Research Article

Synthesis, Characterization, and Application of Magnetite Nanoparticles Coated with Hydrophobic Polyethyleneimine for Oil Spill Cleaning

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Pollution with oil spills, a major contributor to water contamination, has a remarkable effect on the economy, biodiversity, and environment. To protect marine species and environment, efforts should be undertaken for developing efficient ways to remove oil spills. The current work discusses the oil spill removal using magnetite nanoparticles (MNPs) functionalized with hydrophobic polyethyleneimine (HPEA). In this respect, nonylphenol pentatetraethylenehexamine (NTEPA) and nonylphenol triethylenetetramine (NDETA) were prepared by a simple one-step method and used as capping agents in the synthesis of hydrophobically modified magnetite nanoparticles designated as NDETA/Fe₃O₄ (magnetite as a core and NDETA as a shell) and NTEPA/Fe₃O₄ (magnetite as a core and NTEPA as a shell). The prepared MNPs were characterized using FTIR, XRD, TEM, DLS, TGA, and DSA to determine their physical and chemical properties. Additionally, MNPs were applied as oil spill collectors with high efficiencies that reached 93% and 90% for NDETA/Fe₃O₄ and NTEPA/Fe₃O₄, respectively, at low magnetite to oil ratios.

1. Introduction

Nowadays, nanotechnology is involved in various fields due to its ability to control the molecular structure of materials to change their intrinsic characteristics that lead to enhancing and revolutionizing their applications [1, 2]. Among nanomaterials, iron oxide nanoparticles (MNPs) have become an area of intensive research in various fields like energy, engineering, and environmental applications such as heavy metal removal and petroleum oil spillage remediation due to their distinguished magnetic characteristics [3–8]. Because of the high biocompatibility and low toxicity of magnetite nanoparticles (Fe₃O₄), they are the most commonly used iron oxide [9, 10]. By altering the surface chemistry of magnetite nanoparticles with different polymeric materials such as polyethylene glycol, chitosan, cellulose, and polyamine, the produced hybrid materials can be applied in multiple areas [11–14]. As a biocompatible coating agent, polyethyleneimine (PEI) has been utilized in nanomaterial synthesis to prevent their aggregation and decorate their surfaces with amino groups [15, 16].

The pollution by oil spills usually occurs during the production and transportation of crude oil, and it has harmful environmental consequences on aquatic life, economy, tourism, and leisure activities as a result of the coating properties of these materials [17, 18]. Moreover, oil spreading on marine environment is subjected to drifting, evaporation, dissolution, photolysis, biodegradation, and formation of water-oil emulsions [8, 19, 20]. Due to the harmful effects of oil spill disaster, oil cleanup has been a research focus on diverse areas of knowledge [21–23]. The most common chemical methods used to clean up oil are dispersants, absorbents, and collectors [8, 24, 25]. Dispersants are chemical agents with surface activity that are sprayed onto oil spills by specially equipped boats or planes to help break up an oil slick into very small droplets, which dilute throughout the water. The main drawback of this method is that smaller oil particles remain on the water surface and
need long time to degrade [26]. Oil absorbents are porous three-dimensional hydrophobic or oleophilic network structure able to absorb huge amount of oil. Their main disadvantage is that they degrade very slowly and are not naturally occurring as mineral products [27, 28].

Recently, multifunctional nanomaterials have gained a great attention for their technological and biological applications [29]. Various nanomaterials like silica, carbon nanotubes, and magnetite have been synthesized aimed at oil spill removal from the water [30–33]. The functionalization of MNPs with hydrophobic or hydrophilic capping agents can be carried out by simple chemical modification of Fe₃O₄ surfaces during or after their synthesis [34–37]. Hydrophobic magnetic nanoparticles with excellent magnetic properties can be applied in several petroleum and environmental processes such as demulsification, enhanced oil recovery, and oil spill containments [8, 38, 39]. Thanks to the unique characteristics of magnetite nanoparticles like low cost and easy production, chemical stability, good biocompatibility, superparamagnetism, and reusability, they were used for oil removal by applying an external magnet [40–42].

As stated in the first paragraph, polyethyleneimine (PEA) was utilized successfully as organic coating on the magnetite surface to control its particle size and for functionalizing the magnetite surface. In the present work, pentaethylene hexamine and triethylene tetramine were modified with a long chain glycidyl ether by a facile one-step method to prepare hydrophobic polyethylene amines (HPEAs) that were used as capping agents to prepare monodisperse hydrophobic magnetite nanoparticle. The prepared MNPs were well characterized and applied for the collection of heavy petroleum crude oil spills from sea water surfaces with high efficiency.

2. Experiment

2.1. Materials. Pentaethylene hexamine, triethylene tetramine, glycidyl 4-nonylphenyl ether (GNPE), hydrated ferric chloride (FeCl₃·6H₂O), hydrated ferrous chloride (FeCl₂·4H₂O), and ammonium hydroxide (NH₄OH) were supplied by Sigma-Aldrich, while ethanol (99.9%) was purchased from Sinopharm Chemical Reagent Co. Riyadh refinery unit (Aramco Co.) was the supplier for Arabian heavy crude oil with specifications mentioned in our previous work [43], and sea water was brought from Arabian Gulf at Dammam coast.

2.2. Synthesis Procedure

(a) Synthesis of hydrophobic polyethyleneimine

Hydrophobic polyethyleneimines (HPEA), NTEPA and NDETA, were synthesized according to the method mentioned in our previous work [44] with some modifications. Pentaethylene hexamine (10 mmol, 2.32 g) or triethylene tetramine (10 mmol, 1.46 g) were separately mixed with glycidyl 4-nonylphenyl ether (20 mmol, 5.52 g) in three neck flasks with stirring under nitrogen atmosphere at 120°C for 4 h. After the reaction completed, the reaction mixture was cooled down, dissolved in isopropanol, and salted out several times with supersaturated NaCl solution to remove the unreacted polyethyleneimine. The isopropanol layer was separated and evaporated using a rotary evaporator to get viscous brown liquids of NDETA and NTEPA as shown in Scheme 1.

(b) Synthesis of magnetite nanoparticles capped with HPEA

Magnetite nanoparticles were synthesized by coprecipitation of ferric chloride hexahydrate (FeCl₃·6H₂O, 5.4 g) and ferrous chloride tetrahydrate (FeCl₂·4H₂O, 2.0 g) dissolved in 100 mL of distilled H₂O using ammonia solution as reported in our previous work [45]. The formed black suspension of MNPs was collected using an external magnet and washed several times with distilled H₂O to get rid of the excess ammonia solution. The obtained MNPs were dispersed again in 50 mL of ethanol using a probe sonicator for 10 min and then mixed with HPEA (1 g dissolved in 10 mL ethanol) under continuous mechanical stirring for further 2 h at 60°C. The prepared MNPs were collected using an external magnet, washed several times with ethanol to remove unreacted HPEA, and then dried in a vacuum oven at 60°C to get NDETA/Fe₃O₄ (magnetite as a core and NDETA as a shell) and NTEPA/Fe₃O₄ (magnetite as a core and NTEPA as a shell).

2.3. Characterization Methods of NDETA/Fe₃O₄ and NTEPA/Fe₃O₄ Nanoparticles. Fourier transform infrared (FTIR) spectrum was carried out via Shimadzu FTIR 8000 spectrometer (Kyoto, Japan) using KBr pellets; the polydispersity index (PDI) in chloroform was determined using DLS (Zetasizer Nano ZS, Malvern Instrument Ltd., Malvern, UK). Transmission electron microscope images of NDETA/Fe₃O₄ and NTEPA/Fe₃O₄ were recorded using TEM (JEM-2100F, Jeol Co., Tokyo, Japan). The crystalline structure was determined using an X-ray powder diffractometer (BDX-3300 diffractometer; Eindhoven, Netherlands). The thermal degradations of the prepared MNPs were recorded using TGA-50 (SHIMADZU, Tokyo, Japan) under N₂ flow with a heating rate of 10°C/min. Contact angle was determined using a drop shape analyzer (DSA-100, Krüss GmbH, Hamburg, Germany). The magnetic properties were obtained using vibrating-sample magnetometry (VSM) with a LD9600 magnetometer (LD Electronics, MI, USA).

2.4. Efficiency of NDETA/Fe₃O₄ and NTEPA/Fe₃O₄ as Oil Spill Collectors. To apply MNPs as oil spill collectors, the magnetite powder was spread over Arabian heavy crude oil spot (2 g), placed on 250 mL of seawater in a 500 mL beaker, with mixing slowly using a glass rod for 1 minute. Magnetite to oil ratios ranged from 1 : 10 to 1 : 50 Wt%, respectively, to detect the effect of magnetite concentration on the collecting efficiency. Then, the oil spill/magnetite mixture was collected using a permanent magnet of Nd–Fe–B (4300 Gauss).

The noncollected oil remaining on the sea water surface was extracted from water using chloroform which was distilled off using a rotary evaporator under reduced pressure
to isolate the oil residue. The collection efficiency was determined using the following equation:

$$CE(\%) = \frac{W_{ti} - W_{tr}}{W_{ti}} \times 100,$$

where $W_{ti}$ is the initial weight of crude oil spill and $W_{tr}$ is the remaining weights of oil on the sea water surface after the collection process.

### 3. Results and Discussions


The chemical properties of the prepared HPEAs were investigated using $^1$HNMR and $^{13}$CNMR spectra of NTEPA (Figures 1 and 2) as both NTEPA and NDETA have almost similar structures except the ethyleneamine units. The $^1$HNMR spectra (Figure 1) showed the presence of triplet signal at 0.30-0.42 ppm of CH$_3$ protons and multiplet signals at 0.44-0.51 ppm, 0.7-0.96 ppm, 1.12-1.29 ppm, and 1.98-2.16 ppm of CH$_2$ protons of the nonyl alkyl chains. The multiplet peaks at 2.25-2.45 ppm are related to NCH$_2$CH$_2$N protons to verify the amination of glycidyl groups. The doublet and multiplet peaks at 3.82 ppm and 3.97 ppm are related to the alcoholic and phenolic CH$_2$O, respectively, that verify epoxy ring opening. Doublet and multiplet peaks at 6.52 ppm and 6.82-6.89 ppm are related to the aromatic protons. Peaks at 49 and 53 ppm in the $^{13}$C NMR spectra due to CH$_2$NH and CH$_2$NHCHOH to verify epoxy ring opening by amino group attack as shown in Scheme 1. The FTIR spectra of NDETA and NTEPA, depicted in Figures 3(a) and 3(b), respectively, present signals at 3401 cm$^{-1}$, 2959 cm$^{-1}$, and 1660 cm$^{-1}$ that correspond to alcoholic hydroxyl and secondary amine, stretching bands of aliphatic C-H and stretching bands of aromatic C=C bonds, respectively. The strong absorption bands for both NDETA/Fe$_3$O$_4$ and NTEPA/Fe$_3$O$_4$ at about 580 cm$^{-1}$ (Figures 3(c) and 3(d)) are due to Fe–O stretching vibration for the MNPs [46, 47]. The lowering in the intensities of N–H, C–H, and C=C bonds in both NDETA/Fe$_3$O$_4$ and NTEPA/Fe$_3$O$_4$ (Figures 3(c) and 3(d)) confirms the interaction and capping of MNPs with NDETA and NTEPA, respectively [8].

X-ray diffraction was used to characterize the crystalline structure of the prepared MNPs. Figure 4 shows the XRD pattern of magnetite nanoparticles coated with hydrophobic polyethyleneimines (NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$). The X-ray diffractograms of both samples have the characteristic profiles of magnetite with peaks at $2\theta$ values of 30.1\textdegree, 35.4\textdegree, 37.0\textdegree, 43.0\textdegree, 53.6\textdegree, 57.1\textdegree, and 62.3\textdegree corresponding to crystal planes (220), (311), (222), (400), (422), (511), and (440), respectively, to confirm the formation of magnetite without other oxides.

The diameter and dispersity of the magnetite nanoparticles can be further evaluated in chloroform, as a nonpolar solvent, using DLS measurements. The hydrodynamic diameters of NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$ (Figures 5(a) and 5(b)) were 134±8 nm and 243±180 nm, respectively. The use of the two prepared HPEI for the coating of MNPs yielded highly stable colloidal solutions in chloroform solvent to indicate the ability of the prepared HPEA to alter the magnetite surface, control the particle size, and form highly stable colloidal solution. Samples of NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$ were further characterized using transmission electron microscopy (TEM) (Figures 6(a) and 6(b)) which shows that Fe$_3$O$_4$ particles capped with NTEPA, with longer ethyleneamine units, have less aggregations than those of NDETA/Fe$_3$O$_4$. These results are in good agreement with the characterization of HPEA and the magnetite nanoparticles coated with it.
Figure 1: $^1$H-NMR spectra of NTEPA.

Figure 2: $^{13}$C-NMR spectra of NTEPA.

Figure 3: FTIR spectra of (a) NTEPA, (b) NDETA, (c) NTEPA/Fe$_3$O$_4$, and (d) NDETA/Fe$_3$O$_4$. 
with those obtained from DLS study (Figures 5(a) and 5(b)) which indicated the formation of some aggregates in NDETA/Fe$_3$O$_4$ with higher particle size compared with NTEPA/Fe$_3$O$_4$.

The thermal decompositions of the prepared magnetite nanoparticles and their coating agents were determined by thermogravimetric analysis. Figure 7 displays the thermogravimetric analysis (TGA) of Fe$_3$O$_4$ nanoparticles and their hydrophobic HPEA coatings in order to study the weight percentage of the coating layer [48]. From this, it was determined that hydrophobic HPEA mass loss happened at the temperature range 250-650°C and 300-600°C for NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$, respectively. The high temperatures that the hydrophobic HPEA coating started to be removed from the magnetite surfaces in both NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$ indicate that HPEA was chemically bonded to Fe$_3$O$_4$ surfaces [49]. Furthermore, in order to determine the precise percentages of the coating agents on the magnetite nanoparticles, the residual weights at 700°C for both NTEPA and NDETA were determined to be found around 0% for the former and 2% for the latter. Additionally, the residual weights at 700°C for NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$ were 76.4% and 77.8%, respectively, so it can be concluded that the percentages of the
Figure 6: TEM micrographs of (a) NTEPA/Fe₃O₄ and (b) NDETA/Fe₃O₄.

Figure 7: TGA thermograms of NTEPA/Fe₃O₄, NDETA/Fe₃O₄, NTEPA, and NDETA.
coating agent, considering the degradation of the pure organic materials, are 23.6% and 20.2% for NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$, respectively.

3.2. Oil Collecting Efficiency Using MNPs/HPEA. The prepared magnetite nanoparticles were applied as oil spill collectors by the method mentioned in the experimental part.

![Figure 8: Contact angles of a water droplet placed on a thin film of (a) NTEPA/Fe$_3$O$_4$ and (b) NDETA/Fe$_3$O$_4$.](image)

![Figure 9: VSM loop of NTEPA/Fe$_3$O$_4$ and NDETA/Fe$_3$O$_4$ at 25°C.](image)

<table>
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<tr>
<th>MNPs</th>
<th>Oil spill collecting efficiency using different MNPs/crude oil Wt%</th>
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<tr>
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<tr>
<td>NTEPA/Fe$_3$O$_4$</td>
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<tr>
<td>NDETA/Fe$_3$O$_4$</td>
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High hydrophobicity, magnetism, and monodispersity of MNPs are crucial characteristics that magnetite nanoparticles should possess to be efficient in oil spill cleaning application. The hydrophobicity of the synthesized MNPs was tested by measuring the contact angle of seawater drop placed on a compressed magnetite disk as displayed in Figures 8(a) and 8(b). Surfaces are considered to be hydrophilic when its water \( \theta \) is <90\(^\circ\) and hydrophobic when \( \theta \) is >90\(^\circ\) [50]. The contact angle measurements were 118 and 120\(^\circ\) for sea water droplet in contact with compressed disks made from NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\), respectively, to substantiate the hydrophobicity of the prepared magnetite nanoparticles. Additionally, the high dispersity and the formation of stable and low particle sized magnetite colloids in chloroform solvent as shown from DLS studies (Figures 5(a) and 5(b)) indicate the hydrophobicity of the magnetite surfaces. The cleaning of oil spill after spreading MNPs on its surface was carried out using an external magnet, so the strong magnetic properties of the prepared material are crucial to achieve the target [18, 51, 52]. The magnetization values of NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\) were determined from Figure 9, and they were 48 and 52 emu/g, respectively. The high magnetization values of NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\) implied the facile collection of the prepared MNPs using an external magnet and the capability to be applied for oil cleaning. The small difference in their magnetism may be related to the higher percentage of HPEA coating in NTEPA/Fe\(_3\)O\(_4\) as indicated from TGA measurements (Figure 7) which cause more insulation against the external applied magnetic force [53, 54].

The prepared MNPs were applied for oil collection using different magnetite to oil ratios ranging from 1:4 to 1:50 Wt% to indicate the best economical ratio, and the efficiencies are tabulated in Table 1. The data shows a high collection efficacy even at low magnetite to oil ratios (1:10) to validate the ability of both NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\) with higher activity to NTEPA/Fe\(_3\)O\(_4\). The higher efficiency of NTEPA/Fe\(_3\)O\(_4\) as compared to the NDETA/Fe\(_3\)O\(_4\) can be attributed to the smaller particle size and the higher ability of the former to disperse in the oil that was in agreement with measurements obtained from DLS studies (Figure 5).

4. Conclusion

In the current work, two hydrophobic polyethyleneimines (HPEAs) were prepared by the reaction of pentaethylene hexamine and triethylene tetramine with glycidyl 4-nonylphenyl ether to produce NTEPA and NDETA, respectively. These two HPEAs were successfully applied as capping agents to MNPs by the postsynthesis method. The prepared MNPs (NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\)) were characterized using FTIR, XRD, TEM, DLS, TGA, and DSA. The hydrophobicity is an important factor in the application of MNPs as oil spill collectors; therefore, it was measured for both NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\) using DLS. The contact angles of sea water droplet on thin films of NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\) were 118 and 120\(^\circ\), respectively, to indicate the hydrophobicity of the prepared material. Moreover, both magnetite materials formed stable and monodisperse colloids in chloroform to further indicate the low particle size and hydrophobicity. The high magnetism, low particle size, and hydrophobicity of NTEPA/Fe\(_3\)O\(_4\) and NDETA/Fe\(_3\)O\(_4\) suggested the ability to be applied as oil spill collectors. NDETA/Fe\(_3\)O\(_4\) and NTEPA/Fe\(_3\)O\(_4\) were applied as oil spill collectors with efficiencies reaching 93% and 90%, respectively, at low magnetite to oil ratios.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no competing financial interest.

Authors’ Contributions

Abdelrahman O. Ezzat was responsible for the conceptualization, methodology, and investigation and edited the paper. Mohd Sajid Ali reviewed and edited the paper. Hamad A. Al-Lohedan was responsible for the supervision and resources.

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