Journal Homepage: http://ijcpe.uobaghdad.edu.iq
Iraqi Journal of Chemical and Petroleum Engineering
Vol. 25 No. 4 (December 2024) 15 – 25
EISSN: 2618-0707, PISSN: 1997-4884

Oil spill cleanup using EDTA-coated magnetite magnetic nanoparticles

Maha J. Awda [a, *], Basma A. Abdulmajeed [a], Zaid Nidhal Shareef [b]

a Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq
b Curtin University, Chemical Engineering Department, Australia

Abstract

As a result of the critical importance of crude oil in modern industrial society, oil spills, specifically those involving crude oil, generate substantial environmental and ecological difficulties. In contrast to conventional treatment approaches, nanotechnology has demonstrated its efficacy in remedying oil spills This type of pollution could occur during oil investigation, transit, or storage. This study adopted a straightforward and economical method utilizing iron oxide magnetic nanoparticles for oil spills cleanup. Magnetite Fe_3O_4 MNPs were synthesized using the co-precipitation technique, which involved combining ferric and ferrous ions in an alkaline solution at 80°C and a pH of 14. MNPs were characterized using X-ray diffraction (XRD), Fourier-Transform Infrared Spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and vibrating sample magnetometer (VSM). To improve their stability and efficacy, MNPs were coated with ethylenediaminetetraacetic acid (EDTA). Three samples of crude oil with different APIs (23, 28.4, and 40.3) were used to study the ability of coated MNPs for oil spill cleanup. Removal experiments were conducted at 25°C with a mass range of adsorbent (0.02-0.06 g). A neodymium magnet was utilized to extract the oil-contaminated magnetic nanoparticles from the water. The gravimetric oil removal (GOR) for APIs 23, 28.4, and 40.3 were 11.4 - 3.35, 7.19- 2.15, and 4.81 to 1.16 g/g, respectively. Experimental results demonstrated an inverse relationship between GOR and the API value, indicating that as the API value decreased, GOR increased, and vice versa. Furthermore, as the mass of the adsorbent material increased (0.02-0.06g), the GOR value decreased.

Keywords: oil spill; magnetic nanoparticles; crude oil; EDTA; magnetite.

Received on 26/12/2023, Received in Revised Form on 28/04/2024, Accepted on 28/04/2024, Published on 30/12/2024

https://doi.org/10.31699/IJCPE.2024.4.2

1- Introduction

Water is a key element needed for life on Earth. Today's aquatic environment is heavily contaminated, and natural watercourses have been seriously damaged [1]. Due to the high global oil consumption (Iraq, like many other countries, depends on oil for both energy and financial resources [2]), it is challenging to prevent oil spills. Millions of tons of energy were wasted as a result. Globally, it's estimated that 400.000 tons of oil leak annually. For example, the tanker BFC2, transporting 4,750 tons of Basrah petroleum oil, capsized near Khor Al-Zubair on the 22th August 2006. A crack measuring 1.5 meters in length developed in the bump room of the cargo pump tanker due to this calamity; approximately 10–15 tons of oil were spilled, instantly causing substantial leakage in this area [3]. In 2019, oil spread from Brazil's northeast and southeast, impacting about 2,000 kilometers of shoreline [4]. The Gulf of Mexico had the most significant unintentional release of oil in history, commencing on the 20th of April, 2010. This incident occurred when a sudden outburst of natural gas ruptured a cement well cap that had been recently fitted to seal a well drilled by the Deepwater Horizon oil platform. A crude oil disaster transpired in the Gulf of Mexico, releasing around 4.9 million barrels of oil [5]. These disasters, among numerous others, caused environmental damage and economic destruction.

In response to this tendency, several researchers have focused on oil recovery in the regions where oil spills have occurred to avoid the dispersal of pollutants, which causes additional issues [6]. Effective decontamination and rapid cleanup are critical for protecting the ecology and aquatic biota. The oil-slick layers that cover the water's surface must be removed. Since the traditional methods, which classified into booms and skimmers as mechanical techniques, dispersants, and in-situ burning as chemical, in addition to biological treatment, proved to be ineffective, the utilization of nanotechnology in the remediation of oil spills in water is becoming increasingly important [7–11]. Adsorption is regarded as a straightforward, practical, and cost-effective method for treating oil spills, in contrast to other procedures utilized. Typically, sorbents are most efficiently employed in the latter phase of oil spill remediation and for retrieving small accumulations of oil that are not easily recoverable by alternative oil cleanup methods [12]

Nanomaterials with distinctive characteristics such as superparamagnetism, minuscule dimensions, excellent

*Corresponding Author: Email: maha.awda2107m@coeng.uobaghdad.edu.iq

recyclability, environmentally friendly properties, exceptional stability, low toxicity, and robust adsorption capacity have the ability to remediate water tainted with oil [13, 14]. The outstanding oil recovery efficiency and remarkable magnetic characteristics of nanostructured magnetic nanoparticles (MNPs) and nanocomposites make them ideal candidates for oil spill cleanup.

Iron oxide nanoparticles have desirable characteristics such as small size, stability, superparamagnetic capabilities, rapid response to magnetic fields, and superb dispersion in oils. These qualities make them highly effective for collecting oil spills and treating water. Iron oxides that have been extensively researched in the domains of oil and gas are hematite -(α-Fe_2O_3), magnetite -(Fe_3O_4), and maghemite -(γ-Fe_2O_3) [15, 16]. Magnetite MNPs are superparamagnetic (1 to 100 nanometers) in the nanometer range. This indicates that magnetite at the nanoscale cannot retain its magnetization once the external magnetic field is removed. This made magnetite nanoparticles widely used in technology, science, and medicine due to their distinct properties. The extensive utilization of magnetite nanoparticles has prompted the advancement of diverse techniques for their production. Several conventional methods for magnetite nanoparticle production include pyrolysis of organometallic compounds, polyol-process, microemulsion, hydrothermal, sol-gel, and co-precipitation [17].

Co-precipitation is the most commonly employed technique. Through the utilization of bivalent and trivalent hydrated salt ions, magnetite nanoparticles are produced in a controlled atmosphere with the presence of a strong base. Eq. 1 reveals the chemical reaction.

$$2\,Fe^{+3} + Fe^{+2} + 8\,OH^{-} \longrightarrow Fe_3O_4 + 4\,H_2O \qquad (1)$$

Due to their chemical activity, MNPs easily oxidize in air, which causes a loss of general dispersibility and magnetism. Therefore, developing protective strategies to chemically stabilize MNPs against degradation after synthesis is crucial for many applications. These approaches include greasing or coating with organic species, including surfactants or polymers, or coating with an inorganic layer, such as silica or carbon. Notably, in many cases, the protecting shells stabilize the nanoparticles. Depending on the desired application, they can also be used for further functionalization, for instance, with other nanoparticles or various ligands [18].

Ethylenediaminetetraacetic acid (EDTA) is environmentally friendly, stable at high temperatures, salinity, and pH conditions, and a relatively cheap chemical. With these properties, EDTA has gained significant importance in nanoscience, being used as a stabilizer in the fabrication of nanoparticles. It efficiently controls the morphology and size of nanoparticles [19]. EDTA functionalization adsorbent not only possesses good adsorption behaviors, but it also does not cause any secondary pollution [20]. Many studies have shown that EDTA has a strong affinity for iron oxide nanoparticles, which might make it easier for colloids to spread out, lower high surface energy, and stop nanoparticles from sticking together [21,22]. EDTA surface chemistries on the Fe3O4 nanoparticles are shown to be highly effective, and magnetic active sorbent materials [23]

No reports of oil spill recovery using coated magnetite with EDTA as an adsorbent have yet been published. In this work, Fe_3O_4 MNPs were synthesized and coated with EDTA to study their efficiency in oil spill removal from the water surface, employing three samples of Iraqi crude oil with different APIs (23,28.4,40.3).

2- Experimental work

2.1. Material

The materials used in this study included the following: All substances utilized were of the analytical grade reagents and required no additional processing. Ferric chloride hexahydrate ($FeCl_3.6H_2O$ 99%), ferrous chloride tetrahydrate ($FeCl_2.4H_2O$ 98%), ethylenediaminetetraacetic acid (EDTA, $C_{10}H_{18}N_2O_8$, 99%) and HCl (37% concentration) are from CDH, India. Sodium chloride (NaCl 99.5%) is from Alpha Chemika, India. The properties of crude oil, which was taken from Al-Dura Refinery (Basrah crude oil), (Location: EBS-OM-S2 Site), and (Naft Khana) in Iraq are displayed in Table 1.

Table 1. Crude oil properties

Property	Basrah Crude Oil	Naft Khana	East Baghdad S2
Sp.Gr. at 15.6 ºC	0.88490	0.823	0.9158
API	28.40	40.3	23
Viscosity (Cst) at 26.7C	19.4	3.056	58.5

2.2. Preparation of Fe_3O_4 MNPs

MNPs were synthesized by co-precipitating ferric and ferrous ions in an alkaline medium as follows: 6.5 g of $FeCl_3.6H_2O$ and 5.56 g of $FeCl_2.4H_2O$, representing a 1:2 (Fe^{2+}/Fe^{3+}) molar ratio, were dissolved in 50 ml of 0.5 M HCl solution. Subsequently, 500 ml of 1.5M NaOH was added dropwise to the solution while vigorously mixed (600 rpm) and heated to 80 degrees Celsius as a precipitation agent. The reaction environment's pH value was 14. A black precipitate of Fe_3O_4 was generated. After being separated by a neodymium magnet, the Fe_3O_4 precipitate was repeatedly cleaned with deionized water until the suspension turned neutral. Finally, the precipitate was dried for four hours at 50°C and then permitted to rest for a few hours at room temperature.

2.3. Coating with EDTA

EDTA was used to coat Fe_3O_4 MNPs. After adding 0.615 g of EDTA to a solution of 4.48 g of MNPs in water, the suspension was agitated for 1 hour at 50°C [24]. The precipitates were separated magnetically. The solution was rinsed with deionized water until its pH had been eliminated to seven. Subsequently, the residue was dispersed in 200 ml of deionized water and subjected to ultrasonic treatment for 30 minutes. The resultant substance was a black precipitate comprising EDTA-MNPs, which was subsequently isolated from the liquid phase. Then, it was subjected to drying at a temperature of

80 °C for a duration of 3 hours. The dried material was then pulverized using a mortar. Fig. 1 shows the synthesis of Fe_3O_4 and coating with EDTA.

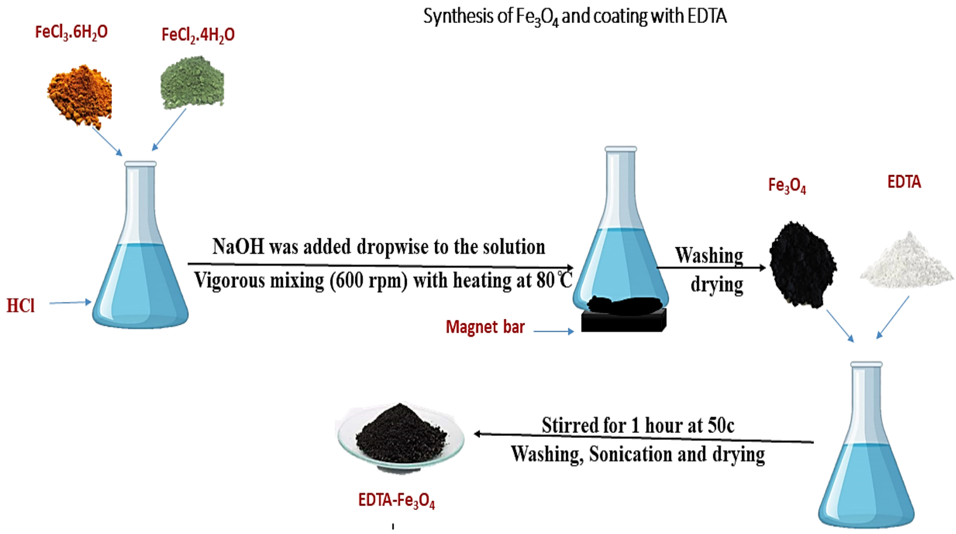

Fig. 1. Synthesis of Fe_3O_4 and coating with EDTA

2.4. Characterization techniques

The resulting magnetic nanoparticles (MNPs) underwent characterization using XRD analysis. This analysis used an X-ray diffractometer (Shimadzu SRD 6000, Japan). This characterization aimed to confirm the structure and presence of the magnetite phase in the MNPs. The TEM investigation used the electron microscopy instrument (EM 900, Zeiss). The SEM pictures were acquired using the Oxford instrument model TE SCAN, Vega III lm-CZECK. The average particle size and the particle size distribution of MNPs and coated-MNPs were determined by AFM (type Angstrom, Scanning Probe Microscope, Advanced Inc, AA 3000, USA), The surface area was quantified with the Brunauer-Emmett-Teller (BET) technique., employing a micrometric ASAP 2020 equipment. The magnetism at room temperature was measured using a VSM, MDK6). FTIR was conducted using a spectrometer (IR-Affinity-1, Shimadzu, Japan). This analysis aimed to verify the presence of the maghemite phase and ascertain that the magnetic nanoparticles (MNPs) were coated with EDTA.

2.5. Oil removal experiment

The investigation on oil removal was conducted utilizing the GOR technique, which is outlined in Fig. 2, as reported elsewhere [25]. A solution of (80 ml) of artificial seawater containing 3.5% sodium chloride (NaCl) was carefully poured into a 100 ml beaker. A quantity of crude oil (API 23, 28.4, 40.3) weighing 0.2 g was dropped into the water surface. Subsequently, a measured amount of EDTA- Fe_3O_4 weighing 0.02-0.06 g was evenly distributed over the oil spill. The oil's EDTA-(MNPs) were retrieved using a magnet bar after 5 minutes. The experiments were performed three times to ensure accuracy, and Eq. 2 was utilized to measure the GOR, g/g)

$$GOR = \frac{m_2 - m_3}{m_1} \quad (2)$$

The variable m_1 represents the mass of the adsorbent, while m_2 represents the entire mass of the beaker, which includes the oil spot, adsorbent, and water. Alternatively, m_3 specifies the mass of the remaining oil (the mass of the beaker after removal).

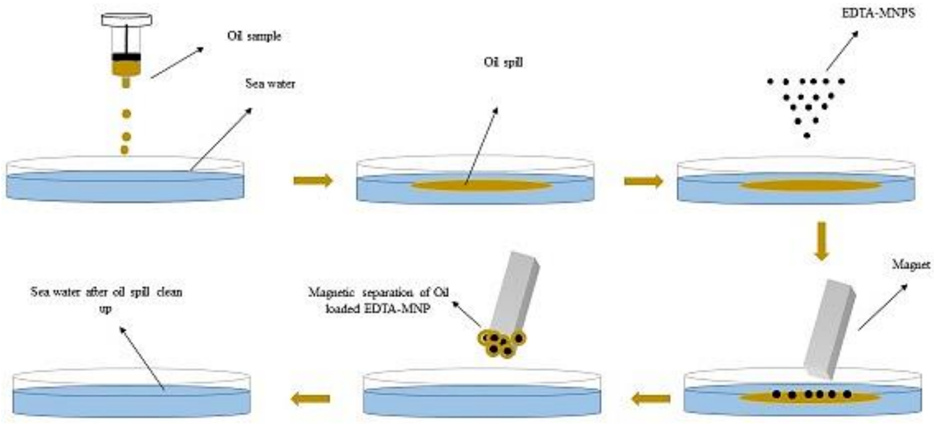

Fig. 2. Illustration depicting the process of gravimetric oil spill removal

3- Result and discussion

3.1. Characterization

The crystal structures of Fe_3O_4 were analyzed using XRD techniques, which provided evidence for the presence of the magnetite phase. Fig. 3 illustrates the X-ray diffraction patterns of MNPs showing that the magnetite Fe_3O_4 possessed a highly crystalline structure. The observed peaks at 2θ values of 30.3, 35.7, 43.4, 53.8, 57.3, and 62.9 correspond to the diffractions of 220, 311, 400, 422, 511, and 440° crystal faces of Fe_3O_4 spinel structure, which agree with (Al-Alawy et al., 2018)[26]. The crystallite size of MNPs was determined using Scherer's Eq. 3:

$$D = \frac{K * \lambda}{\beta * COS\theta} \qquad (3)$$

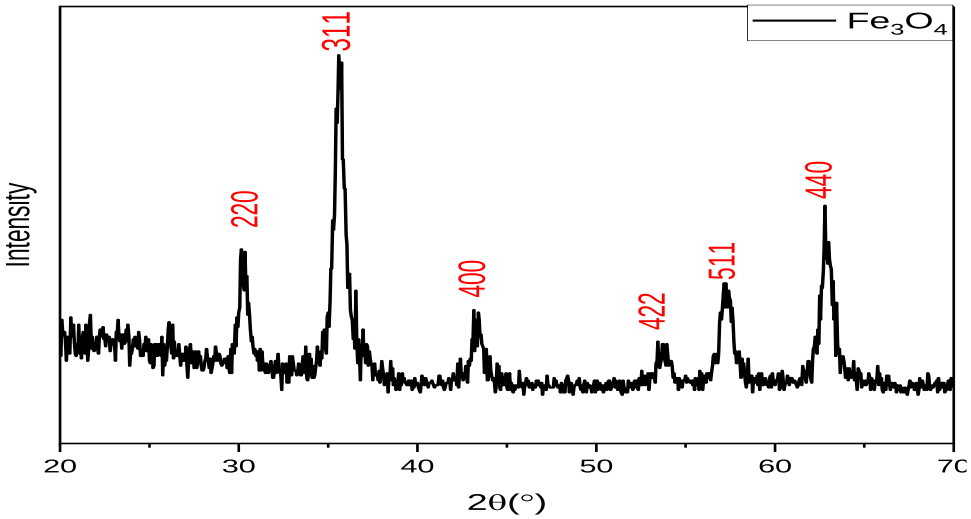

Fig. 3. XRD pattern of magnetite nanoparticles

Where D is the mean size of crystallite (nm), K is the form factor (around 0.9 for magnetite and maghemite (dimensionless) [27], λ is the X-ray wavelength (nm), β is the FWHM (radians), and θ is the XRD angle (degrees). The crystallite size of MNPs is (15.1 nm) using Scherer's formula and the FWHM the strongest peak values obtained from XRD.

SEM and TEM images of the Fe_3O_4 nanoparticles were presented in Fig. 4, and, Fig. 5, to visually depict the shape of the nanoparticles and provide information on their particle size distribution. Based on the (SEM) pictures, it can be shown that the nanoparticles tended to adhere to one another, resulting in the formation of agglomerates, ultimately assuming a spherical morphology (refer to Fig. 4).

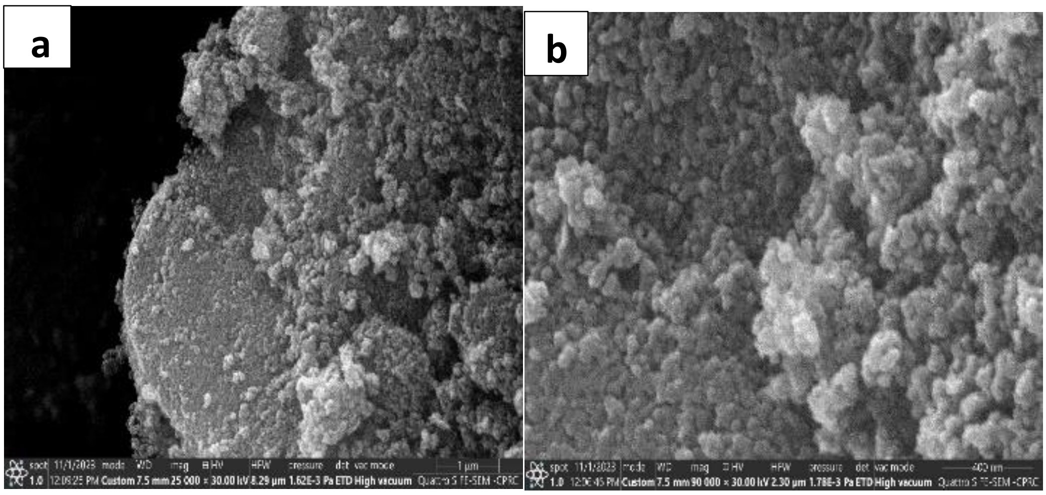

Fig. 4. SEM images of magnetite

The TEM picture demonstrates the presence of ultrafine particles with irregular forms (Fig. 5). Based on the diminutive dimensions of particles, it can be posited that their morphology exhibits a dot-encircled, nearly spherical configuration.

The particle size distribution analysis indicates that the particles are dispersed throughout a range of approximately 7-18 nm, with an average size of around 15.1 nm. The particle sizes detected in the (TEM) micrograph were consistent with the (XRD) analysis results. The particles exhibit a mostly spherical morphology and tend to overlap, forming an aggregated structure.

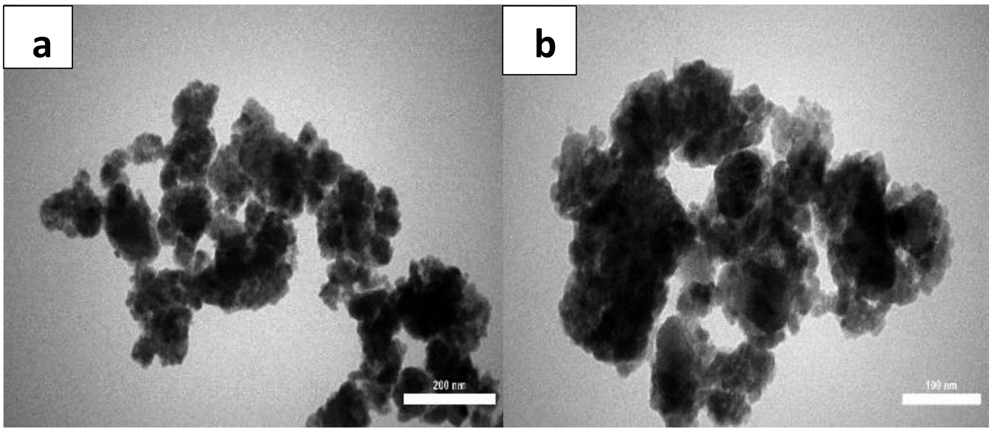

Fig. 5. TEM images for magnetite

As shown in Fig. 6, the presence of peaks corresponding to iron (Fe) and oxygen (O) in the EDX spectra provides evidence supporting the development of magnetite nanoparticles, according to the percentages listed in Table 2.

Table 2. Elements in the EDX examination

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
O	67.3	0.5	37.1	0.3
Fe	32.7	0.1	62.9	0.1

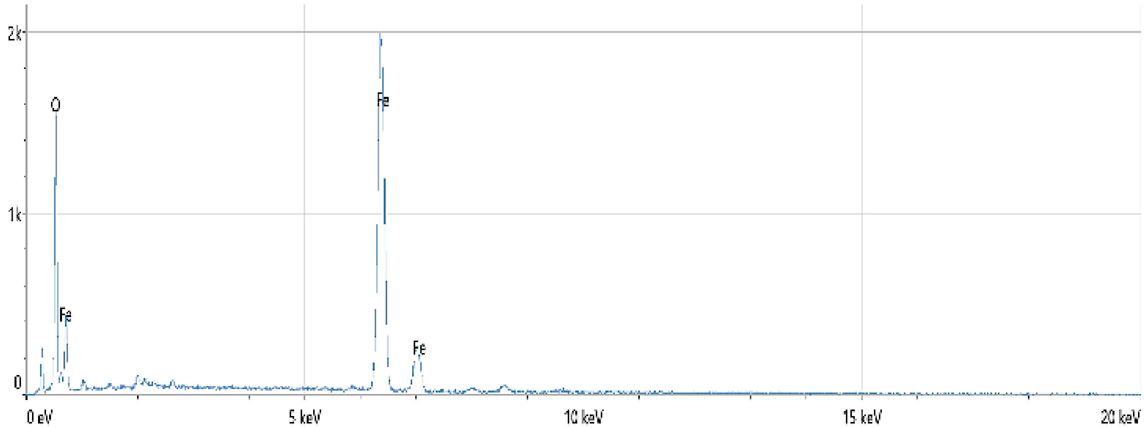

Fig. 6. EDX pattern of magnetite nanoparticles

The results obtained from the BET approach indicate that the specific surface area of MNPs was 83.85 m^2 /g; this can lead to a conclusion that the synthesized magnetite exhibits the properties of nanoparticles with a vast specific surface area compared to the surface area of commercial magnetite, which was 3.36 m^2/g. additionally, the surface area of EDTA-magnetite was found to be 97.64 m^2/g which proved that EDTA enhanced the surface area of magnetite.

According to Fig. 7, the saturation magnetization (Ms) of the synthesized magnetite MNPs powder was 42.4745 emu/g, obtained from the VSM test at ambient temperature.

The result of the AFM test, picture of particles, and particle size distribution for MNPs and coated MNPs are shown in Fig. 8 and Fig. 9, respectively. The mean diameters of magnetite and EDTA-magnetite were found to be 30.8 and 78.9 nm, respectively.

FTIR was utilized to validate the occurrence of the magnetite phase and verify the attachment of functional groups from EDTA to the surface of the iron oxide. Fig. 10 displays the (FTIR) spectra of (a) pure MNPs, (b) (EDTA), and (c) EDTA- Magnetite.

3.2. Gravimetric oil removal

This work employed three crude oil samples with varied APIs (23, 28.4, and 40.3) in oil removal tests. It is well known that raising the API facilitates more excellent oil dispersion. One possible explanation for the dispersive behavior that has been found is that the oils being studied have different chemical compositions. As evidenced by the data in Table 1, the oil's API and viscosity value exhibit an inverse correlation.

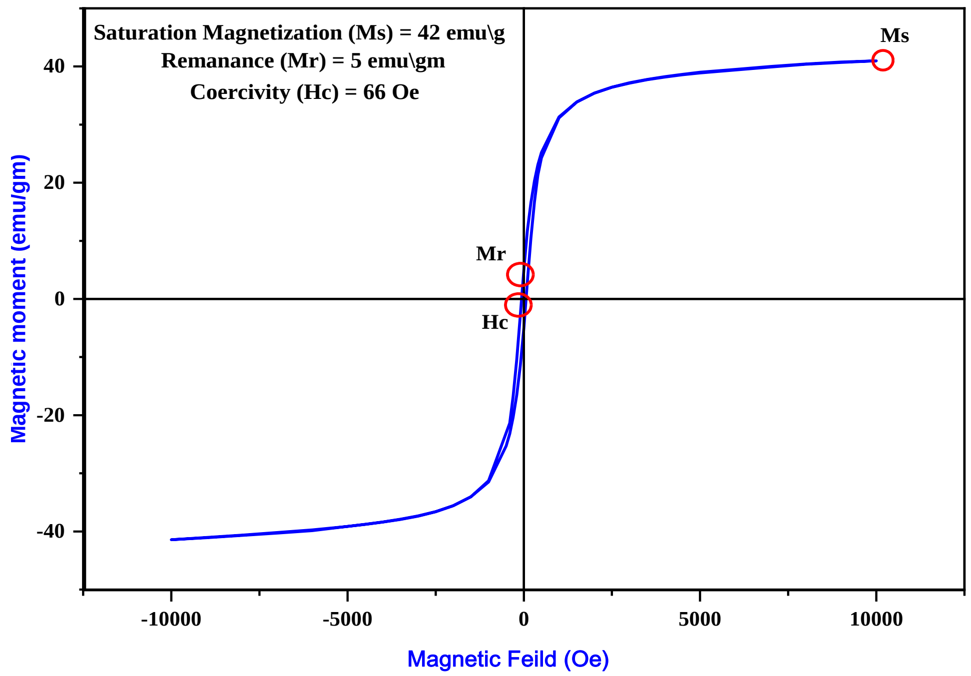

Fig. 7. Magnetization curve of magnetite

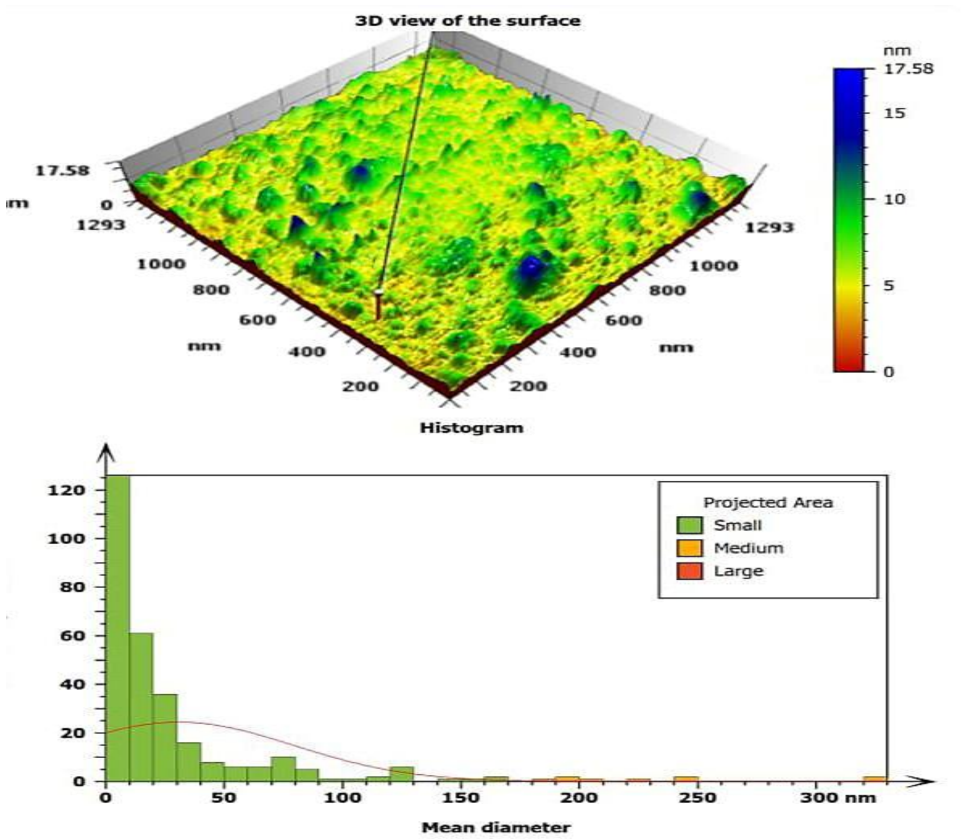

Fig. 8. AFM picture and particles size distribution for magnetite

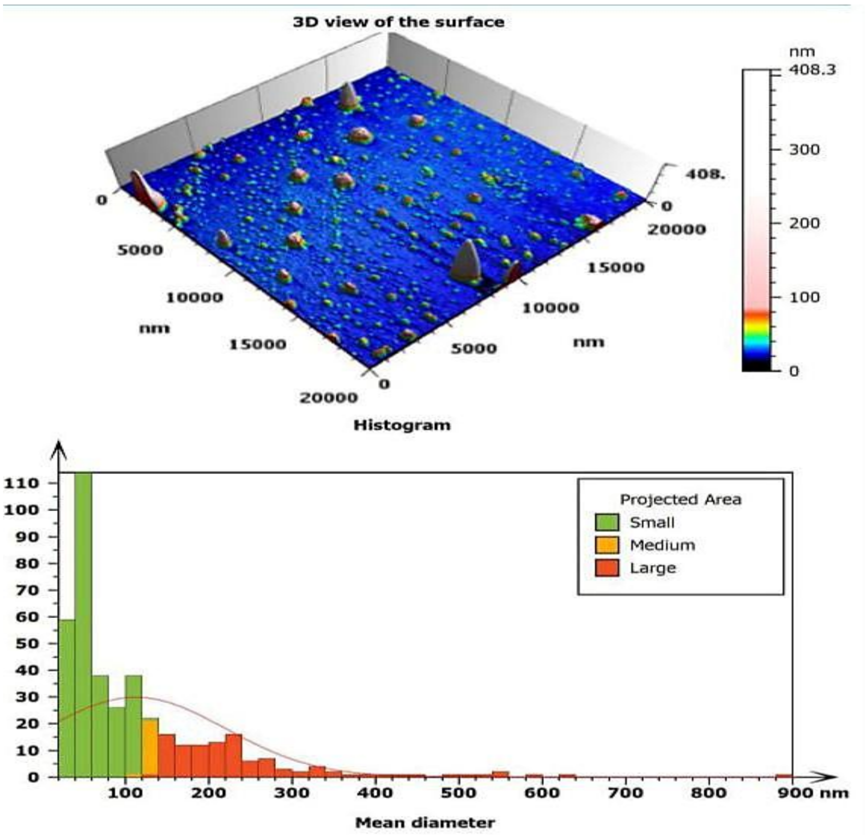

Fig. 9. AFM picture and particles size distribution for EDTA-magnetite

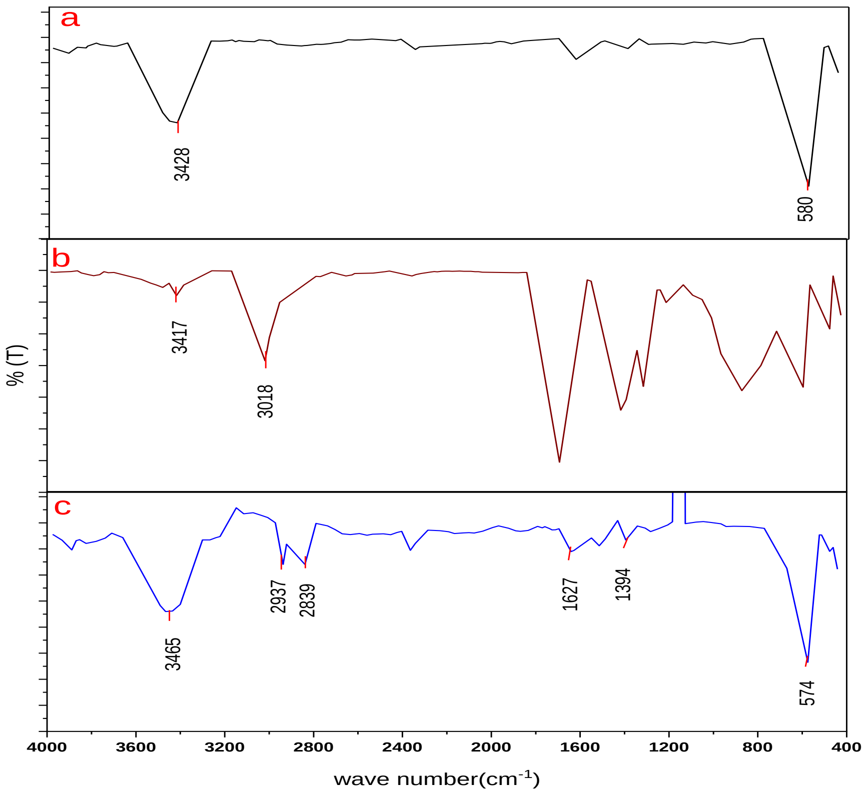

Fig. 10. FTIR spectra of (a) Magnetite (b) EDTA (c) EDTA- magnetite

That is to say, the viscosity decreases as the API increases It is plausible that oils with weaker intermolecular cohesion forces exhibit a higher degree of dispersion [31]. Oil sorption is a multifaceted phenomenon influenced by various characteristics of the oil, such as its API, density, viscosity, and adsorbent material, including its porosity and surface area. Fig. 11 (Error bar) depicts the impact of API on the (GOR, g/g) of the oil samples under investigation, with adsorbent quantities of 0.02g and 0.06g. As evidenced, the oil with the lowest API (23) exhibited the highest (GOR) values (11.4 and 3.35 g/g), in contrast to samples with the highest APIs (28.4 and 40.3), which had a lower GOR (7.19, 2.15 and 4.81, 1.16 g/g). These results can be attributed to the inverse relationship between API and viscosity. Lower viscosity decreases oil adherence to the adsorbent surface, resulting in reduced oil adsorption capacity [32]

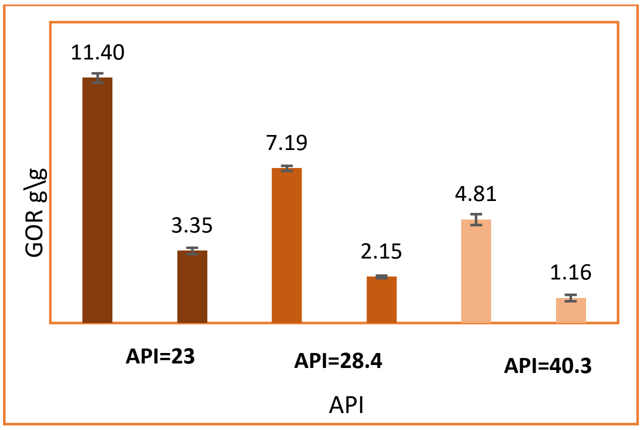

Fig. 11. Dependence of GOR on the tested oil API(at m_1=0.02and 0.06)

Fig. 12 illustrates the relationship between (GOR g|g) and the quantity of adsorbent materials ranging from 0.02 g to 0.06 g. The results demonstrate a clear trend of decreasing (GOR) when the adsorbent amount increases from 0.02 to 0.06 g. specifically, the GOR values fell from 11.4 to 3.35 g/g, 7.19 to 2.15 g/g, and 4.81 to 1.16 g/g for crude oil samples with (APIs) 23, 28.4, and 40.3, respectively.

Previous studies have also documented this decline in oil adsorption capacity (g/g) as the quantity of adsorbent increases [33–35]. The observed decline in adsorption capacity may be due to the aggregation of the adsorbent. Consequently, the sorbent's surface area experienced a reduction, thereby impeding the infiltration of oil spills into the interior pores that are accessible for oil sorption [36].

The high GOR of EDTA-magnetite nanoparticles can be attributed to their nanosize and low density, which allow them to float with the oil on the water surface. Additionally, organic species (EDTA) enhanced the dispersion of iron oxide particles and facilitated penetration into the oil. The high surface area of coated nanoparticles led to high adsorption, and the superparamagnetic properties of magnetite nanoparticles allowed for easy removal using an external magnetic field [37]

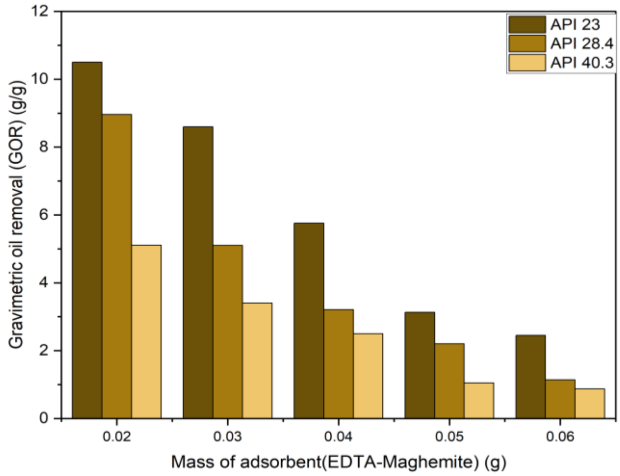

Fig. 12. Correlations between the GOR and the mass of EDTA-magnetite

4- Conclusions

Fe_3O_4 MNPs were synthesized using a co-precipitation process at a temperature of 80°C. The resulting MNPs were then coated with EDTA. The coated MNPs exhibited a high adsorption capacity (GOR g/g) and effectively removed oil spills from water surfaces. GOR experiments were conducted at room temperature using three crude oil samples with different (APIs) (23, 28.4, and 40.3). The results indicated that the crude oil sample with the lowest API gravity (23) exhibited the highest values of oil removal efficiency (10.5 and 2.45 g/g).

The XRD and FTIR analyses conducted on the magnetic nanoparticles (MNPs) provided evidence of the presence of the magnetite phase. The determined crystallite size was approximately 15.1 nm. The particles exhibit a mostly spherical morphology.

EDTA-Magnetite shows less agglomeration when compared with bare MNPs synthesized. So, EDTA acts as a surfactant (reducing the MNP's agglomeration) and leads to an enhanced surface area, as shown in the BET test.

The superparamagnetic character of the synthesized MNPs was confirmed using the VSM test, resulting in improved oil separation efficiency using the magnetic separation technique. The BET analysis revealed that EDTA enhanced the surface area of the synthesized magnetite. FTIR was employed to confirm the presence of functional groups of (EDTA) on the iron oxide surface. The analysis revealed that the crystal structure of magnetite remained unaltered.

In addition to being low-cost, biocompatible, and easily prepared, EDTA-Magnetite exhibits paramagnetic properties, a high surface area, low toxicity, and ease of application.

References

[1] H. M. Ibrahim and R. H. Salman, "Study the Optimization of Petroleum Refinery Wastewater Treatment by Successive Electrocoagulation and Electro-oxidation Systems," *Iraqi Journal of Chemical and Petroleum Engineering.*, vol. 23, no. 1, pp. 31–41, 2022, https://doi.org/10.31699/IJCPE.2022.1.5

[2] R. H. Salman and A. H. Abbar, "Optimization of a combined electrocoagulation-electro-oxidation process for the treatment of Al-Basra Majnoon Oil field wastewater: Adopting a new strategy," *Chemical Engineering and Processing - Process Intensification*, vol. 183, p. 109227, Jan. 2023, https://doi.org/10.1016/j.cep.2022.109227

[3] M. J. Awda and B. A. Abdulmajeed, "Synthesis, Characterization, and Application of EDTA-Coated Maghemite Magnetic Nanoparticles for Oil Spill Cleanup from Water Surface," *International Journal of Engineering.*, no. Articles in Press, 2024. https://doi.org/ 10.5829/IJE.2024.37.08B.04

[4] M. D. S. L. Mendes, L. C. D. S. Coutinho, A. B. Araujo, M. A. F. E. S. Neves, and M. S. Pedrosa, "Comprehensive Review of Magnetic Polymeric Nanocomposites with Superparamagnetic Iron Oxide Nanoparticles for Oil Removal from Water," *Revista de Chimie (Rev. Chim.)*, vol. 74, no. 1, pp. 40–57, 2023, https://doi.org/10.37358/RC.23.1.8562

[5] I. Ali, Z. Mohamed, and M. Alsalheen, "Oil Spill Removal from Water by Absorption on Zinc-Doped Cobalt Ferrite Magnetic Nanoparticles," *Advanced Journal of Chemistry-Section A*, vol. 2, no. 4, pp. 365–376, 2019. https://doi.org/10.33945/sami/ajca.2019.4.9

[6] S. Mirshahghassemi and J. R. Lead, "Oil Recovery from Water under Environmentally Relevant Conditions Using Magnetic Nanoparticles," *Environmental Science and Technology.*, vol. 49, no. 19, pp. 11729–11736, 2015, https://doi.org/10.1021/acs.est.5b02687

[7] K. W. Wirtz and X. Liu, "Integrating economy, ecology and uncertainty in an oil-spill DSS: The Prestige accident in Spain, 2002," *Estuarine, Coastal and Shelf Science.*, vol. 70, no. 4, pp. 525–532, 2006, https://doi.org/10.1016/j.ecss.2006.06.016

[8] J. D. Orbell, L. Godhino, S. W. Bigger, T. M. Nguyen, and L. N. Ngeh, "Oil spill remediation using magnetic particles: An experiment in environmental technology," *Journal of Chemical Education*, vol. 74, no. 12, pp. 1446–1448, 1997, https://doi.org/10.1021/ed074p1446

[9] C. Jiang, R. Wang, and W. Ma, "The effect of magnetic nanoparticles on Microcystis aeruginosa removal by a composite coagulant," *Colloids and Surfaces A: Physicochemical and Engineering Aspects.*, vol. 369, no. 1–3, pp. 260–267, 2010, https://doi.org/10.1016/j.colsurfa.2010.08.033

[10] B. I. Kharisov, H. V. R. Dias, and O. V. Kharissova, "Nanotechnology-based remediation of petroleum impurities from water," *Journal of Petroleum Science and Engineering*, vol. 122, pp. 705–718, 2014, https://doi.org/10.1016/j.petrol.2014.09.013

[11] J. Ross, D. Hollander, S. Saupe, A. B. Burd, S. Gilbert, and A. Quigg, "Integrating marine oil snow and MOSSFA into oil spill response and damage assessment," *Marine Pollution Bulletin.*, vol. 165, p. 112025, 2021. https://doi.org/10.1016/j.marpolbul.2021.112025

[12] U. Anwana Abel, G. Rhoda Habor, and O. Innocent Oseribho, "Adsorption Studies of Oil Spill Clean-up Using Coconut Coir Activated Carbon (CCAC)," *IOSR Journal of Applied Chemistry*, vol. 8, no. 2, p. 36, 2020, https://doi.org/10.9790/5736-1303024256

[13] A. F. Al-Alawy and M. K. Al-Ameri, "Treatment of simulated oily wastewater by ultrafiltration and nanofiltration processes," *Iraqi Journal of Chemical and Petroleum Engineering.*, vol. 18, no. 1, pp. 71–85, 2017. https://doi.org/10.31699/IJCPE.2017.1.6

[14] K. H. Mnaty and A. M. Saleem, "Using the nanotechnology method to remove oil spill pollution of water," in *AIP Conference Proceedings*, 2023, vol. 2809, no. 1. https://doi.org/10.1063/5.0151527

[15] S. Ko *et al.*, "Amine functionalized magnetic nanoparticles for removal of oil droplets from produced water and accelerated magnetic separation," *Journal of Nanoparticle Research*, vol. 19, no. 4. Springer Science and Business Media B.V., Apr. 01, 2021. https://doi.org/10.1007/s11051-021-05355-6.

[16] A. Akrami and A. Niazi, "Synthesis of maghemite nanoparticles and its application for removal of Titan yellow from aqueous solutions using full factorial design," *Desalination and Water Treatment*, vol. 57, no. 47, pp. 22618–22631, Oct. 2016, https://doi.org/10.1080/19443994.2015.1136693

[17] S. Majidi, F. Zeinali Sehrig, S. M. Farkhani, M. Soleymani Goloujeh, and A. Akbarzadeh, "Current methods for synthesis of magnetic nanoparticles," *Artificial Cells, Nanomedicine, and Biotechnology.*, vol. 44, no. 2, pp. 722–734, 2016. https://doi.org/10.3109/21691401.2014.982802

[18] S.-M. Taghizadeh, A. Berenjian, M. Zare, and A. Ebrahiminezhad, "New perspectives on iron-based nanostructures," *Processes*, vol. 8, no. 9, p. 1128, 2020. https://doi.org/10.3390/pr8091128

[19] D. B. Fumis, M. L. D. C. Silveira, C. Gaglieri, L. T. Ferreira, R. F. C. Marques, and A. G. Magdalena, "The Effect of EDTA Functionalization on Fe 3 O 4 Thermal Behavior," *Materials Research.*, vol. 25, 2022. https://doi.org/10.1590/1980-5373-MR-2022-0312

[20] D. I. Sandoval-Cárdenas *et al.*, "Sargassum@magnetite Composite EDTA-Functionalized for the Potential Removal of Mercury," *Polymers (Basel).*, vol. 15, no. 6, 2023, https://doi.org/10.3390/polym15061405

[21] J. A. Ramos-Guivar, E. O. López, J. M. Greneche, F. Jochen Litterst, and E. C. Passamani, "Effect of EDTA organic coating on the spin canting behavior of maghemite nanoparticles for lead (II) adsorption," *Applied Surface Science*, vol. 538, no. October 2020, p. 148021, 2021, https://doi.org/10.1016/j.apsusc.2020.148021

[22] B. Hirani, P. S. Goyal, S. S. Sagare, S. H. Deulkar, A. Dsouza, and S. Rayaprol, "Magnetic properties of Fe3O4 nanoparticles having several different coatings," *Bulletin of Materials Science.*, vol. 46, no. 4, p. 216, 2023. https://doi.org/10.1007/s12034-023-03049-4

[23] W. Cai and J. Wan, "Facile synthesis of superparamagnetic magnetite nanoparticles in liquid polyols," *Journal of Colloid and Interface Science*, vol. 305, no. 2, pp. 366–370, Jan. 2007, https://doi.org/10.1016/j.jcis.2006.10.023

[24] M. Shahrekizad, A. G. Ahangar, and N. Mir, "EDTA-Coated Fe 3 O 4 Nanoparticles : a Novel Biocompatible Fertilizer for Improving Agronomic Traits of Sunflower (Helianthus Annuus)," *Journal of Nanostructures*,vol. 5, pp. 117–127, 2015. https://doi.org/10.7508/JNS.2015.02.006

[25] I. A. Amar, S. I. Faraj, M. A. Abdulqadir, I. A. Abdalsamed, F. A. Altohami, and M. A. Samba, "Oil spill removal from water surfaces using zinc ferrite magnetic nanoparticles as a sorbent material," *Iraqi Journal of Science*, vol. 62, no. 3, pp. 718–728, 2021, https://doi.org/10.24996/ijs.2021.62.3.2

[26] A. F. Al-Alawy, E. E. Al-Abodi, and R. M. Kadhim, "Synthesis and Characterization of Magnetic Iron Oxide Nanoparticles by Co-Precipitation Method at Different Conditions," *Journal of Engineering*, vol. 24, no. 10, pp. 60–72, Oct. 2018, https://doi.org/10.31026/j.eng.2018.10.05

[27] A. Afkhami and R. Moosavi, "Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles," *Journal of Hazardous Materials*, vol. 174, no. 1–3, pp. 398–403, Feb. 2010, https://doi.org/10.1016/j.jhazmat.2009.09.066

[28] [28] H. Namduri and S. Nasrazadani, "Quantitative analysis of iron oxides using Fourier transform infrared spectrophotometry," *Corrosion Science*, vol. 50, no. 9, pp. 2493–2497, Sep. 2008, https://doi.org/10.1016/j.corsci.2008.06.034

[29] W. Cai and J. Wan, "Facile synthesis of superparamagnetic magnetite nanoparticles in liquid polyols," *Journal of Colloid and Interface Science*, vol. 305, no. 2, pp. 366–370, Jan. 2007, https://doi.org/10.1016/j.jcis.2006.10.023

[30] R. M. Cornell and U. Schwertmann, *The iron oxides: structure, properties, reactions, occurrences, and uses*, vol. 664. Wiley-vch Weinheim, 2003. https://doi.org/10.1002/3527602097

[31] D. S. Cardona,KB.Debs,SG.Lemos,G. Vitale,NN.Nassar,EN.Carrilho,D.Semensatto,G.Labuto , "A comparison study of cleanup techniques for oil spill treatment using magnetic nanomaterials," *Journal of Environmental Management*, vol. 242, pp. 362–371, Jul. 2019, https://doi.org/10.1016/j.jenvman.2019.04.106

[32] F. Damavandi and J. B. P. Soares, "Polystyrene magnetic nanocomposite blend: an effective, facile, and economical alternative in oil spill removal applications," *Chemosphere*, vol. 286, p. 131611, 2022. https://doi.org/10.1016/j.chemosphere.2021.131611

[33] I. A. Amar, A. Alzarouq, W. Mohammed, M. Zhang, and N. Matroed, "Oil spills removal from seawater surface by magnetic biochar composite derived from Heglig tree bark and cobalt ferrite," *World Journal of Engineering*, Sep. 2023, https://doi.org/10.1108/WJE-11-2022-0459

[34] F. da Silveira Maranhão,F. , Gomes,S. Thode,DB.Das,E. Pereira ,N.Lima,F. Carvalho,M Aboelkheir,V.Costa,and,K.Pal,"Oil Spill Sorber Based on Extrinsically Magnetizable Porous Geopolymer," *Materials*, vol. 14, no. 19, p. 5641, Sep. 2021, https://doi.org/10.3390/ma14195641

[35] F. Gomes de Souza, J. A. Marins, C. H. M. Rodrigues, and J. C. Pinto, "A Magnetic Composite for Cleaning of Oil Spills on Water," *Macromolecular Materials and Engineering*, vol. 295, no. 10, pp. 942–948, Aug. 2010, https://doi.org/10.1002/mame.201000090

[36] E.Elias,R.Costa,F.Marques,G.Oliveira,Q.Guo,S.Thomas,and Jr.Souza "Oil-spill cleanup: The influence of acetylated curaua fibers on the oil-removal capability of magnetic composites," *Journal of Applied Polymer Science*, vol. 132, no. 13, Dec. 2014, https://doi.org/10.1002/app.41732

[37] O. Saber, N. H Mohamed, and A. Aljaafari, "Synthesis of magnetic nanoparticles and nanosheets for oil spill removal," *Nanoscience Nanotechnology-Asia*, vol. 5, no. 1, pp. 32–43, 2015. https://doi.org/10.2174/2210681205666150601215445

تنظيف الانسكابات النفطية باستخدام الجسيمات النانوية المغناطيسية المطلية بـEDTA

مها جلال عودة [١، *]، بسمة عباس عبد المجيد [١]، زيد نضال شريف [٢]

١ قسم الهندسة الكيمياوية، كلية الهندسة، جامعة بغداد، بغداد، العراق
٢ جامعة كيرتن، قسم الهندسة الكيمياوية، استراليا

الخلاصة

تعد الانسكابات النفطية أحد المصادر الرئيسية لتلوث المياه، والتي تؤثر سلبًا على البيئة والاقتصاد. قد تحدث الانسكابات النفطية أثناء التنقيب أو النقل أو التخزين. نظراً للأهمية الكبيرة للنفط الخام في الحضارة الصناعية المعاصرة، فإن الانسكابات النفطية، وخاصة تلك الناتجة عن النفط الخام، تؤدي إلى تحديات بيئية وإيكولوجية كبيرة. وعلى النقيض من أساليب المعالجة التقليدية، أثبتت تكنولوجيا النانو فعاليتها في معالجة الانسكابات النفطية. اعتمدت هذه الدراسة طريقة بسيطة واقتصادية باستخدام الجسيمات النانوية المغناطيسية لأكسيد الحديد. تم تصنيع المغنتيت Fe_3O_4 MNPs باستخدام تقنية الترسيب المشترك، والتي تتضمن دمج أيونات الحديديك وأيونات الحديدوز في محلول قلوي عند (٨٠ درجة مئوية ودرجة الحموضة ١٤)، والتي تم تشخيصها باستخدام حيود الأشعة السينية (XRD)، التحليل الطيفي للأشعة تحت الحمراء لتحويل فوريه. (FTIR)، المجهر الإلكتروني النافذ (TEM)، المجهر الإلكتروني الماسح (SEM)، التحليل الطيفي للأشعة السينية المشتتة من الطاقة (EDX)، ومقياس مغناطيسية العينة الاهتزازية (VSM). تم طلاء الجسيمات النانوية المغناطيسية (MNPs) بحمض الإيثلين ثنائي أمين رباعي الأسيتيك (EDTA) لتحسين ثباتيتها وفعاليتها. تم استخدام ثلاث عينات من النفط الخام ذات قيم API (مقياس الكثافة النوعية حسب معهد النفط الأمريكي) مختلفة (٢٣،٢٨,٤،٤٠,٣) لدراسة قدرة MNPs المطلية على تنظيف الانسكاب النفطي. أجريت تجارب الإزالة عند درجة حرارة الغرفة باستخدام اوزان مختلفة من المادة المازة (٠,٠٢–٠,٠٦ جم). تم استخدام مغناطيس النيوديميوم لفصل الجسيمات النانوية المغناطيسية الملوثة بالنفط من الماء. كانت قيم الإزالة الوزنية (GOR) لنماذج النفط ذات قيم:API ٢٣ ,٢٨,٤ و٤٠,٣ هي ١١,٤ – ٣٥.٣، ٧,١٩ – ٢,١٥، و٤,٨١ – ١,١٦ جم/جم، على التوالي. وجد من التجارب أن الازالة الوزنية (GOR) تزداد كلما قلت قيمة API بينما زيادة وزن المادة المازة كان له تأثير معاكس.

الكلمات الدالة: الانسكاب النفطي، الجسيمات النانوية المغناطيسية، النفط الخام، EDTA، المغنتيت.