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Biosynthesis, Characterization and Removal Efficiency for Petroleum Leakage of the Cofe$_2$O$_4$ Nanoparticles

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Abstract

Magnetic nanoparticles are widely used in areas such as biosensors, data storage devices, waste water treatment and biomedicine due to their biocompatibility and low toxicity. In this study, biosynthesis of the $CoFe_2O_4$ nanoparticle (NP) was carried out using the bark extract of *Aesculus hippocastanum* plant as a reducing and capping agent. Synthesized NPs were characterized by ultraviolet-visible spectrophotometer (Uv-Vis.), Dynamic Light Scattering (DLS), zeta load, X-Ray Dust Diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy, Raman, BET, and Thermogravimetric Thermal Analysis (TGA). The Lethal dose value (LD_{50}) and the crude oil removal efficiency were examined. The characteristic light absorption of the $CoFe_2O_4$NP has been measured at 330 nm, surface charge of +14.4 mV, mean size of 75 nm and effective diameter of 432 nm. The XRD analysis revealed that the particle structure was in the cubic spinel structure with functional groups bound by FT-IR analysis and Raman data. It has been noted that the $CoFe_2O_4$NP, which was synthesized by biological method, can remove a 78.5% of the crude oil from the contaminated water. It has been determined that the NP's have a low toxic effect on *D. magna* (LD_{50}= 728.267 ppm). In this study, it has been suggested that the $CoFe_2O_4$ NP with *A. hippocastanum* bark extract could be synthesized by a cheap, relatively easy and environmentally friendly method which used for purification of contaminated water bodies.

Keywords: Aesculus *hippocastanum*, $CoFe_2O_4$, Biosynthesis, Crude oil treatment, Daphnia *magna*, lethal dose.

Introduction

The nanoparticles with sizes less than 100 nm have high surface energy, surface area, and different physical and chemical properties than micro equivalents and ionic states. With its unique optical, magnetic, electrical and mechanical properties, it has a wide use in fields such as biomedical, biotechnology, biosensor, diseases diagnosis, wastewater treatment applications and medical food industry.

For many years, nanoparticles have been synthesized by physical and chemical methods. However, these methods require high cost, energy and time and have the disadvantage of using toxic chemical agents in synthesis process. For example, in the synthesis of nanoparticles hydrazine, sodium borohydride (NaBH4) and dimethyl formamide (DMF), are widely used in chemistry as reducing agents, but in general, these chemicals have high reactivity, posing environmental and biological risks.

In the recent years, the use of biological agents (bacteria, algae, fungi, lichens and plant extracts) as reductive and coating agents in the synthesis of nanoparticles has become more attractive with the prospect of having various advantages. Biological synthesis is cheaper, easier, and more environmentally friendly than other conventional methods.

Ferrous nanoparticles have application areas such as biocompatibility, low toxicity and stable structure due to biosensors, catalysis, data storage devices, waste water treatment, biomedical applications. Among the magnetic nanoparticles, cobalt ferrite ($CoFe_2O_4$) is used in the construction of sensors, sound and video cassettes, high density digital recording discs due to its high electromagnetic properties, stable structure and high cubic magneto crystalline properties. Magnetic nanoparticles can be synthesized by chemical reduction agents such as precipitation, solvothermal reaction, high temperature hydrolysis reaction, hydrazine and carbon monoxide. However, these methods have the disadvantages of containing toxic reactive substances and requiring high cost. Biosynthesis of magnetic nanoparticles with biological agents such as Sargassum muticum and Hordeum vulgare has been carried out in the previous studies.

Oil wastes which derived from oil can mainly come from the fast shipping vessels, especially as a result of industrial activities such as leaks. In this way, many water sources are polluted in the world. There are many methods to control the spillage including physical, chemical, biological methods, or their combination which are commonly used to clean up the oil spills.

There are many studies in the literature about the usability of nanoparticles for oil wastes treatment in the water systems. The use of nanoparticles as sorbent material to remove the contaminants from water systems is of a great importance in terms of toxicity and water ecosystem, which may be caused by aquatic organisms. *Daphniamagna* is used as a model organism in the toxicity studies in the aquatic ecosystems due to its sensitivity to pollutants like heavy metals comparing with the other aquatic organisms, which plays an important role in the ecosystem to conserve the crucial position in the food chain.

The aim of this study is to find a new, cheap and echo friend method to remove the crude oil waste from the water bodies.

Materials and Methods

Collection of the Plant Samples

The *Aesculus hippocastanum* fruit, which has been found in the garden of the Faculty of Science in Erciyes University (Kayseri/ Turkey), it has been collected in August 2016. The fleshy fruit shells of the plant have been washed with tap water followed by deionized water then dried in the open air in the laboratory for 2 weeks. The dried samples were powdered and stored in storage cabinet for use in nanoparticle synthesis (Figure 1).

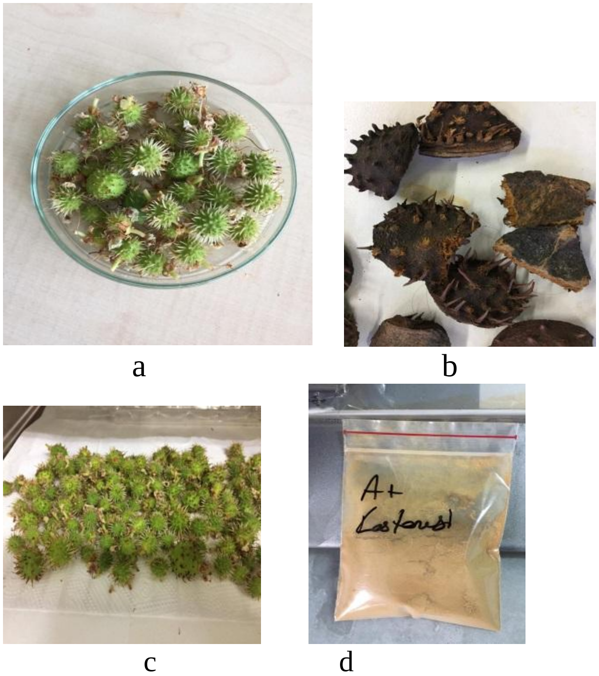

Figure 1- Collected A. hippocastanuma and b: Fruits, c: Dried fruit bark, d: fruit bark dust

Preparing the Plant Extracts

The grits were weighed 10g from the shells of the milled plant and transferred into the beaker. 100 ml of distilled water (dH_2O) was added and the mixture was stirred at 100 ° C for 30 minutes. The boiled mixture was allowed to warm to room temperature and then cooled mixture was filtered through Whatman No: 1 filter paper. The resulting *A. hippocastanum* fruit husk extract was stored at 4°C for use in the synthesis of the $CoFe_2O_4$ nanoparticles.

Nanoparticle synthesis

12.07 g of $FeCl_3$ and 5.34 g of $CoCl_2.6H_2O$ were dissolved in 150 ml of deionized water in separate beakers in an ultrasonic bath. In another beaker, 300 ml of the previously prepared *A. hippocastanum* fruit husks were first added to $CoCI_2$ followed by $FeCl_3$ solvates and stirred at 100 ° C for 1 hour in a magnetic stirrer. The mixture was then boiled in a microwave oven for 1 hour at medium level (460 watts) and cooled to room temperature. The solution was centrifuged at 5000 rpm for 5 minutes, and then ethanol was washed twice with distilled water. The pellet was burnt in an ash furnace at 400 ° C for 2 hours.

Removal of Crude Oil from Water

The crude oil sample used in the experiment was obtained from the laboratory located in ATAŞ Anatolian Disposal House in Mersin in July 2016. In the laboratory, 20 ml of dH_2O, 2 g of crude protein and 0.002 g of $CoFe_2O_4$ nanoparticle were added to the petri dishes, which were weighed orderly. The nanoparticle-petroleum mixture was collected by magnetic force on the edge of the petri dish with the help of a magnet.

Uncollected oil and water were removed with the aid of a pipette and the remainder was dried and weighed until the water was removed at 100 ^oC. The formula: $k = (b - a) / a$ is used to determine the oil holding capacity. Where 'a' is the adsorbent material placed on top of the oil layer, and 'b' is the weight of the adsorbed material (in grams) after drying.

Toxicity studies

To determine the toxic effect of the synthesized particle on *Daphniamagna*, the LD50 value of the obtained nanomaterial was calculated. The synthesized $CoFe_2O_4$ nanoparticles were dissolved in ultrasonic bath to prepare 1000 ppm stock solution. The solutions were set up in Petri dishes to be 500, 250, 100, 50, 25 and 10 ppm (concentrations determined by literature review) and each solution have been incubated at 27 ° C for 24 hours with the addition of 10 *Daphniamagna* in each case. After exposure, *Daphniamagna* live and dead individual numbers have been counted and recorded in petri dishes and the LD50 concentrations were determined. The experiment was carried out as 3 replicates.

Statistical Analysis

For the determination of LD50 concentrations, live and dead individual numbers obtained after 24 hours exposure were used. Probity analysis was performed using the SPSS 15.0 program to determine LD50 concentrations.

Results and Discussion

- The $CoFe_2O_4$ nanoparticles were successfully synthesized by bark extraction of *A. hippocastanum* plant. Comparing with the conventional synthesis methods, this method is easy, inexpensive, short time and environmentally friendly using biological waste instead of chemical agent.
  It was confirmed by the FT-IR analysis that A.*hippocastanum* plants participated in the particle structure of the functional groups in the bark extract. The surface load of the $CoFe_2O_4$ nanoparticles measured by biosynthesis was measured as +14.4 mV and it was decided that the particle was stabilized for a short period of time.
- The CoFe2O4 nanoparticles were found to be round in shape and 72 nm in length.
- The tendency of synthesized nanoparticles to form small clusters was determined by the SEM images and the DLS analysis.
- The crystal structure of $CoFe_2O_4$ nanoparticles was confirmed by the XRD analysis.
- Particulate cubic spinel structure was determined with active RAMAN modes.
- 78.5% of the contaminated crude oil of biologically synthesized $CoFe_2O_4$ nanoparticles is removed from the environment.
- It has been observed that the toxic effect of biosynthesized $CoFe_2O_4$ nanoparticles to D. magna is low.

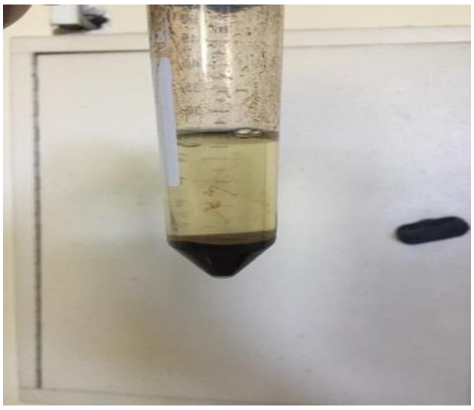

Figure 2- Nanoparticles before entering the centrifuge device

Figure 3- Samples after a prank of distilled water and put it on the fire for one hour and at a temperature of moderate 60 degrees

Figure 4- The nanoparticles produced before being placed in the oven to be transformed into a small nanoparticle by heating 400 degrees

Figure 5- nanoparticles produced after being placed in the oven under 400 degrees heating

Figure 6- Models of nanoparticles extracted with plant extracts for the purpose of isolating the material by centrifugation

Discussion

$CoFe_2O_4$ Nanoparticles Characterization.

The morphological, physical and chemical properties of the particles synthesized by biological methods are important in determining the areas of use of the particles. The morphological characteristics of the particles synthesized by the biologic method are affected by the species, parts, concentration, reaction time, ambient pH, concentration of the reduced metal, and variety. At the end of the synthesis of the $CoFe_2O_4$ nanoparticles, the color of the solution turned brown to gray. The color change is a sign of nanoparticle formation. In the UV Vis analysis, a peak at a wavelength of 330 nm was observed.

The functional groups binding to the structure of the nanoparticle were determined by comparing the FT-IR analysis data with the characteristic IR Absorption Frequency. Alcohol (O-H), amine (N-H) and amide (N-H) of 3346.9 cm^{-1} band vibrations; Amine (N-H) of 1600.1 cm^{-1} band vibrations; 1012,3 cm^{-1} band vibrations are alkyl halide (C-F), ether (C-O), ester (C-O); It has been determined that band vibrations observed in the 594,64 cm^{-1}, 558,91 cm^{-1} and 549,84 cm^{-1} spectra correspond to the alkyl halide (C-Br) functional groups. Gingasu *et al.* observed band vibrations at 3338, 2920, 1647, 1384 and 1046 cm^{-1} by FT-IR analyzes of $CoFe_2O_4$ nanoparticles synthesized by *Hibiscus rosa-sinensis* leaf extract.

These bands were OH, CH_2, COO, COO and COC band vibrations. In the same study, they identified functional groups incorporated into the structure of particles by band vibrations observed at 3387, 3177, 1601, 1384, 1228, 1077, 963, 914, 847 and 790 cm^{-1} by FT-IR analysis of $CoFe_2O_4$ nanoparticles synthesized by flower extract. The researchers reported that the bands observed at 591, 386 and 423 cm^{-1}waves are corresponded to the characteristic $CoFe_2O_4$ bands. It is thought that the band vibrations observed in our findings are correspond to metal oxygen ($CoFe_2O_4$) band vibrations which observed at 594,64 cm^{-1}, 558,91 cm^{-1} and 549,84 cm^{-1}.

The electron microscopes are used to determine the morphological characteristics (such as size, shape, and cluster status) of nanoparticles. It has been determined that the CoFe2O4 nanoparticles synthesized by biological methods have an average size of 72 nm and a round structure. It was also observed with the SEM images where the particles formed small clusters. Zi *et al.*[1] observed that the CoFe2O4 nanoparticles obtained by chemical method are round in shape, 20-30 nm in length, and do not clump.

Pervaiz *et al.* [2] reported that $CoFe_2O_4$ nanoparticles synthesized had a diameter of 60-80 nm, a length of 800-900 nm, and a particle beam shape. Phumying *et al.* [3] observed that the Fe_2O_3 nanoparticles synthesized by extracting *Aloevera* plant are in the 25-50 nm size and tend to cluster. In the same study, the researchers reported that the size of the particles identified in the SEM analysis is larger than the size calculated by the XRD analysis, and this is due to the cluster of particles. Çolak *et al.* [4] observed that the ZnO nanoparticles synthesized by crust extraction of *A.hippocastanum* fruits were in the dimensions of 50-100 nm. As a result, the resulting $CoFe_2O_4$ NPs were found to be larger in size, bringing them to the cluster.

Diffraction peaks at 30.3^o, 35.5^o, 45.0^o and 62.8^o of $CoFe_2O_4$ nanoparticles synthesized by crustal extraction of *A.hippocastanum* fruits were obtained at 2θ position. Waje *et al.* [5] reported that the diffraction peaks observed in the XRD analysis at the 2θ position observed at 35, 52 and 53,91^o are in the (3 1 1) and (5 1 1) planes, respectively, and that these peaks may point to $CoFe_2O_4$ nanoparticles. Maaz *et al.* [6] (2007) reported that at the 2θ position observed at 18,05^o, 30,2^o, 35,7^o, 37,4^o, 43,45o, 57,55o and 63,05^o, Mostaghni *et al.* [7] , 30,22^o, 57 0, 43, 14 ^{o}, 53, 69 ^{o}, 57, 22 ^{o}, 62, 85 ^{o} and 74, 32 ^{o} have determined that the particles are in a crystalline structure. This confirms that the biosynthesized particles belong to $CoFe_2O_4$ NP in the crystal structure.

10% of the mass loss to 380 C by TGA analysis of the $CoFe_2O_4$ nanoparticle powder on which the biosynthesis is performed; Mass loss from 380 ^{o}C to 900 ^{o}C was found to be 16% (total 26%). Similar to our findings, Pui *et al.* [8] reported that about 20% mass loss occurred in the particle structure together with a temperature increase of up to 700 ° C. El-Remaily and Hamad reported that the mass loss to the $CoFe_2O_4$ nanoparticle was about 7% at 25-120 ^{o}C due to the dehydration of mass loss, and 7% at 120-270 ^{o}C, they predicted that the structural loss was due to water loss and they noted that there was no mass loss above 600 °C. Shirsath *et al.* reported that the $CoDy_{0.1}Fe_{1.9}O_4$ nanoparticles had a mass loss of about 17% at about acidic (pH 2.5) ambient conditions of 700 °C, about 17% of mass loss at acidic (pH 5)) around 12% of the mass loss. They observed that mass loss was caused by loss of gel, nitrate and compressed gases. Idrees *et al.* reported that the $NiFe_2O_4$ nanoparticles were water-lost to 100 °C, water hydrate to 100-250 °C, and the activity caused by the formation of oxides of hydroxides of various metals up to 300-650 °C. This information is to be due to the mass loss observed in the $CoFe_2O_4$ nanoparticle in the light due to the transformation into water, compressed gases and oxide form.

Zeta potential is an important parameter used to determine the stability of suspensions by measuring the surface load of nanoparticles. If the particles in the solution have a large negative or positive zeta potential, the pushing force between the particles prevents the nanoparticles from clustering. However, if they have a low surface load, it leads to the aggregation of the particles together with the weak pushing force between the particles. Nanoparticles with a surface charge higher than +25 mV or a surface charge lower than -25 mV are considered to be high and those with a surface charge between -10 and +10 mV are considered to be near the neutral value. In this case, $CoFe_2O_4$ nanoparticles synthesized by bark extract of *A. hippocastanum* fruits have a short-term stability.

As a result of the DLS analysis performed to determine the hydrodynamic size distribution of the nanoparticle, the effective diameter was measured as 432 nm on average. Similar to our findings, Sankar *et al.* determined the average effective diameter of CuO nanoparticles synthesized by Ficusreligiosa leaf extract as 577 nm by the DLS analysis. Nanoparticles of very small size tend to cluster if the environment is acidic. It is believed that the large diameter of the $CoFe_2O_4$ nanoparticles synthesized by crust extraction of A. *hippocastanum* fruits is due to the formation of small clusters due to acidic (pH4) environmental conditions and the small size confirmed by the SEM analysis.

RAMAN modes obtained by the RAMAN analysis were 131, 52, cm^{-1}, 317 cm^{-1}, 471 cm^{-1}, 616,72 cm^{-1} and 674,16 cm^{-1} and the particulate structural characteristic was determined. The regions in the range of 650-710 cm^{-1} show the tetrahedral sub-cage structure of the particles while those below 650 cm^{-1} show the octahedral sub-cage structure. 217,83 cm^{-1}, 311 cm^{-1}, 471 cm^{-1}, 616,72 cm^{-1}. It can be said that this information beam has a particleic cubic spinel structure.

Petrol Treatment

The aquatic ecosystems are threatened by oil spills from different sources such as oil spills, exploration, processing and transport. It is obvious that marine life and ecosystem are facing a great danger, considering that about 5 million tons of petrol per year is carried on the seas around the world. The purification of pollutant-derived petroleum derivatives is provided by biological agents such as dispersants or mechanical processes using microbubbles, emulsifiers, on-site combustion, bombs, scrapers, oil-water separators or sorbents.

Properties such as the hydrophobic nature of the materials used as sorbents and the ability to rapidly retain high oil retention at the same time must be considered during sorbent material selection. In addition, the recycling of used materials and the biocompatibility of oil are very important in terms of their utility in environmental applications. Sorbent materials can enhance the efficiency of the synthesis by facilitating the collection of petroleum derivatives in the presence of a magnet. There are many studies on the use of oil wastes as sorbent materials in nanoparticles. It has been determined in previous studies that $CoFe_2O_4$ nanoparticles are heavy metal removed.

For example, Srivastava *et al.* [9] reported that $CoFe_2O_4$ nanoparticles removed Cr (VI) from waste water. In this study, it was determined that $CoFe_2O_4$ nanoparticle synthesized by bark extract of *A.hippocastanum* fruits removed 78.5% of crude oil from water. Atta *et al.* [10] reported that uncoated Fe_3O_4 nanoparticles remove 40% of the oil when the magnetite and fat ratio is 1:1, but the efficiency of the treatment is reduced by increasing the fat concentration. At the same time, researchers reported that crude oil was increased by 95% with the particles surrounding it.

Palchoudhury *et al.* [11] reported that petroleum-derived oils from the water environment of polyvinylpyrrolidone which coated the iron nanoparticles had optimum conditions (12 hours exposure time, 307.6 mg nanoparticle, 0.8 g / l fat and 12 hours exposure time, 623.9 mg nanoparticle, 0.8851 g / l oil). The high reactivity of zero-valence iron nanoparticles (ZVI), together with their large surface area, makes them a potential candidate for adhesion. Bimetallic nanoparticles contain catalytic and reactive metal atoms, which react directly to the oxidation of pollutants. The iron nanoparticles are used as chemical catalysts for oil residues from oil spills. The reactive OH- ions of the particles react with the reaction of the particles and can oxidize this product and its petroleum components. As a result, it is suggested that the biosynthesized $CoFe_2O_4$ nanoparticle can be used effectively in the treatment of petroleum derivatives from water systems.

Toxicity

Acute toxicity tests of the magnetic nanoparticle biosynthesis were performed using *Daphniamagna* model organisms, which are widely used in the toxicity studies in the aquatic ecosystems for its rapid growth, its susceptibility to pollutants such as heavy metals, and its ability to play an important role in the ecosystem. Moreover, the grounds for being in a crucial position in the food chain and the level of pollution to be determined in the genus Daphnia provide preliminary information on the water ecosystem. Heavy metals and nanoparticles have been studied by toxicity experiments carried out in aquatic organisms. Okamoto *et al.* [12] reported that the Fe ion ($FeCl_{3.6}H_2O$) has low toxicity by detecting acute toxicity value to D. magna as 2300 μg / L. Blinova *et al.* [13] reported that Fe_2O_3 nanoparticles in the artificial freshwater environment died approximately 9% at 100 ppm exposure and 45% at 1000 ppm exposure, and Fe_2O_3 nanoparticles were toxic at low levels.

González-Andrés *et al.* [14] determined that the D. magna acute inhibitor effect of iron oxide nanoparticles coated with humic acid was higher than 943 mg / L, and based on the physical interaction of the particles with D. magna. The most digestive systems are affected by the fact that the nanoparticles are usually taken by D. magna for ingestion. In some other studies it has been reported that nanoparticles and Fulleren-C60 accumulate in the intestines of Daphnia.

The very small size of the particles allows the passage of the medium intestine through the patotropic membrane. The iron oxide nanoparticles passing through the cell initiate the formation of reactive oxygen species with reactive surfaces, causing oxidative damage, Baumann *et al.* [15]. Within this information, it has been determined that the $CoFe_2O_4$ nanoparticles biosynthesized cause low-level toxicity. At high concentrations (728,267 ppm) the particle can be bound to cause oxidative stress-induced toxicity by entering the reactive oxygen species after ingestion by Daphnia magna.

Suggestions

The availability of A. *hippocastanum* plant for the synthesis of bark extract and other magnetic and metal nanoparticles should be assessed. Biosynthesis of various nanoparticles with different biological wastes should be performed. Thus, the cost of synthesis can be reduced by evaluating organic wastes. • Antimicrobial, anticancer, antifungal and photocatalytic properties of $CoFe_2O_4$ nanoparticles synthesized by biological methods can be evaluated and used in industry. The genotoxic and cytotoxic properties of the particles synthesized by plant extracts should be determined on various model organisms. Studies on the ability of $CoFe_2O_4$ nanoparticles synthesized by bark extract of A. *hippocastanum* plant and other plant extracts to remove toxic contaminants such as heavy metals from the ecosystem can be studied. The toxic effects of particles biologically synthesized on aquatic organisms such as *Daphnia*, *Paramecium*, *Lemna* and *Elodea* must be completed before the material is used.

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