Removal of Microplastics in Water using Oil-based Ferrofluid solution

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Abstract

This study focuses on resolving the growing issue of microplastic pollution found in the ocean using oil-based ferrofluid solutions. Using the fact that most microplastics are hydrophobic, ferrofluid, magnetic nanoparticles, are synthesized and dispersed in various oil solutions. The prepared solutions were used to remove microplastics in water and retrieved using a magnet. Our study showed that the vegetable oil-based ferrofluid solution showed promising results, removing a large number of microplastics. Ferrofluid solutions using other oils were also prepared and their effect on the removal of microplastics was studied.

Introduction

Plastics are everywhere. It has become one of the most useful, yet harmful products utilized around the world. The excessive use of plastic has been polluting the environment impacting various wildlife habitats, particularly the marine habitat. Over time, plastic debris can break down into smaller particles less than 5 mm in diameter. These forms of plastics are known as microplastics. Fishes, zooplankton, crustaceans, and other aquatic species have been mistakenly consuming these microplastics, which has been blocking their digestive tract and changing their eating behaviors. Likewise, microplastics are passed between organisms through the food chain, where predators, such as humans, have been eating these infected species.

Recently, 18-year-old, Fionn Ferreira, discovered a way to save aquatic life from the growing plastic pollution problem. He found that microplastics can be extracted to oil when ferrofluid was used. Ferrofluid is a magnetic nanoparticle solution which was first discovered by NASA. Using the facts that most microplastics are hydrophobic and ferrofluid can be controlled by an external magnetic field, he was able to successively remove microplastics from water.

This study aimed to further investigate this great finding and prepare the most optimized ferrofluid solution that can maximize the effect of microplastics removal. To start with, ferrofluid solutions were prepared and their effect on the removal of microplastics was investigated. Ferrofluid was first synthesized and dispersed in various oil solutions such as vegetable oil, sunflower oil, grapeseed oil and canola oil. These oil solutions are solvents that exhibit a high percentage of oleic acid, one of polyunsaturated fatty acids (PUFA). Due to the unsaturated π-bonding and alkyl chains, oleic acid can serve as a good surfactant for ferrofluid dispersed in hydrophobic solvents. The oils were chosen based on this knowledge.

To test the feasibility of ferrofluid solution, microplastic solutions were prepared by grinding and dissolving plastics in water. The prepared ferrofluid solutions were added to microplastic water, stirred and the ferrofluid solution was separated using a magnet. The water samples were then investigated using an optical microscope.

Experimental Methods

Preparation of oil-based ferrofluid solutions

Ferrofluid was synthesized using the synthesis method reported by Churchhouse et al. Iron (II) chloride and iron (III) chloride solutions in 2.0 M HCl were prepared and mixed with 2:1 molar ratio. Subsequently, 0.7 M ammonia solution was slowly added to the mixture with vigorous stirring to ensure nanoparticle formation. The color of the solution turned black, which proved successful synthesis of magnetite, $FeO{\cdot}Fe_2O_3$. The following shows the chemical reaction of the synthesis:

$$2\,FeCl_{3(aq)} + FeCl_{2(aq)} + 8\,NH_{3(aq)} + 4\,H_2O_{(l)} \rightarrow Fe_3O_{4(s)} + 8\,NH_4Cl_{(aq)}$$

After the addition of ammonia solution, a magnet was put underneath the solution to collect magnetite nanoparticles and the supernatant solution was decanted. DI water was added and decanted several times to remove any residual byproducts and ammonia solution. Cleaned ferrofluid was then dispersed in decane ($C_{10}H_{22}$) with 0.5 mL of oleic acid, which served as a surfactant to help dispersion of magnetite nanoparticles in nonpolar solvents and prevent aggregation. The solution was then heated to 90°C using a hot plate for approximately 2 hours and 30 minutes and left to cool. Once cooled, decane was added to the solution. As a result, a decane layer formed above the magnetite, and was removed using a pastured pipette. The same procedure was repeated with vegetable oil, grapeseed oil, sunflower seed oil and canola oil as a solvent.

When oils were used as solvents, there was a slight modification due to their viscosity: oils were too viscous and caused overboiling when heated. To prevent this issue, the solution was not heated nor decanted after 0.7 M NH_3 solution was added. Likewise, DI water was also added to prevent the solution from overboiling. After these slight changes, the oil-based ferrofluid was successfully prepared.

Preparation of water samples with microplastics

Microplastics were prepared by grinding a polystyrene petri dish. This plastic product was grinded using a coarse sandpaper (grit 60-80) and fine sandpaper (grit 1500). The powder residue was collected in two separate beakers and dispersed in DI water to prepare microplastic solutions. Although tiny shavings were being made by the sandpaper, large macro-plastics were also made. To remove these, the microplastic solution was poured onto a grade 2 filter paper (8 µm pore size) to allow the microplastics to pass through. To analyze the size of the microplastics, drops of the solutions was added to a microscope slide and gently heated on a heating plate to evaporate the water. These slides were then further analyzed using the optical microscope.

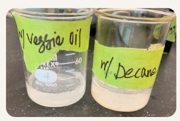


Figure 1: Microplastic solutions prior adding the ferrofluid solutions.

Experimental Methods (continued)

Removal of microplastics using organic + oil-based ferrofluid

By using the coarse sandpaper, a 40-mL solution of polystyrene microplastics in DI water was created. Then, 20-mL of the solution was poured into another 100-mL beaker to create two solutions of microplastics. Prepared decane-based ferrofluid and vegetable oil-based ferrofluid solutions were added to each beaker (see Figure 2 a+b). The mixtures were then vigorously stirred to ensure complete interaction between ferrofluid and microplastics. Subsequently, a magnet was used to retrieve ferrofluid solution from the water samples (see Figure 2c).

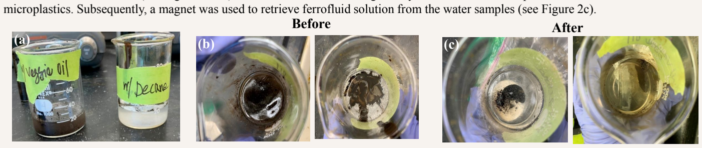


Figure 2: (a) When adding vegetable oil-based and decane-based ferrofluids to the microplastic solutions; (b) before magnet: top-view of the veggie oil-based ferrofluid (left) and decane-based ferrofluid (right); (c) after magnet top-view of veggie-oil based ferrofluid (left) and decane-based ferrofluid (right).

Analyzing the removal of microplastics

To observe the removal of the microplastics at a micro-level, 4-drops of the untreated and treated samples were placed on a 1 x 1" microscope slide and gently heated on a heating plate to evaporate the water (see Figure 3). These samples were then placed under an optical microscope to investigate whether the microplastics were removed.

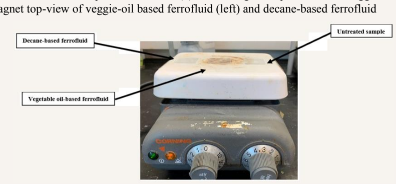


Figure 3: Treated and untreated samples heated-up using the hot plate: veggie oil-based ferrofluid (left), decane-based ferrofluid (middle), and untreated microplastic solution (right).

Results/Discussion

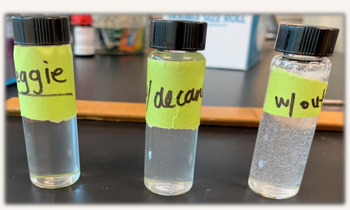


Figure 4: Treated and untreated solutions: veggie oil-based ferrofluid (left), decane-based ferrofluid (middle), and untreated microplastic solution (right).

When comparing the treated and untreated solutions, it was observed that there was a significant decrease in the number of microplastics within the treated solutions. However, the vegetable oil-based ferrofluid was the clearest solution amongst the three samples, as illustrated in Figure 4. At the microscopic level, it was also observed that the vegetable oil-based ferrofluid successfully removed a significant amount of microplastics. As shown in Figure 5b, the red circles highlight the significant decrease in microplastics despite the large presence of water droplets. However, there were still various regions that contained a large presence of microplastics. Unlike the vegetable-oil sample, the sample treated with decane contained a large presence of microplastics, thus causing the solution to remain cloudy. Ultimately, this was also visible under the optical microscope (See Figure 5c). It was also observed how the ferrofluid gathered the microplastics into groups. After comparing the treated and untreated samples, it was concluded that the vegetable oil-based ferrofluid removed more micro- and macro-sized plastics than the decane-based ferrofluid. As a result, the vegetable oil-based ferrofluid holds promise for future innovative approaches on the removal of microplastics in water.

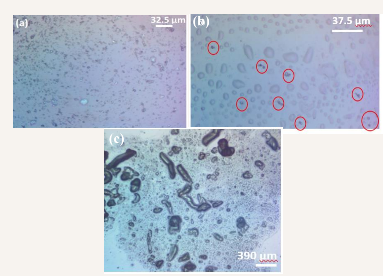
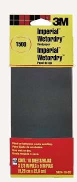


Figure 5: Microscopic image of a) untreated sample (40 x 0.60); b) sample treated with vegetable oil-based ferrofluid (40 x 0.60); c) treated sample with decane-based ferrofluid (10 x 0.25)

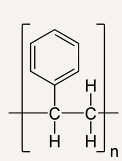
Materials and Apparatus

- Iron (II) and (III) chloride ($FeCl_2$ & $FeCl_3$)
- 2 M HCl
- 0.7 M $NH_3(OH)$
- Oleic acid (technical grade, 90%)
- Decane, 99+%
- Vegetable oil
- Canola Oil
- Grapeseed Oil
- Sunflower Oil
- Polystyrene petri dish
- 1500 grit sandpaper
- 60-80 grit sandpaper
- OMAX Optical Microscope

OMAX optical microscope



1500-grit sandpaper



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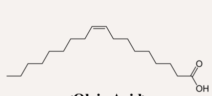

<Oleic Acid>

<Decane>

Conclusions / Future Directions

Furthermore, the purpose of this research was to determine which organic based solvent in ferrofluid best removed microplastics in water. The solvents analyzed were the following: decane, vegetable oil, sunflower oil, canola oil, and grapeseed oil. Each solvent was chosen due to their low toxicity and viscosity when creating ferrofluid. In addition, these oils were chosen for their high percentage of oleic acid, the surfactant used to improve the quality of ferrofluid. Overall, this study demonstrated that decane and vegetable oil were promising solvents that interacted well with the ferrofluid. It was also observed that the vegetable oil-based ferrofluid was able to remove a large number of microplastics. In the future, it is hoped to use other oils such as safflower oil and flaxseed oil, as an organic solvent, which also show high percentages of oleic acid.

Acknowledgment

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