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Analysis of microplastics and their removal from water

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<p>Removal of microplastics from water was studied using extraction with oil. The aim of the thesis was to remove microplastics from water using an organic medium, and to analyse the amount of microplastics in the media involved. The separation of different microplastic types was done by conducting experiments in the laboratory. The microplastics were made by grinding and sieving plastics with a grinding machine before adding them to water and oil, which serves as the organic medium.</p> <p>Two experiments were done: in Experiment 1, the microplastic solution was not mixed in the oil solution, and in Experiment 2, the solution was mixed vigorously in oil. The resulting solution then underwent separating funnel method for separation into two phases. The water phase was filtered in order to know the amount of microplastics in the water medium. The analysis of the amount of microplastics in the water medium was done by weighing the mass of the filter paper containing the microplastics substrate after drying. Replicate experiments and measurements were done.</p> <p>Results show that microplastics could be successfully extracted from water by the filtration method. However, when the polystyrene microplastics in water were mixed vigorously in the oil (Experiment 2), more polystyrene were cleaned from the water by the oil. This observation was supported by the results of the quantitative analysis, which indicate that an organic medium can be used to clean high density microplastics to some degree.</p>	
Keywords	microplastics, water, oil, filtration, HDPE, LDPE, PP, PS

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Abiola Oladejo

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Abbreviations

WWTPs	Wastewater Treatment Plants
MPs	Microplastics
<	less than
>	greater than
PPCPs	Pharmaceuticals and Personal care products
PET/PETE	Polyethylene terephthalate
HDPE	High Density Polyethylene
PVC	Poly Vinyl Chloride
PVAc	Polyvinyl acetate
LDPE	Low Density Polyethylene
PP	Polypropylene
PS	Polystyrene
PC	Polycarbonate
AS	Acrylonitrile styrene
ABS	Acrylonitrile butadiene styrene
SPI	Society of Plastic Industry
H ₂ O ₂	Hydrogen Peroxide
FTIR	Fourier Transform Infrared spectroscopy
α	alpha

μ	micro
CCl_4	Carbon tetrachloride
DWL	Dishwashing Liquid
H_2O	Water
M_1	Measurement 1
M_2	Measurement 2
M_3	Measurement 3
Σ	Sum or total

Units

mm	millimetres
μm	micrometres
g/cm^3	gram per cubic centimetre
$^{\circ}\text{C}$	degree Celsius
psi	pounds per square inch
%	percentage
%w/w	% mass per mass
g	gram

1 Introduction

There is a need for wastewater treatment plants to treat effluents from households and commercial sectors before they are being reused or released into the rivers. One of the important wastes only partially removed by the wastewater treatment plants (WWTPs) are microplastics, which are small plastic fragments which can be found in water and in the environment. However, there is a reasonable amount of microplastics (MPs) which still escape the treatment processes. These microplastics (MPs) which evade treatment at the WWTPs then pose a danger to aquatic life, hence, to human health as well. [1]

In a literature reviewed, it was concluded that most WWTPs which have a tertiary treatment process do remove a significant amount of microplastics compared to secondary plants. [2] In other previous researches, emphasis was mainly on the size and colour of only one type of microplastic and pays less attention to different microplastic types using a different method of separation. Thus, this thesis attempts to fill that gap by focusing on the behaviour and separation of different types of microplastics (MPs) using a two-phase system composed of microplastic contaminated aqueous phase and an organic phase such as vegetable oil. [2]

The aim of this thesis was to remove microplastics (MPs) from water using an organic phase and to analyse the microplastics. This was achieved by conducting experiments in the laboratory. Some research questions that were addressed in this study were as follows:

- How can microplastics be removed from water?
- How much microplastics remain in the aqueous phase after separation?

The experiments and the results from the experiments acknowledged the above questions.

The rest of this thesis follows a structure which is divided into various chapters. Chapter 2 gives background information on microplastics and their classification. Chapter 3 is a literature review which describes the sources of MPs, the types of plastics and how MPs have been analysed and removed from water. Chapter 4 includes the experimental sections, results and discussion. Chapter 5 discusses the results further and makes conclusions.

2 Background

Plastic is a wide term used to describe synthetic organic polymers formed by polymerization process. Plastics may be nanoparticles, microplastics, mesoplastics, macroplastics or megoplastics based on their classification by size. Microplastics are those which have a size of less than 5 mm (the minimum size depends on the laboratory test and reporting, usually from nano proportions to 5 mm). Nanoparticles are usually less than 1 μm , mesoplastics are those whose size are greater than 5 mm, macroplastics are centimetres in size, and megoplastics are more than 1 metre size. [5; 6]

Microplastics tend to be easily swallowed by aquatic animals, thereby posing danger to aquatic life in general and in turn danger to human health. The Figure 1 shows microplastics and how small they can be in size.



Figure 1: Microplastics [7]

There are two classes of microplastics based on how they are produced (primary and secondary):

Primary microplastics are virgin plastic pellets, nurdles, and microplastic scrubbers, which are deliberately manufactured for use in cosmetics, abrasives, hand and exfoliating cleansers.

Secondary microplastics are little plastics particles which result from wear, tear, abrasion, breakdown and degradation of large plastic debris. The debris is produced through the fragmentation of larger plastic materials. [6; 8]

Reasons for removing microplastics from wastewater treatment plants

Microplastics (MPs) need to be removed from wastewater before being discharged or reused because they are of great danger to health. Aquatic and filter feeding organisms may ingest MPs because they mistake these for food. MPs are usually similar in colour and shape to the food these organisms consume, but the digestive systems of these organisms cannot digest microplastics. Thus, MPs are absorbed into the body tissues of these organisms thereby causing adverse effects to their health and life.

It is important to note that these microplastics being ingested usually contain additives used in their manufacture. These small organisms which already have MPs in their guts and system are, however, food for other animals which feed on them; consequently, MPs affect the lives of most organisms across the marine trophic levels. [3] The relevant distribution coefficients for organic chemicals are several orders of magnitude in favour of the plastic medium meaning that microplastics in municipal and industrial wastewater are enriched in toxic organic chemicals; thus, posing an eminent threat to environment and human health. [5] This is why it is necessary to remove microplastics in wastewater treatment plants in order to ensure they do not get into the ecosystem.

3 Literature review

This chapter focuses on the general overview of plastics, the various sources of microplastics as these sources have to be known in order to help reduce the means by which they enter water. The review includes methods which have been used to analyse MPs and to remove them from water as well as resistance of MPs to chemicals.

3.1 Sources of microplastics pollution

- Microplastics are usually intentionally caused by the use of household products such as pharmaceuticals and personal care products (PPCPs) and cosmetic products such as toothpaste, exfoliating cream, hand cleaners, face cleaners

and shaving foams because plastic microbeads are used in the manufacture of these products. These microbeads are usually washed through sinks and drains which then lead them to wastewater treatment plants.

- Industrial spills and transport: Plastic pellets are lost from the plastic manufacturing processes be it during pre-production, actual production or post production (transport and delivery). Scraps and fragments during pre-production, small pieces of plastic resins such as nurdles, mermaid tears, cracked pellets, tails and dust during raw material production and transportation. This source of microplastic pollution is unintentional [9].
- Construction work and everyday activities: MPs also arise from wear and tear from plastic items used indoors. This can for example include toys, electronics, kitchen utensils and carpets. Abrasion of textiles and fabrics during laundry also gradually leads to creation of microplastics which are released into wastewater. Microplastics also result from plumbing and electricity activities during construction as in the use of pipes, wires, wall and cable insulation, conveyor belts. Artificial turfs for sport centers and pitches can in turn contribute to MPs in seas or wastewater through leaching/erosion or unintentional carriage from someone who has been on the turf.
- Waste management and recycling: Municipal waste used for landfills contains a certain amount of plastics in form of plastic additives which leach out from plastics. Plastic litter can end up in the sea from plastic recycling facilities, private companies and the reverse vending machines of polyethylene terephthalate (PET) bottles. MPs may be air-drifted from overloaded plastic waste containers by water or wind.
- Littering: Human lazy and lackadaisical attitudes of littering on the streets or into the air also leads to microplastics pollution [10].
- Sea activities: Microplastics are produced as a result of floating devices, wear from boat paints, coatings or antifouling paint, plastic fishing equipment, large plastic fragments, by waves and grinding on high energy shorelines [11].



3.2 Types of plastics





There are 7 main types of plastics.


- Polyethylene terephthalate (PET or PETE), which was discovered in the 1900s and derived from ethylene monomer.
- High Density Polyethylene (HDPE), which was commercialized in 1957.
- Poly Vinyl Chloride (PVC), which was invented in 1835 and patented in 1933. It is the leading plastic in Europe which is manufactured usually by suspension process and mass polymerization. It can also vary as rigid PVC, flexible PVC, Polyvinyl acetate (PVAc) amongst others.
- Low Density Polyethylene (LDPE), which was commercialized in 1939.
- Polypropylene (PP), which was discovered in 1955 by the addition reaction of propylene gas with Titanium chloride.
- Polystyrene (PS), which was first manufactured in 1851 by the passing of benzene and ethylene through a red hot tube. [12]
- Others is a category which is dependent on resin or combination of resins. The types of plastics in this category include Polycarbonate (PC), Acrylonitrile styrene (AS) and acrylonitrile butadiene styrene (ABS). [13]

Table 1 below shows the various properties which distinguishes the different types of plastics. These properties include mechanical, physical and processing properties.

Table 1: A table showing the plastic types, SPI codes (Society of Plastic Industry), properties and their applications [12; 13; 14; 15; 29]

SPI code	Properties	Applications
 PET	Density: 1.38 g/cm ³ Strong and clear Resistant to heat	Beer bottles, water bottles, beverage bottles, textile fibre and carpet fibre
 HDPE	Density: 0.97 g/cm ³ Tensile strength of 5000 – 6000 psi Strong and stiff Moisture permeability to gas Easily forming Resistance to chemicals Melting temperature of 130 – 137 °C Resistant to solvent below 60 °C	Retail bags, cereal bag liners, detergent bottles, compost bins, crates, milk containers

	<p>Density: 1.40 g/cm³</p> <p>Tensile strength of 1500 – 3500 psi (flexible) and 6000 – 7500 psi (rigid PVC)</p> <p>Strong and clear</p> <p>Flexibility</p> <p>Versatility</p> <p>Resistance to chemicals, grease or oil</p> <p>Melting temperature of 75 – 105 °C</p> <p>Soluble in acetone and cyclohexanol but partially in toluene</p>	<p>Toys, shampoo bottles, plumbing pipes, construction pipes, construction flooring and fittings</p>
	<p>Density: 0.92 g/cm³</p> <p>Tensile strength of 600 – 2300 psi</p> <p>Flexible and soft</p> <p>Ease of processing and sealing</p> <p>Barrier to moisture</p> <p>Melting temperature of 98 – 115 °C</p> <p>Resistant to solvent below 60 °C</p>	<p>Frozen food bags, bin bags, squeezable bottles, rubbish bins, plastic grocery bags</p>
	<p>Density: 0.90 g/cm³</p> <p>Tensile strength of 4500 – 5500 psi</p> <p>Strong and versatile</p> <p>Flexible</p> <p>Resistance to chemicals, grease or oil and heat</p> <p>Melting temperature of 175 °C</p> <p>Resistant to solvent below 80 °C</p>	<p>Medicine bottles, yoghurt containers, ketchup bottles, margarine containers</p>
	<p>Density: 1.05 g/cm³</p> <p>Tensile strength of 5000 – 7200 psi</p> <p>Versatile</p> <p>Rigid and brittle plastic</p> <p>Clear and light weight</p> <p>Styrofoam</p> <p>Thermal insulation</p> <p>Melting temperature of 100 °C</p>	<p>Meat tray, plastic cutlery, disposable cups, compact disc cases, egg cartons, packaging foam</p>

	Soluble in acetone, benzene, toluene and methylene dichloride	
	Made with a resin other than the above mentioned or combination of resins	Baby bottles, automobile parts,

3.3 Analysis of Microplastics from water

Different methods have been used to analyse microplastics in the previous literatures reviewed in this thesis. Usually sampling was done using either water samples, beach samples, subtidal sediments or biota.

- The floatation method was used to extract microplastics which were counted and then grouped according to shapes and sizes. Water samples were collected using a teflon pump and a neuston net. The samples containing organic matter then underwent oxidation for cleansing using 30% hydrogen peroxide (H₂O₂). Zinc chloride solution was then used to separate plastic particles from organic matter through the floatation method before being filtered over cellulose nitrate filters. [16]
- Sediment sampling in which mineral salt or saline water is added to the sediment sample allowing for the separation of low-density microplastics. Meanwhile the denser particles can be removed after being observed under a microscope. The Fourier transform infrared spectroscopy (FTIR) technique is then used to identify plastics after staining the plastics with a lipophilic dye such as Nile red. Other techniques which may be used are Raman spectroscopy, electron spectroscopy or optical spectroscopy. [6]

In the case where the microplastics are in a water sample containing other larger plastic particles, coarse filtration was used to remove the macro particles. Then the plastic particles underwent salt addition, filtration and eventually microspectroscopy in order to isolate the microplastics.

Figure 2 shows that microplastics are subjected to a series of separation techniques including filtration, in order to ensure separation from a water sample.

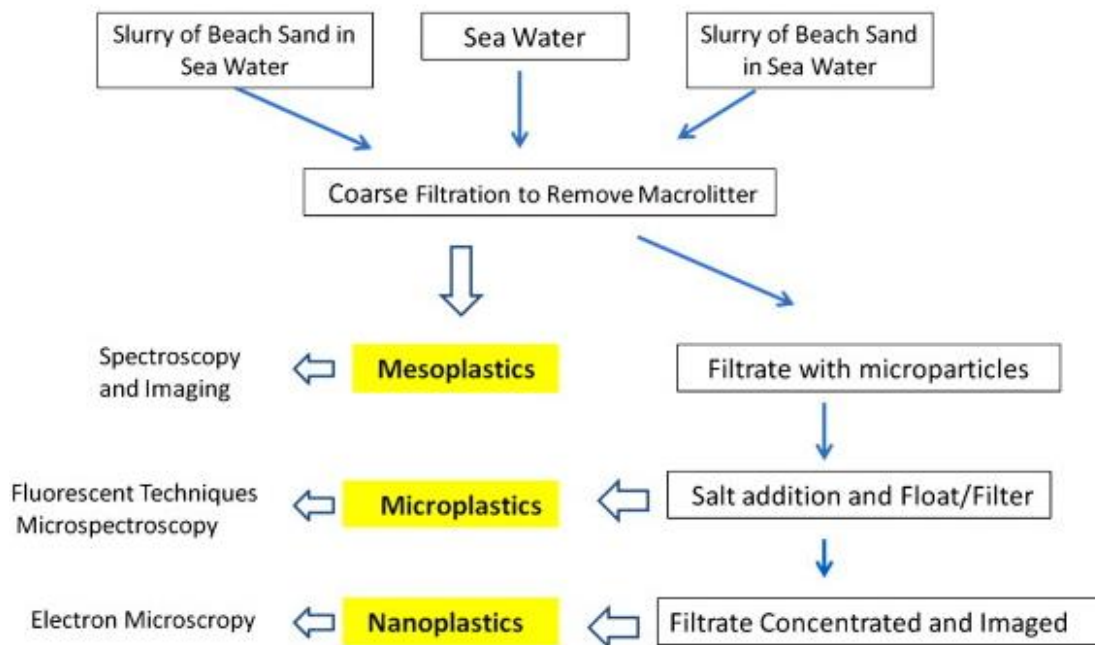


Figure 2: Isolation of plastics from samples of water or sand [17]

- Marine trawling is trawling along a transect of a water column. It involves using manta trawls to sample surface water, bongo nets for sampling of mid-water levels, and benthic trawls to assess the sea bed. The microplastics in the samples were identified by evaporating the seawater and testing the residue left or by using a microscope to examine the sample.
- Biological sampling is conducted on marine animals. Organisms that are suspected to have mistaken microplastics for food are studied to detect the presence of MPs. Beached organisms and seabirds are dissected or their guts are analysed to check for microplastics. The fulmar is one seabird which has been used to assess the presence of plastics. [6]

- Neuston net was used to sample small plastic fragments with mesh size of 0.35 mm in a study made by Isobe, Uchida, Tokai and Iwasaki [18]. It was taken to the laboratory to separate the plastic particles from suspended matter. These samples were then monitored on a monitor display and visually identified by shape and colour. Polymer materials are thus identified using a FTIR spectrophotometer (Fourier transform infrared).
- Mussels are very susceptible to microplastics and are therefore the most common benthic species for identifying or studying microplastics in Li et al [19]. Mussels (*Mytilus edulis*) were collected from water sites and taken to the laboratory where it was stored at -20 °C for MPs analysis. After that, salt water, fresh water and hydrogen peroxide underwent filtration with 1 µm filter paper before being used. The soft tissues of 2-5 mussels were placed in a glass bottle before 200 mL of 30 % H₂O₂ (Hydrogen peroxide) was added. The bottle was left in an oscillation incubator set at 65 °C, 80 rpm for a period of 24 hours. It was then removed and placed at room temperature for 24 - 48 hours. The dissolved liquid of the mussels' soft tissue was then separated from microplastics using pre-filtered sodium chloride solution. It was allowed to stand for hours before further analysis was done using FTIR spectroscopy (Fourier transform infrared spectroscopy).

3.4 Chemical resistance of microplastics

The microplastics to be separated from water and to be analysed have to be chemically resistant to the separation media. The organic media chosen has to be one which does not dissolve or break down the plastic material in order to ensure accuracy of results during experimentation. The organic medium used should be a non-polar organic medium, they usually have low polarity index compared to water's polarity index of 9. [20]

Polar organic mediums will dissolve the water, thereby, no two-phase solution is created which makes separation difficult. Non-polar organic solvents are hexane, pentane, cyclohexane, carbon tetrachloride (CCl₄), isooctane (also known as 2, 2, 4 – trimethyl pentane), trichloroethylene and petroleum ether. [21]

Table 2 presents the solubility of immiscible non-polar organic solvents in water

Table 2: Solubility of immiscible non-polar organic solvents in water [20; 21; 22; 23; 24]

Solvent	Dielectric constant	Solubility in water (%w/w)
Pentane	1.84	0.004
Hexane	1.90	0.001
Cyclohexane	2.01	0.0055
Isooctane	1.94	0.00022
Carbon tetrachloride	2.2	0.08
Benzene	2.28	0.18
Toluene	2.38	0.051
Water	80.10	100

The solvents which are highly soluble in water usually dissolve in water and then no two-phase media is formed. Some chemicals also affect the microplastic itself. For example, pure toluene usually causes immediate damage to polystyrene. [25]

4 Experiments

This chapter describes methods and procedures carried out in the laboratory. The results and discussions are also presented in this chapter.

The purpose of the experiment was to extract or separate microplastics from water and to analyse its amount in the media. The principle which the experiment follows is summarised in Figure 3 below.

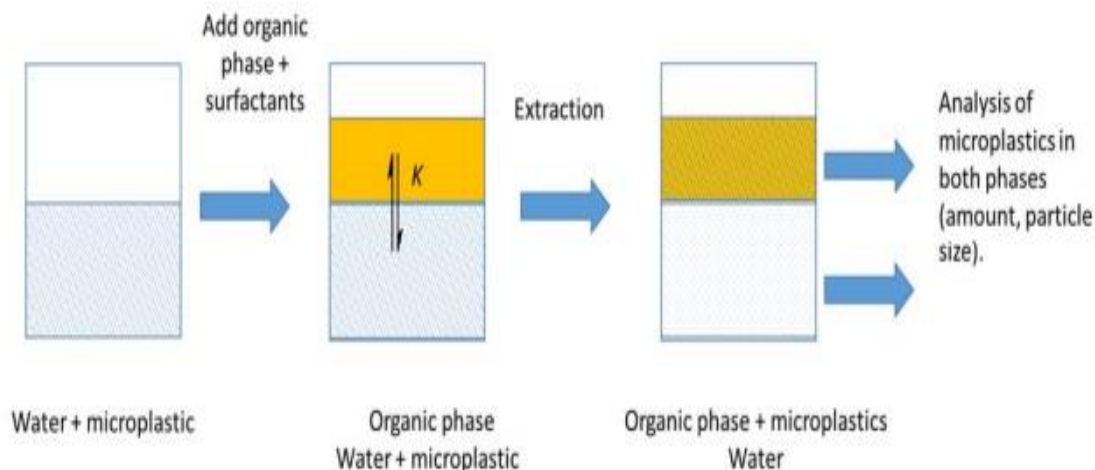


Figure 3: Microplastics extraction experiments. [26]

Figure 3 shows that the first step is to mix water and microplastics together. Depending on how well they both mix together determines if a surfactant will be added. A surfactant reduces the surface tension of water, which thus allow for even mixing of MPs with water. Then an organic phase/medium is added; this is done in order to provide a medium which has a density different from that of water and to ensure that extraction of MPs is possible. After partitioning of MPs between aqueous and organic phases, the phases are separated and the microplastic content is analysed.

4.1 Pre- experiments and factors considered for the laboratory experiments

There were many factors considered in order for the experiment to take place.

- **Temperature:** Ambient temperature will be adequate for the experiment. If the experiments were to be done at a different temperature, it would be difficult to notice when some microplastic types start dissolving in the organic or water phase. Some plastic types also start dissolving at a much lower temperature than their melting point. For example, PVC starts distorting at 92 °C when the melting point is 160 °C. [27]
- **Microplastics used:** Nurdles and cracked plastic pellets were not easy to get; likewise, it would have been tedious to obtain MPs from the sea or water bodies using trawls. Polyethylene microbeads were first extracted from a body scrub by

first mixing in warm water before filtration, but it was tedious to extract an amount of microplastics which would be enough for the whole experiment. [28] Another method for getting microplastics for use is by cutting plastic materials into very small pieces using scissors. This was also not successful because a separating funnel was planned for use in the experiments, and these MPs would be too large to pass through the tap of the separating funnel. Therefore, a decision was made to resort to using several household plastics which were ground into powder and used as sources of MPs for separation and analysis.

- Particle size: Microplastics size of <5 mm was used for the experiment. In this case, mesh/filter of the appropriate size was used to sieve the MPs in order to ensure the adequate size. However, the problem with having larger particles closer to the upper limit of size 5 mm is that the microplastics would not be able to leave through the tap of the separating funnel (This was also addressed in the previous paragraph). On the other hand, MPs were ground into powder of even less than 0.25 mm using a sanding machine so that they pass through the separating funnel. These powdery and extremely small particles, however, were not easy to analyse or weigh in the separating media compared to larger particles.
- Buoyancy and plastic type: Buoyancy is important here because different plastic types have different densities. For example, PET, PVC and PS are denser than water; thus, they are expected to mostly sink in water. HDPE, LDPE and PP are less dense than water and would float on water. Separation and moving of different types of plastics into the organic phase and in the aqueous phase would be different. [28]
- Chemical resistance of microplastics: The chemical resistance of MPs is necessary as it helps to determine what plastic types are resistant to what chemicals, and which organic medium to use. This helps to know what kind of damage a chemical would cause to microplastics and to avoid decomposition/dissolution of microplastics. However, most of the non-polar organic phases in their pure form in Table 2 usually cause immediate damage to the different plastic types. [25] Therefore, cooking oil was used as the organic medium for the experiment as it does not disintegrate the MPs and it allows for distinct organic (oil) and aqueous (water) phases.

4.2 Method

Four different microplastic types were separated from water;

- High Density Polyethylene (HDPE)
- Low Density Polyethylene (LDPE)
- Polypropylene (PP)
- Polystyrene (PS)

The first three plastic types listed above have a lower density compared to water, whereas PS has a higher density than water. This helped to notice how the difference in density affects buoyancy and actual separation of microplastics from water. The properties of the plastic types are illustrated in Table 3.

Table 3: Properties of materials used [29]

Plastic types	Densities (g/cm ³)	Material used
HDPE	0.97	Food container
LDPE	0.92	Water bottle
PP	0.90	Food package
PS	1.05	Disposable cup

PET was not used because it was melting during the sanding process. This is as a result of the friction as well as the low thickness of the PET material used. Figure 4 shows the plastic materials used in the experiments.

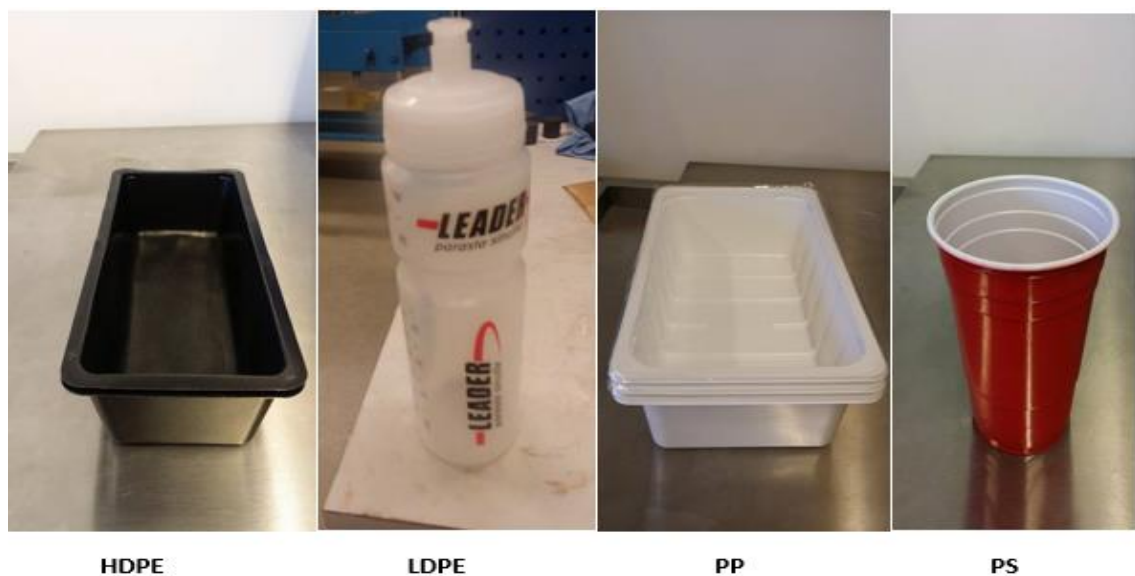


Figure 4: Four plastics materials used for the experiment

Figure 4 shows the four different microplastic materials used for the experiment after they were ground into powdery form. However, the main steps in the removal of MPs which follows the extraction processes in Figure 3 can be further subdivided into specific procedures as shown in Figure 5.

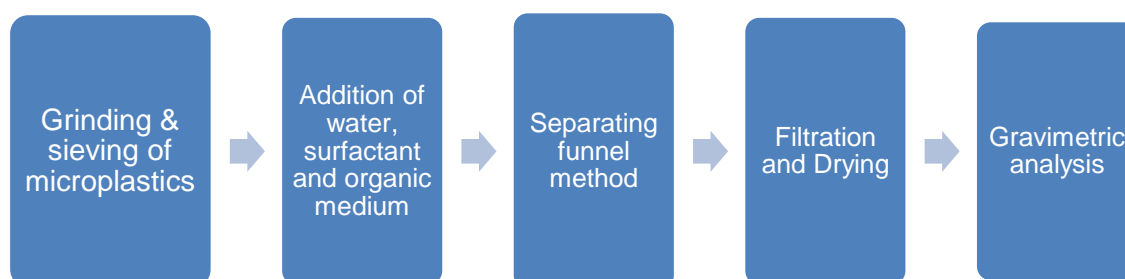


Figure 5: Step by step method used in separating the microplastics from water

Plastics were first ground and sieved before adding water. Then, the microplastics solution was passed through a separating funnel method, filtration and drying processes. The results were then analysed gravimetrically in order to know the amount of microplastics in the water and oil phase. [4]

Equipment and used materials

The following equipment and material were used in the experiments: separating funnels and corks, separating funnel rings, beakers, glass vials, spatulas, a grinder, a sanding machine, a sieving machine, an analytical balance, a drying oven, retort stands, 125 mm filter papers, filter funnels, cooking oil, distilled water, paper tape, a scissors, a knife, a wash bottle, dishwashing liquid, conical flasks, a sieving machine, a 5 mm sieve size.

The procedures followed in the experiments are described in the following sections.

4.3 Grinding and Sieving

- The plastics were first ground into powdery form using the sanding machine.
- The microplastics were passed through the sieving machine using mesh size of 5 mm to ensure any larger particles was collected on the mesh, while the smaller particles needed for the experiment were collected below.

- The plastic powder was then transferred into clean glass vials and labelled accordingly (Figure 6).



Figure 6: The microplastics stored in glass vials

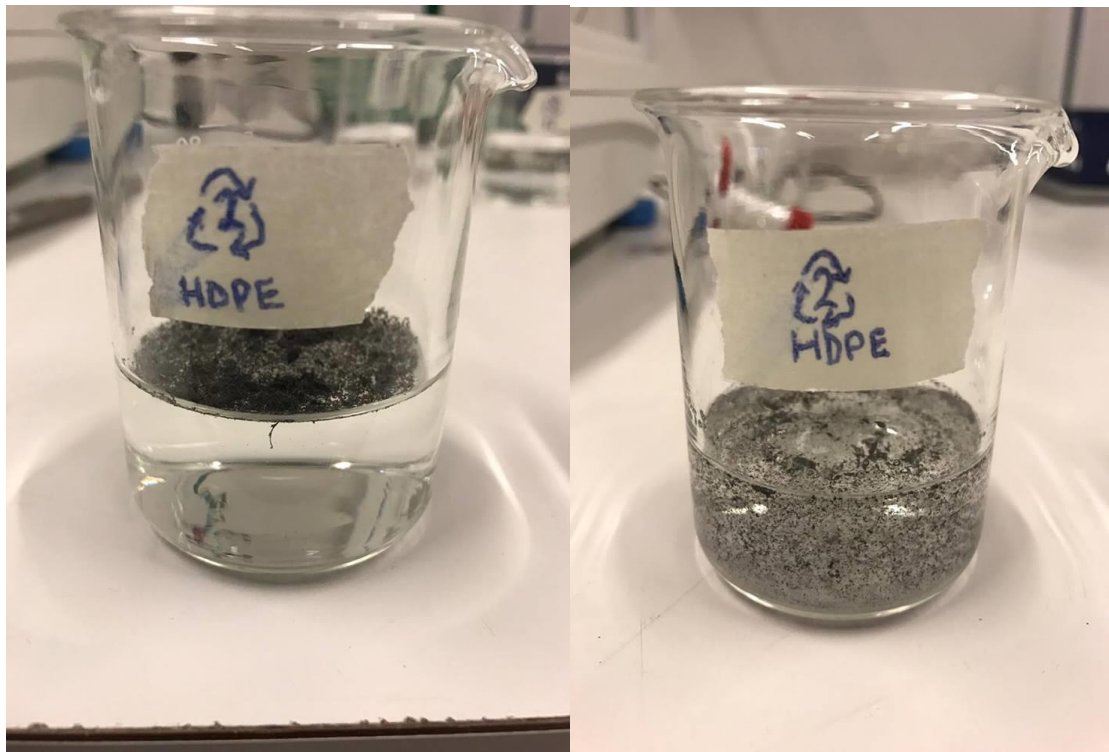
The microplastics were then ready for use in the experiment (mesh size 5 mm was used to sieve the ground plastics)

4.4 Addition of water and surfactant

- A beaker was taken and the mass of the beaker was measured on the analytical balance.
- Some microplastic powder were then added into the beaker and the total mass was noted.
- The difference between the mass of beaker and mass of beaker + microplastics is the mass of the microplastics used.
- Distilled water was added into the beaker containing microplastics.
- The resulting solution was then mixed with a spatula; they did not mix. HDPE, LDPE and PP mostly float, whereas a very little amount of PS sinks. This is at-

tributed to the density of the microplastics compared to that of water; lower density MPs float while MPs with a density higher than water sink. The surface tension of the water did not allow the microplastics to mix.

- One drop of dishwashing liquid was then added to act as a surfactant in order to reduce the surface tension of the water. This allowed for the microplastics to mix properly in water. Microplastics mixed better when dishwashing liquid was added.



(a)

(b)

Figure 7: (a) HDPE microplastics in water; (b) HDPE microplastics in water after adding dishwashing liquid

Figure 7 indicates that the HDPE microplastics mix better due to the effect of the dishwashing liquid on the water. It is the same situation for LDPE and PP microplastics; they do not mix unless one drop of dishwashing liquid was added. However, when the dishwashing liquid was added to PS in water, they did mix, but most of the microplastics sank almost immediately as shown in Figure 8 below.

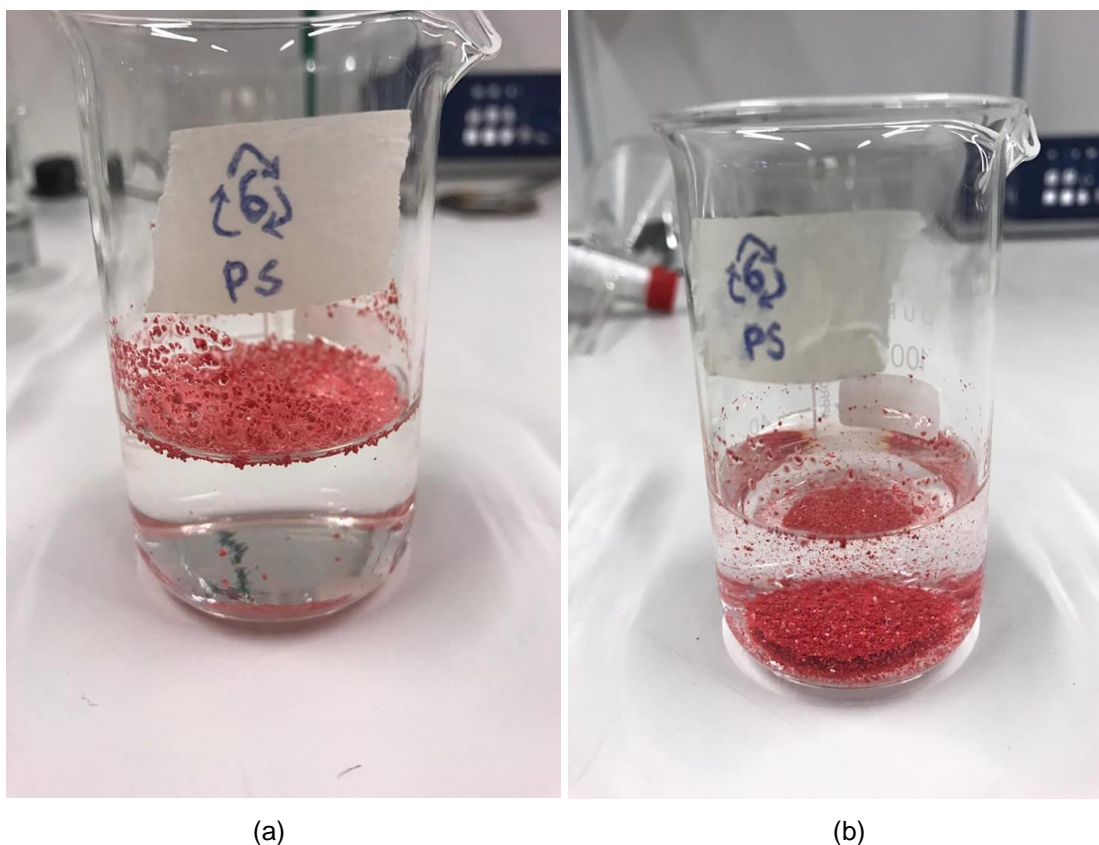


Figure 8: (a) PS microplastics in water; (b) PS microplastics in water after adding dishwashing liquid

Figure 8 shows the behaviour of the MPs sinking almost immediately is expected because PS has a higher density than water; whereas, HDPE, LDPE and PP all have densities lower than that of water. Density of water is 1 g/cm^3 .

4.5 Organic medium addition and separating funnel method: Case I (Solution was not mixed)

At this stage of the experimental process, results of the experiments were influenced by vigorous mixing of the solution containing water, microplastics, one drop of dishwashing liquid and oil. The difference in results caused by vigorous mixing lead to separate experiments being done in order to observe the water – oil separation behaviour

Case I: The solution was not mixed

Case II: The solution was mixed vigorously with oil

This section focuses on Case I, while the following section 4.6 concentrates on Case II.

4.5.1 High Density Polyethylene (HDPE)

A separating funnel was fixed to the retort stand firmly, and the tap closed.

20 ml of cooking oil was measured and transferred into the separating funnel.

The mixture of all water + HDPE microplastics + surfactant was poured into the separating funnel containing oil. The surfactant used is dishwashing liquid (DWL).

Water was used to spray the microplastics stuck on the walls of the beaker into the solution in the separating funnel. This was to ensure that all or most of the HDPE particles get into the separating funnel.

The solution was not mixed vigorously in the separating funnel. However, it was allowed to stand for a few minutes. The separating funnel opening was covered with a cork.

After the 2 layers were properly formed, the cork was removed in order to release the pressure.

Then the tap was slightly opened to collect the water phase in a beaker for further analysis. The oil phase was discarded because there were no known methods to analyse the microplastics in the oil phase.

The solution of all four types of plastics was not vigorously mixed for three reasons.

- When mixing was done, most of the microplastics move into the non-polar organic medium. This would not allow for testing of the microplastics in the water medium since all the microplastics to be removed from the water have already moved into the cooking oil in the top layer. This raises an important idea of using oil to clean water off MPs by vigorous mixing.

The method used to ensure both phases in the separating funnel passed through each other is the sequence of pouring water and oil in the separating funnel. That is why the cooking oil was initially poured into the separating funnel before the solution of microplastics + H₂O + dishwashing liquid (DWL) was added. This allowed both phases to pass through each other because the oil phase would rise to the top of the water.

- The MPs get stuck to the walls of the container which introduces experimental errors in the measurements. It made analysis of the amount of microplastics in the water medium more difficult.

- Bubbles: Dishwashing liquid began to form bubbles with water because of the mixing/shaking. The bubbles attracted some microplastics and more time would have been needed to allow the bubbles disappear.

HDPE + H₂O + DWLHDPE + H₂O + DWL + oil

Figure 9: HDPE microplastics in water containing dishwashing liquid, before and after adding oil

Figure 9 shows the before and after addition of oil. However, it can be observed from the picture on the right that most of the HDPE microplastics are in the top oil medium. The slightly larger HDPE particles are in the oil medium, whereas, the tiny particles can be seen in the water medium. Visual observation shows that most of the microplastics are in the organic medium (oil).

4.5.2 Low Density Polyethylene (LDPE)

The same steps as in HDPE were followed.

Some LDPE microplastics were stuck to the walls of the container while pouring them into the separating funnel. These HDPE on the walls of the container were washed into the solution by spraying with distilled water from the wash bottle.

LDPE + H₂O + DWLLDPE + H₂O + DWL + oil

Figure 10: LDPE microplastics in water containing dishwashing liquid, before and after adding oil

Figure 10 shows that most of the microplastics were in organic medium (top oil phase) while a little amount was in the water medium.

4.5.3 Polypropylene (PP)

The same steps as in HDPE were followed.

Almost all the PP microplastics remained in the oil phase even without mixing. This is because when the PP material was ground, most of the powder particles tend to mould into tiny balls (PP particles in Figure 6). These larger moulded PP microplastics remained in the oil medium alongside some fine powdered particles.

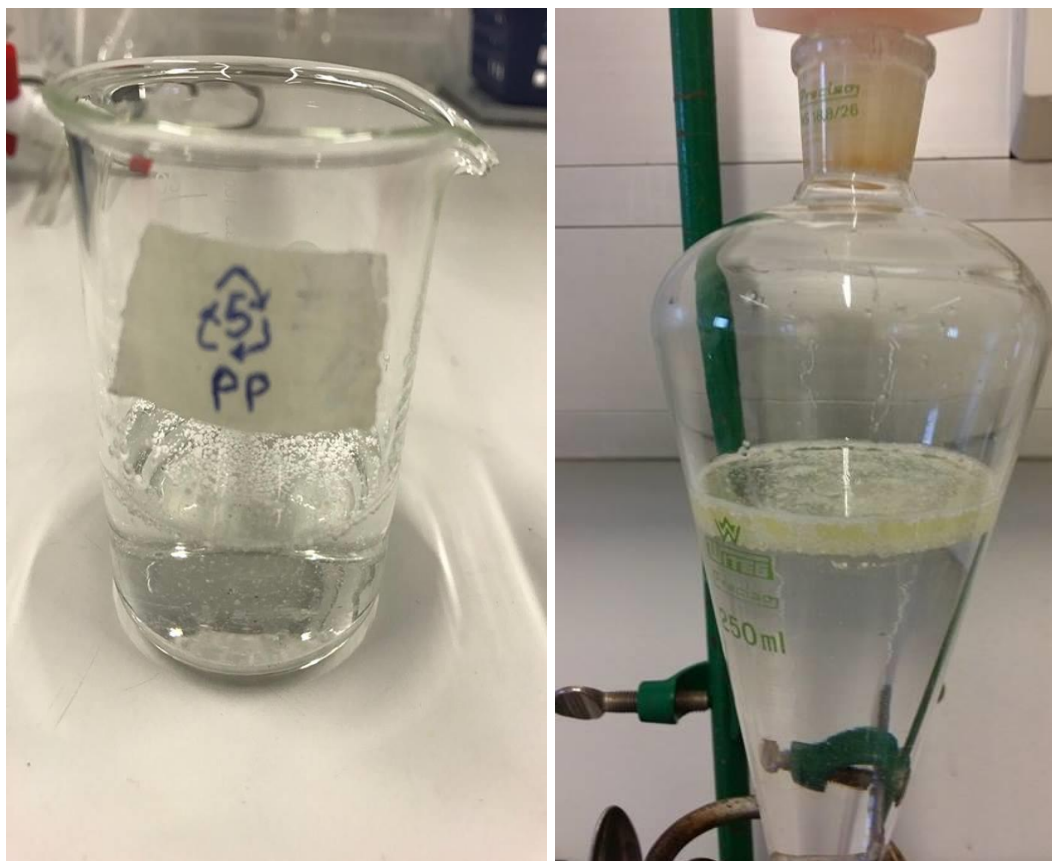
PP + H₂O + DWLPP + H₂O + DWL + oil

Figure 11: PP microplastics in water containing dishwashing liquid, before and after adding oil

Some fine PP particles were in the water medium.

4.5.4 Polystyrene (PS)

The same steps as in HDPE were followed.

PS has a higher density than water; thus, when PS was mixed with water, the PS settled at the bottom but some heavier particles stayed at the top. It was observed that a reasonable quantity of the PS microplastics was retained in the oil medium.

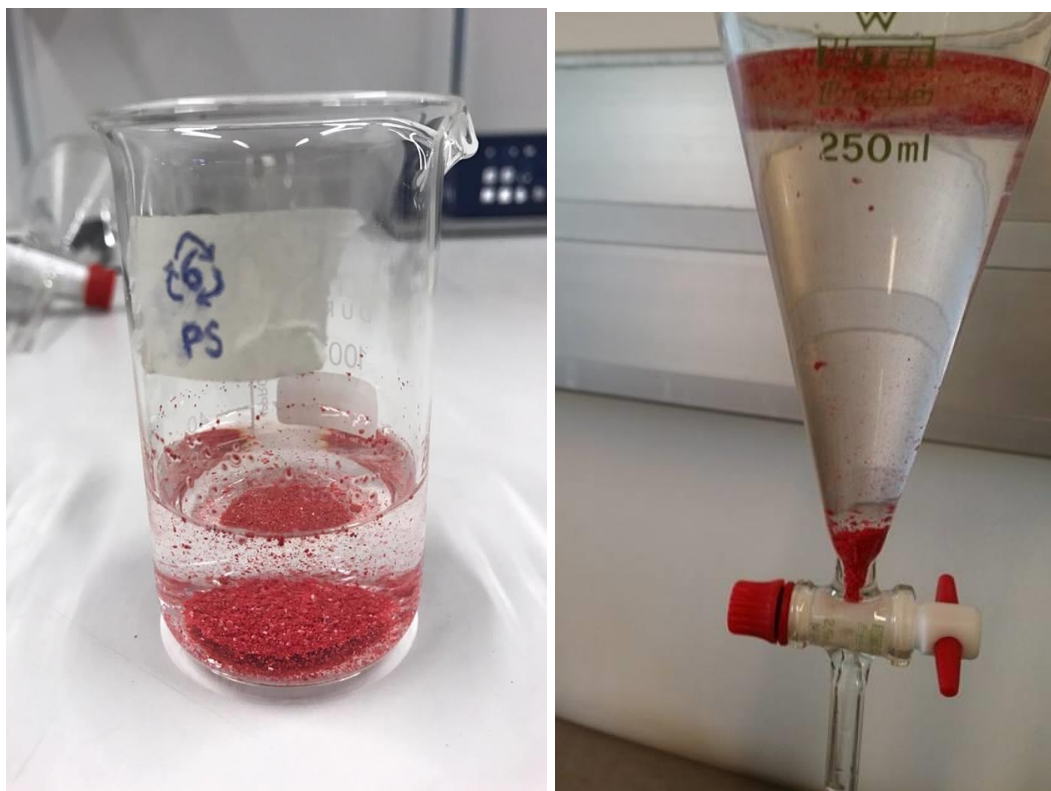
PS + H₂O + DWLPS + H₂O + DWL + oil

Figure 12: PS microplastics in water containing dishwashing liquid, before and after adding oil

Similar to the oil medium, there was a reasonable amount of PS microplastics in the water medium. Most of the PS microplastics accumulated at the bottom of the funnel as seen in Figure 12.

4.6 Organic medium addition and Separating funnel method: Case II (Solution was mixed vigorously with oil)

All the same steps except vigorous mixing as in Case I were followed for all four types of microplastics. In this Case II, there was vigorous mixing of the microplastics + H₂O + dish washing liquid (DWL) + oil using a spatula. Case II was done in order to observe the water - oil separation behaviour when it was vigorously mixed together.

Unlike Case I where the oil was first poured into the separating funnel, in this Case II, the oil was added into the beaker containing the microplastics + water + dishwashing liquid. The resulting solution was then mixed together vigorously using a spatula.

It was difficult to visually notice the difference in the amount of LDPE, HDPE and PP microplastics in the water medium when comparing Case I and Case II.



Case I: HDPE not mixed in solution

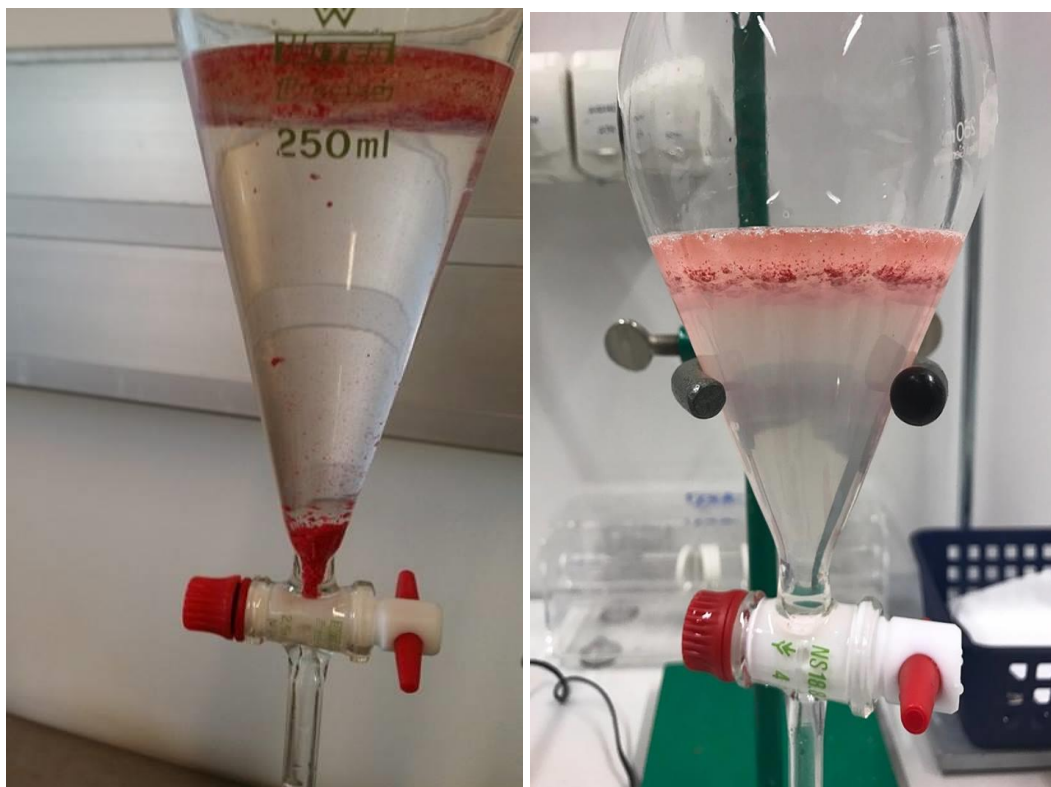
Case II: HDPE vigorously mixed in solution

Figure 13: Comparison of HDPE in solution without mixing and when mixed vigorously

Figure 13 indicates that the water phase in Case II was cloudy because of the vigorous mixing since it already contains dishwashing liquid. It can also be observed that there was not much difference in the amount of HDPE in the water phase in Case I and Case II. This was the same when LDPE and PP microplastics were involved. This was due to HDPE, LDPE and PP all having a density lower than that of water; thereby exhibiting similar characteristics.

*The images of LDPE and PP in the separating funnel was not added to the report because they were acquired from white plastic materials and the cloudiness of the water phase would make it difficult to interpret the picture

However, the observation was different when PS was mixed in the solution containing water, oil and dishwashing liquid as shown in Figure 14.



Case I: PS not mixed in solution

Case II: PS mixed vigorously in solution

Figure 14: Comparison of PS in solution without mixing and when mixing occurs.

Figure 14 shows that the water medium in Case I contains more polystyrene microplastics than in Case II where there was vigorous mixing. The significance of mixing the solution together was mostly noticed when PS was the microplastic type involved.

The more the PS microplastics were mixed in solution with the oil, the more the PS microplastics move into the organic medium as shown in Figure 15 below.



(a) Before mixing

(b) After mixing vigorously (before standing)

Figure 15: PS microplastics in water and oil before and after mixing using a spatula

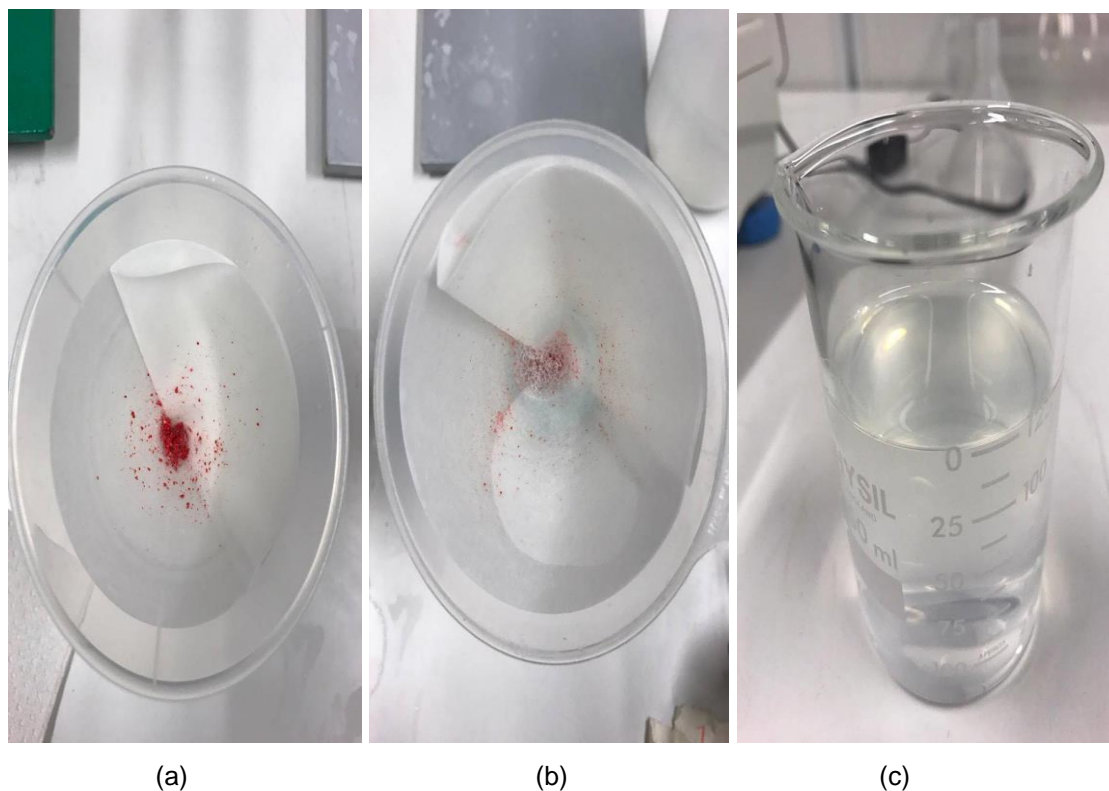
The (a) and (b) in Figure 15 were from the same experiment, the (b) picture was taken just few seconds after mixing vigorously. The purpose of the Figure 15 is to show the organic phase's (oil) high affinity for PS microplastics; thus, it expands briefly before shrinking back to its normal volume. When the solution in (a) was mixed vigorously using a spatula, the top organic phase expands and mixes with the water to attract the PS particles into the top phase. However, Figure 15 (b) is the expansion stage and can only be observed for a very short while after mixing vigorously, because the top phase shrinks back as the solution is allowed to stand for few minutes.

4.7 Filtration and Drying

An oven was preheated to 90 °C.

The filter paper was first placed in the oven for a few minutes to ensure dry weight. The weights of all the filter papers used in the experiment was noted for gravimetric analysis. After collecting the water phase into a beaker, a filtration setup was done.

The water phase was then transferred into the filter funnel containing filter paper. Water from a wash bottle was used to wash any visible MPs on the beaker walls into the filter funnel. This filtration method retained the microplastics substrate on the filter paper and the water went into the beaker.



- (a) PS microplastics residue in Case I
- (b) PS microplastics residue in Case II
- (c) water filtrate from the filtration process

Figure 16: PS microplastics residue and filtrate

The water filtrate did not contain visible microplastics confirming that the filtration method removed the microplastics.

*The pictures of the other MPs residue (LDPE and PP) was not in this report because both of these microplastics are white in colour, just like the filter paper; thus, cannot be observed through a picture.

When filtration was complete, the filter paper containing MPs was placed in the pre-heated oven at 90 °C until its visibly dry.

The filter paper + MPs was then weighed on an analytical balance.

The mass of the microplastics is calculated by subtracting the mass of the filter paper from the mass of filter paper and microplastics (filter paper + microplastics)

This process of filtration and drying was repeated for all the four plastic types.

4.8 Gravimetric analysis and Results

This analysis was done in order to know the quantity of MPs in the separation media. Only the water phase was filtered as the purpose of the thesis was to remove the MPs from water. It was also easier to analyse MPs in the water medium than in the oil medium.

Three measurements were done for each case (the original and two replicates). [30]

Key for Tables 4 - 7:

M_1 – First measurement, M_2 – Second measurement, M_3 – Third measurement

All values in the tables are masses in g

HDPE (all) = (Beaker and HDPE) - Beaker

HDPE left on filter paper = Filter paper and HDPE after drying – Filter paper

The logic of the above formulas was also applied in the cases of LDPE, PP and PS.

Table 4: HDPE Results

Mass of	Beaker	Beaker and HDPE	HDPE (all)	Filter paper	Filter paper and HDPE after drying	HDPE left on filter paper
Case I						
M_1	75.2539 g	75.3605 g	0.1066 g	0.9505 g	0.9577 g	0.0072 g
M_2	58.0453 g	58.1251 g	0.0798 g	0.9705 g	0.9991 g	0.0286 g
M_3	58.0475 g	58.1275 g	0.0800 g	0.8990 g	0.9122 g	0.0132 g
Σ			0.2664 g			0.0490 g
Case II						
M_1	50.1117 g	50.2833 g	0.1716 g	0.8975 g	0.9050 g	0.0075 g
M_2	50.1140 g	50.2260 g	0.1120 g	0.9306 g	0.9605 g	0.0299 g
M_3	50.1135 g	50.1987 g	0.0852 g	0.9282 g	0.9580 g	0.0298 g
Σ			0.3688 g			0.0672 g

The HDPE in water medium is the HDPE left on filter paper.

Thus, HDPE in water medium = HDPE left on filter paper

Mean amount of HDPE microplastics in water medium as a percentage;

Case I (no mixing)

$$= \left(\frac{\sum \text{HDPE in water medium}}{\sum (\text{HDPE all})} \right) * 100$$

$$= \left(\frac{0.0490 \text{ g}}{0.2664 \text{ g}} \right) * 100 = 18.39 \%$$

Case II (vigorous mixing)

$$= \left(\frac{\sum \text{HDPE in water medium}}{\sum (\text{HDPE all})} \right) * 100$$

$$= \left(\frac{0.0672 \text{ g}}{0.3688 \text{ g}} \right) * 100 = 18.22 \%$$

Table 5: LDPE Results

Mass of	Beaker	Beaker and LDPE	LDPE (all)	Filter paper	Filter paper and LDPE after drying	LDPE left on filter paper
Case I						
M ₁	75.2541 g	75.5423 g	0.2882 g	0.9923 g	1.0038 g	0.0115 g
M ₂	58.0474 g	58.2015 g	0.1541 g	0.8923 g	0.9186 g	0.0263 g
M ₃	58.0474 g	58.2707 g	0.2233 g	0.9187 g	0.9527 g	0.0340 g
Σ			0.4423 g			0.0378 g
Case II						
M ₁	51.9891 g	52.4598 g	0.4707 g	0.9383 g	0.9563 g	0.0180 g
M ₂	50.1190 g	50.3664 g	0.2474 g	0.8861 g	0.9210 g	0.0349 g
M ₃	50.1133 g	50.4288 g	0.3155 g	0.9018 g	1.0665 g ^{a)}	0.1647 g^{a)}
Σ			0.7181 g			0.0529 g

^{a)} Error in the measurement

All M_3 readings are not used in the summation (Σ) calculation because of the error. Thus, in Table 5, the summations are $M_1 + M_2$ throughout.

Reason for the error

There was an error in the third measurement (M_3) in Table 5. There was a systematic error in the value of filter paper and LDPE after drying, the value was unusually higher. This is due to an error made during the experiment when releasing the tap of the separating funnel to collect the water phase. Some oil dropped into the water collected. [31]

When the filtration was done, oil prints were observed on the filter paper after drying, thereby, increasing the weight. This shows how the measurement could be greatly affected or altered by carelessness of allowing few oil drops into the water. That is why only M_1 and M_2 results were used in the calculation. M_3 values were just included in the table in order to show what causes the error and the error effects on the result.

The LDPE in water medium is the LDPE left on filter paper.

Thus, LDPE in water medium = LDPE left on filter paper

Mean amount of LDPE microplastics in water medium as a percentage;

Case I (no mixing)

$$= \left(\frac{\Sigma \text{LDPE in water medium}}{\Sigma (\text{LDPE all})} \right) * 100$$

$$= \left(\frac{0.0378 \text{ g}}{0.4423 \text{ g}} \right) * 100 = 8.55 \%$$

Case II (vigorous mixing)

$$= \left(\frac{\Sigma \text{LDPE in water medium}}{\Sigma (\text{LDPE all})} \right) * 100$$

$$= \left(\frac{0.0529 \text{ g}}{0.7181 \text{ g}} \right) * 100 = 7.37 \%$$

If the third measurement were included in the calculations; the mean amounts in Case I and Case II would have been 10.79 % and 21.05 % respectively. The result when the errors were included in the calculations are unusual.

Table 6: PP Results

Mass of	Beaker	Beaker and PP	PP (all)	Filter paper	Filter paper and PP after drying	PP left on filter paper
Case I						
M ₁	75.8090 g	75.9786 g	0.1696 g	0.9460 g	0.9687 g	0.0227 g
M ₂	58.0475 g	58.3854 g	0.3379 g	0.9002 g	0.9081 g	0.0079 g
M ₃	58.0452 g	58.3027 g	0.2575 g	0.9208 g	0.9379 g	0.0171 g
Σ			0.7650 g			0.0477 g
Case II						
M ₁	58.0468 g	58.4707 g	0.4239 g	0.8930 g	0.9202 g	0.0272 g
M ₂	50.1132 g	50.4563 g	0.3431 g	0.9273 g	0.9364 g	0.0091 g
M ₃	50.1113 g	50.3374 g	0.2261 g	0.9225 g	0.9472 g	0.0247 g
Σ			0.9931 g			0.0610 g

The PP in water medium is the PP left on filter paper.

Thus, PP in water medium = PP left on filter paper

Mean amount of PP microplastics in water medium as a percentage;

Case I (no mixing)

$$= \left(\frac{\sum PP \text{ in water medium}}{\sum (PP \text{ all})} \right) * 100$$

$$= \left(\frac{0.0477 \text{ g}}{0.7650 \text{ g}} \right) * 100 = 6.24 \%$$

Case II (vigorous mixing)

$$= \left(\frac{\sum PP \text{ in water medium}}{\sum (PP \text{ all})} \right) * 100$$

$$= \left(\frac{0.061 \text{ g}}{0.9931 \text{ g}} \right) * 100 = 6.14 \%$$

Table 7: PS Results

Mass of	Beaker	Beaker and PS	PS (all)	Filter paper	Filter paper and PS after drying	PS left on filter paper
Case I						
M ₁	75.2565 g	75.6393 g	0.3828 g	0.9474 g	1.1322 g	0.1848 g
M ₂	58.0467 g	58.3676 g	0.3209 g	0.8978 g	1.1183 g	0.2205 g
M ₃	52.0021 g	52.4467 g	0.4446 g	0.9079 g	1.0607 g	0.1528 g
Σ			1.1483 g			0.5581 g
Case II						
M ₁	50.1145 g	50.6133 g	0.4988 g	0.9243 g	0.9719 g	0.0476 g
M ₂	50.1124 g	50.4377 g	0.3253 g	0.9480 g	0.9971 g	0.0491 g
M ₃	58.0516 g	58.6035 g	0.5519 g	0.9396 g	0.9931 g	0.0535 g
Σ			1.3760 g			0.1502 g

The PS in water medium is the PS left on filter paper.

Thus, PS in water medium = PS left on filter paper

Mean amount of PS microplastics in water medium as a percentage;

Case I (no mixing)

$$= \left(\frac{\sum PS \text{ in water medium}}{\sum(PS \text{ all})} \right) * 100$$

$$= \left(\frac{0.5581 \text{ g}}{1.1483 \text{ g}} \right) * 100 = 48.60 \%$$

Case II (vigorous mixing)

$$= \left(\frac{\sum PS \text{ in water medium}}{\sum(PS \text{ all})} \right) * 100$$

$$= \left(\frac{0.1502 \text{ g}}{1.3760 \text{ g}} \right) * 100 = 10.92 \%$$

Table 8: Amount of microplastic fraction remaining in the aqueous phase

	Case I (no mixing)	Case II (vigorous mixing)	Percentage difference
HDPE	18.39 %	18.22 %	0.17 %
LDPE	8.55 %	7.37 %	1.18 %
PP	6.24 %	6.14 %	0.10 %
PS	48.60 %	10.92 %	37.68 %

The results in Case I and II from Table 8 are the microplastic percentages out of the total MPs that were left in the water phase. The percentage of microplastics left in the water medium when the solution was not mixed (Case I) is more than when it was vigorously mixed for all types of microplastics. Thus, more microplastics move into the oil medium when vigorous mixing occurs.

In HDPE, LDPE and PP, the percentage differences are small when comparing vigorous mixing and when there was no mixing. That percentage is too small to guarantee that vigorous mixing does influence how much MPs are left in the water medium by the attraction of the MPs into the oil medium. However, mixing the solution containing PS vigorously in oil has a significant effect because more PS particles move into the oil medium. This can be seen from the 37.68 % difference between Cases I and II in Table 8.

4.9 Particle Size Analysis

There was not much difference in the behaviour of the microplastics based on size when in solution since the mesh size of 5 mm was already used to achieve the appropriate MPs size. All microplastic types showed expected behaviours in water except in the case of PP sizes. From section 4.5.3, the PP particles which form into spherical agglomerates tend to float in the oil medium more often than the particles which do not mould together.

Overall, in all the four types of microplastics, particle sizes on the upper size limit close to 5 mm was easier to analyse because they were easier to weigh. Whereas, the extremely small microplastics were not easy to analyse gravimetrically because some could have been blown away by air during weighing or from the filter paper when drying. MP sizes that are large also tend to get stuck in the tap hole of the separating funnel when releasing the water phase.

5 Discussion and Conclusions

This chapter contains more discussions on the result and on the whole thesis. The limitations are in this section, as well as research that can be done to gain further knowledge on the removal of microplastics from water.

5.1 Discussions

The aim of the study was to remove microplastics from water and to analyse the microplastics in the separation media. Plastics of four different types were ground into powdery form and sieved into the appropriate size in order to get the required <5 mm size microplastics. Water was then added to the microplastics, before a drop of dishwashing liquid was added to the solution in order to reduce the surface tension of water, subsequently allowing for proper mixing. The solution then underwent separating funnel method, using cooking oil as the organic medium in order to ensure two phases was created. Filtration method is used to separate the MPs from water and the substrate is dried in an oven before quantitative analysis was done.

The methodology used for the experiment can be compared to the research highlighted in Figure 2, which involves the use of filtration, salt addition and microspectroscopy in isolating the microplastics, albeit only filtration method and the idea of density separation is well represented in this thesis. [17]

The results from the filtration process where microplastics were accumulated by the filter paper and water containing dishwashing liquid passed through the funnel suggest that microplastics can be removed from water successfully.

At the start of the experiment, it was not expected that vigorous mixing of the solution would have an impact on the amount of microplastics that go into the water and oil medium. This led to separate experiments, Case I (no mixing) and Case II (vigorous mixing) being done.

In the separating funnel, there were more PS microplastics in the water phase than the other microplastic types in the water phase. This was expected because it is known that PS has a higher density than that of water. The other 3 MPs (HDPE, LDPE, PP) have

densities lower than that of water; therefore, they tend to float and stay at the top oil phase in the separating funnel.

There are more discussions and conclusions that can be deduced from Table 8.

HDPE, LDPE and PP were not affected much by mixing the oil vigorously in oil as shown in the quantitative result. This is because there were very minimal differences in the amount of particles that were found in the water phase in Case I and Case II.

On the other hand, there was a large difference in the amount of PS left on the filter paper when the PS solution was mixed vigorously in oil (10.92 %) and when there was no mixing (48.02 %). This 37.68% difference indicates that the more the PS solution is mixed vigorously, the more the PS particles are attracted into the oil medium.

The previous point thus brings up the idea that oil can in fact be used to some extent to remove microplastics from water, albeit mostly high density microplastics. This was demonstrated by the results of PS since PS has a higher density than that of water. It can be used in the removal of low-density microplastics also but not as effectively as microplastics with a high density.

5.2 Limitations and Further research

During the experiment, MP losses to the walls of the container, losses during solution transfer, and air/breeze interference were not taken into account in the calculations. These are factors which are quite important in order to analyse the microplastics accurately. A decent percentage of the microplastics were stuck to the walls of the container; also partly attributed to the viscous nature of cooking oil.

There were random errors during the experiments. The MPs already have very small weights such that when the same amount of microplastics is weighed several times on the same analytical balance, it gives a different reading on the analytical balance. Even the readings of the beakers contained random errors because the same beaker gives a slightly different value when weighed several times. [32]

It is important to note that the results of the amount of microplastics in the water medium was also based on the weight of the filter paper; not just only on the mixing. Hence, to

assume the complete accuracy of the microplastics residue left on the filter paper after drying would seem uninformed.

There was no room for rounding off the weight readings of the microplastics when weighed on the analytical balance because they are already micro in size and every figure on the analytical balance reading has to be taken into account in calculations. Thus, any slight mistake done in the procedure usually leads to a wrong reading or result and the experiment has to be repeated. This is also a positive because one can easily notice the reliability or abnormality of the results because of the small margin allowed for mistakes or wrong procedures. Such is the situation when the oil slightly dropped from the tap in Case I separation of LDPE (second measurement).

Another limitation is in the case of using PET as another type of microplastics in the experiment. The use of PET was limited because there was no available device that could be used to grind the PET bottles/materials into powdery form without it melting. The friction from the sanding machine during grinding melted the PET bottles. This would have allowed for experimentation with another high density plastic other than PS; the other three MPs used (HDPE, LDPE and PP) have densities lower than that of water. It would have greatly helped in further comparison of the behaviours of high density and low density MPs during separation.

Wastewater in the WWTPs are not as clean as the water used for the experiments in the laboratory. Thus, when considering microplastics removal on a large scale in wastewater treatment plants, it is important to note that there are various other kinds of materials and chemicals in the wastewaters which would affect the behaviour of MPs especially in terms of buoyancy.

This method of microplastics removal is also worthy of further research especially in wastewater treatment plants. It initiates the idea of incorporating this method as a sub process in the tertiary treatment process or as a new fourth treatment process in WWTPs mainly to remove the microplastics.

To also know how effectively MPs can be removed from water, more research should be done on how effective microplastics can be removed by combining the microplastics removal method in this thesis with other methods such as Raman spectroscopy, centrifugation, Fourier transform infrared (FTIR) spectroscopy. A combination of these other

methods with the filtration method using an organic medium could effectively remove microplastics from water.

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