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Full Paper

An Investigation of the Effects of Dopamine on the Superhydrophobicity of Carbonyl Iron Particles with Stearic Acid

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ABSTRACT

Many industries produce large volumes of effluent which are made of oil and its derivatives; very common pollutants in the environment. The use of hydrophobic magnetic particles due to their low cost, low toxicity, and availability is one of the preferred methods for separating oil from water in oil spillage issues. This research aims at evaluating the effects of dopamine as a link in the hydrophobicity of carbonyl iron (CI) particles with stearic acid. In this connection, CI @ stearic acid and CI @ dopamine @ stearic acid have been synthesized. The FESEM analysis was used to observe the surface modification and structure of the particles. The magnetic properties of hydrophobic particles were also measured and the magnetic saturation of CI, CI @ stearic acid, and CI @ dopamine @ stearic acid were 200, 169, 131 emu/g respectively. Finally, the contact angle and adsorption capacity of two modified particles were measured. Based on the result, the static contact angles of water drops placed on the beds of the CI, CI @ stearic acid, and CI @ dopamine @ stearic acid were found to be 0°, 162.9°, and 168.24° respectively. The adsorption capacity range for CI@ stearic acid particles was 1.5 to 2.2 and for CI@ dopamine@ stearic acid particles was 1.8 to 3.2. Therefore, the result showed that dopamine had a good effect as a link to the hydrophobicity of carbonyl iron particles.

1. Introduction

Many industries including mining, textiles, food, petrochemicals, and metal industries produce large volumes of effluent. Nowadays, oil and its derivatives are very common pollutants and have become a global environmental concern. Frequent oil spillages during the maritime transportation or the oil production are a disaster for the marine environments, ecology, and also cause the depletion of valuable resources. Russia Norilsk diesel oil spill (2020), the explosion of China's Huangdao due to the oil pipeline accident (2013), America's Kalamazoo River oil spillage (2010), Gulf of Mexico spillage (2010), and the Persian Gulf spill (2007) are some of the most significant historical oil spillage events in the world. Generally,

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absorbent layers which are made up of scrap cellulose and recycled polypropylene having very porous structures are used for tackling this problem. The layers containing the absorbed oil are then collected and disposed of by the direct combustion. It will however add waste and contaminants to the environment. Therefore, it is necessary to provide a new method for collecting and separating oils spilled on the sea [1, 2].

Different methods have been investigated for oil/water separation. Various types of mechanical equipments, such as skimmers or booms have been used to purify industrial oil/water mixtures. This equipment requires high energy and pressure for which it is not considered to be suitable for being used in emergency oil spillage accidents. In these situations, porous materials such as foams [3, 4], mesh [5, 6], sponges [7, 8], textiles [9], are commonly used to absorb oil from the oil-water mixture. However, these materials have their drawbacks because of their low capacities, poor selectivity, low efficiency, non-recovery, and low adsorption rate. Generally, due to the time-consuming recycling and reuse of these materials, they are burned or buried in the ground which lead to the secondary environmental pollution.

Numerous micro-nano structured hydrophobic particles such as SiO_2 [10], TiO_2 [11], Fe_3O_4 [12], ZnO [13], and Al_2O_3 [14], CuO [15] by different efficiencies have been designed and synthesized for the oil water separations. The high ratio of surface-to-volume, easy-to-control wettability, and the reduction of the interfacial tension make them much more attractive for the oil water separation.

The use of hydrophobic magnetic particles due to their low cost, low toxicity, and availability is one of the preferred methods for separating oil from water in oil spillage issues. Various researches have been carried out having focused on the hydrophobicity of the particles to increase the oil adsorption capacity [16, 17].

Simmons et al. [18] reviewed the potentiality of the magnetic nanoparticles for the oil-water separation in the petroleum industry. They discussed relevant separation applications such as the mixture/emulsion separation, the oil spill clean-up, and the mitigation of the undesired phase separation.

Zhang et al. [19] made superhydrophobic particles and investigated the potential application of them in the oil-water separation. In this regard, they synthesized SiO_2/PD/Ag particles and used dopamine as a linker between SiO_2 and Ag. They showed that 0.01 g of magnetic particles removed 0.02 g of oil from the oil water mixture (Adsorption capacity: 2 g/g).

Doan et al. [20] proposed an easy preparation method for superhydrophilic magnetic particles with stearic acid and oleic acid. The water and oil contact angles on these modified particles are about 160° and 0° respectively. These modified particles were able to separate the oil from the oil water mixture or emulsions.

Zhou et al. [21] developed materials with high selectivity for the oil adsorption using Fe_2O_3@C nanoparticles. The contact angle of a water drop placed on a bed of the Fe_2O_3@C nanoparticles was 162.9° and the oil adsorption capacity for lubricating oil was increased to up to 3.8 g/g.

Dopamine can polymerize or precipitate on a variety of non-stick organic and inorganic surfaces and can be used as a substrate for a variety of secondary reactions. Thus, dopamine has a wide range of applications in encapsulation, free radical scavenging, mineralization, carbon precursors, etc. [19, 22]. Therefore, dopamine can be used as a good linker for the better coating of stearic acid on carbonyl iron magnetic particles. On the other side, the high magnetic permeability, low residual magnetism, high magnetic saturation, low weight, changes in magnetic effects with restructuring, fast and reversible behavior, good stability in a wide temperature range, and ability to rearrange the particles affected by the magnetic field are the features making the use of carbonyl iron in absorbing oil from the oil water in the oil spill process [23-25].

Therefore, the main purpose of this study is the synthesis of superhydrophobic magnetic particles using stearic acid as a hydrophobic coating. In addition, the effect of dopamine as a linker in a proper coating of stearic acid on the surface of carbonyl iron particles was investigated. In this regard, super-hydrophobic magnetic particles of carbonyl iron @ stearic acid and carbonyl iron @ dopamine @ stearic acid have been synthesized. Finally, the hydrophobicity of the two modified particles measured by using the contact angle and adsorption capacity of these particles for different oily contaminants has been also measured.

2. Experimental

2.1. Materials

Carbonyl iron particles (Density:7860 kg/m^{-3}, CS grade, BASF Company, Germany) as a magnetic core and steric acid (Sigma-Aldrich, ST. Louis, MO, USA) as a hydrophobic layer were used. Also, dopamine (Sigma-Aldrich, ST. Louis, MO, USA) was used for the modification of carbonyl iron particles.

2.2. Synthesis of carbonyl iron with stearic acid

About 5 g of carbonyl iron particles were mixed with toluene and stirred for 15 minutes. Then 0.2 g of stearic acid was dissolved in 10 ml of toluene and stirred for 15 minutes and added to the solution containing carbonyl iron and then the resulting mixture was stirred under nitrogen gas for 7 hours at 75 °C. Finally, the product was washed three times with toluene, ethanol, and acetone respectively. The magnetic powder was then separated using a magnet apparatus and dried in an oven at 60 °C for 2 h.

2.3. Synthesis of CI @ dopamine @ stearic acid

For getting a superhydrophobic particle, dopamine was used as a linker between carbonyl iron and stearic acid. The synthesis of dopamine with carbonyl iron particles was done before coating carbonyl iron with stearic acid for better bonding between carbonyl iron particles as the nucleus and stearic acid as the shell.

The dopamine synthesized by the carbonyl iron method is inferred from various researches [22, 26, 27]. About 2.4 g of carbonyl iron particles were mixed with 30 ml of deionized water and stirred for 15 minutes. Then 0.2 g of dopamine was dissolved in 40 ml of deionized water and stirred for 15 minutes and added to the solution containing carbonyl iron and then the resulting mixture was ultra-sonicated under nitrogen gas for 12 hours at 50 °C. Finally, the product was washed three times with deionized water and hexane respectively by the aid of the neodymium magnet. The magnetic powder was then separated with a magnet and dried in an oven at 60 °C for 2 h. After that, to coat the obtained product with stearic acid the method mentioned in sections 2-2 was used.

2.4. Oil-water adsorption capacity

The oil-water mixtures containing different percentages of oil were prepared and the adsorption capacity of them were evaluated. A certain amount of modified samples (m_0) was sprayed to the surface of the oil water mixture. Then, the particles that absorbed the oil were removed from the container using a magnet, and the weight (m_1) was measured. According to the following equation, the amount of the oil adsorption capacity (Q) for different oils contaminants as obtained[12].

$$Q=(M_1-M_0/M_0) \quad (1)$$

2.5. Characterization

The spherical core-shell structure and the size of synthesized particles were observed by using Field Emission Scanning Electron Microscope (FESEM, FEI NOVA NanoSEM450). The magnetic properties of the hydrophobic particles were measured by Princeton Applied Research (Vibrating Sample Magnetometer, Model No. 155, Magnet: Varian, V-7300 Series 12" Electromagnet). The values of the static contact angle for thoes particles were also measured using CAG-20, Jikan Co., and the angles were measured by Jikan Assistant and Image-J software.

3. Results and discussion

The schematic diagram of the different hydrophobic layers on the CI particles is shown in Figure 1. Based on the type of the first coated layer, the second layer can be placed on the coated CI particles. Therefore, the CI particles with dopamine are synthesized and used as a linker for a better coating of these particles with stearic acid.

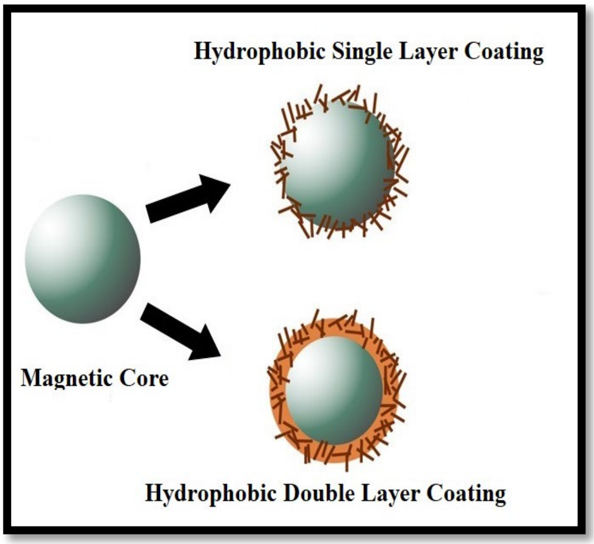


Figure 1. Schematic of the synthesis of carbonyl iron coated by different types of coating layers.

The role of dopamine as a linker between the CI particles and stearic acid was shown in Figure 2. As it can be seen, the amine group of dopamine reacts with the carboxyl group of stearic acid, and a chemical bond is formed between dopamine and stearic acid which increases the hydrophobicity of the particles.

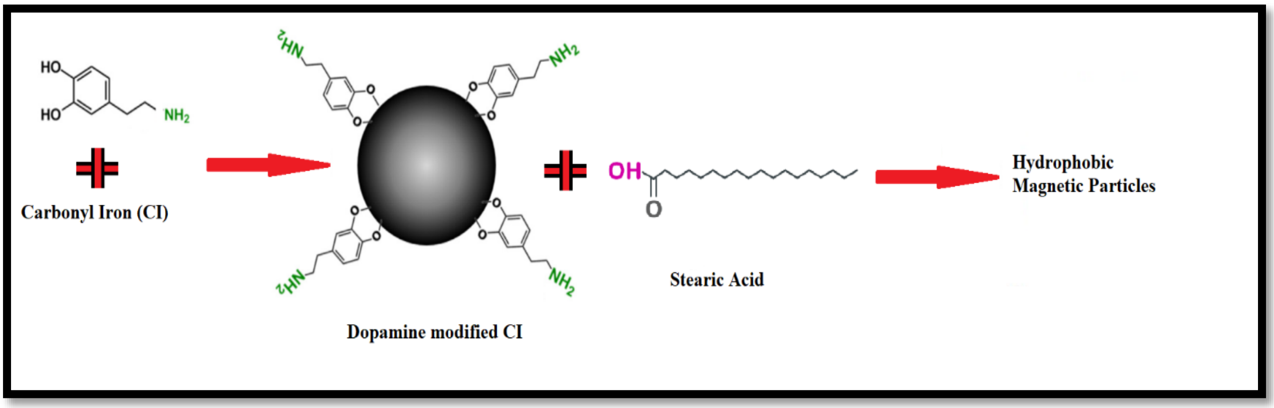


Figure 2. Mechanism of the dopamine on the CI @ dopamine @ stearic acid particles.

The spherical structure of carbonyl iron particles was evaluated by FESEM. The image processing showed that the particle size was between 2 to 3 microns. The spherical structure of carbonyl iron and the core-shell structure of CI @ stearic, and CI @ dopamine @ stearic acid have been illustrated in Figure 3.

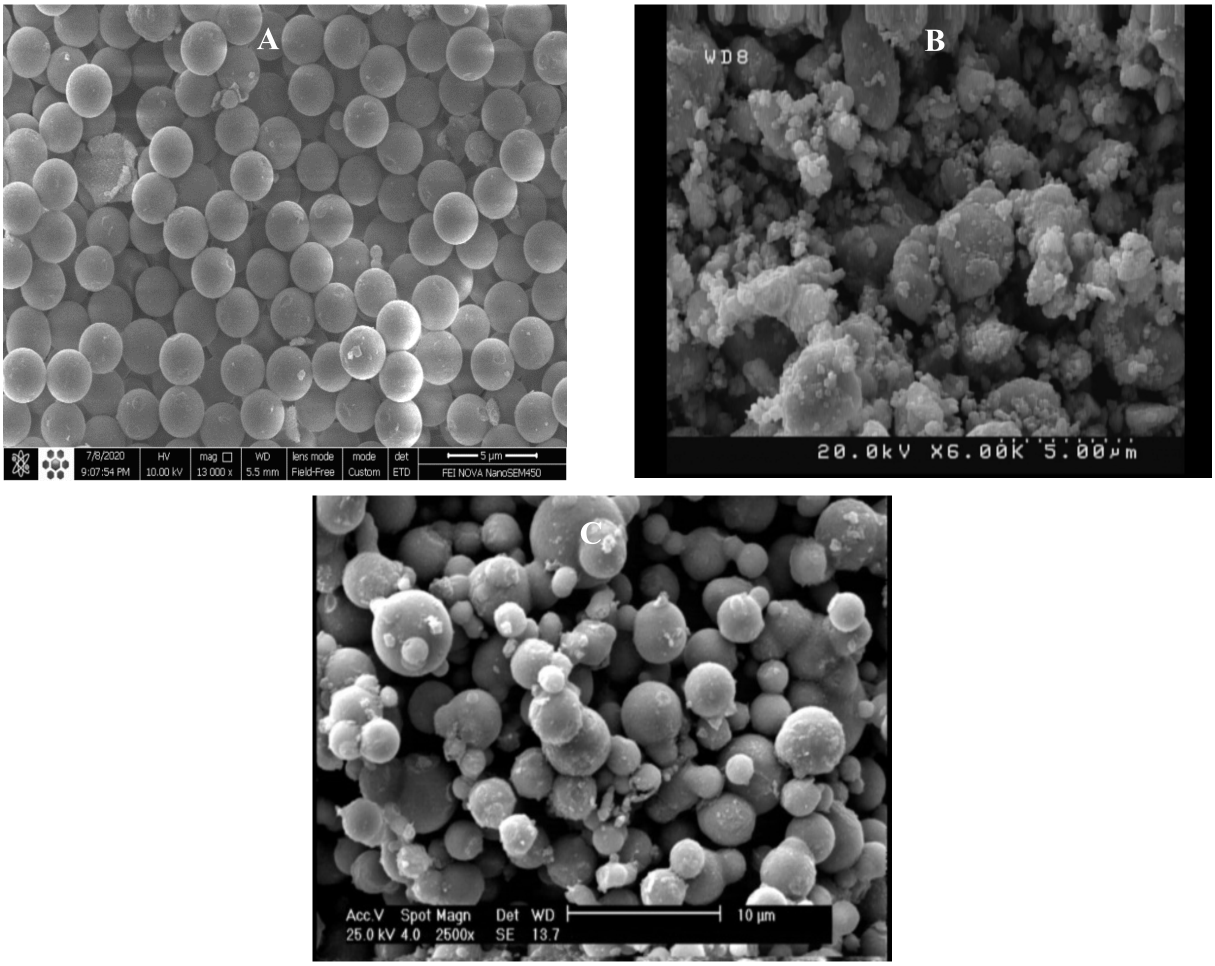


Figure 3. FESEM images of the modified samples: A) Carbonyl iron, B) Carbonyl iron @ stearic acid, C) Carbonyl iron @ dopamine @ stearic acid.

The magnetic properties of the hydrophobic particles were measured by VSM at room temperature. The magnetic curve of the carbonyl iron (CI), CI @ stearic acid, and CI @ dopamine @ stearic acid was shown in Figure 4 and the value of the magnetic saturation for these particles are 200, 169, 131 emu/g respectively. It's obvious that the magnetic saturation of two modified hydrophobic particles is lower than that of pure carbonyl iron particles due to the effect of dopamine and stearic acid layers on the magnetic core. The magnetic saturation of CI @ dopamine @ stearic acid reaches 131 emu/g which is very high in comparison to Fe_3O_4 hydrophobic particles (value of hydrophobic Fe_3O_4 magnetic particles is about 60-100 emu/g) [28-30].

For the assessment of the super-hydrophobicity of the particles, the value of the static contact angle of modified particles was measured. The optical image of a water droplet (5 microliters) placed on a bed for various samples was shown in Figure 5.

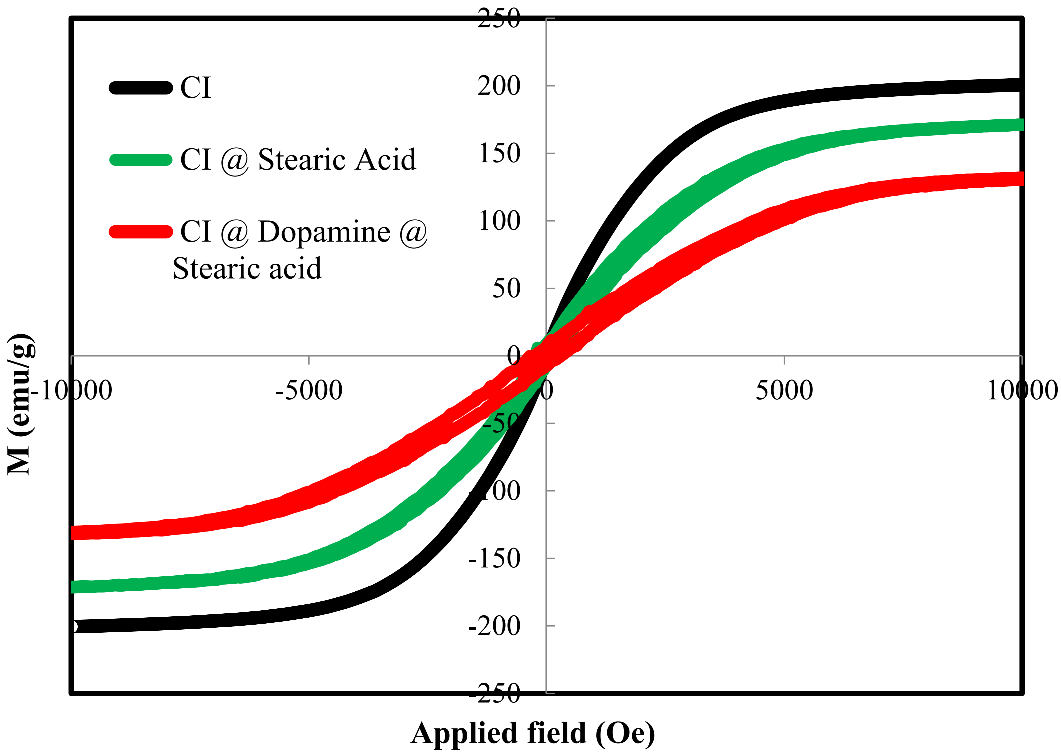


Figure 4. VSM plot of the different hydrophobic layers on the carbonyl iron particles.

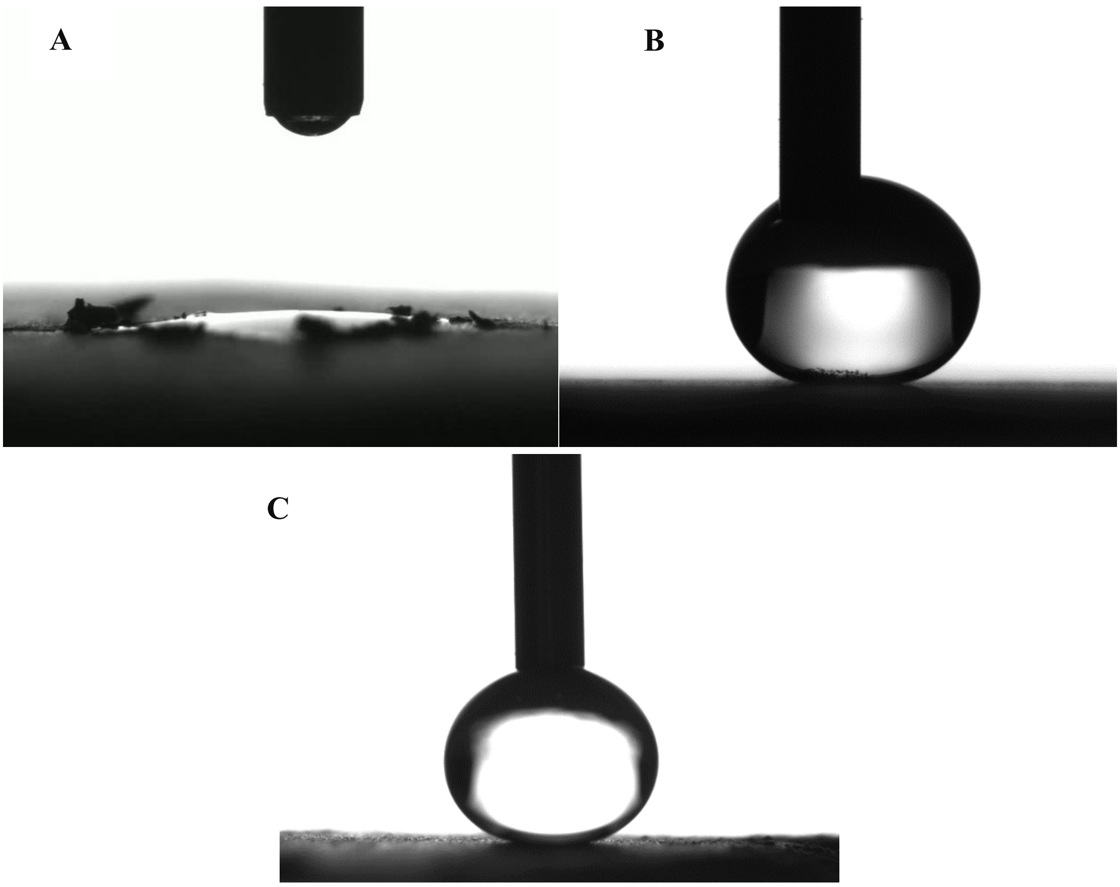


Figure 5. Optical images of a water droplet placed on a bed of the modified particles, A) barer carbonyl iron, B) CI @ stearic acid, C) CI @ dopamine @ stearic acid.

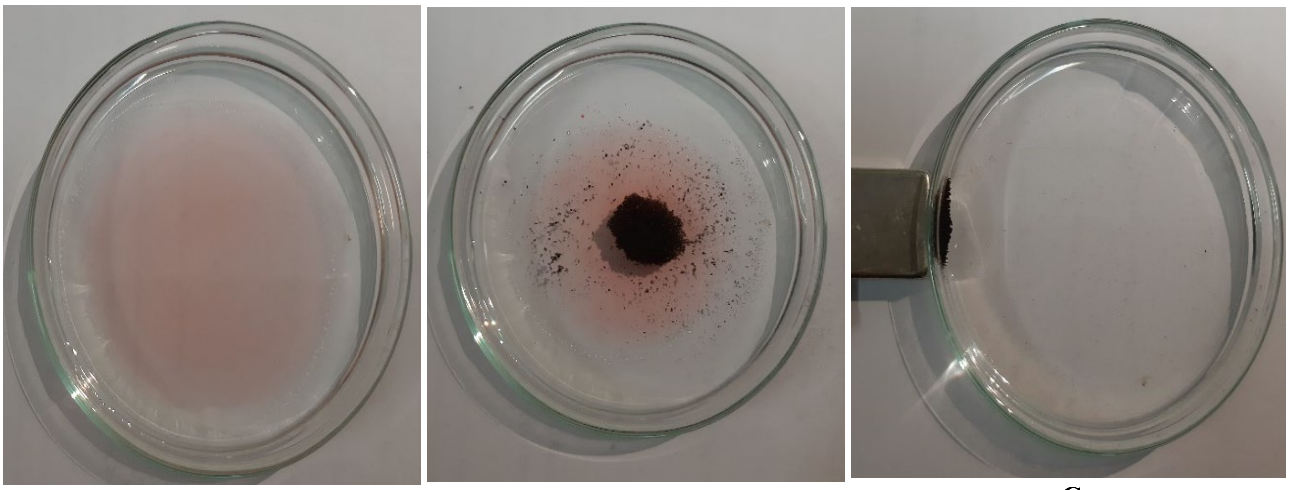
The contact angles of the samples measured by the Jikan Assistant and Image-J software were shown in Table 1. The measurements showed that the particles display high hydrophobic properties as it can be seen in Figure 5. The static contact angles of a water droplet placed on the beds of the carbonyl iron, CI @ stearic acid, and CI @ dopamine @ stearic acid were 0°, 162.9°, and 168.24° respectively.

Table 1

The average contact angle for all samples.

Sample	Test Number	CA (Degrees)	Average CA (Degrees)
Carbonyl iron	**1**	0	**0**
Carbonyl iron @ stearic acid	**1**	161.7-161.7	**162.9**
	2	161.6-166.8	
	3	163.6-161.7	
Carbonyl iron @ dopamine @ stearic acid	**1**	169.022	**168.24**
	2	167.045	
	3	168.64	

The ability of the oil adsorption by modified hydrophobic particles (CI @ stearic acid and CI@ dopamine @ stearic acid.) was evaluated. Various oily contaminants with red oil detectors were selected as analytes for the hydrophobically modified particles. The adsorption process has been shown in Figure 6 (A, B, and C). In this regard, the 100 mg of oil floats on the surface of the water with a red indicator (Figure 6-A), and then 50 mg of the modified particles are sprayed on the surface (Figure 6-B). Then, after a few seconds, the particles that have absorbed the oil are collected using a neodymium magnet (Figure 6-C).



A **B** **C**

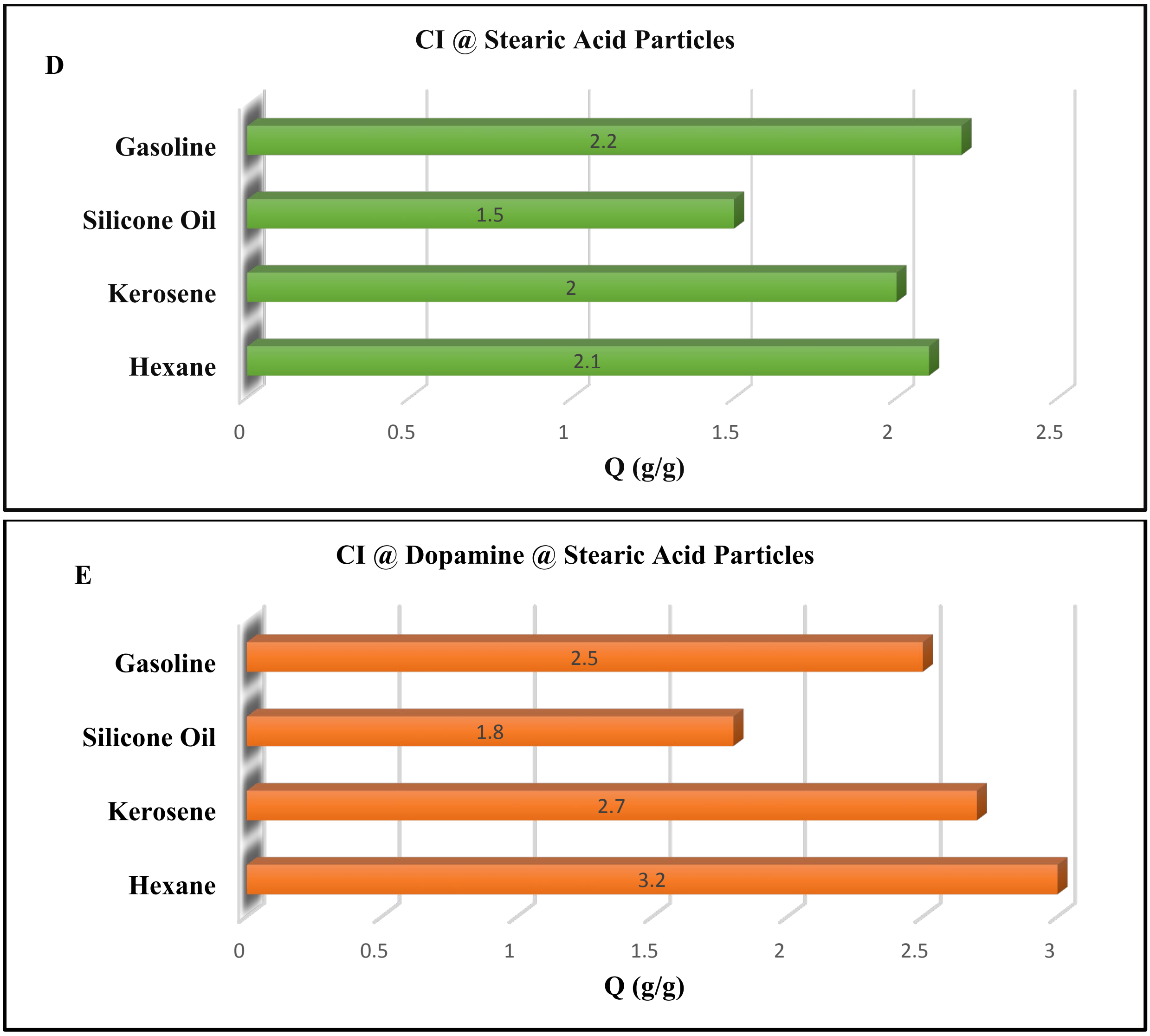


Figure 6. (A, B, and C), Process of the oil adsorption by modified particles, (D) The adsorption capacity for different oil contaminants of CI @ stearic Acid and (E) The adsorption capacity for different oil contaminants of CI @ dopamine @ stearic Acid.

In the Figure 6-D and 6-E, the amount of the adsorption capacity for four different oil contaminants (Hexane, Silicone Oil, Kerosene, Gasoline) by two modified particles was reported. The amount of the adsorption capacity is obtained by using the maximum amount of the adsorption of oil floating on the surface using a specified amount of the modified particle and in accordance with Equation 1. The results show that the CI @ dopamine @ stearic acid particles are more capable of absorbing various oil contaminants than the CI @ stearic acid particles due to their high hydrophobicity and high contact angle.

4. Conclusions

Many industries including mining, textiles, food, petrochemicals, and metal industries produce large volumes of effluent which are made of oil and its derivatives and very common pollutants in the environment. The use of hydrophobic magnetic particles due to their low cost, low toxicity, and availability is one of the preferred methods for separating oil from water in oil spillage issues. In this study, the effect of dopamine as a linker in a proper coating of stearic acid on the surface of carbonyl iron particles was investigated. So, CI @ stearic acid and CI @ dopamine @ stearic acid were synthesized.

The spherical structure of modified carbonyl iron particles was evaluated by FESEM. The result clearly showed the layer of coating on the surface of the carbonyl iron. Also, the magnetic properties of the hydrophobic particles were measured by VSM at room temperature. Magnetic saturation of CI, CI @ stearic acid, and CI @ dopamine @ stearic acid is 200, 169, 131 emu/g respectively.

Finally, the hydrophobicity of the two modified particles (CI @ stearic acid and CI @ dopamine @ stearic acid) was measured by using the contact angle and adsorption capacity of these particles for different oily contaminants.

The contact angles of the samples were measured, and the measurements show that the particles display the high hydrophobic properties and the static contact angles of the water droplets placed on the beds of the CI, CI @ stearic acid, and CI @ dopamine @ stearic acid were 0°, 162.9°, and 168.24° respectively. The adsorption capacity range for CI@ stearic acid particles was 1.5 to 2.2 and for CI@ dopamine@ stearic acid particles was 1.8 to 3.2.

The result shows that dopamine as a linker has a good effect on the hydrophobicity of the particles. Therefore, the CI @ dopamine @ stearic acid is the best choice for the oil water separation approaches in the processes of cleaning- up oil spills.

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