Analysis of the Microplastic Removal Efficiency of Synthesized Ferrofluids and the Development of an Automated Prototype for Aquatic Environments

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Microplastics are proven to be harmful to living organisms. There are about 51 trillion microplastics (< 5mm size) present in water bodies worldwide. Filters, membranes, and sieves currently used to capture aquatic microplastics are costly and labor-intensive, limiting widespread usage. Ferrofluids, made up of iron oxide (Fe_3O_4) and oil, are cheaper alternatives. Ferrofluids exploit the hydrophobic properties of microplastics and oil, allowing the removal of microplastics through magnets. For this research, varying volumes of used and unused cooking oils and engine oils were combined with different weights of Fe_3O_4, to synthesize ferrofluids. These solutions were then used to extract Polypropylene (PP), Polyethylene (PE), and Polyethylene Terephthalate (PET) (< 2mm sized) microplastics from water, and the microplastic removal efficiencies (MRE) were calculated. The goal was to understand the effect of different oils, oil volumes, and Fe_3O_4 weights on microplastic removal efficiency. This study also aimed to determine the ideal ferrofluid composition with a high MRE. This ferrofluid combination was used in an electromechanical prototype, designed using the Raspberry Pi, which was built to fully automate the microplastic extraction process. The results suggest an inverse relationship between oil volume and MRE. Unused cooking oil and used engine oil had the highest and lowest MRE respectively. For each of the three microplastic types extracted using the prototype, the average MRE was observed to be greater than 85%. Laboratory and prototype investigations indicate that a high MRE is possible, illustrating that ferrofluids used to magnetically remove microplastics are a viable solution to the increasing aquatic microplastics problem.

I. INTRODUCTION

Plastics are some of the most useful yet harmful products manufactured. Microplastics are smaller forms of plastic, less than 5 mm in diameter, which are either intentionally created (primary microplastics) or formed when forces such as wind, water, and UV radiation cause larger plastics to degrade (secondary microplastics) [2]. When microplastics travel through wastewater facilities and other waterways, they end up in aquatic ecosystems [5]. The small size of microplastics and their hydrophobic nature cause them to adsorb many harmful hydrophobic pollutants and chemicals also found in aquatic environments. As a result, microplastics can create powerful chemical cocktails which are harmful to organisms and humans that may ingest them [5 & 8]. As microplastics are passed between organisms through the food chain, there is a danger of the bioaccumulation of large amounts of microplastics and toxins in organisms higher up in the food chain [2]. When organisms and humans consume these microplastics, changes in eating behaviors and metabolic processes have been observed [4]. Many laboratory studies have researched the neurotoxicity potential and an increased risk of skin and reproductive disorders in humans due to microplastic intake [13]. Studies of the health, economic and social impacts of microplastic pollution are only recently being investigated. In 2017, the United Nations Environment Assembly estimated that between 4 - 12 million metric tons of plastic make their way into the oceans every year [7]. Despite these statistics, there is no global political consensus yet to limit plastic consumption or to address its disposal [7]. Therefore, there is an urgent need for environmentally friendly ways to remove aquatic microplastics.

Sieves and filters implemented in aquatic environments are costly and target mainly surface microplastics [12]. Recent studies have investigated the magnetic extraction of aquatic microplastics using ferrofluids. Ferrofluids are colloids of a liquid carrier (oil), magnetic nanoparticles (magnetite), and Fe_3O_4 (Iron I + II Oxides) [6]. Magnetite (also known as ferrite) is a mineral, which is biocompatible, cheap, chemically stable with low toxicity and high magnetic strength [10]. The oil component acts as a surfactant, which coats the magnetite particles preventing them from clumping and agglomerating, therefore hindering the magnetic attraction and Van der Waals forces between the particles [10]. Agglomeration would prevent the formation of a ferrofluid emulsion and be ineffective in the extraction of microplastics. When ferrofluids are added to a microplastic suspension, the hydrophobic microplastics adsorb the hydrophobic oils resulting in the formation of microplastic-oil-magnetite complexes, which can easily be extracted with a magnet [6].

This research involved designing and developing a fully automated ferrofluid-based prototype to magnetically extract microplastics. This prototype is powered by a Raspberry Pi 3 Model B, a low-cost, small computer. The automation sequence is coded in Python programming language. The control circuitry around the Raspberry Pi is designed with components purchased from online stores (like Adafruit): motor hats, motors, pumps, GPIO breakout board, etc. Adafruit's software library called Circuit Python helped simplify interfacing with these electronic components. The prototype is targeted for aquatic vehicles, like boats and ships, to facilitate clean up of small and large bodies of water with minimal manual supervision. To determine the cheapest and optimal ferrofluid combination for use in the prototype, different volumes of used and unused cooking and engine oils and weights of ferrites were tested. This was done in order to compare their efficiency in magnetically extracting three microplastic types commonly found in water bodies: Polypropylene (PP), Polyethylene (PE), and Polyethylene Terephthalate (PET), .

II. METHODS

To establish how each ferrofluid component impacts magnetic removal efficiency (MRE) of PE (polyethylene), PP (polypropylene), and PET (polyethylene terephthalate) microplastics, 64 different combinations of ferrofluids (Fig. 1) were synthesized. This was done using varying weights (0. 25 g/L, 0.5 g/L, 0.75 g/L, and 1g/L) of magnetite (Fe_3O_4) and varying volumes (0.5 ml/L, 1.0 ml/L, 1.5 ml/L, and 2.0 ml/L) of four types of oil: cooking (peanut) oil, used cooking (peanut) oil, engine oil, and used engine oil. Microplastics (PE, PP, and PET), < 2mm in size, were used.

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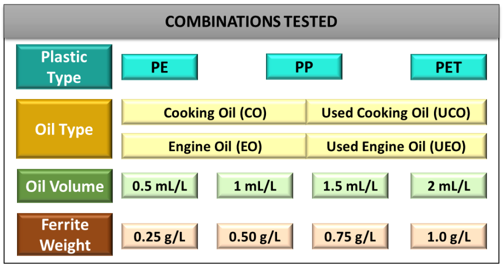
One microplastic type at a time was added to distilled water to make the microplastic suspension (0.5 g/L).



COMBINATIONS TESTED

Plastic Type	PE	PP	PET	
Oil Type	Cooking Oil (CO)	Used Cooking Oil (UCO)		
	Engine Oil (EO)	Used Engine Oil (UEO)		
Oil Volume	0.5 mL/L	1 mL/L	1.5 mL/L	2 mL/L
Ferrite Weight	0.25 g/L	0.50 g/L	0.75 g/L	1.0 g/L

Figure 1. This table shows the different oil types, oil volumes, and ferrite weights used to make the varying ferrofluid combinations. Each of these ferrofluid combinations was tested on three types of microplastics, PE, PP, & PET.

Ferrofluid Synthesis and Magnetic Extraction

The predetermined volume of a given type of oil and the predetermined weight of ferrite (magnetite) were added to each microplastic suspension, forming the ferrofluid. This was followed by vigorous stirring to mix the suspension and ferrofluid. A neodymium magnet-test tube device (20 small neodymium magnets held together by wire in a glass test tube) was immersed into the solution to attract and extract the ferrofluid (with or without adsorbed microplastics). To remove all traces of ferrites, the solution was stirred and allowed to settle. The magnet-test tube device was immersed again (for a total of 3 times), with cleanup of the device between immersions (magnetic extraction). After magnetic extraction, the solution was vacuum filtered on a previously weighed filter paper. Additional distilled water was added to ensure that any particles adhering to the glass of the beaker were transferred. The filter paper was removed and transferred to a previously weighed petri dish and allowed to dry in an incubator (24 hours). The weight of the dried filter paper in the petri dish was measured and compared with the weight of the filter paper and petri dish before filtration. The difference of the weight of microplastics remaining in the water after magnetic extraction was used to calculate the % magnetic removal efficiency (MRE) using the percent-change formula (Fig.3).

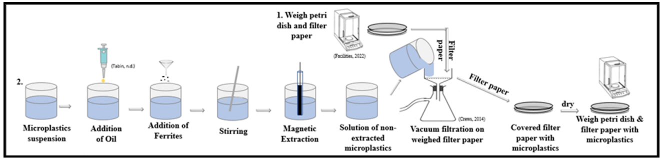


Figure 2. Schematic of methodology for MRE Analysis of Ferrofluid combinations and Prototype

$$\boldsymbol{MRE}\ \% = \frac{C_i - C_f}{C_f}(100)$$

C_i = *Initial weight of microplastics added to solution* (g/L)

C_f = *Weight of microplastics in solution after magnetic extraction* (g/L)

Figure 3. Magnetic Removal Efficiency Formula

As shown in Figure 2, ferrofluid synthesis and analysis of magnetic removal efficiency was performed five times for each combination of microplastic, oil type, oil volume, and ferrite weight. The two positive controls used were the addition of only ferrites to the microplastic suspension without adding any oil and the use of a 1mm sieve to filter the microplastic suspension (with no oil or ferrites) followed by vacuum filtration and weight analysis. The negative control used was microplastic suspensions without adding any oil or ferrites. Statistical analysis was carried out using MiniTab and Microsoft.

Prototype Design & Sequence

The prototype design schematic is shown in Figure 4. The base platform used a particle board (1ft x 1.5 ft) and two vertical square structures 1 ft apart. Three stepper motors [3] were mounted above one of the vertical structures. Stepper motor 1 (lowest of the three motors) controlled a pulley and vertical movement of an electromagnet [4]; stepper motor 2 controlled the horizontal movement of the electromagnet, and stepper motor 3 enabled the horizontal movement of the ferrite (magnetite) dropper. Five glass containers (C1, C2, C3, C4, and C5) were used: C1 (representing an external body of water), held the microplastic (MP) water, C2 was the site of magnetic extraction, C3 held waste ferrofluids in water, C4 is where the water after microplastic removal was transferred to, and C5 contained oil. Two electric pumps [11] transferred water and oil into C2 respectively while a third pump transferred water after MP extraction to C4. Motors, pumps, stirrer and electromagnet were electronically controlled using a Raspberry Pi where the control sequence was coded in Python.

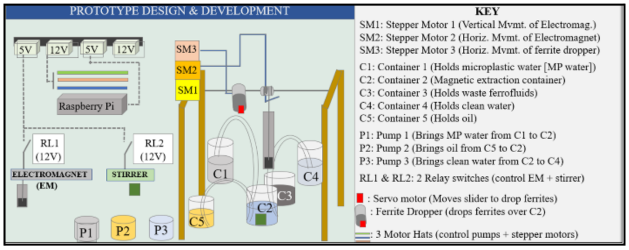


Figure 4. Prototype schematic and key illustrating the various components of the prototype and their purpose

SEQUENCE

1. MP water from C1 to C2
2. Oil from C5 to C2
3. Ferrites from ferrite dropper into C2
4. Stirrer stirs
5. Electromagnet descends into C2
6. Electromagnet moves in C2 and picks ferrofluids
7. Electromagnet is raised
8. Electromagnet moves to C3 & turns off
9. Electromagnet drops ferrofluid into C3
10. Clean water from middle of C2 to C4

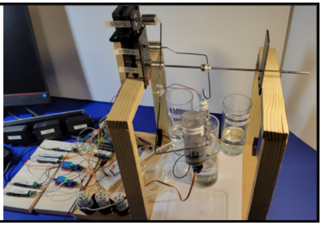


Figure 5. Image of Developed Prototype, sequence indicating automation and movement of individual parts and materials

The MP water was transferred into C2 (magnetic extraction container). Oil (1 drop) and ferrites (~0.5 g) were added to C2, and the stirrer [9] was turned on to mix the ferrofluids and increase contact between microplastics and ferrofluids. The water was allowed to settle (2 min). The electromagnet was turned on and lowered into C2 (where it moved around the bottom of the container) to pick up the ferrites/ferrofluid. Then, it was slowly raised to skim the water surface and attract floating ferrofluids. The electromagnet was then transferred above C3 and turned off to allow disposal of ferrites into C3. To ensure all ferrites on the electromagnet's surface were disposed of, it was rapidly lowered in and out of the water in C3. The water in C2 was allowed to settle (2 min). Finally, about 70% of the water from C2 (to prevent the transfer of ferrofluids that were floating at or around the bottom of the container) was transferred to C4. The sequence was programmed to be repeated as many times as required. To test the microplastic extraction ability of the prototype, the program was run for 3 trials per plastic type. A neodymium magnet was inserted into the final C4 solution(to remove ferrite traces, if any. The solution was then vacuum filtered on a weighed filter paper, dried, and MRE was calculated.

III. RESULTS AND DISCUSSION

To find the cheapest and most environmentally friendly ferrofluid combination with the highest MRE for use in the prototype, factorial analysis using MiniTab was first conducted to understand the effects of the four main factors: oil volume (OV), oil type (OT), ferrite concentration (FC), and plastic-type (PT) on MRE.

Statistical Analysis

As seen in Figure 6, all Interaction plots are almost parallel. They do not appear to intersect, suggesting no perceivable interactions of any two factors are influencing MRE among the six two-factor interactions [oil volume with: ferrite concentration, plastic type, and oil type; ferrite concentration with: plastic type and oil type; and plastic type with oil type]. Therefore, while each of the four factors individually affect MRE, it is not necessary to take into consideration any combination of factors when attempting to understand the effects of ferrofluid composition on MRE.

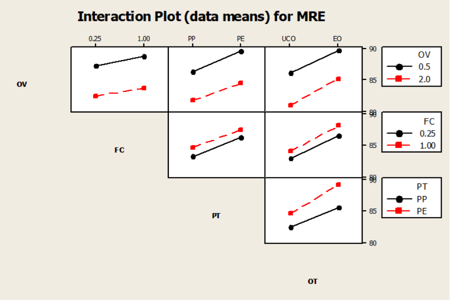


Figure 6. The Interaction Plot indicates that since the interaction plots are almost parallel and do not appear to intersect, there is no perceivable interaction among the 6 two-factor interactions.

Effect of different Ferrite Concentrations on MRE

The comparison of the average MRE for all oil types, oil volumes, and plastic types at 4 ferrite concentrations, ranging between 0.25 g/L to 1.0 g/L (Fig. 7) shows no significant effect of changing the ferrite concentration on MRE in the ferrite ranges tested. Further testing is necessary to determine if the MRE values drop when ferrite concentrations are decreased below 0.25 g/L. From an environmental standpoint, lesser ferrite usage is better. Therefore, establishing the minimum threshold of ferrite concentration required to yield high MRE is necessary. The slope of the FC graph of the Main Effects Plot (Fig. 8, top right) confirms that it is not possible to establish a relationship between ferrite concentration (FC) and MRE in the range of ferrite concentrations tested.

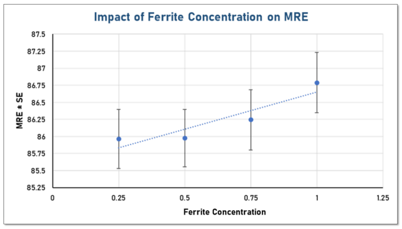


Figure 7. Graph demonstrating average MRE of all oil types, oil volumes, and plastic types at four ferrite concentrations.

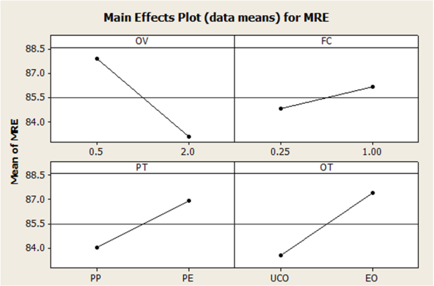


Figure 8. The Main Effects Plot demonstrates that as the oil volume (OV) increases, the MRE decreases. [Ferrite Concentration (FC), Plastic Type (PT), Oil Type (OT)]

Effect of different Oil Volumes on MRE

The comparison of the average MRE at all four oil volumes tested (for all oil types) is seen in Figures 9a-9c. For all three microplastic types tested, PE, PP, and PET, and for all oil types tested, the MRE values at 0.5 ml/L oil volume were found to be greater than those at 2.0 ml/L oil volume. The slope of the Main Effects Plot (Fig. 8), confirms a strong negative correlation between oil volume (OV) and MRE. This strong negative correlation is in agreement with the findings of Gheit et. al. (2006), who state that smaller oil volumes have higher sorption efficiencies on plastics. They found that high oil absorbency on plastics is achieved when the plastic to oil ratio is between 0.5 and 2.0. Two proposed mechanisms have been suggested to understand how microplastics act as oil sorbents: the hydrophobic interactions between oils and microplastics and the filling of oil by capillary action in the pores of microplastics [15] . Greater sorption efficiencies at lower oil volumes result in the formation of stronger ferrofluid-microplastic complexes, leading to better magnetic extraction of the microplastics, and therefore higher MRE values. Based on these results, only 1 drop of oil was added at a time to the prototype's microplastic suspension. These results contribute to the environmental friendliness of this mechanism of microplastic extraction. Using the least amount of oil necessary for ferrofluid synthesis and extraction will not only help keep costs low, but also help control the release of oil into the ecosystem.

Positive and Negative Controls and MRE

The MRE of the microplastic suspension for the no ferrites and no oil (negative control) group and that of the microplastic suspension using ferrites but no oil (positive control) is seen in Figures 9a-9c. Since the MRE of the negative control did not exceed 2.5%, it is clear that without the addition of ferrofluids, magnetic extraction of microplastics is not viable. For the first increasing ferrites but no oil added (first positive control), the average MRE did not exceed 24%. The increasing ferrite concentration probably creates a stronger magnetic field between the ferrites and neodymium magnets leading to more plastics (that are in contact with or in the proximity of the ferrites) extracted from the solution as they are trapped by the strong magnetic field. These MRE values are significantly lower than that of the ferrofluids, indicating that the oils making up ferrofluids are necessary for better magnetic extraction of microplastics. The average MRE using the 1 mm sieve (used as 2nd positive control because of its current use to remove aquatic microplastics) was in the range of 68% to 70% (Fig.10).

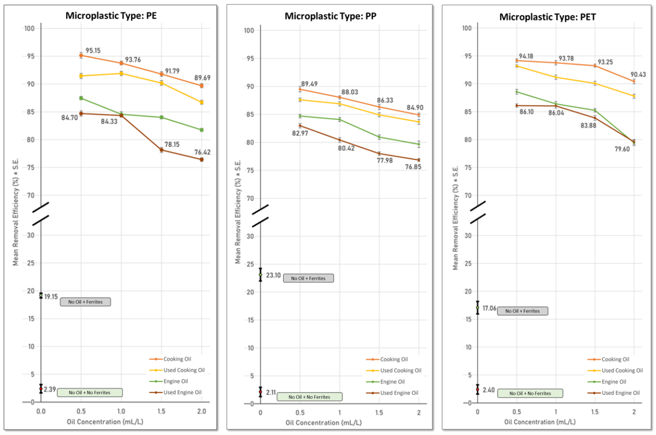


Figure 9. (9a - PE, 9b - PP, 9c - PET) Graphs demonstrating effects of varying Oil Volumes, Oil Types, and Plastic Types on MRE. The average MREs of the positive control (no oil & ferrites) and the negative control (no oil & no ferrites) are displayed.

Effect of different Oil Types on MRE

A comparison of the average MRE for all four oil types tested (cooking oil, used cooking oil, engine oil, and used engine oil) at oil volumes ranging from 0.5 ml/L to 2.0 ml/L for each of the three microplastic types tested is seen in Figures 9a-9c.

For all plastic types tested, cooking oil showed the highest MRE. Cooking oil, both used and unused, also had higher MRE values (between 90-97% and 88-93%, respectively) than engine oil (88-93%). Used engine oil had the lowest MRE (83-86%). The oils in a ferrofluid act as a surfactant on the magnetite (ferrites). The proposed mechanisms of surfactant action of the oils on magnetite are physisorption and chemisorption. Physisorption involves the electrostatic attractions between the carbonyl group of the fatty acid and the protonated and deprotonated hydroxyl groups on the surface of the magnetite particle [14]. Chemisorption involves the formation of chemical bonds between the carbonyl group of the fatty acid and the magnetite surface that results in complex formation [1]. The cooking oil used in the experiment was peanut oil with a higher fatty acid content than engine oil. The higher fatty acid content of cooking oil could increase its surfactant ability, accounting for its higher MRE [7]. Another important and noteworthy point is that peanut oil, used in testing, is cheap and abundantly available worldwide.

It was also seen that used oils resulted in lower MRE than unused oils. Heating of oil (during cooking or running a car) could have altered chemical bonds in the oil altering its ability to adsorb microplastics effectively. Additionally, used oils were observed to be more viscous, which could negatively impact their surfactant ability. A one-tailed independent t-test analysis (α = 0.05) of the average MRE for cooking oil was used in prototype testing.

Prototype Testing

The prototype had MRE values ranging from 86% to 88%. A comparison of the MRE values for the prototype and the 1 mm sieve (Fig. 10) showed a 28.89% , 21.52%, and 27.30% greater MRE for the prototype, for PE, PP, and PET microplastics respectively. Considering that the prototype is fully automated whereas the 1 mm sieve besides being labor intensive is also time-consuming, there is a need to further explore the prototype’s potential as a method to extract aquatic microplastics.

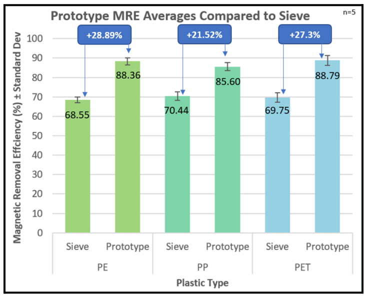


Figure 10. Prototype vs Sieve Results (MRE averages for PE, PP, PET microplastic removal using prototype & comparison to MRE averages for 1mm sieve).

IV. CONCLUSION

The next step will involve analysis of the water after magnetic extraction by the prototype under different conditions of pH, temperature, and salinity to ensure no release of either oil or ferrites into the environment. Further improvements to the prototype involve the use of a stainless-steel oil skimmer in the final solution after magnetic extraction, to extract any remnant oil. It will also be important to investigate using a Y-type strainer or an electromagnetic device that surrounds the pipe releasing water into the environment (as is currently being utilized in some water treatment plants) to prevent the release of ferrites into the environment. Also, a sieve added at the water inlet pipe will prevent living organisms and other organic matter from entering the prototype. This prototype design can be scaled up with heavier pumps and motors, and additional sensors.

The automated Raspberry Pi powered prototype using an electromagnet and ferrofluids synthesized from cooking oil showed MRE >85% for all plastics tested, indicating that automated magnetic removal of MPs from water is possible and effective. Since magnetic extraction of microplastics shows potential to be cheaper, less labor-intensive, and fully automated, further investigations are necessary to help reduce the increasing number of aquatic microplastics that pose a danger to human health and the ecosystem.

V. ACKNOWLEDGMENTS

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