ions using KOH-activated carbon derived from water hyacinth. *Bull. Chem. Soc. Ethiop.* **2023**, 37, 1369-1382.
3. İrdemez, Ş.; Yeşilyurt, D.; Ekmekyapar, F.; Kul, S. Determination of parameters affecting kinetic and thermodynamic values for lead removal using wastewater treatment plant sewage sludge ash. *Bull. Chem. Soc. Ethiop.* **2022**, 36, 935-948.
4. Silva-Holguín, P.N.; Ruíz-Baltazar, Á.J.; Medellín-Castillo, N.A.; Labrada-Delgado, G.J.; Reyes-López , S.Y. Synthesis and characterization of α-$Al_2O_3$/Ba-β-$Al_2O_3$ spheres for cadmium ions removal from aqueous solutions. *Materials* **2022**, 15, 6809.
5. Jacopo, B.; Cristina, H.; Christophe, F.; Hilke, P.; Jan,T.; Claudia, W.; Amol , A.; Ferdi, S. Surface and bulk chemistry of mechanochemically synthesized tohdite nanoparticles. *J. Am. Chem. Soc.* **2022**, 144, 9421-9433.
6. Gao, H.; Zhang, M.; Yang, H.; Li, Z.; Li, Y.; Chen, L. A novel green synthesis of γ-$Al_2O_3$ nanoparticles using soluble starch. *Modern Phys. Lett. B* **2019**, 33, 1950182.
7. Abyzov, A.M. Scientific research and development aluminum oxide and alumina ceramics (review). Part 1. Properties of $Al_2O_3$ and commercial production of dispersed $Al_2O_3$. *Refractories Ind. Ceram*. **2019**, 60, 24-32.
8. Tabesh, S.; Davar, F.; Loghman-Estarki, M.R. Preparation of γ-$Al_2O_3$ nanoparticles using modified sol-gel method and its use for the adsorption of lead and cadmium ions. *J. Alloys Compd.* **2018**, 730, 441-449.
9. Ramakrishnan, S. Antimicrobial study on gamma-irradiated polyaniline–aluminum oxide (PANI–$Al_2O_3$) nanoparticles. *Int. Nano Lett.* **2020**, 10, 97-110.
10. Gholizadeh, Z.; Aliannezhadi, M.; Ghominejad, M.; Tehrani, F.S. High specific surface area γ-$Al_2O_3$ nanoparticles synthesized by facile and low-cost co-precipitation method. *Sci. Rep.* **2023**, 13, 6131.
11. Ahmed, M.A.; Bishay, S.T.; Ramadan, R. Water detoxification using gamma and alfa alumina nanoparticles prepared by micro emulsion route. *Nanosci. Technol.* **2015**, 9, 064-074.
12. Mohamad, S.N.S.; Mahmed, N.; Halin, D.S.C.; Razak, K.A.; Norizan, M.N.; Mohamad, I.S. Synthesis of alumina nanoparticles by sol-gel method and their applications in the removal of copper ions ($Cu^{2+}$) from the solution. Proceedings of the Electronic Packaging Interconnect Technology Symposium, 2019, Penang, Malaysia, 24–25 November, 012034.
13. Rigoberto, L.; Neftalí, R.; Teresita, P.; Orlando, H.; Simón, Y. Synthesis of α-$Al_2O_3$ from aluminum cans by wet-chemical methods. *Results Phys.* **2018**, 11, 1075-1079.
14. Chu, T.P.M.; Nguyen, N.T.; Vu, T.L.; Dao, T.H.; Dinh, L.C.; Nguyen, H.L.; Hoang, T.H.; Le, T.S.; Pham, T.D. Synthesis, characterization, and modification of alumina nanoparticles for cationic dye removal. *Materials* **2019**, 12, 450.
15. Jwad, K.H.; Saleh, T.H.; Abd-Alhamza, B. Preparation of aluminum oxide nanoparticles by laser ablation and a study of their applications as antibacterial and wounds healing agent. *Nano Biomed. Eng.* **2019**, 11, 313-319.
16. Marlina; Yanto; Triyatna, F.; Lestari, E.; Sarmini, E.; Mujamilah; Awaludin, R.; Yulizar, Y. Green synthesis of alumina nanoparticle using *Hibiscus rosa-sinensis* leaf extract as a candidate for molybdenum-99 adsorbent. *Appl. Radiat. Isot.* **2023**, 193, 110644.

17. Abd Al-Khodor, Y.A.; Albayati, T.M. Employing sodium hydroxide in desulfurization of the actual heavy crude oil: Theoretical optimization and experimental evaluation. *Process Saf. Environ. Prot.* **2020**, 136, 334-342.
18. Omar, R.A.; Verma, N. Review of adsorptive desulfurization of liquid fuels and regeneration attempts. *Ind. Eng. Chem. Res.* **2022**, 61, 8595-8606.
19. Maegan, T.; Angelo, Ch.; Nathaniel, D.; Meng-Wei, W. A review on the adsorptive performance of bentonite on sulfur compounds. *Chem. Eng. Trans*. **2023**, 103, 553-558.
20. Kondyli, A.; Schrader, W. Study of crude oil fouling from sulfur-containing compounds using high-resolution mass spectrometry. *Energy Fuels* **2021**, 35, 13022-13029.
21. Shi, Q.; Wu, J. Review on sulfur compounds in petroleum and its products: State-of-the-art and perspectives. *Energy Fuels* **2021**, 35, 14445-14461.
22. AL-Bidry, M.; Rana, A. Removal sulfur components from heavy crude oil by natural clay. *Ain Shams Eng. J.* **2020**, 11, 1265-1273.
23. Zaid, S.M.A.; Razak, A.A.A.; Abid, M.F. Desulfurization of a model liquid fuel by adsorption over zinc oxide/activated alumina assisted with ultrasonication. *Egypt. J. Chem.* **2022**, 65, 807-825.
24. Rezaee, M.; Kazemeini, M.; Fattahi, M.; Rashidi, A.M.; Vafajoo, L. Oxidation of $H_2S$ to elemental sulfur over alumina-based nanocatalysts: Synthesis and physiochemical evaluations. *Sci. Iran. C* **2016**, 23, 1160-1174.
25. Zaid, S.M.A.; Abdulrazak, A.A.; Abid, M. A review of nano-catalyst applications in kerosene desulfurization techniques. *J. Appl. Sci. Nanotechnol*. **2022**, 2, 86-102.
26. Xunjun, Ch. Modeling of experimental adsorption isotherm data. *Information* **2015**, 6, 14-22.
27. Rania, F.; Yousef, N. Equilibrium and kinetics studies of adsorption of copper (II) ions on natural biosorbent. *Int. J. Chem. Eng. Appl.* **2015**, 6, 319-324.
28. Alamouti, A.; Nadafan, M.; Dehghani, Z.; Majles, M.; Noghreiyan, A. Structural and optical coefficients investigation of $\gamma$-$Al_2O_3$ nanoparticles using kramers-kronig relations and Z–scan technique. *J. Asian Ceram. Soc*. **2021**, 9, 366-373.
29. Rozita, Y.; Ismail, Z.; Anwar, Ul.; Hasliza, B.; Raja, M.; Muhammad, H.; Radiah, S. Synthesis of facetted gamma alumina nanoparticles from waste beverage aluminium cans for potential catalyst support applications. *Malay. J. Microsc.* **2021**, 17, 78-87.
30. Asghar, A.; Nemati, O.; Alidadi, H.; Yazdani, M.; Asghar, A.; Fezabady, N.; Taghavi, M. Optimization of ciprofloxacin adsorption from synthetic wastewaters using $\gamma$-$Al_2O_3$ nanoparticles: an experimental design based on response surface methodology. *Colloids Interface Sci. Commun.* **2019**, 33, 100212.
31. Fatemeh, G.; Bahri, M.M. Adsorption of Cr(VI) from aqueous solution by adsorbent prepared from paper mill sludge: Kinetics and thermodynamics studies. *Adsorpt. Sci. Technol.* **2017**, 36, 149-169.
32. Yuannan, Z.; Qingzhao, Li.; Chuangchuang, Y.; Qinglin, Tao.; Yang, Z.; Guiyun, Z.; Junfeng, Li. Influence of temperature on adsorption selectivity: Coal-based activated carbon for $CH_4$ enrichment from coal mine methane. *Powder Technol.* **2019**, 347, 42-49.
33. Liang, M.; Mushi, Q.; Qing, Z.; Shuiping, Xu.; Dunqiu, W. Study on the dynamic adsorption and recycling of phosphorus by Fe–Mn oxide/mulberry branch biochar composite adsorbent. *Sci. Rep.* **2024**, 14, 1235.