Separation of Crude Oil and Its Derivatives Spilled in Seawater by using Cobalt Ferrite Oxide

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Abstract: Oil spills can cause a wide range of impacts in the marine environment and are often portrayed by the media as 'environmental disasters' with dire consequences predicted for the survival of marine flora and fauna. The purpose of this paper is to study the possibility of using spinel oxide (CFO) as an oil absorbent material with the aim of removing crude oil and its derivatives from aqueous solutions. Spinel oxide from cobalt ferrite nanoparticles with formula CoFe2O4 (CFO) was prepared by sol-gel method. Functional groups were also identified on the surface of the oxide using the infrared spectrum (FTIR). In addition, crude oil and its derivatives were diagnosed using FTIR, and the density and viscosity of crude oil and its derivatives at 15° C temperature. In this study, three samples of seawater were used from different Libyan regions (Gemens Seawater, Abo Sitta Port, Elbrega Anchorage), and Two samples of crude oil were used from different Libyan fields (Light, Medium). The samples of crude oil used at three different concentrations (0.01g, 0.03g, 0.05g). However, the oil removal was calculated for different scenarios as gm / gm and as percentage. The oil removal capabilities of the prepared absorbent were found to be 10.966 2.3651 g/g to 4.5426 ± 0.113 g/g, 31.8333 ± 5.324 g/g to 7.02053 ± 1.1271, 14.7333 ± 3.1988 g/g to 6.01 ± 0.1287 g/g, 47.1033 ± 6.0222 g/g to 9.2122 ± 2.8177, 10.8833 ± 2.1840 g/g to 4.5786 ± 0.1921 g/g, 42.96 ± 1.4046 g/g to 10.5020 ± 1.3172 g/g for Gemmens Seawater (light oil), Gemmens Seawater (medium oil), Port Abu Sitta (light oil), Port Abu Sitta (meduim oil), Elbrega Anchorage (light oil) and Elbrega Anchorage (medium oil), respectively. The results suggest that the prepared magnetic nanoparticles can be used as absorbent materials for removing oil spills from sea water especially at medium oil.

1 INTRODUCTION

Environmental pollution is the pollution of air, land and water in many ways. There are several reasons for environmental pollution, such as from agriculture and industry. Environmental pollution has drastically changed the air, water and terrestrial ecosystems as a result of the industrial revolution in Europe, North America and China in the 19th century. Moreover, different types of toxic gases and different forms of carbon components were produced from factories, transport, and energy sectors has resulted in different changes in the global climate and weather patterns, and become a source of contamination of land, as well as the ocean environment where the average temperature and acidity are increasing. In addition, many other chemicals like fertilizers used in the agricultural industry also contribute to the pollution of the seas over vast areas (Fartoosi and M., 2013).

Oil spills can have devastating effects on waterways and oceans. In the oil it is the polycyclic aromatic hydrocarbons (PAHs) that cause most of the toxicity for human life, but the physical nature of oil, i.e. the stickiness is a major problem for a number of organisms such as birds. Spills of oil has a numerous negative impacts both short and long term, resulting in economic and financial losses. Also, the recovering and clean-up processes are very costly; see for example cases such as the clean-up from the Exxon Valdes or the Deep Water Horizon (Fartoosi and M., 2013). Oil spills could be removed through many methods such as mechanical, chemical and treatment

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by burning in situ, this study will include a part of the chemical methods spinel oxide nanoparticles (magnetic spinal compounds).

1.1 Magnetic Spinel Compounds

The mixed transition elements of the general formula AB2O4 are called spinel's. These oxides take their name from spinel metal (MgAl2O4). A is a binary ion (Fe^2 +, Co^2 +, Ni^2 +, Zn^2 +, Mg^2 +, etc.), while B is a trivalent ion (Fe^3 +, Co^3 +, Cr^3 +, Al^3 +, Mn^3 +, etc.) (Smart,). Spinel oxides are among the most important magnetic nanomaterial's. Spinel ferrite, SF Magnetic nanoparticles are spinel oxides containing tri-iron ions. These oxides have the general formula M^2+ Fe^3 + O_4 (Where M^2 + represents Mn^2 +, Fe^2 +, Co^2 +, Ni^2 +, Zn^2 +, Mg^2 + etc.). These oxides have distinct chemical and physical properties (Reddy, 2016). Excellent magnetic properties, Large surface area, its surface has a large number of effective sites, high chemical stability, easy to prepare and convert to the desired shape (Smart, ; Gomez-Pastora et al.,).

Spinel oxides has wide applications in several fields including: gas sensors, magnetic devices, water purification, medicine, catalysts, recharging batteries and ammonia production by electric stimulation (Amar, 2014), as shown in figure 1.

In the field of water treatment, spinel nanomagnetic nanoparticles on the list of materials can be used as absorbent materials, because it can be removed quickly and easily from the solution after absorption using an external magnetic field, after separating the pollutants can be removed and reused several times, Water Purification.

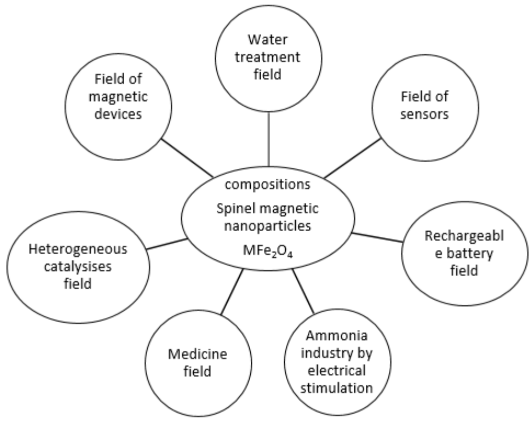

Figure 1: Some applications of spinel ferrite oxides (Amar, 2014)

2 MATERIALS AND CHEMICALS

$CoFe_2O_4$ were used in this study. Seawater three samples were used after routine testing and distilled water. Light and Medium crude oil were also used with (density: 0.8245, API: 40, viscosity: 5.6136 and Boris 3.5915 @ 25° C and @ 37.5° C, Sp.Gr @ 60/60Fo :0.8249) for light. While the (density: 0.8368, API: 37.5, viscosity: 19.5970 and Boris 9.7102 @ 25° C and @ 37.5° C, Sp.Gr @ 60/60 Fo:0.8372) for medium.

2.1 Cobalt Ferrite Oxide Nanoparticle Particles ($CoFe_2O_4$)

The magnetic spinal Cobalt ferrite oxide powder was prepared 10 gm from magnetic spinal Nanoparticle formula CFO)$COFe_2O_4$ (by Sol-gel method (Amar et al., 2018), and The required quantities of cobalt nitrate (12.4041g) and iron nitrate (34.4369g) were weighed, Then add it in a small amount of distilled water. Then add citric acid in amount of (36.8486g) and EDTA in amount of (37.34g) as complication factors, the ammonia solution ($NH_3.H_2O$) was added to pH control to 6, The solution was then evaporated using an electric heater with the solution moving continuously by a magnetic mold to distribute heat. And by continuously heating and stirring solution (mixture) to thick black gel, the magnetic stirrer was then removed and the gel left on the electric burner completely burned and turned into a solid component (ash), The component was milled solid obtained and placed in ceramic seals and burned in the air in the furnace at 600° C for 2 hours to remove the remaining organic compounds and obtain a pure phase of powder (Cobalt ferrite oxide), which will later be used as a maze material to remove the blue methylene dye from its solutions water. Figure 2 Shows the procures to prepare the spinal oxide (Scheffe et al., 2011; Scheffe et al., 2013).

2.2 Sea Water and Crude Oil

Three samples of seawater were obtained from different parts of Libya, Tripoli, Benghazi and Al Brega as shown in the figure 3. The parameters of seawater were calculated at the Faculty of Science University of Sebha, as shown in Table 1. Two samples of crude oil were collected from different fields of Libya (Light, Medium) As shown in the figure 4, Crude oil properties were calculated at the Tripoli Petroleum Research Center as shown in table 2.

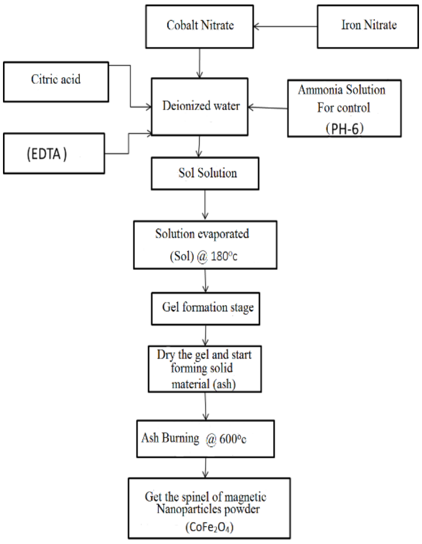

Figure 2: Steps of Preparation Spinal oxide


Figure 3: Shows seawater samples that used in this study


Figure 4: Shows oil samples that used in this study

3 RESULTS AND DISCUSSION

3.1 FTIR Result

Functional groups on the surface of the spinel oxide prepared by the sol-gel method and then identified using the infrared absorption spectrum (FTIR). The car-

Table 1: The Properties of seawater for three samples

Type	Marsa al-Briga	Sea Gmines /Benghazi	Mina Abo-seta /Tripoli
Conductivity (mc/cm)	183.9	186.7	180.7
pH	7.34	7.9	7.52
Salinity (ppm)	1222810	1314210	1132110

Where:
MC/CM = Milli Cemence/Centimeter
Ppm = Pond per Million

Table 2: The Properties of Crude Oil.

Test Method	TestDescription	Unit	Result	
			X- field	X-field
ASTM D 5002	Density @ 15°CSp.Gr 60/60FAPI	g/cc////	0.8368 0.8372 37.5	0.8245 0.8249 40
ASTM D 445	K.Viscosity@25°C K.Viscosity@ 37.8°C	m m^2/s	19.597 9.7102	5.6136 3.5915

Where:
ASTM = American Society for Testing And Material.
K.Viscocity = Kinematic Viscocity Sp.Gr = Specific Gravity

bon nanotube (CFO) oxide after burning the ash compounds in preparation in air at 600°C for two hours. Figure 5 shows the FTTR results for Nanoparticles, it is clearly seen that there are bundles of the terminals at 3968 cm^{-1} and 2928 cm^{-1}; these packets can be attributed to the Co-O and Fe-O bonds, respectively. These specialty packs are characteristic of all spinel oxides. Figure 6 and figure 7 have shown the FTTR results for different oil type, where the range of wavenumber from 600 to 4000 cm^{-1}.

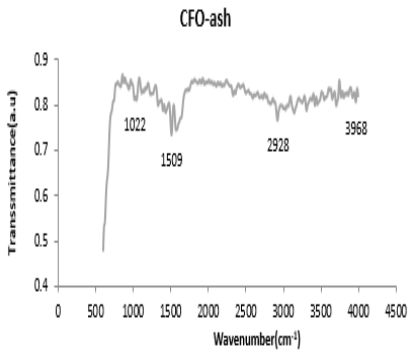

Figure 5: FTIR results for nanoparticles

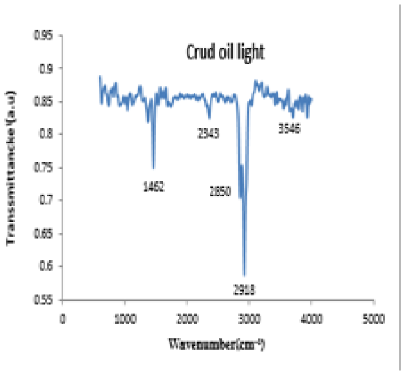

Figure 6: FTIR Results for light oil.

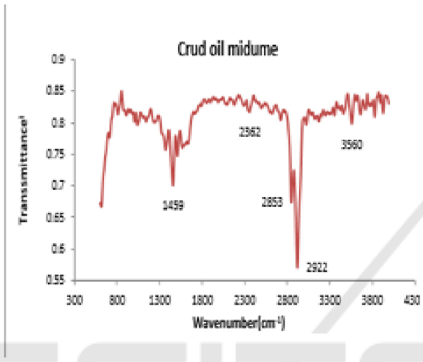

Figure 7: FTIR Results for medium oil.

3.2 Results of Oil Removal as gram/gram g/g

The technique of remove the oil from the sea water a by using magnetic rod has shown in the figure 8.

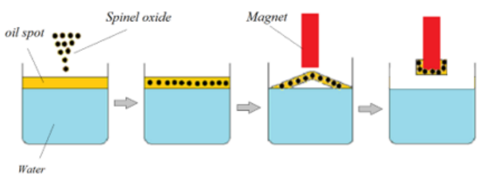

Figure 8: Shows the step of removal oil spot from water surface (Amar et al., 2019)

The following equation for calculating the oil removed:

$$OR = (m2 - m1)/m1 \qquad (1)$$

Where:
OR=Oil Removal (gm/gm).
m1= Concentration of the spinal (gm).
m2= The weight of the spinal and oil (gm).

3.2.1 Gemmens Seawater

Figure 9,10 and table 3 display the gravimetric oil removal (OR, g/g) or the oil absorption capacity of the tested oily samples (light and medium) of Gemmens Seawater as a function of absorbent amount. As can be seen, in all cases the gravimetric oil removal of Gemmens Seawater decrease with the increase in the amount of the adsorbent from 0.01 to 0.05 g. In the case of light oil (Figure 9), the OR decreased from 10.966 ± 2.3651 g/g to 4.5426 ± 0.113 g/g as the amount of absorbent material. For the medium oil, the OR was about 31.8333 ± 5.324 g/g at the absorbent amount of 0.01 g and reached a value of 7.02053 ± 1.1271 g/g when the absorbent amount increased to 0.05 g (Figure 10).

Table 3: The Properties of Crude Oil.

Gemmens					
Meduim				**Light**	
Sd	**O.R**	Concentrate	**Sd**	**O.R**	Concentrate
5.324	31.8333	0.01	2.36	10.966	0.01
1.5565	13.8388	0.03	0.3967	5.6955	0.03
1.1271	7.2053	0.05	0.113	4.5426	0.05

Where:
OR=Oil Removal.
Sd=Standard Devition.

3.2.2 Port Abu Sitta

Figure 11,12 and table 4 display the gravimetric oil removal (OR, g/g) or the oil absorption capacity of the tested oily samples (light and medium) of Port Abu Sitta Seawater as a function of absorbent amount. As can be seen, not all cases the gravimetric oil removal of Abu Sitta Seawater decrease with the increase in the amount of the adsorbent from 0.01 to 0.05 g. In the case of light oil (Figure 11), the OR decreased from 14.7333 ± 3.1988 g/g to 6.01 ± 0.1287 g/g as the amount of absorbent material. For the medium oil, the OR was about 47.1033 ± 6.0222 g/g at the absorbent amount of 0.01 g and reached a value of 9.2122 ± 2.8177 when the absorbent amount increased to 0.03 g, while 10.0593 ± 0.8987 g/g when the absorbent amount increased to 0.05 g (Figure 12).

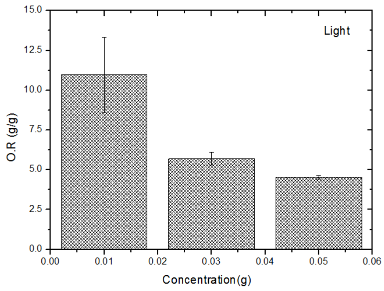

Figure 9: Shows The Crude Oil (Light) Concentration, Oil Removal Gemmens

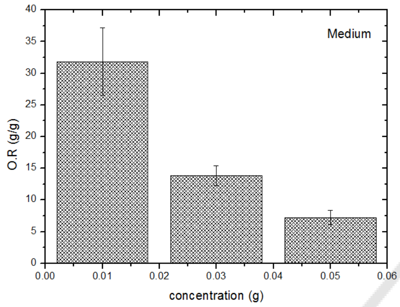

Figure 10: Shows the Crude Oil (Medium) Concentration, Oil Removal Gemmens

3.2.3 Elbrega Anchorage

Figure 13,14 and table 4 display the gravimetric oil removal (OR, g/g) or the oil absorption capacity of the tested oily samples (light and medium) of Elbrega Anchorage Seawater as a function of absorbent amount. As can be seen, in all cases the gravimetric oil removal of Elbrega Anchorage Seawater decrease with the increase in the amount of the adsorbent from 0.01 to 0.05 g. In the case of light oil (Figure 13), the OR decreased from 10.8833 $\pm$ 2.1840 g/g to 4.5786 $\pm$ 0.1921 g/g as the amount of absorbent material. For the medium oil, the OR was about 42.96 $\pm$ 1.4046 g/g at the absorbent amount of 0.01 g and reached a value of 10.5020 $\pm$ 1.3172 g/g when the absorbent amount increased to 0.05 g (Figure 14).

Table 4: The Properties of Crude Oil.

PORT ABU SITTA					
	Medium			Light	
Sd	O.R	Concentrate	Sd	O.R	Concentrate
6.0222	47.1033	0.01	3.1988	14.7333	0.01
2.8177	9.2122	0.03	1.598	6.8199	0.03
0.8987	10.0593	0.05	0.1287	6.01	0.05

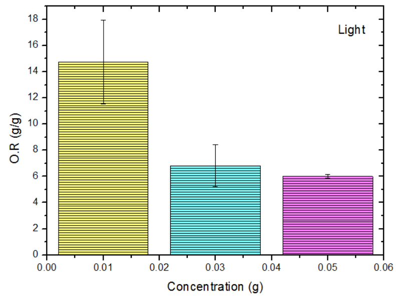

Figure 11: Shows the Crude Oil (Light) Concentration, Oil Removal Port Abu sitta

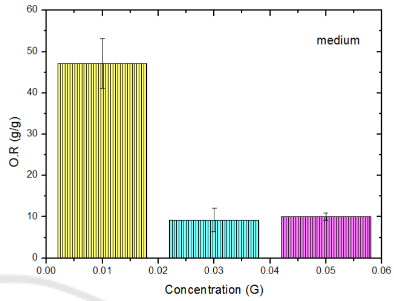

Figure 12: Shows the crude oil (medium) concentration, oil removal port Abu sitta

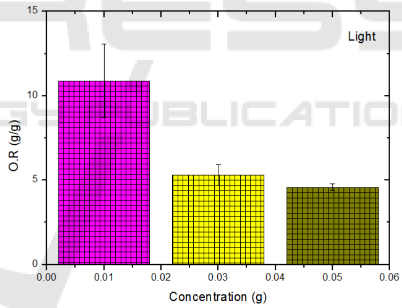

Figure 13: Shows the crude oil (light) concentration, oil removal Elbrega Anchorage

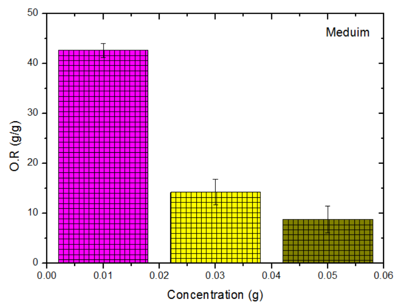

Figure 14: Shows the crude oil (medium) concentration, oil removal Elbrega Anchorage

Table 5: The Properties of Crude Oil.

Elbrega Anchorage					
Medium			Light		
Sd	O.R	Concentrate	Sd	O.R	Concentrate
1.4046	42.69	0.01	2.184	10.8833	0.01
2.5788	14.2086	0.03	0.6217	5.3132	0.03
1.3172	10.502	0.05	0.1921	4.5786	0.05

3.3 Results of Oil Removal as Percentage

The following equation for calculating the percentage:

$$Remaining = ((Woil + Powder) - Wremoval)/(Woil + Powder) \tag{2}$$

$$OilRemovalPercentage = (1 - Remaining) * 100 \tag{3}$$

3.3.1 Gemmens Seawater

The highest percentage of oil removal was (52.73%) at the powder concentration (0.05gm) during the light oil, when using the medium oil, the highest oil removal percentage was (79.43%) at the powder concentration(0.03gm) as shown in the table 6.

Table 6: Shows the Oil Removal Percentage of Gemmens Seawater

Gemmens			
Light		Medium	
Concentration	Percentage %	Concentration	Percentage %
0.01	24.65	0.01	60.92
0.03	33.74	0.03	79.43
0.05	52.73	0.05	65.09

3.3.2 Port Abu Sitta

When we use the light oil was the highest removed (66.69%), It was when the powder concentration (0.05gm), When using the medium oil was the highest removal rate (91.1%), It was when the powder concentration (0.05gm) as shown in the table 7.

Table 7: Shows the oil removal percentage of Abu Sitta port

Port Abu Sitta			
Light		Medium	
Concentration	Percentage %	Concentration	Percentage %
0.01	32.41	0.01	89.25
0.03	46.41	0.03	54.81
0.05	66.69	0.05	91.1

3.3.3 Elbrega Anchorage

The light oil was the highest removed about (53.08%), It was when the powder concentration (0.05gm), When using the medium oil was the highest removal rate (93.1%), It was when the powder concentration (0.05 gm) as shown in the table 8.

Table 8: Shows the oil removal percentage of Abu Sitta port

Port Abu Sitta			
Light		Medium	
Concentration	Percentage %	Concentration	Percentage %
0.01	25.17	0.01	82.79
0.03	37.47	0.03	80.92
0.05	53.08	0.05	93.1

4 CONCLUSION

The properties of iron oxide were studied and functional groups were identified using the infrared spectrum. Two types of oil samples (Light and Medium) were used as water pollutants model. Within the absorbent amount of 0.01 to 0.05 g, the gravimetric oil removal capabilities were between the 24.5% to 93.1%. The obtained results suggest that Cobalt Ferrite Oxide Nanoparticle might be promising absorbent materials and can be used for oil-spill cleanup from Sea water specially for medium oil.

- The material must be milled enough to avoid falling into the bottom of the test.
- High-density raw materials must be heated when aggregated in cold temperatures.
- Apply experiments in large vessels for easy handling with magnets and to contribute to the success of the experiment.
- A medium-sized absorbent should be used for easy handling with the addition of oil.

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