Bench-Scale Study into the Effectiveness of Microplastic Removal from Surface Water by Coagulation Flocculation and Sedimentation

By

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A thesis submitted for the degree of

Doctor of Philosophy of University College London (UCL) in
Environmental Engineering

Faculty of Engineering

Department of Civil, Environmental and
Geomatic Engineering

March 2023

I, Chaoran Li confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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ABSTRACT

Microplastics (MPs), mainly of size 10-150 μm, have been found in surface freshwater systems such as tap water, suggesting that water treatment plants are not effectively removing MPs. Furthermore, limited information is available on the removal of MPs in the surface drinking water treatment process. However, the widespread presence of MPs in surface freshwater systems indicates that surface drinking water sources are polluted with MPs.

This research aims to investigate the removal of MPs by conventional surface water treatment using approaches traditionally designed to remove particulate matter from water: coagulation-flocculation and sedimentation.

To measure and understand the mechanism of the MP removal, a new method for overcoming the limitations of visual counting of MPs was developed. During the coagulation-flocculation-sedimentation experiments, the jar testers were used. Total organic carbon (TOC), Zeta potential, Photometric Dispersion Analyser (PDA), Fourier transform infrared (FTIR), turbidity meter, and scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDS) were also used for MP characterization. In order to preliminarily investigate the effects of coagulant-flocculation and sedimentation in surface freshwater, polystyrene beads with a density of 1.04–1.06 g/cm^3 (similar to the water) were selected, resulting in removals as high as 98.9 ± 0.94 %. Microplastics with different sizes (10-1000 μm), densities (0.89-1.38 g/cm^3), and materials were also studied.

The study found that higher density (like PVC) or larger size (over 150 μm) MPs were easier to settle. The optimal removal was achieved when PAC was 0.4 mmol/L, and polyacrylamide (PAM) was 3 mg/L, with the optimal conditions of pH=8 (before adding PAC), mixing at 240 rpm for 1 min, flocculation at 35 rpm for 13 min and sedimentation for 25 min. The removal of mixture MPs in natural freshwater reached 97.1 % with economic considerations.

A proposed flocculation model was successfully applied to the data and the proportionality constant, by fitting the data and using the least-squares method to determine the stoichiometric coefficient and equilibrium adsorption constant for floc formation. In terms of model parameters such as Zeta potential, and plastic content in the flocs, PAC was the most effective flocculant. In conclusion, this research demonstrated a widely used process as a high-efficient method for removing and monitoring MPs from surface water treatment plants. Future research should focus on combining granular activated carbon (GAC), sand filtration, biodegradation, and other means to develop a systematic method for MP removal in treatment plants.

IMPACT STATEMENT

The impacts of this thesis fall into the following areas:

Inside academia:

- A review article has been published in the journal "Science of the Total Environment", evaluating the current research on microplastics in surface freshwater systems. The article summarizes the research progress on microplastic sources, distribution, pollutants, risk assessment, and monitoring methods, and discusses the potential impact of microplastic pollution on freshwater ecosystems and human health. This article provides important references and guidance for the study of microplastic pollution in freshwater ecosystems. The article has a high citation rate of 400, indicating its significant contribution and impact in this field.
- A novel approach utilizing a flow cytometer was devised for the efficient detection of microplastics (MP) in surface water, enabling high throughput analysis. This method can potentially be applied for monitoring MPs in water. A manuscript on this method is under review on Green Analytical Chemistry (Elsevier). Some of the results were also presented in a conference: Microplastics Meeting in University College Cork, 2019.
- The thesis presents a study on the removal of low-density polystyrene microplastic beads from surface drinking water using

coagulation-flocculation and sedimentation methods. The study shows that coagulation-flocculation and sedimentation are effective methods for removing microplastic beads from water, but the removal efficiency varies depending on the water sample. The research provides important references and guidance for the control of microplastic pollution in freshwater ecosystems. The article was published in the Journal of Water Process Engineering in 2021. The results of this study were also presented in two conferences. One presentation was presented at the virtual conference of AQUA≈360: Water for All - Emerging Issues and Innovations in 2021. Additionally, a poster was presented at the Global Research & Innovation in Plastics Sustainability conference, also held in 2021. These presentations demonstrate the importance and relevance of the study in the field of microplastic pollution research and its potential applications in water treatment.

- The Total Organic Carbon (TOC) data has provided confirmation that the pores present on the surface of MPs possess the capability to adsorb and accumulate hazardous substances in water. The use of PAC coagulant in this thesis provides an effective method for removing MPs the pollutants attached to them. A manuscript is underwritten.

- The study also used Fourier transform infrared (FTIR) to examine the floc samples. Through spectral peak analysis, the flocculant coagulates the MP pollutants well and settles. Also, the method of scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDS) was used. The distribution of flocs under different flocculants was compared from the morphological point of view. EDS analysis revealed the distribution of contaminants in the floc structure, thus further revealing the principle of the reaction. In addition, the Zeta potential data demonstrates the electrochemical mechanism of the reaction of different flocculants. At the same time, it also revealed the competition mechanism among various pollutants. A manuscript is underwritten.

- Using the Photometric Dispersion Analyser (PDA) instrument, this study provides a detailed understanding of the kinetic changes of flocs during flocculation. At the same time, this study found that the removal effect of MPs increased after the flocs were broken and reunited. This study also adopted the pH Redox Equilibrium in Aquatic Systems (PHREEQC) mathematical model to simulate the effect of pH on the flocculation process. Last but not least, this thesis elucidated the underlying principles of the flocculation process for the removal of MPs from water, employing Density Functional Theory (DFT) chemical model and Extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) action energy model to examine the reaction mechanism. A manuscript is underwritten.

Outside academia:

- This study developed a simple and efficient solution for tracking MPs in various settings. This approach has the potential to improve data collection and analysis in environmental monitoring stations, while also enabling regulatory bodies to enforce stricter regulations on plastic waste. Additionally, industries can benefit from this method by utilizing it to reduce their plastic footprint and promote sustainable practices. Overall, this novel technique has far-reaching implications for the environment and could play a critical role in addressing the growing issue of plastic pollution.

- The focus of this study is on the conventional water treatment process, which involves coagulation-flocculation and sedimentation, and is widely applied worldwide. The study findings indicate that a significant proportion of the investigated microplastics can be removed by these processes. As a result, the incorporation of microplastic removal processes into existing wastewater treatment plants would require relatively minimal changes and could be a cost-effective solution for the mitigation of microplastic pollution in water resources. These findings can aid in the improvement of full-scale treatment processes used by water utilities.
- The use of poly-aluminium chloride (PAC) for the first time in natural water containing MPs is a ground breaking advancement in water treatment technology that could improve the quality of treated water and reduce plastic waste. Since PAC is already commonly used in water treatment, the implementation of this approach in full-scale water treatment plants could be easily adopted, resulting in substantial environmental benefits for aquatic life and potentially human health.
- The utilization of environmentally friendly reagents in this

study is a significant advancement as it mitigates the issue of secondary pollution caused by chemical treatments. Not only does this approach ease the burden on industry and governments, but it also has a positive impact on the environment by reducing the release of harmful substances and minimizing the ecological footprint.

RESEARCH DISSEMINATION

Peer-reviewed publications

- A novel high-throughput analytical method to quantify microplastics in water by flow cytometry. Chaoran Li, Luiza C. Campos, Rosa Busquets (Corresponding). Green Analytical Chemistry. 2023 (under review)
- Preliminary study on low-density polystyrene microplastics bead removal from surface drinking water by coagulation-flocculation and sedimentation. Li, C., Busquets, R., Moruzzi, R. B., & Campos, L. C. (Corresponding). Journal of Water Process Engineering, 44, 102346. 2021.
- Assessment of microplastics in surface freshwater systems: A review, Chaoran Li, Rosa Busquets, and Luiza Campos (Corresponding). Science of The Total Environment. 2020.

Conferences

- Presentation: Effect of Flocculation and Sedimentation Times on the Removal of Polystyrene Microplastics from Water. Conference: The virtual conference of AQUA≈360: Water for All - Emerging Issues and Innovations. 2021
- Poster: Microplastics Removal from Surface drinking Water by Coagulation-Flocculation and Sedimentation. Conference: Global Research & Innovation in Plastics Sustainability. 2021
- Presentation: Development of a method for the detection of microplastics in water. Conference: Microplastics Meeting in University College Cork. 2019

ACKNOWLEDGEMENTS

The Great Britain-China Educational Trust (Charity No. 269944) and UCL Studentship provided financial support for this research. Additionally, I would like to express my gratitude to my parents for their financial assistance.

I am also deeply grateful to my principal supervisor, Prof. Luiza C Campos, who is an incredibly energetic and accomplished researcher and engineer. Thanks to her guidance, I had the opportunity to pursue my studies in the United Kingdom, an experience that I will cherish for years to come. Prof. Campos provided invaluable support in selecting my research topic, conducting experiments, and writing papers and my thesis. Her vast knowledge and experience, patience, positive attitude, encouraging words, and warm smiles helped me navigate the many challenges of my PhD program.

I would like to express my sincere gratitude to my secondary supervisor, Prof. Rosa Busquets, for her invaluable guidance throughout my research on MP detection. Her expertise and knowledge in this field have been instrumental in shaping my research and helping me to achieve my goals. In addition, I would like to thank her for her assistance in facilitating my collaboration with Dr Simon Crust at Kingston University London. Through her connections and recommendations, I was able to access the necessary equipment and expertise for my project, including the use of SEM-EDS.

Special thanks to to Dr Qizhi (Judith) Zhou, the manager and collaborator of the UCL Environmental Engineering Lab. She not only provided me with

significant technical support throughout my experiments but also assisted me in overcoming various challenges and concerns in my daily life, particularly during times when I was feeling down. Additionally, I am grateful for her guidance in designing my experiments, as well as in writing my research paper and thesis.

Furthermore, I am deeply grateful to the lab managers and technicians in the Department of Civil, Environmental, and Geomatic Engineering, namely Dr Melisa Canales, Dr Utku Solpuker, and Dr Shi Shi, for their indispensable assistance during my experiments.

I would also like to acknowledge and express my gratitude to the other PhD students in Prof. Campos' research group: Dr Dominic Clyde-Smith, Dr Alessandro Lizzul, Dr Oriana Landa Cansigno, Mr Enrique Lopez Arroyo, Dr Zhuojun Li, Dr Fan Huang, Fan Gao, Mingjie Yi, and Dr Jianan Li. Their insightful discussions and advice have been immensely helpful to me, and I wish them all the best in their future endeavours.

I would like to extend my sincere appreciation to The Royal Parks for granting me permission to conduct water sampling at Regent's Park Lake. Without their authorization, my research would not have been possible.

Additionally, I would like to express my gratitude to Dr Hongyi Chen for providing me with instruction on conducting FTIR tests. I am also thankful to Junheng Li from Imperial College for providing guidance on statistical programming. I am also indebted to Prof. Han Wu, Dr Xueming Xia, Dr. Zhi

Li, and Yiting He for their valuable instruction on Zeta potential. Their expertise and knowledge in this area have been instrumental in shaping my research and aiding me in accomplishing my research goals.

During my five-year stay in the UK, I was fortunate to encounter a kind and compassionate community. The people I met left a lasting impact on me with their warmth and friendliness. I want to express my gratitude and well wishes to the UCL faculty and staff, my closest friends, roommates, and even strangers who showed me kindness through their support, encouraging words, and small acts of kindness that brightened my day. Their generosity and camaraderie will always be cherished, and I am grateful for their goodwill.

Last but not least, I would like to take this opportunity to express my heartfelt gratitude to the pillars of my support system - my beloved parents, Dr Weixin Li and Dr Jianling Chai, my girlfriend, Xinran Meng, and all my relatives. Without their unwavering love, encouragement, and guidance, I would not be the person I am today. They have been my strongest backing, providing me with the emotional and financial support I needed to pursue my dreams and aspirations. Their unwavering support has been my safest harbour, providing me with a sense of security and comfort, even during the toughest times. I am truly blessed to have such wonderful people in my life, and I will always be indebted to them for their love and support.

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LIST OF ABBREVIATIONS

ABS: acrylonitrile butadiene styrene

ANOVA: analysis of variance

COD: chemical oxygen demand

DFT: density functional theory

DLVO: Derjaguin-Landau-Verwey-Overbeek

DO: dissolved oxygen

DOE: design of experiments

DLS: dynamic light scattering

DWTP: drinking water treatment plants

EDS: energy-dispersive X-ray spectroscopy

EDTA: ethylenediaminetetraacetic acid

E. Coli: Escherichia coli

ESEM-EDS: environmental scanning electron microscopy-energy dispersive X-ray analysis

FC: forward scatter

FPA-FTIR: Fourier transform infrared spectroscopy with focal plane array detector

FTIR: Fourier-transform infrared spectroscopy

GAC: granular activated carbon

GC-MS: gas chromatography-mass spectrometry

GGA: generalized gradient approximation

IR: infrared

LCAO: linear combination of atomic orbitals

LOD: limit of detection

LOQ: limit of quantification

MFs: microfibers

MS: mass spectrometry

MPs: microplastics

NMR: nuclear magnetic resonance

NTU: nephelometric turbidity unit

PA: polyamide

PAC: polyaluminium chloride

PAM: polyacrylamide

PBE: Perdew-Burke-Ernzerhof

PDA: Photometric Dispersion Analyser

PET: polyethylene terephthalate

PE: polyethylene

PEst: polyester

PHREEQC: PH Redox Equilibrium in Aquatic Systems

PP: polypropylene

PS: polystyrene

PU: polyurethane

PVDF: polyvinylidene difluoride

PVC: polyvinyl chloride

PFS: polyferric sulphate

RSD: relative standard deviation

SCAN: Strongly Constrained and Appropriately Normed

SC: Side Scatter

SD: standard deviation

SEM: scanning electron microscopy

SEM-EDS: scanning electron microscopy-energy dispersive X-ray analysis

SPME: solid phase microextraction

SWCNTs: single-walled carbon nanotubes

TED-GC-MS: thermal extraction desorption gas chromatography-mass spectrometry

TOC: total organic carbon

TGA-DSC: thermogravimetric differential scanning calorimetry

TLC: thin layer chromatography

UTOTAL: total interaction energy

UV: ultraviolet

UV-254: absorbance at 254 nm

UEDL: electrical repulsion energy

UVDW: van der Waals attraction energy

U_AB: Lewis acid-base interaction energy

U_VDW: Van der Waals interaction energy

WWTP: wastewater treatment plant

XDLVO: extended Derjaguin-Landau-Verwey-Overbeek...

CHAPTER 1 INTRODUCTION

1.1 Motivation behind the research

Microplastics (MPs) have become a global concern due to their widespread presence in various water sources. A study conducted by the non-profit journalist group Orb Media in 2017 revealed that MPs were detected in 83% of tap water samples and 93% of bottled water samples across five continents (Tyree and Morrison, 2017). This alarming discovery has sparked extensive research efforts to understand the implications of MPs on both human health and the environment.

The accumulation of MPs in ecosystems, disruption of food chains, and harm to marine life are among the key environmental concerns associated with MP pollution. Aquatic organisms can ingest MPs, resulting in physical harm, reduced reproductive success, and altered behaviour (Issac et al., 2021). Furthermore, MPs have the ability to adsorb and transport toxic chemicals, potentially introducing pollutants into the food web (Li et al., 2020).

Concerning human health, MPs have been detected in various food products, raising apprehensions about their potential ingestion by humans. Although the long-term health effects of MPs are not yet fully understood, there are concerns about their capacity to act as carriers of harmful substances, potentially leading to inflammation or other health issues (Pironti et al., 2021).

In response to this emerging issue, the Department for Environment, Food and Rural Affairs (Defra) in the UK has funded several studies investigating MPs in sewage treatment and rivers (Wu et al., 2020). However, there is still a significant knowledge gap when it comes to the presence and removal of MPs in surface freshwater systems, particularly in the context of drinking water treatment.

One trend in legislative efforts is the implementation of bans or restrictions on the use of microbeads in personal care products. These small plastic particles have been recognized as a significant contributor to MP pollution. By prohibiting or limiting their use, countries can reduce the release of microplastics into the environment (Naiara et al., 2023).

Another trend is the focus on improving plastic waste management. Effective waste management is crucial for preventing the entry of MPs into water sources. Some countries (such as UK) have implemented regulations that promote proper disposal and recycling practices, set recycling targets, and establish extended producer responsibility (Wu et al., 2020).

Furthermore, upgrading water treatment infrastructure and filtration systems is being pursued as a strategy to address MP pollution (Naiara et al., 2023). By enhancing water treatment plants, it becomes possible to capture and remove microplastics from water sources, reducing their presence in drinking water supplies.

Lessons can be learned from other countries that have implemented successful strategies to tackle MP pollution. For instance, the European Union has taken a comprehensive approach, including bans on microbeads and single-use plastics, as well as measures to improve plastic waste management (Li et al., 2020). The EU's approach highlights the importance of a holistic strategy combining regulation, consumer awareness, and international collaboration.

Countries like Canada and Australia have focused on labelling requirements and consumer education to raise awareness about the presence of MP in products. These efforts aim to empower consumers to make informed choices and reduce their contribution to MP pollution (Li et al., 2020).

The existing literature review indicates a scarcity of information regarding the effectiveness of conventional water treatment processes in removing MPs from surface water (Naiara et al., 2023; Li et al., 2020). Conventional treatment methods, such as coagulation-flocculation and sedimentation, have been widely employed globally to eliminate suspended particles from water. These processes exploit the use of positively charged coagulants, such as alum and ferric salts, to destabilize negatively charged particles and form larger flocs, which can be efficiently removed through sedimentation.

Therefore, it is imperative to explore whether these conventional treatment processes are capable of effectively removing MPs from water. Understanding the efficiency and limitations of coagulation-flocculation and sedimentation in eliminating these microscopic plastic particles is crucial in safeguarding the quality of drinking water resources. By addressing this research gap, more informed strategies and technologies for mitigating the presence of MPs in freshwater systems can be developed.

In light of the above, the primary objective of this research is to investigate the removal of MPs from surface water using coagulation-flocculation and sedimentation processes. The research aims to assess the effectiveness of these treatment methods in reducing MP concentrations from drinking and freshwater samples, elucidate the underlying mechanisms of MP removal, and evaluate the potential impacts on overall water quality. Through comprehensive experimentation and analysis, this research seeks to provide valuable insights into the removal efficiency of conventional treatment processes, thereby informing future policies, guidelines, and practices related to the management of MPs in drinking water supplies.

In summary, this research aims to bridge the knowledge gap regarding the removal of MPs from surface water and contribute to the overall understanding of the challenges associated with the presence of MPs in fresh water sources. By investigating the efficacy of coagulation-flocculation and sedimentation, the ability to ensure safe and clean water for communities worldwide is enhanced.

1.2 Aim and Objectives

This research aims to investigate whether the conventional treatment processes (coagulation-flocculation-sedimentation) are effective in removing MPs from surface water. So, the specific objectives are:

(1) The first objective of the research is to understand the types and sizes of the MPs found in surface water (Chapters 2 and 6);

The maximum and median size ranges were observed in the environment and included fibres and spheres (beads). The study was focused on the treatment surface water contaminated with a mixture of 7 particle types (polystyrene (PS) (10-1000 μm), polypropylene (PP) (10-1000 μm), polyvinyl chloride (PVC) (10-1000 μm), polyethylene terephthalate (PET) (10-1000 μm), polyamide (PA) (10-1000 μm), polyethylene (PE) (10-1000 μm) and polyurethane (PU) (10-1000 μm)) covering the ranges of concentrations expected to occur in UK rivers. At the same time, a literature review (Li et al. 2020) on MPs in surface freshwater was conducted at the first stage of the research.

(2) The second objective of the research is to develop a method for detection and measuring of MPs (Chapter 4);

Through the collaboration of UCL Environmental Engineering Laboratory, UCL Healthy Infrastructure Research Group (HIRG) Laboratory, and Environmental Health and Food Safety Group at Kingston University, a simple and inexpensive method that allows high-throughput detection and automated quantification of small MP particles (< 100 μm) was developed, using the flotation method, hydrogen peroxide solution method and flow cytometry. This method addresses the limitations of the traditional manual counting method by microscope, which are time-consuming and prone to inaccuracies. This method was further tested by using FTIR, Raman and SEM-EDX at UCL and Kingston University.

(3) The third objective of the research is to optimize the removal of MPs by coagulation, flocculation and sedimentation (Chapters 5 and 6);

Through initial tests, synthetic water prepared with MPs to mimic the concentrations usually found in surface water, and kaolin was used to simulate suspended colloid particles found in surface water. Jar testers were used to treat the contaminated water by coagulation-flocculation-sedimentation. Samples were taken after each treatment stage as well as method blank samples to assess the potential impacts of the study design on background interferences. MPs and flocs were characterized.

(4) The fourth objective of the research is to analyse the reaction principle and competition mechanism through chemical analysis methods and mathematical models (Chapter 7).

River water and water supply tank water were used in natural water tests to estimate the efficiency of the treatment methods. Their removal rates were compared and the better treatment methods, their condition for validity, and cost were optimized. A simulation experiment was conducted as appropriate. The reaction mechanisms were explained by analyses of PHREEQC mathematical model, DFT chemical model and XDLVO action energy model.

However, the research conducted herein also bears certain limitations. It has been specifically validated for microplastic beads. As for other microplastic variants like microfibers, additional testing and validation are imperative to ascertain their suitability and applicability within the scope of this study.

1.3 Thesis outline

Chapter 2: the focus of this chapter is to firstly assess the magnitude of global MP pollution in surface freshwater environments, containing information compiled from recent research associated with the sources, occurrence, fate, and effects of MPs in surface freshwater environments. Section 2.1 provides an introduction to microplastics, including their definition, types, and sources. Section 2.2 examines the sources of microplastics in freshwater and discusses the distribution of microplastics in freshwater environments. Section 2.2.1 discusses the distribution of microplastics in freshwater, including rivers, lakes, and groundwater. Section 2.2.2 describes the characteristics of microplastic pollution. Section 2.3 reviews the methods used to detect, analyse, and quantify microplastics in water samples. Section 2.3.1 describes the sampling and separation methods used to collect microplastic samples from water. Section 2.3.2 examines the morphological characteristics of microplastics. Section 2.3.3 discusses the different techniques used to characterize microplastics. Section 2.4 evaluates the methods used to quantify microplastics in water samples. Section 2.5 examines technologies for the remediation of microplastics and analyses the advantages and disadvantages of different techniques. Section 2.6 provides a conclusion to the chapter.

Chapter 3: This chapter discusses the general methodology used in the whole research. It includes Jar tester, TOC, Zeta potential, PDA, FTIR, turbidity meter, and SEM-EDS. Section 3.1 provides an introduction to the chapter. Section 3.2 introduces the materials used in the study. Section 3.3 describes the manual counting of microplastics by microscope. Section 3.4 describes the coagulation-flocculation and sedimentation tests. Section 3.5 describes the floc breakage and re-growth experiment. Section 3.6 describes the determination of pH. Section 3.7 describes the weighting of microplastics after treatment. Section 3.8 describes the determination of COD, TOC and turbidity. Section 3.9 describes the determination of Zeta potentials. Section 3.10 describes the Fourier-transform infrared spectroscopy experiments. Section 3.11 describes the scanning electron microscopy experiments. Section 3.12 describes the general analytical methods used.

Chapter 4: This chapter focuses on the MP measurement methods by flow cytometer. materials and methods used in the study, including the chemicals and equipment used and the design of the experiments. The section also includes information on SEM-EDS analysis and quality parameters. Section 4.3 presents the results and discussions on the method development for the analysis of microbeads and the quantification of microbeads with flow cytometry. Specifically, Section 4.3.1 details the method development for the analysis of microbeads in the 10-100 μm range, and Section 4.3.2 discusses the quantification of microbeads with flow cytometry. Lastly, Section 4.4 provides a conclusion to the chapter.

Chapter 5: This chapter focuses on the preliminary investigation on the potential impacts of coagulation-flocculation and sedimentation. Section 5.1 provides an introduction to the chapter. Section 5.2 describes the materials and methods used in the study, including coagulation-flocculation and sedimentation tests, floc breakage and re-growth experiment, and quantification of microplastics. Section 5.3 presents the results and discussions on the effect of flocculation stirring intensity, flocculation time, initial water pH, sedimentation time, and floc-breakage and regrowth on the removal of polystyrene microplastics. Specifically, Section 5.3.1 examines the effect of flocculation stirring intensity on the removal of polystyrene microplastics, while Section 5.3.2 discusses the effect of flocculation time on the removal of polystyrene microplastics. Section 5.3.3 investigates the effect of initial water pH on the removal of 100 μm PS beads, and Section 5.3.4 studies the effect of sedimentation time on the removal of polystyrene microplastics. Lastly, Section 5.3.5 examines the effect of floc-breakage and regrowth on the removal of polystyrene microplastics. Section 5.4 provides a conclusion to the chapter.

Chapter 6: This chapter focuses on MPs with different sizes, densities, and materials. Section 6.1 introduces the chapter. Section 6.2 describes the materials and methods used in the study, including the comparison of coagulants, the effect of microplastic size on removal efficiency, and the determination of reaction conditions and removal efficiency of different microplastics. Section 6.2 also discusses the application of optimal conditions in natural water and tap water and compares them with the current industrial treatment effects. Section 6.3 presents the results and discussions, which are organized into four subsections. Section 6.3.1 examines the effect of the type of coagulant on microplastic removal, while Section 6.3.2 investigates the effect of microplastic size on removal efficiency. Section 6.3.3 determines the reaction conditions and removal efficiency of different microplastics, and Section 6.3.4 applies the optimal conditions in natural water and tap water and compares them with the current industrial treatment effects. Lastly, Section 6.4 provides a conclusion to the chapter.

Chapter 7: This chapter focuses on TOC, Zeta potential, PDA, FTIR, turbidity meter, and SEM-EDS characterization. Section 7.1 examines the impact of microplastics and coagulants on TOC levels in the Thames River and Regent's Park Pond. Section 7.2 discusses the zeta potential of microplastics and its impact on coagulation for their removal from aquatic environments. Section 7.3 investigates floc breakage and regrowth for the removal of microplastics in water treatment. Section 7.4 observes microplastics in water using microscopy and coagulation-flocculation for their removal. Section 7.5 uses FTIR analysis for characterization and removal of microplastics in water. Section 7.6 examines the impacts of microplastics on turbidity and the efficiency of coagulation-flocculation in their removal. Section 7.7 uses SEM-EDS analysis for optimization of coagulation-flocculation for microplastic removal from water. Section 7.8 investigates the efficiency of polystyrene removal in the presence of competing pollutants. Section 7.9 investigates competitive reaction mechanism by XDLVO model. Section 7.10 optimizes pH for coagulation-flocculation: insights from PAC hydrolysis products simulation using PHREEQC. Section 7.11 studies the mechanism of PAC coagulation-flocculation with polystyrene microplastics using DFT. Section 7.12 provides practical applications of PAC coagulation-flocculation and sedimentation for the removal of microplastic particles from market products and microfibers in water.

Chapter 8: This chapter focuses on conclusions and future work. Section 8.1 provides a conclusion to the study and summarizes the key findings of the research. Section 8.2 suggests future work to advance the research on microplastics, including the development of new technologies for microplastic remediation, the investigation of microplastic interactions with other pollutants, and the evaluation of the impact of microplastics on the environment and human health.

CHAPTER 2 LITERATURE REVIEW

Globally, MP pollution has become a serious environmental threat due to its numerous sources, widespread occurrence, persistence, and adverse effects on ecosystems and human health. Addressing this multifaceted threat requires innovative technologies that can effectively remove MPs from the environment. In this review, the source, distribution, properties of MPs, and methods of detection and analysis of MPs are firstly outlined. Subsequently, the identified promising technologies for the removal of microplastics were classified into three categories: physical, chemical, and biological methods. A detailed analysis of the advantages and limitations of different techniques is provided. Finally, current challenges and future research priorities to guide in addressing MP pollution are summarized.

2.1 Introduction to MPs

Plastics are synthetic polymers in many forms with a wide range of sizes, shapes, compositions, properties, and potential for use. MPs refer to small plastics that have a particle size smaller than 5 mm. This definition encompasses nano plastics, which are even smaller with a particle size below 1 micron. In addition to primary MPs used in household and personal care products (Padervand et al., 2020), secondary MPs are formed in the environment due to the degradation, transformation, and deterioration of parent (micro)plastics driven by photo-oxidation and physical processes. (Barnes et al. 2009). MPs have been detected in nearly all environments affected by human interaction, including aquatic, terrestrial, and atmospheric environments (Abbasi et al., 2019; Hurley and Nizeto, 2018; Zhou et al., 2018). It has been reported that MPs have a negative impact on organisms, hindering their growth, development, and reproduction. (Lambert et al., 2017; Strungaru et al., 2019). MPs can also enter the human food chain through ingestion, inhalation, and digestion (Revel et al., 2018). Once it enters the food chain, it will bioaccumulate up the chain, eventually threatening human health. What's more, (micro)plastics can remain in the environment for hundreds to thousands of years; they may live longer in the deep ocean and polar environments (Barnes et al., 2009). Therefore, there is an urgent need to develop technologies to remove MPs from the environment.

Plastic products have been widely used nowadays – for example in 2017, the annual output of plastic products worldwide exceeded 3.48 × 10^8 tonnes and is increasing at a rate of 0.2 × 10^8 tonne acre $^{-1}$ (Statista, 2017). Based on their mass production and usage, plastic products inevitably enter the aquatic environment: for example, more than 2.5 × 10^5 tonnes of plastic waste were estimated to be floating on the global ocean surface (Eriksen et al., 2014). In the aquatic environment, plastic waste can be fragmented into MPs (debris $<$ 5 mm in diameter) by physical, photo and biodegradation (Law and Thompson, 2014).

The investigation of MP pollution has mainly focused on the marine environment (Cole et al., 2011; Ivar do Sul and Costa, 2014), including Canada (Desforges et al., 2014), Brazil (Santana et al., 2016), the UK and neighbouring countries such as The Netherlands (Barnes et al., 2009), China (Zhang et al., 2017; Zhang et al., 2019), Antarctica (Cincinelli et al., 2017) and in deep-sea Artic sediments (Kanhai et al. 2019).

Marine MP debris can be a possible contributing factor to biodiversity loss and a potential threat to human health. The impacts of MPs on aquatic life are influenced by the size of the debris: large plastic debris, such as discarded fishing lines and nets, often cause entanglement among invertebrates, birds, mammals and turtles (Gall and Thompson, 2015; A. Lusher, 2015). Smaller plastic items, such as bottle caps and less dense plastics can cause intestinal obstruction (Law and Thompson, 2014). MPs are ingested by a variety of aquatic life ranging from invertebrates to fish with varied consequences, many of which are under current investigation – for example, a trend of fishes, mussels, turtles, seabirds, etc. to consume less prey has been observed (Cannon et al., 2016; Foley, et al., 2018; Lusher et al., 2013). Human health could be affected via the food chain transmission of MPs (Hollman et al., 2013). Furthermore, the physical and chemical properties of MPs have been found to facilitate contaminant sorption to their surfaces, hence MPs may serve as a vector of contaminants to organisms following ingestion (Carbery et al., 2018; Kontrick, 2018). The presence of plastic debris in the environment is considered among the main environmental issues and an emerging threat that may affect the ability of humans to conserve biodiversity (Sutherland et al., 2010; Auta et al., 2017).

MP pollution is particularly acute in estuaries, indicating that terrestrial river input is an important source of MPs to coastal and marine environments (Gallagher, et al., 2016; Sadri and Thompson, 2014; Vendel et al., 2017). However, knowledge of the impacts that MP pollution has in freshwater environments is still in its infancy when compared to that of marine environments, even though freshwater is a source of drinking water. Recent reviews of MP pollution in freshwater environments have focussed on methodology (Koelmans et al. 2019; Pico and Barcelo, 2019; Mendoza and Balcer, 2019; monitoring occurrence of MP in biota (Connor et al., 2019; Triebskorn et al. 2018); toxicity and methodology (Horton, 2017); occurrence, impact and analysis (Li et al. 2018); overarching discussion of MP pollution, however not focused on distribution (Wagner and Lambert, 2017) or focused in a specific geographic area (Fu and Wang, 2019; Shahul Hamid et al. 2018).

2.2 MP sources

The rate of fragmentation and degradation of plastics is unknown even for marine environments (Law and Thompson, 2014). Varying degrees of physical forces, such as waves in oceanic systems; environmental conditions, such as sunlight, pH, and temperature; and the physical and chemical properties of the plastic itself are thought to play a role in plastic degradation. Plastics in freshwater systems also undergo physical and environmental degradation despite milder physical forces than in marine environments (Andrady, 2011). Some environmental conditions may have a larger impact on freshwater, for example, Free et al. (2014) showed that plastic fragments may undergo relatively intense weathering because of high ultraviolet penetration in poorly nourished lakes (Free et al., 2014). However, overall the degradation patterns of MPs in freshwater were found to be similar to those in the marine environment: cracks, pits, and adherent particles (Imhof et al., 2013; Zbyszewski and Corcoran, 2011).

The degree of weathering to the surface of MPs can be used to track the history of the particles. Hence, surface features can show whether plastic debris underwent mechanical degradation, for example from the action of waves, sand friction (Zbyszewski et al., 2014), oxidative weathering such as from exposure to UV-B (Zbyszewski et al., 2014), or biodegradation such as by the action of hydrocarbon-degrading microorganisms (Zettler et al., 2013). Insights into the effect of organic matter on MP degradation in sedimentary environments such as beaches and muddy rich coastlines were also reported by Zbyszewski et al. (2014). Identifying the degradation patterns of plastics in different environments is important as this can reveal how particles interact with the environment and how various factors affect their stability, transport, fate, and indicate potential effects on organisms (Ballent et al., 2016).

A spatial correlation has been found between the types of MPs found at particular sites and human activities in surrounding areas (Lechner et al., 2014). In addition, the type of polymer and their concentration can be used to link MPs with their origin. For example, MPs found in the Great Lakes of North America are similar in size, shape, colour, and elemental composition to those found in facial cleansers (Eriksen et al., 2013). At the same time, MP particles in the effluent of a sewage treatment plant were very similar in colour, shape, and size to those in toothpaste formulations, revealing that the plastic particles in personal care products may be among the sources of MP pollution in freshwater environments (Carr et al., 2016). Industrial sources of MPs can also be identified even in large rivers such as the Danube River (Lechner et al., 2014). As opposed to rivers, stationary bodies of water such as lakes may accumulate more MPs (Free et al., 2014; Imhof et al., 2013). Industrial resin particles and microspheres were found to be abundant in Lake Erie near the Huron Lake industrial zone (Eriksen et al., 2013; Zbyszewski and Corcoran, 2011). Large amounts of secondary MPs (or MPs derived from the fragmentation of other plastics) were found along the shores of sparsely populated mountain lakes, where there was scarce primary MP pollution (Free et al., 2014). Areas near tourist sites are also especially affected by MP pollution, and a representative example is a concentration of MPs (i.e. 5,000-757,500 units Km^{-2}) found in China's Qinghai Lake (Xiong et al., 2018).

Direct sources of MP pollution encompass various factors, such as the discharge from sewage treatment plants (Browne, 2015), the weathering and degradation of plastic waste in water bodies (Eerkes-Medrano et al., 2015), and the terrestrial input originating from soil erosion or surface runoff (Horton et al., 2017). The contribution of these sources remains controversial. Carr et al. (2016) found that nearly no MPs were detected in the discharge of a tertiary sewage treatment plant in Southern California, and the abundance of MPs in the effluent of the secondary sewage treatment plant was also low (with an average of only one MP particle per 1.14 liters of effluent). In contrast, most MPs were found in the primary treatment stage (oil skimming). Also, Murphy et al. (2017) investigated a large secondary sewage treatment plant in Glasgow, Scotland (daily capacity 260,954 m^3) and found that although the final removal rate of MPs was as high as 98.41 %, approximately 6.5×10^7 MP particles per day were still discharged into the receiving water, indicating that the sewage treatment plant was an important source of the MP pollution (Murphy et al., 2017). Therefore, the different operative conditions applied in each plant could lead to varied efficiencies in the removal of MPs, and sewage treatment plants can be an important source of MPs. Additionally, more data is needed to understand the magnitude of the problem. Comparable removal rates of fibres were found in the Seine Aval (Paris, France) wastewater treatment plant, which was estimated to be 83-95 %. Regarding the treated effluents, the number of fibres in the samplers used for their monitoring was $\times 10^5$ greater than the number irregular MP fragments, which ranged between $6\cdot\times 10^{-5}$ and $3 \times\cdot 10^{-4}$ MP units L^{-1} in average (Dris et al., 2017). Hence, it can be concluded that the contribution of sewage treatment plants to MP pollution may be related to their scale, location, residence time, and type of influent.

MPs can also enter rivers and lakes through surface runoff and atmospheric deposition (Dris et al., 2017). An example is the large amount (with a maximum abundance of 660 units. kg^{-1}) of large-size (1-4 mm) MPs in sediments downstream of storm drainage outlets that input into the Thames River, UK. These MPs were mainly sheet-shaped, which the authors thought might be from painted roads in the surrounding urban area. After being washed away by rainwater, the MPs were eventually deposited in the sediments of the Thames River (Hortonet al., 2017). In addition, Klein et al. (2015) also found high concentrations of MPs (228-3,763 units kg^{-1}) in sediments along the banks of the Rhine River in Germany, which further confirms the importance of the terrestrial input to MP pollution of freshwater environments.

Among the origins of MPs entering wastewater, the cleaning of synthetic fabrics such as clothing (grey water) constitutes a major contribution (Browne, 2015; Peng et al., 2017). When the process of washing clothes in a household washing machine was simulated in the laboratory, the drainage of the washing machine contained a large amount of fibre-like MPs (Hernandez et al., 2017). By using detergent, the content of MPs in the drainage of the washing machine was much higher than that of washing without detergent. For example, washing a five-year-old PET fleece jacket released microfibers as 0.00111 weight percentage (wt %) (with no detergent); 0.00123 wt % (with detergent); and 0.00136 wt % (with detergent and softener), with a much higher effect of detergent and fabric softener use (10.8 % and 22.5 % increases respectively) (Pirc et al, 2016). The various sources contributing to MP pollution of freshwater environments have been summarized in the Graphical Abstract.

2.2.1 MP distribution in freshwater

In marine environments, properties of MPs such as their small size and low density result in transport over long distances, particularly via ocean currents (Ballent, et al., 2016; Cole et al., 2011). Their occurrences have been reported along the coasts of continents (Browne, 2015; Ivar do Sul and Costa, 2014), in remote areas such as the central Atlantic Islands (Ivar do Sul and Costa, 2014), sub-Antarctic region (Eriksen et al., 2014), the Arctic (Obbard et al., 2014), and even in deep-sea habitats (van Cauwenberghe et al., 2015; Kanhai et al., 2019). The different units of concentration used throughout the research and within review papers hinder comparison between findings (Kang et al., 2018; Li et al., 2018). For example, recent review papers (e.g. van Cauwenberghe et al., 2015) tabulate research findings with different units, which does not allow comparison among the concentrations. According to the approximate average of plastic of 1 g mL^{-1} and the size of particles, a calculation – $C_{\text{number per volume}} = C_{\text{mass per volume}} / (d_{\text{plastic}} \times V_{\text{plastic}})$ – can be made, to derive comparable concentration results from different studies in the same unit, i.e. number per volume. Thus, all results can be compared and analysed intuitively. Table 1.1 compiles recent studies that report MPs in freshwater environments, and highlights that this type of contamination is a global issue. It is noticeable that the concentration of MPs in sediments is higher than that in water, this may be due to a combination of factors including their hydrophobic nature and density, and as a result, they tend to accumulate in sediments. Figure 2.1 intends to show where MP research is currently focussed and also highlights places where MP monitoring is currently lacking, e.g. South America, the Middle East, Africa, and Russia.

From the data and map, one of the most striking studies are from the Great Lake Basin of North America, where the average abundance of MPs floating on the surface was as high as 43,000 units km^{-2} (Eriksen et al., 2013). The greatest presence of MPs in Europe, to the best of our knowledge, has been reported in Lake Geneva, Switzerland, reaching 48,146 units km^{-2} (Florian Faure, 2012). However, MP pollution in freshwater environments of Asia may be more serious than those from other parts of the world (Wu et al., 2018). Notably, Free et al. (2014) found MP contamination in the surface water of Lake Hovsgol in northern Mongolia, Asia, with an average abundance of 20,264 units km^{-2}. As the geographical location of the region is remote, and the population is sparse, this study suggests that MP pollution here may be more influenced by runoff, monsoon rains, and atmospheric fallout, among other factors. Concentrations and location of MPs in recent monitoring studies (period 2011-2019) in the freshwater environment are compiled in Table 1.1. MPs detected in these studies include data from water and sediments, and different compositions (Table 1.1). In the table, the average original concentrations mean the average data of concentrations with original units in the studies.

Table 2. 1 Concentrations and sizes of MPs found in samples from freshwater environments.

Lat, Lon	Country	Location	Average Original Concentration	MP units · L^{-1}	Sample	Size	Methods	Reference
55.367, -3.96142	UK	Kelvin River	0.26685 g/L	296.5	Sediment	Size classes: 2.8 mm-11μ m	SEM-EDS	Blair et al. (2019)
29.00896, 116.69785	China	Poyang Lake	0.2034 g/L	226	Sediment and Surface water	Size classes:< 0.5 mm	Raman	Yuan et al. (2019)
44.37996, -108.03899	Europe	Carpathian basin	0.4716 g/L	524	Sediment and Surface water	Size classes: <0.3mm	FTIR	Bordós et al. (2019)
37.27442, 9.87391	Tunisia	the lagoon of Bizerte	2.106 g/L	2340	Sediment	Size classes: 5 mm – 0.2 mm	FTIR	Toumi et al. (2019)

34.37526, 107.09683	China	Wei river	0.918 g/L	1020	Sediment and Surface water	Size classes: <5 mm	Microscope with digital camera	Ding et al. (2019)
4.74974, 6.82766	Belgium	Flemish rivers	0.0153 g/L	17	Water	Size classes: <5 mm	FTIR and Raman	Slootmaekers et al. (2019)
-32.1058579, 115.9381508	Australia	Bloukrans River	0.216 g/L	240	Sediment	Size classes: 500µm	Visual Inspection	Nel et al., (2018)
2.3923759, 112.8471939	Malaysia	Surface water in Malaysia	0.108 g/L	120	Surface water	Size classes: 3 µm - 178 µm	Visual Inspection	Praveena et al., (2018)
-37.718524, 145.234919	Australia	Maribyrnong and Yarra Rivers	2.5803 g/L	2867	Surface water	Size classes: <2 mm	Visual Inspection	Kowalczyk et al. (2017)
52.13191, -97.26176	Canada	Lake Winnipeg	1.7397 g/L	1933	Surface water	Size classes: <5 mm	SEM-EDS	P. J. Anderson et al. (2017)

9.5949193, 76.3942857	India	Vembanad Lake	0.27 g/L	300	Sediment	Size classes: 0.2 mm – 1 mm	Raman	Sruthy and Ramasamy (2017)
52.2379891, 5.5346074	Netherlands	Dutch wastewater treatment plant effluent	0.00297 g/L	3.3	wastewater treatment plant effluent water	Size classes: <5 mm	Visual Inspection	van Wezel et al., (2016)
61.0666922, -107.9917071	Canada	Canadian lakes and rivers	0.495 g/L	550	Sediment and Surface water	Size classes: 2 mm - 5 mm	Visual Inspection	J. C. Anderson et al, (2016)
32.0000002, 89.9999998	China	Remote lakes in Tibet plateau	0.5067 g/L	563	Sediment	Size classes: <5 mm	Raman	Zhang et al. (2016)

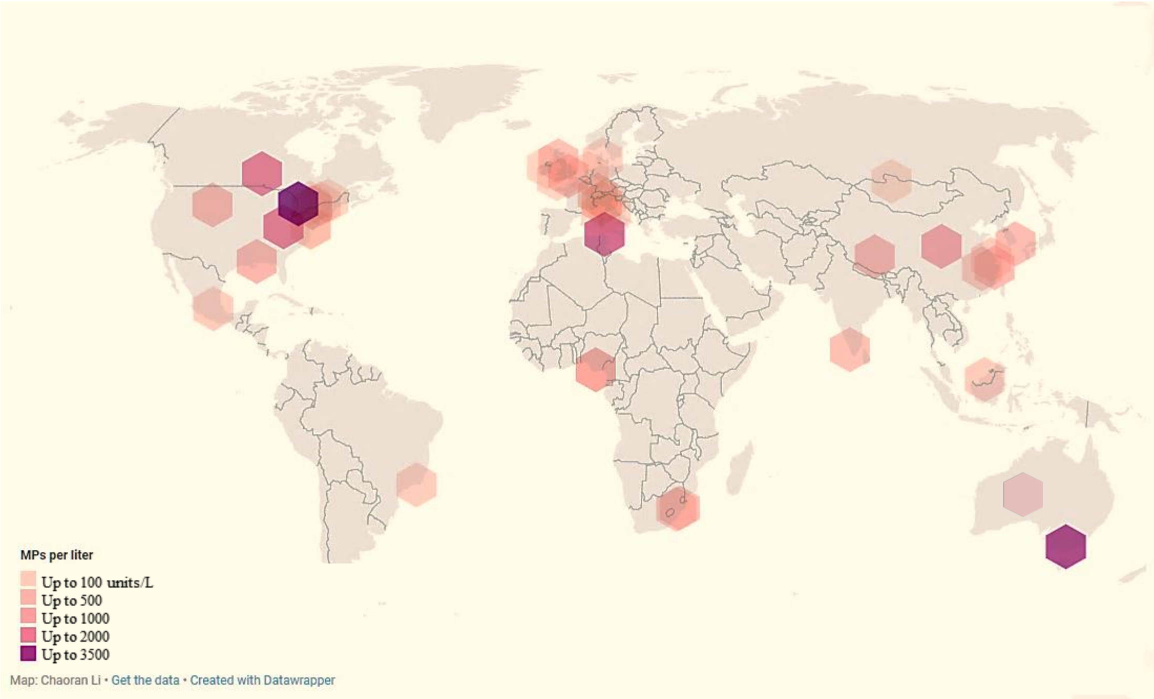
42.64326, 11.98514	Italy	Lake Chiusi and Lake Bolsena	2.5 particles / m^3	0.025	Sediment and Surface water	Size classes: <5 mm MPs	Visual inspection	Fischer et al. (2016)
31.23825, 120.1414	China	Taihu Lake	123 particles / L	123	Sediment and Surface water	MPs with a size of 100–1000 µm	FTIR and SEM/EDS	Su et al. (2016)
-22.9333191, -43.1147684	Brazil	Jurujuba Cove, Niterói, RJ	0.099 g/L	110	Sediment and Surface water	Size classes: <5 mm	FTIR	Castro et al., (2016)
-28.816623, 24.991639	South Africa	Five urban estuaries of KwaZulu-Natal	0.288 g/L	320	Sediment and Surface water	Size classes: <5 mm	Visual Inspection	Naidoo et al., (2015)
44.83141, 9.41722	France	River Seine, urban area	3 particles / m^3	0.03	River water	100–5000 µm	Visual inspection	Dris et al. (2015a)

23.1118934, 113.3341061	China	Pearl River Estuary	0.468 g/L	520	Sediment and River water	Size classes: 0.315 mm – 5mm	Visual Inspection	Fok and Cheung (2015)
50.22062, 99.91705	Mongolia	Lake Hovsgol	1.2 x 10^4 particles/ km^3	0.00012	Lake water	Size classes: 0.355–0.999 mm, 1.00–4.749 mm, and >4.75 mm	Visual inspection	Free et al. (2014)
-27.11667, -109.36667	Chile	Easter Island	0.072 g/L	80	Sediment and Surface water	Quadrat: 0.25 m^2; Depth: 2 cm; Sieve: 1 mm	Visual Inspection	Hidalgo-Ruz and Thiel (2013)
46.91807, -104.00437	South Korea	Heungnam beach	0.3285 g/L	365	Sediment and Surface water	Quadrat: 0.25 m^2; Depth: 5 cm; Sieve: 2 mm	Visual Inspection	Heo et al. (2013)

55.670249, 10.3333283	Denmark	Danish waters	0.0324 g/L	36	Sediment	Size classes: 38 µm – 1 mm, 1 – 5 mm and >5 mm	FTIR	Strand et al., (2013)
45.66132, 10.6851	Italy	Lake Garda	1.7 x 10^3 particles/ m^3	17	Sediment	Size classes: 9–500 µm, 500 µm–1 mm, 1–5 mm, >5 mm	Raman	Imhof et al., (2013)
42.30919, -87.8501	USA	Great Lakes	1.6 x 10^7 particles / km^3	0.016	Surface water	Size classes: 0.355–0.999 mm, 1.00–4.749 mm, >4.75 mm	SEM/EDS	Eriksen et al., (2013)
61.60713, -149.309	Switzerland	Various lakes	2 x10^3 particles / m^3	20	Sediment and Surface water	Size classes: <2 mm, <5 mm (sediments)	Visual inspection	Faure et al., (2012)

44.65031, -82.2819	USA and Canada	Lake Huron	3.5 x 10^{11} particles / km^3	3499	Sediment	<5 mm, >5 mm (water) Size classes: <5 mm plastic pellets, >5 mm broken plastic, polystyrene	FTIR	Zbyszewski and Corcoran, (2011)

Whilst there are numerous reports of MPs in freshwater environments such as in the Great Lakes basin of North America; the Thames and Rhine rivers of Europe; and the Taihu basin of China (Table 1.1), MP pollution of freshwater environments has been studied to a lesser extent when compared with marine environments. However, MP contamination of freshwater environments has been found even in remote regions; although studies are limited, which suggests that MPs are distributed in freshwater systems throughout the world. Therefore, more systems should be studied to fill the gap in our knowledge of the distribution of MP pollution in freshwater environments globally.



Map: Chaoran Li • Get the data • Created with Datawrapper

Figure 2. 1 Map of distribution of MPs in freshwater systems (based on data in Table 1.1)

2.2.2 Characteristics of MP pollution

MP pollution in freshwater environments is global and generalized. This can be observed from a sample of published data (Figure 2.2). Data in Figure 2.2 were collected from the Web of Science database and included information from every research article that was retrieved with keywords MPs and freshwater from 2016 to 2019. From the results, MP pollution has been mainly reported in North America and Western Europe (Horton, et al., 2017) and parts of China (Peng et al., 2017; K. Zhang et al., 2018) (Figure 2.1 and Figure 2.2). In addition, MPs have been reported in Brazil (Castro et al., 2016), Mongolia (Wu et al., 2018), and India (Sruthy and Ramasamy, 2017).

Figure 2.3 and Figure 2.4 illustrate the percentage of composition and type of MPs found in freshwater. These figures were constructed based on the papers listed in Table 1.1 that included the percentage value of composition (Ballent et al., 2016; Bordós et al., 2019; Burns and Boxall, 2018; Horton et al., 2017; Imhof and Laforsch, 2016; Martin et al., 2017; Naji et al., 2017; Peng et al., 2018; Sruthy and Ramasamy, 2017; K. Zhang et al., 2016; W. Zhang et al., 2017) and type (P. J. Anderson et al., 2017; Aytan et al., 2016b; Baldwin, et al., 2016; Ballent et al., 2016; Burns and Boxall, 2018; Cincinelli et al., 2017; Gewert et al., 2017; Leslie et al., 2017; Peng et al., 2018; Lei Su et al., 2018; L. Su et al., 2016; Sutton et al., 2016; Wang, et al., 2018; Wang, et al., 2017b; K. Zhang et al., 2018; W. Zhang et al., 2017) of MP. The percentages here were then calculated as the average of the percentages given by those papers.

As it can be seen, PP, PE, PS, and PET collectively contribute to approximately three-quarters of the pollution observed in freshwater systems (Figure 2.3). PP and PE have the highest detection rate possibly because of the high production and utilization of these two types of plastic products, so it is urgent to improve the current sewage treatment methods and reduce the pollution of PP and PE MPs (Lechner and Ramler, 2015).

Based on the morphological characteristics of MPs, fibres and fragments constitute the majority of the pollution (Figure 2.4). Fibres make up approximately 59% of the MPs, potentially due to significant discharge of laundry wastewater (Kole et al., 2017). This is a concerning issue as fibres are not effectively removed by current wastewater treatment processes (Browne, 2015). Fragments account for around 20% of the MPs, likely resulting from the crushing of larger plastic pieces due to runoff impact (Auta et al., 2017). Additionally, beads, films, and foams have been detected in freshwater, each contributing to less than 10% of the total pollutants.

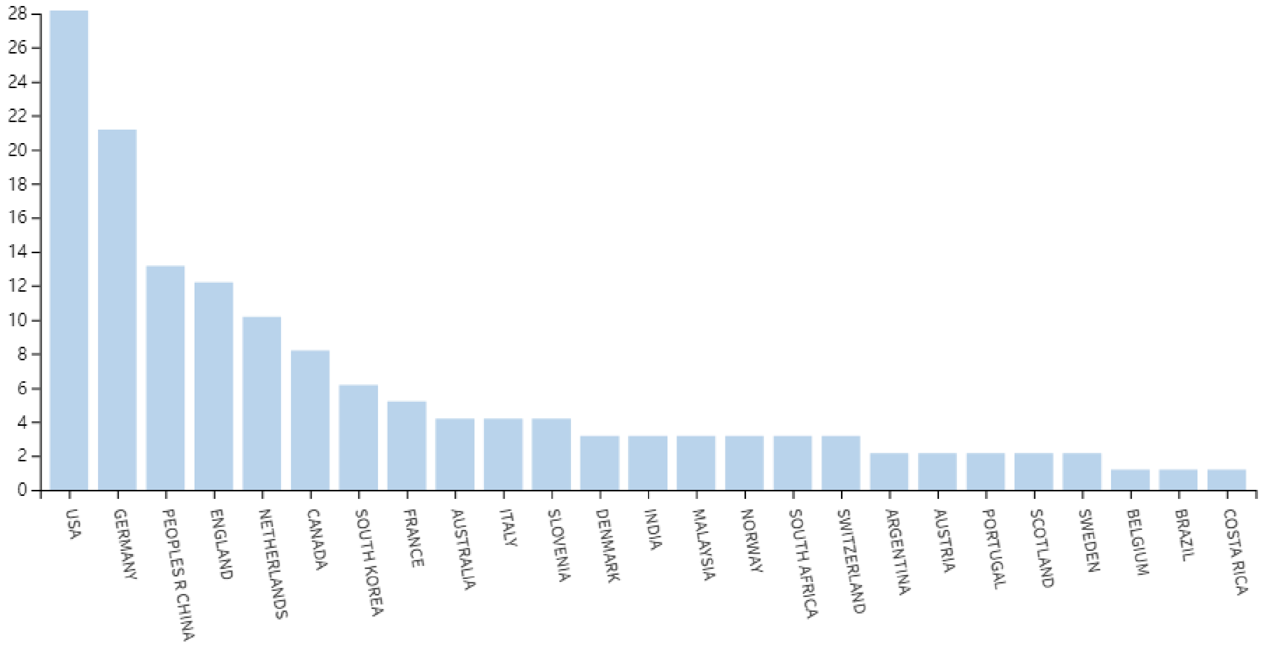


Figure 2. 2 Reports on MPs in freshwater worldwide (Y axis indicates the number of published relevant papers)

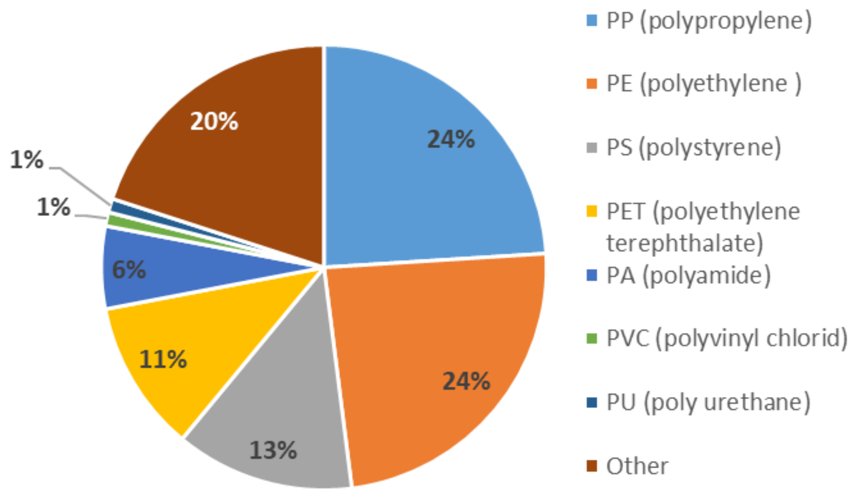


Figure 2. 3 Composition of MPs found in freshwater samples

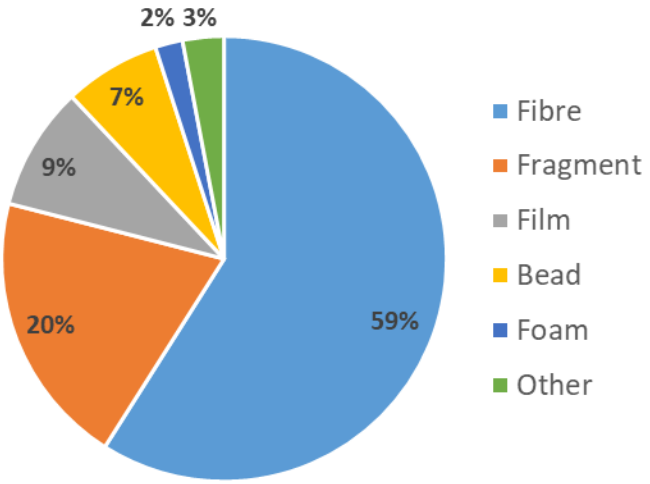


Figure 2. 4 Proportion of MPs in freshwater samples according to their type

2.3 Detection and analysis of MPs

The difficulty in separating MPs from benthic and planktonic habitats has limited the available knowledge of their spatial and temporal distribution (Galgani, et al., 2013; Hidalgo-Ruz et al., 2012). The majority of current methods used for the detection and monitoring of MPs are time-consuming and insufficient in accurately identifying all particles (Galgani et al., 2013; Mendoza and Balcer, 2019). The challenges associated with MP detection primarily revolve around three aspects: effectively capturing plastic particles from water or sediment samples, distinguishing plastic fragments from other substances (both organic and inorganic), and accurately identifying the types of plastic present (Eriksen et al., 2013; Hidalgo-Ruz et al., 2012). MPs are not regularly monitored as there is a lack of understanding of their possible effects on humans (Wright and Kelly, 2017). For this reason, further research on the spectrum of MPs in freshwater (i.e. size range, type, and effects of MPs) is required.

2.3.1 Sampling and separation methods

The sampling methods used for capturing MPs have consisted of selective sampling (such as sieving, filtration, floatation, density separation, and charge separation) and bulk or volume-reduced sampling (Hidalgo-Ruz et al., 2012). Selective sampling (consisting of visual sorting) has been mainly utilized for surface sediments, whereas bulk or volume-reduced sampling, has been used to analyse MPs from sediments or water samples (Eerkes-Medrano et al., 2015).

Separating MPs from other particles such as sand can be achieved through different flotation methods because plastics are relatively less dense compared to other particulate matter. Fine filters (generally with a cut-off of 150 μm) and salts (such as NaCl and NaI) are added to the water samples to increase water density (Hidalgo-Ruz et al., 2012) and facilitate the separation of MPs. However, separating low-density MPs, with diameters < 500 μm, is still challenging (Imhof et al, 2012). Some methods may be able to overcome this difficulty, however. For example, through the use of dense fluid, the Munich Plastic Sediment Separator is a specialized tool capable of isolating

MP particles of various sizes (ranging from 1 μm to 1 mm), types, and densities present in water (Imhof et al., 2012), and has been used in the analysis of MPs in freshwater from Lake Calda (Italy) and made possible the identification of MPs as small as 9 μm (Imhof et al., 2013). An effective way for separating MPs from sediment involves washing samples with nitric acid, which led to an extraction efficiency of 93-98 % (Claessens et al., 2013). A low-cost approach proposed used castor oil to separate MPs from sea and river water. This method was found applicable for the extraction of MPs larger than 300 μm. Methods for improving the separation of MPs of all sizes and types are emerging and improving our ability to effectively sample and separate MPs. As the new methodology is still emerging, it is too early to reach a unified approach.

2.3.2 MP morphological characteristics

Morphological characteristics of MPs are important parameters for the classification of MPs and the determination of their source. Particle size is closely related to the migration behaviour of MPs in the environment. It also directly determines the ease of entry of MPs into organisms. On a practical note, it also determines the required mesh size (0.038–5.000 mm) of sampling sieves (Hidalgo-Ruz et al., 2012). Particle size grading is mainly achieved through sieving and filtering during the sample pre-treatment stage. According to Hidalgo-Ruz et al. (2012). sediment samples usually pass through 2-4 sieve nets, while water samples pass through 4-9 sieve nets.

MP morphological features are a good indicator of MP degradation and can be important in identifying their source. MP degradation is largely driven by external forces such as biodegradation, photodegradation, and chemical weathering. Chemical weathering causes cracks on the surface of the plastic and can break particles into smaller pieces. Different morphologies of MPs can be found in Figure 2.5. The characterization of surface morphology needs to be conducted at high magnification (50-10,000 times) (Wang et al., 2017a). For this reason, current methods employ SEM techniques (Aytan et al., 2016a) such as scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDS), and environmental scanning electron microscopy-energy dispersive X-ray analysis (ESEM-EDS). However, characteristics such as shape and colour are still predominantly reliant on visual inspection, with tools such as fluorescence labelling that can be used to enhance the distinction between MPs and environmental substrates in cases where they are difficult to distinguish.

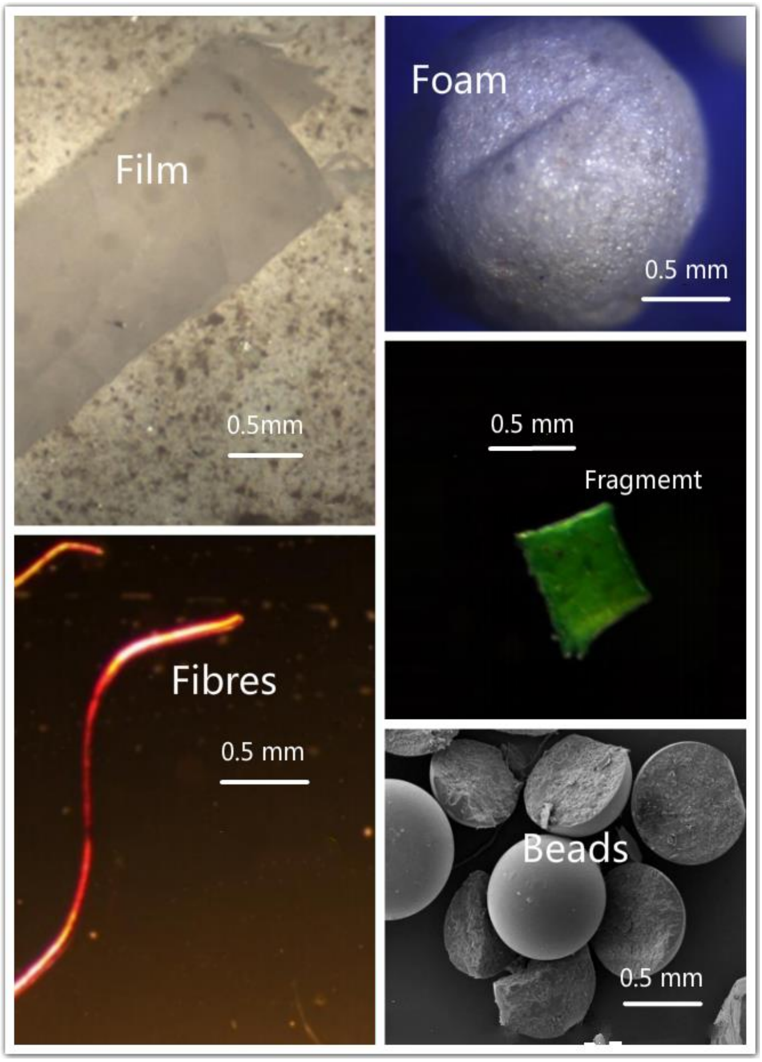


Figure 2. 5 Examples of types of morphologies in MPs (Katsnelson, 2015; Wuhan, 2017; Wageningen, 2014)

2.3.3 Characterization methods of MPs

The most common approaches used for the characterization of MPs often utilize complementary techniques. For example, Fourier Transform Infrared Spectroscopy (FT-IR) or Raman, which are primarily stand-alone techniques, are often employed coupled with optical microscopy (micro-spectrometer) (Song et al. 2015). MPs of >20 µm from drinking water were characterized with µFTIR imaging (Mintenig et al. 2019). Despite their high selectivity, differentiating MPs with smaller particle size (i.e. in the low micrometre-range) from natural matter becomes difficult with μFTIR and μRaman imaging and can cause overestimation of the number of identified MPs (Mendoza and Balcer, 2019). In addition, as a result of the reduction of light transmittance through MPs, the use of an attenuated total reflectance crystal attached to the microscope (ATR-μFTIR) is preferred. This modality is affected by limited sensitivity, however (Pico and Barcelo, 2019), and although it does not require sample treatment, the characterization of MPs with this technique is still time-consuming.

SEM-EDS (or ESEM-EDS) (Zhao et al., 2017) provide greater spatial resolution than μFTIR and μRaman imaging Compared to the visualization of specimens (from ~10 μm in the case of optical microscopy) SEM modalities make possible resolutions > 1 nm (Busquets, 2017) at the same time than their inorganic compositional analysis can be carried out by EDS. The qualitative analysis that they offer is much localized; hence the lack of homogeneity of the MP sample can become an issue if the goal is quantitative analysis. This is also problematic in the analysis of nanoparticles, and it can be overcome by characterizing a very high number of sites within every sample (Dudkiewicz et al., 2015).

In addition to FTIR and Raman-based techniques, Pyr-GC-MS has been used to identify the composition of MPs (Dierkes et al., 2019). Unlike the spectroscopic approach, this technique is destructive; the characterization is based on the pyrolysis of the polymer (0.1-0.5 mg polymer i.e., at 700 °C for 60 s (Nuelle et al. 2014) which leads to cleavage of chemical bonds and generation of low molecular weight volatile moieties from the non-volatile polymer. These thermal degradation products can be cryo-trapped, separated, and identified by their mass spectrum. The identification is carried out by matching the retention time and mass spectrum with that of standards of polymers or the use of spectral libraries. The advantage of this approach is greater sensitivity and selectivity in the identification than when using spectroscopic techniques, but it has drawbacks: Pyr-GC-MS requires high maintenance of the equipment because the relatively heavy moieties arising from the degradation of the polymer can condensate in the capillary between the pyrolysis chamber and the GC and cause blockages and cross-contamination. Nuelle et al. (2014) used these techniques to identify the polymer in MPs from sediments collected from Norderney island beach after a two-step (fluidization-flotation) sample treatment method that separates MPs based on their density in saturated solutions of NaCl and NaI. The MP in the samples was probably made of polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC).

Pre-treating the sample before the chromatographic analysis can allow for increasing the sample size (up to 100 mg) and overcoming the obturation problems when using Pyr-GC-MS for the analysis of MPs. This is achieved with TED-GC-MS (Dumichen et al., 2014), which consists of a combination of thermogravimetric analysis (at temperatures of about 600 °C) where the volatile products generated are pre-concentrated onto fibres by adsorption. These volatile degradation products will be subsequently desorbed and introduced into the GC-MS (Dumichen et al., 2017).

2.4 Quantitative analysis of MPs

At present, MPs concentrations are given in weight of MPs/volume and number of MPs/volume (Picó & Barceló, 2019; Liu, Li et al. 2021). When expressing the results in the number of MPs, it implies the specific number (or a fraction of it) is manually and converted into the concentration in environmental samples. MPs' quantitative concentration determination methods mainly include the microscopy visual method and spectroscopic method (microIR, microRaman) (Lin, Xu et al. 2021). For MP particles with a particle size of 1-5 mm, manual counting by microscope can be used for direct identification; for MP particles with a size in the micron scale, it needs to be identified under a microscope (Jung, Cho et al. 2021). The visual method is simple to operate, but due to many impurities in the sample and the similar appearance, it is easy to cause misjudgement (Jung, Cho et al. 2021), and it is time-consuming and implies very low throughput as well. Fourier transform infrared spectroscopy (FTIR) and Raman are commonly used to identify the polymers in MPs. In a study Eriksen et al.'s (2013) research on MP pollution in the Laurentian Great Lakes, about 30 % of the particles in the samples manually counted by microscopy were aluminium silicates, which were misidentification as MPs. In addition, the differences in the observers themselves are also the reasons for the misjudgement. When three different observers identified MPs in the same sediment with the same sample treatment and same detection methods. different results were obtained: the number of MP particles in the sample was 1 to 4 in a 0.25 m^2 sediment (Dekiff, Remy et al. 2014). This exemplifies the method of identifying plastics based on visual inspection could be suitable just for MPs' screening or preliminary identification method.

The fluorescent staining method has been used to optimize the analysis that involves the visual identification of MPs. The method involves dyeing MPs with hydrophobic fluorescent dyes (such as Nile red) by adsorption on MPs' surface (Lv, Qu et al. 2019). Density extraction and filtration are performed, and they are irradiated with UV254 under a fluorescence microscope to make them emit fluorescence. The fluorescent staining method is simple, fast, and can be used to identify and quantify polymer particles in laboratory control samples (Schwaferts, Niessner et al. 2019). However, because some biological organic matter is stained by dyes or naturally has fluorescent properties, the results are false positive (Schwaferts, Niessner et al. 2019). At present, there is no method that can completely remove organics from environmental samples. As a result, fluorescent staining can be utilized as a supplementary technique for quantitative analysis, complementing other methods.

A complementary way to follow MPs is using labelled MPs that are labelled with a metal. For instance, in Pulido-Reyes et al.'s (2015) research, synthetic samples of polyacrylonitrile cores labelled with palladium (Pd) and polystyrene shells were used to obtain core/shell nanoparticles with similar physicochemical properties, which were determined by the hydrodynamic diameter and Zeta potential. However, this method can't detect MPs in natural water and the costs of the materials and devices are expensive.

Due to the brittle nature of MPs in the environment, the accidental fragmentation of particles can change the number of particles and affect the calculation of their number concentration (Gillibert, Balakrishnan, et al. 2019). The fact that MPs are constantly fragmented in the environment means that particle number cannot be considered a conserved fundamental quantity. Relative to particle number, mass is not affected by the physicochemical processes when MPs are exposed to the environment (Wang, Bolan et al. 2021). Therefore, mass concentration determination of MPs allows quantification of the environmental load of MPs and direct comparison of contributions from different sources. For MPs in number concentration, to convert it to mass concentration, the MPs need to be weighed. However, the small density and volume of individual MPs and the variety of types bring difficulties to weighing measurements. Based on this, Simon et al. (2018) proposed a method to quantify the quality of MPs using FPA-FTIR imaging. They measured the size of the MP particles on the infrared image, simulated the volume of the sample, and then multiplied the density of the corresponding species to obtain the mass of the detected MPs (Simon, van Alst et al. 2018). The researchers found that mass concentration was a more reliable method for characterizing MPs and was less affected by the analysis method and target size (Simon, van Alst et al. 2018). However, this method can only roughly estimate the quality of MPs, and the quantitative analysis method is mainly thermal analysis.

Thermal analysis is another method to analyse the components and mass of MPs, but it can’t give the number of MPs in environmental samples. It determines the MP components based on spectrums. It is an analytical technique that complements IR and Raman for the identification of polymers constituting the MP. This method does not require complex pre-treatment of the sample and do direct analysis (Majewsky, Bitter et al. 2016). The principle of Pyr-GC-MS is that the MPs are thermally decomposed in an inert atmosphere, and the formed gases are separated on a chromatographic column and identified by mass spectrometry (Rai, Kumar et al. 2021). At present, thermal analysis methods used thermal analysis of MPs include thermogravimetric differential scanning calorimetry (TGA-DSC), pyrolysis gas, chromatography-mass spectrometry (Pyr-GC-MS), thermal extraction desorption gas chromatography- Mass spectrometry (TED-GC-MS) (Velimirovic, Tirez et al. 2021). TGA-DSC combines differential scanning calorimetry (DSC) and the different advantages of thermogravimetry (TGA) (Velimirovic, Tirez et al. 2021). DSC is used to understand the thermodynamic properties of phase transitions such as enthalpy, heat capacity and temperature (Velimirovic, Tirez et al. 2021). When the sample is endothermic or exothermic, it will cause a temperature change (Velimirovic, Tirez et al. 2021). A peak will be observed in the DSC system, and the area under this peak can be used for quantitative analysis of the quality of MPs (Velimirovic, Tirez et al. 2021). TGA is to perform quantitative analysis by monitoring the change of the mass of the sample in an inert atmosphere with time or temperature at a programmed temperature. Majewsky et al. (2016) studied several plastics (polyethylene, polypropylene, polyvinyl chloride, polyamide, polyethersulfone, polyethylene terephthalate, and polyurethane) using TGA-DSC. Majewsky et al. (2016) successfully performed the Quantitative analysis was performed, but the remaining MPs were not successfully analysed due to phase transition overlap problems (Majewsky, Bitter et al. 2016). TGA and DSC can also be used with other instruments for quantitative detection. For example, combining DSC with Pyr-GC-MS can achieve quantitative analysis according to the change of sample mass in DSC while the polymer is cleaved. Each polymer has specific degradation products and indicator ions that can be used for qualitative and quantitative judgments (Majewsky, Bitter et al. 2016). The advantage of this method is that it can analyse the chemical properties of the MPs themselves and the chemical properties of other additives, which cannot be effectively identified by spectroscopy. But for synthetic MPs, due to their tiny mass and poor sensitivity to characteristic indicator ions, the method cannot identify them, requiring the aid of FTIR spectroscopy. In addition, due to the small amount of a single sample (0.1~0.5 mg), this method is not suitable for detecting a large number of samples containing impurities. Based on this, some scholars have used TED-GC-MS, combined with TGA and solid-phase extraction, to thermally degrade MP degradation products (100-600 °C) and conduct thermal desorption analysis in GC-MS. Compared with Pyr-GC-MS, the method can process samples with a mass of up to 100 mg and analyse complex heterogeneous matrices without pre-screening samples for MPs (Okoffo 2021). The method can rapidly analyse and quantify five common polymers (polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyamide) within 2–3 h (Okoffo 2021). Although its effectiveness has been preliminarily verified, the selection of characteristic peaks for different MPs and the preparation of standard curves still needs to be continuously improved. The advantage of thermal analysis is that there is no need for complex pre-treatment of the sample before sample analysis. It can be directly injected for analysis, is not affected by MPs' shape, size, and surface morphology, and can provide the chemical composition of its particles and additives. Compared with the spectroscopic method, the disadvantage of the thermal analysis method is that the high-temperature conditions will destroy the sample and cannot obtain other information such as size, shape, colour, etc., which brings difficulties to the traceability analysis of MPs (Okoffo 2021). Both spectroscopic and thermal analysis methods have obvious and serious shortcomings, and they all have extremely high requirements for instruments, samples, and costs. A simple, efficient, and low-cost, high-throughput detection method is urgently needed. For these reasons, in chapter 4, a rapid and low-cost MPs detection method was introduced.

2.5 Technologies for the remediation of MPs

Technologies for MP remediation can be classified into three categories: physical, chemical, and biological methods. In each category, the process (physical, chemical or biological), removal efficiency of different types of MPs, operating media, and conditions are summed up in Figure 2.6, Figure 2.7 and Figure 2.8. Besides, a specific analysis of the benefits and limitations of each method is provided.

In the industry of drinking water from a river with an initial concentration of 6614 ± 1132 MPs/L, conventional treatment processes' removal efficiency (including coagulation/flocculation, sedimentation, and sand filtration) was roughly 58.9-70.5 % (Wang et al. 2020). There, MPs > 10μm were removed with 50.7-60.6 % efficiencies which were greater than for the rest of the MPs (Wang et al. 2020). Polyacrylamide (PAM) was the coagulant that was applied, and it caused much PAM in the sedimentation tanks' sludge (Wang et al. 2020). There currently are no legal restrictions on content of the MP in drinking water, and there is no treatment technology targeting

MPs' removal directly. MPs' relatively high percentages can be removed by agglomeration strategies and coagulation on a lab scale, but not in the WWTP process, and in large MP particles which will be less efficient. These techniques need extra chemicals (Herbort et al., 2018; Ma et al., 2019).

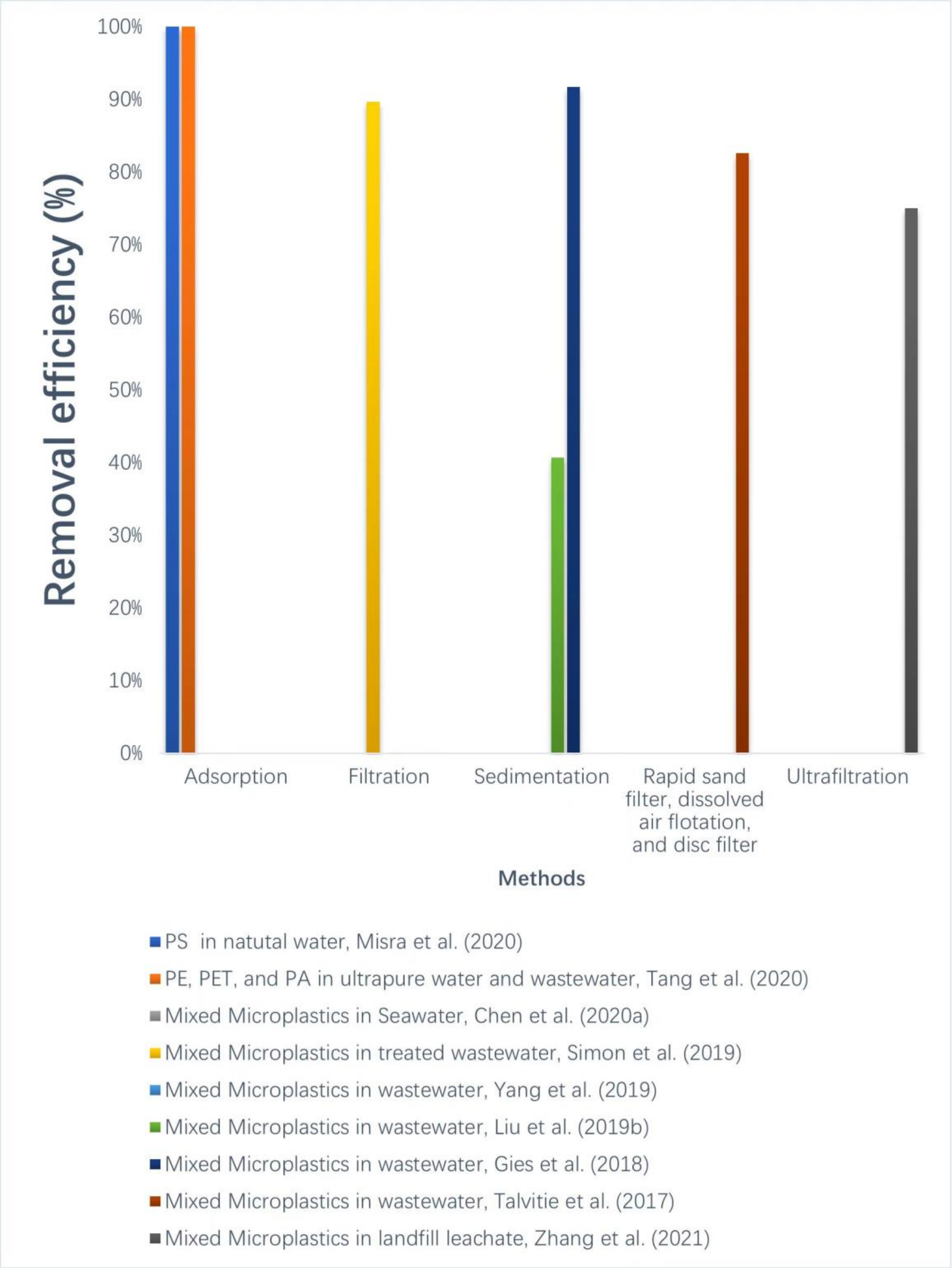


Figure 2. 6 Physical techniques for the removal of MPs. These water treatment processes have been applied with non-comparable water quality and microplastics.

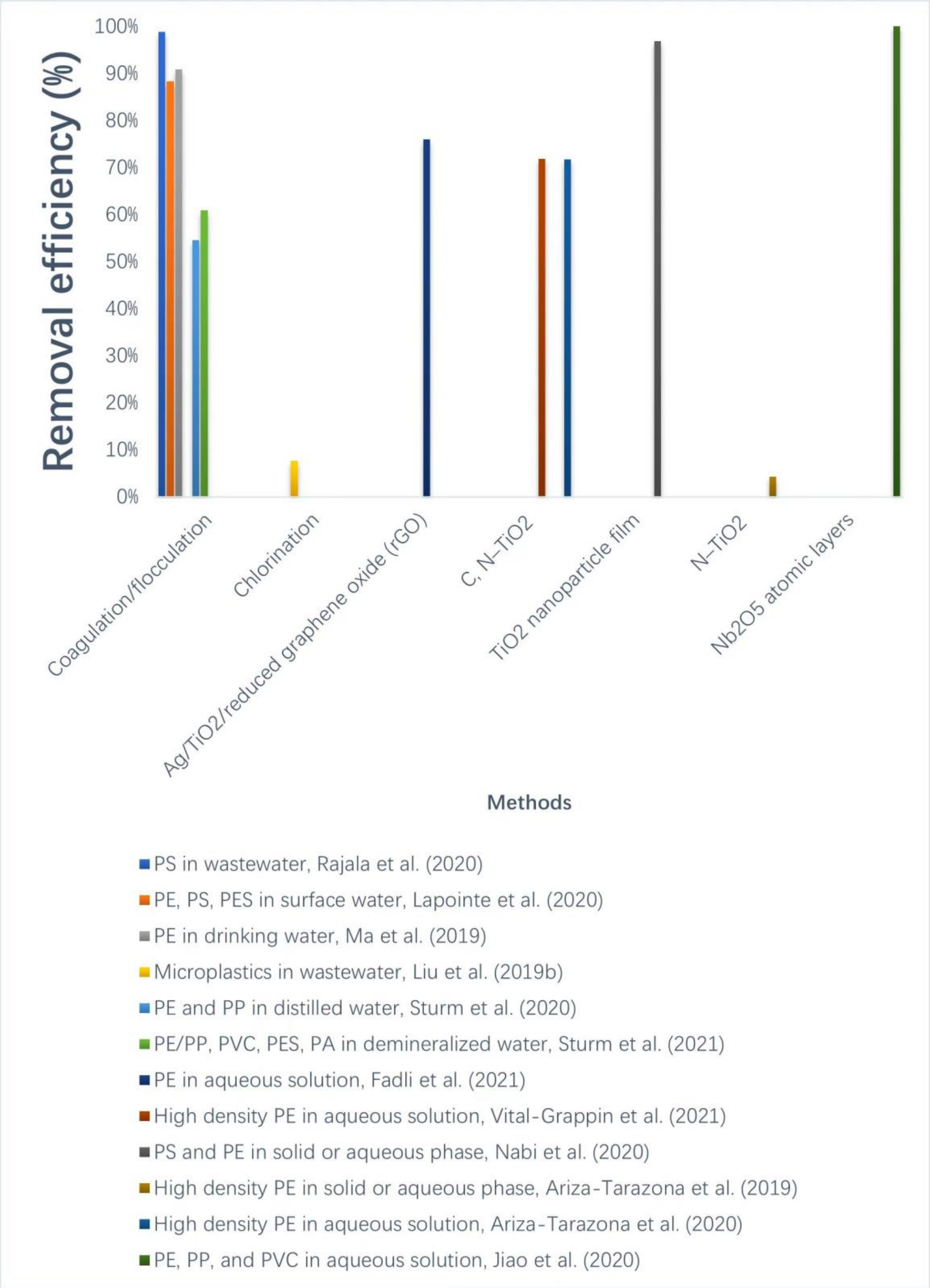


Figure 2. 7 Chemical techniques for the removal of MPs. These water treatment processes have been applied with non-comparable water quality and microplastics.

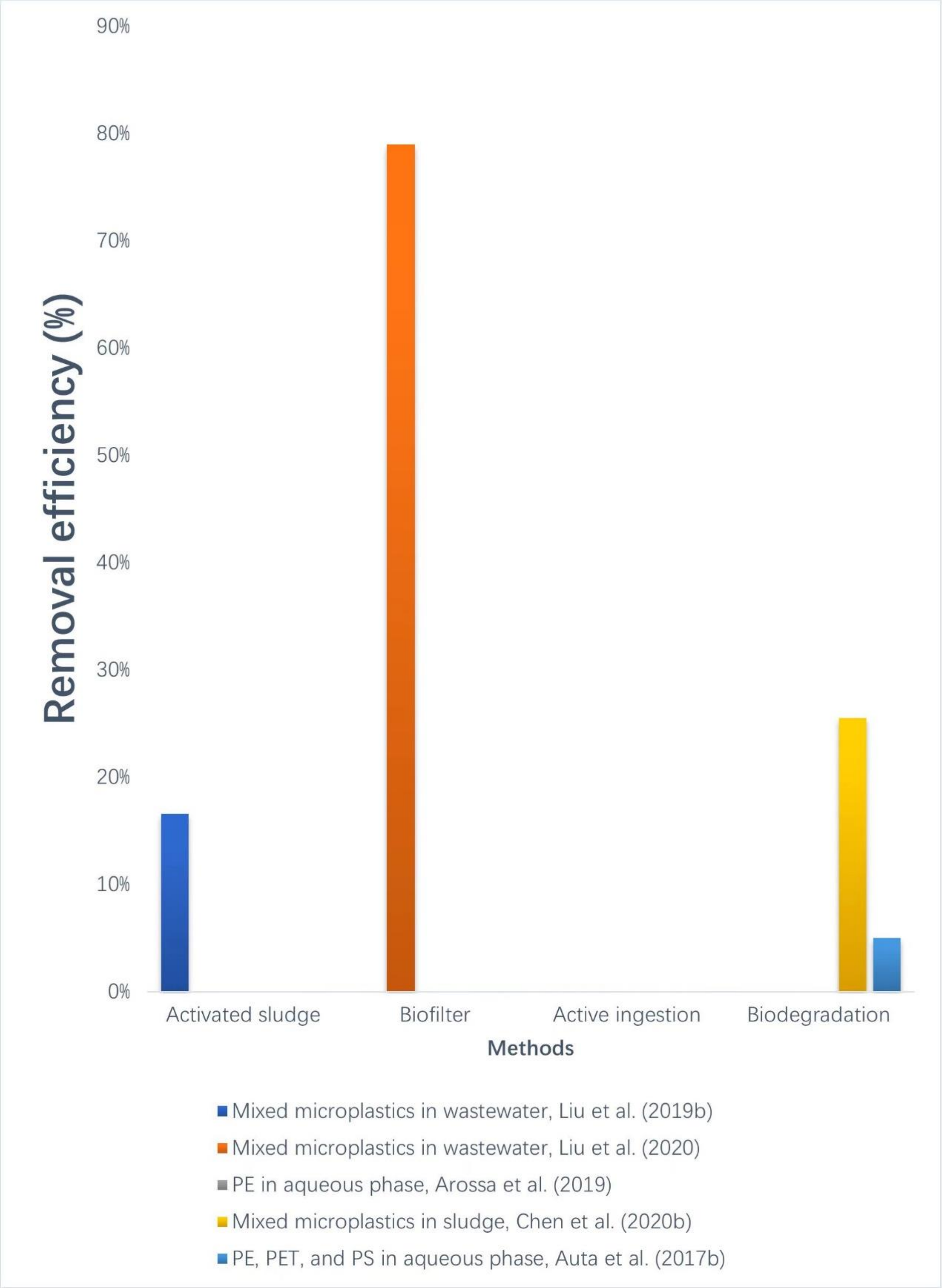


Figure 2. 8 Biological techniques for the removal of MPs. These water treatment processes have been applied with non-comparable water quality and microplastics.

All of the methods mentioned above for removing MPs have their own limitations and advantages. Physical approaches such as adsorption, membrane filtration, sedimentation, and other methods can be employed to remove MPs. Adsorption is a cost-efficient method compared to membrane filtration and reverse osmosis, which require high maintenance costs and energy for membrane descaling (Li et al., 2020). However, the disadvantage of adsorption is that the adsorbent used requires regeneration.

Chemical methods, including coagulation, agglomeration, and photocatalytic degradation, have also been discussed for MPs removal. Photocatalytic degradation, which may utilize solar energy, is an application technology with the potential to remove MPs. However, it has limitations in terms of selectivity for different types of MPs and a higher chance of secondary pollution (Wang et al., 2019; Ariza-Tarazona et al., 2019).

Biological techniques mainly rely on activated sludge, biodegradation, and the intake of MPs by organisms. Although the biofiltration method shows 80% removal efficiency, the overall biological removal efficiency of MPs is comparatively low and can be affected by treatment conditions and biological species (Auta et al., 2017b; Arossa et al., 2019; Liu et al., 2019b). Also, as shown in the Figure 2.8, the method of active ingestion cannot remove PE MPs in aqueous phase (Arossa et al., 2019).

Several studies have explored the efficacy of coagulation-flocculation methods for MP removal. Skaf et al. (2020) found a high removal efficiency (99%) of paper flocs using aluminium through sedimentation and coagulation-flocculation at pH 6.5.

However, the generalizability of their results is limited due to the wide variety of MP types, sizes, and densities, as well as the difference in density between kaolin (used as a reference) and MPs.

In the case of coagulation-flocculation as a tertiary wastewater treatment process for treating secondary sewage containing MPs (~10 μm), Rajala et al. (2020) investigated the use of different coagulants (iron, polyamine-based, and aluminium). They achieved optimal MP removal (93%) using PAC as the coagulant. Shahi et al. (2020) and Lapointe et al. (2020) emphasized the influence of plastic types, sizes, densities, solution conditions, and coagulants on the flocculation effect, highlighting the need for further research in this area.

While some studies have focused on different polymer MPs such as PE, PP, PVC, or mixed solutions of MPs (Wang et al., 2020; Skaf et al., 2020), there is a lack of research specifically addressing the treatment of low-density PS MPs through sedimentation and coagulation-flocculation. PS is characterized by rigidity and brittleness, properties that favour its degradation (British Plastics Federation, 2021b). Photooxidation is a significant weathering process that affects the structure of plastic debris, and these fragments can potentially enter freshwater sources used for drinking water. Therefore, considering the various techniques and the need for in-depth research on flocculation treatment methods, this thesis focuses on the use of efficient flocculants and controlled reaction conditions for MPs treatment.

2.6 Current Policies in the UK and Worldwide

Efforts to address MP pollution have resulted in the development of policies and strategies by governments and organizations globally. In the UK, the government has recognized the urgency of addressing MP pollution and has taken steps to combat it. The Environment Agency, responsible for regulating and enforcing environmental policies, has been actively involved in monitoring and managing MP pollution (Environment Agency, 2021). Furthermore, the UK government has proposed the ban of certain single-use plastics and microbeads in cosmetic and personal care products, which are significant sources of MP pollution (Gov.uk, 2020). On an international scale, numerous countries have implemented policies to combat MP pollution. For example, the European Union has introduced the Single-Use Plastics Directive, aiming to restrict the use of certain single-use plastic products, including microplastic microbeads, which contribute to marine litter (European Commission, 2019). Additionally, the United Nations Environment Programme (UNEP) has established the Clean Seas campaign, urging governments, industries, and individuals to take action to reduce plastic pollution (UNEP, 2018).

Water companies play a crucial role in managing and reducing MP pollution at its source. To control the release of MPs into water systems, these companies have implemented various strategies. One strategy is source control, which focuses on identifying and addressing the sources of MPs within their operations. Measures include improving infrastructure and processes to prevent the release of MPs from wastewater treatment plants and reducing the shedding of MPs from pipes and equipment (Chapman, 2019).

In addition to controlling MP pollution at its source, water companies employ treatment strategies that could remove MPs from wastewater and drinking water. However, MPs are not yet included as priority pollutant in treated water or freshwater and are not legislated anywhere in the word, to the best of our knowledge. This is a barrier for investigating strategies targeting for their removal.

Advanced filtration technologies, such as granular activated carbon filters, membrane filtration, and microfiltration, are implemented in water treatment plants to effectively capture and remove MPs from water supplies (Yao et al., 2021). Coagulation and flocculation, which involve the addition of chemicals that cause MP particles to clump together, are used to enhance MP removal through sedimentation or filtration (Yao et al., 2021). Furthermore, UV irradiation and ozone treatment are being explored as potential methods for degrading and reducing the concentration of MPs in water (Vikrant et al., 2021). These technologies can break down the polymer chains of MPs, leading to their degradation and removal.

2.7 Conclusion

MP pollution in the marine environment has been a matter of concern for. However, related research has just largely launched from 2014, and it there is an urgent need to study on the reference standard, cheap high-throughput monitoring methods, and treatment to address these problems.

Second, as discussed above, an efficient and low-cost MP monitoring method needs to be invented. When evaluating MP treatment methods, pre- and post-treatment concentrations must be determined. Flow cytometry has matured as a reliable technique for cell detection in biological experiments, and it is commonly utilized for cell counting and calibration using plastic microbeads, which are MPs. Its mechanism of action can also be used to monitor MP particles. However, microorganisms or other inorganic particles in the water can interfere with the judgment of the flow cytometer, and this problem will be solved in chapter 3.

Finally, by comparing different methods for MP removal, the methods of coagulation, flocculation, and sedimentation were selected. These methods were chosen based on their affordability (suitable for existing drinking water/wastewater treatment equipment without the need for repurchasing), effectiveness, absence of secondary pollution, and ease of industrial application. Additionally, it is worth noting that these methods exhibit low pollution emissions during the removal process, because the flocculants used are also commonly used in water/wastewater treatment plants. Specific flocculant comparisons, control of reaction conditions, characterization of flocs, and reaction mechanisms will be discussed in detail in successive chapters.

CHAPTER 3 METHODOLOGY

3.1 Introduction

This chapter gives the general methodology details of the whole thesis, including materials, manual counting MPs by microscope, coagulation-flocculation and sedimentation tests, floc breakage and re-growth experiment, determination of pH, weighting MPs after treatment, determination of COD, TOC and turbidity, determination of Zeta potentials, FTIR spectroscopy experiments, SEM-EDS experiments, and general analytical methods.

3.2 Materials

All chemical reagents used were analytical grade and obtained from Sigma-Aldrich (UK), including $Al_2(SO_4)_3 \cdot 18H_2O$, Na_2CO_3, NaCl, 37 % HCl, NaOH, and Kaolin, polyacrylamide (PAM), $AlCl_3$, $Fe_2(SO4)_3$, $FeCl_3$, Nile red, 99.8% methanol. Beads made of PS (10-100 μm), PP (10-1000 μm), PVC (10-1000 μm), PET (10-1000 μm), PA (10-1000 μm), PE (10-1000 μm) and PU (10-1000 μm) were purchased from Dongguan Xingwang Plastics Co., Ltd. PE microfibres (MF) (Diameter: 23 μm, Length: ~ 60 μm) was provided by University College Cork. PAC powders were purchased from Tianjin Dingshengxin Chemical Co., Ltd. Water used in this research was tap water (pH 7.7±0.1; turbidity: 0.2±0.1 NTU; UV-254, 0.177±0.001), Thames River water and Regent's Park Pond water (detailed in Section 4.2.1) for other tests. All MPs stock solutions were prepared at 5 mg/L (concentration that led to a suspension with maximum concentration without suffering aggregation). Such stock was diluted further to prepare other standards and were stored in the dark at 4 °C. Standards and stock solutions included 2 % methanol.

3.3 Manual counting MPs by microscope

For the quantification of MPs, an optical microscope (model Euromex Oxion Material Science) and Countess^{TM} cell counting chamber slides (C10228, Thermo Fisher Scientific, UK) were used for the visual inspection of MPs with microscopy. A glass graduated pipette (5 mL) was used to draw the diluent (0.85 % NaCl aqueous solution) into a test tube. An aliquot (1 mL) of water sample with suspended MPs was taken (using PP micropipette tips) and it was added to a glass test tube. The suspension was shaken to resuspend the MPs adhered inside the test tube. Then, the test tube was manually shaken several times. An aliquot of the tube was placed in between the flat counting chamber and the cover glass, allowing the suspension to flow naturally into the counting chamber for up to 2 min. The concentration of MPs in the suspension was done by visually counting the MPs and considering the volume of sample. The percentage removal was obtained from the difference between the concentration of MPs before and after the treatment and was normalized by the starting concentration of MPs.

3.4 Coagulation-flocculation and sedimentation tests

A PB-900 programmable Jar tester (Phips & Bird, USA) was used with a total of six beakers (1 L) with one flat-bladed mixer with a diameter of (d) = 0.0504 m. PS beads (100 μm) stock solutions (Dongguan Xingwang Plastics Co., Ltd., China) were added to different types of water (Tap water, Regent's Park Pond water, Thames River water) at 5 mg/L (or different concentrations mentioned in following chapters). For imaging and MPs counting purposes only, MPs were dyed with red acrylic paint before the coagulation-flocculation experiment; the optimization of the treatment steps was carried out with undyed beads.

The coagulant used as $Al_2(SO_4)_3 \cdot 18H_2O$ (or other coagulants in different Chapters) at 3.4 mg Al/ L (or different types of coagulant mentioned in following chapters) based on previous work (Yu et al. 2010). During coagulation, the solution pH was adjusted with 0.1 M $NaHCO_3$, and the pH of the untreated water (before adding the coagulant) was adjusted to 1, 3, 5, 7, 12, and 13 by adding 0.1 M HCl or 0.1M NaOH (Fisher Scientific).

To investigate the effect of flocculation mixing speed and sedimentation time, coagulation speed was maintained at 300 rpm (G = 345 s^{-1}) for 1 min, and then the mixing intensity decreased to seven individual test speeds (50, 100, 150, 200, 250 rpm; G = 23, 66, 122, 188, 263 s^{-1}) for 7 min of flocculation (Zhou et al. 2021). The mixing intensities were converted into velocity gradient using Equation (1) (Rushton et al. 1950) and Equation (2) (Camp 1954):

Equation 3.1 $P = N_p \rho N^3 d^5$**Equation 3.2** $G = \sqrt{\frac{P}{\mu V}}$

Where P is the power requirement (W), N is the rotational speed of the impeller (rpm), N_p is the power number (dimensionless), d is the impeller diameter (m), V is the tank volume (m^3), and ρ and μ are the density and absolute viscosity of the water (kg/m.s) at temperature ‘T’. The following parameters were used: $N_p = 7$ (Cornwell and Bishop 1983); $V = 8x10^{-4}$ m^3; water temperature 25 ºC; $\rho = 1x10^3$ kg/m^3; μ = 0.0091 kg/m.s; d = 0.0504 m. Finally, the sedimentation step spanned 30 min (Ma et al. 2019a). All experiments were carried out in triplicate. The effect of the duration of the different flocculation speeds was investigated from 100 s to 800 s (Ma et al. 2019a) with increments of 100 s. In all tests, the coagulation speed was set at 300 rpm (G = 345 s^{-1}) for 1 min. Sedimentation time was screened and the optimum time, based on the maximum number of MPs separated from the solution and counted, was selected.

3.5 Floc breakage and re-growth experiment

In a dynamic test, the PDA 3000, Photometric Dispersion Analyser (Rank Brothers Ltd., Cambridge) (Figure 4.1) was sampled every two seconds. 50 mg/L kaolin and 10 mg/L PS MPs were prepared in 800 mL of central London tap water to simulate the real natural water treatment process. Coagulant (0.8L) was prepared as specified in Section 4.4. The pH of the suspension was adjusted to 5 with 0.1M HCl and stirred at 300 rpm (G = 345 s^{-1}) for 1 min. Then, the stirring speed was reduced to 50 rpm (G = 23 s^{-1}) for 10 min. Next, it increased to 300 rpm (G = 345 s^{-1}) for 1 min to break the flocs and then back to 50 rpm (G = 23 s^{-1}) for 10 min for flocs re-growth. In the case of the addition of coagulant for a second time, the additional dosage of alum (0.8 mg/L) was added into the stirred suspension during the floc breakage phase (Yu et al. 2010). All experiments were carried out in triplicate.

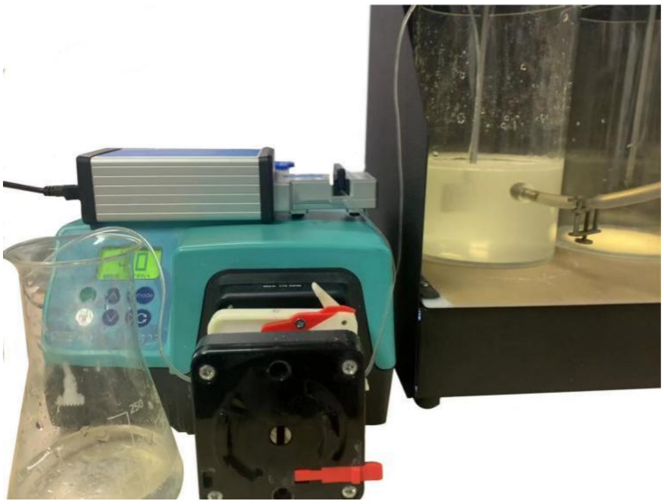


Figure 3. 1 PDA device and jar tester flocculator assembly

3.6 Determination of pH

General water parameter, pH was determined using Mettler Toledo SevenMulti meter (method APHA 9221). Probe head was immersed in the water samples until the readings were stable. The solutions' pH was adjusted by adding 0.1 M HCl or 0.1M NaOH (Fisher Scientific). All readings were conducted three times and average values were calculated.

3.7 Weighting MPs after treatment

An HWIR200A drying oven (Thermo Fisher, UK) was used for sample preparation in recovery experiments (105°C, 12h) before weighting MPs on an analytical laboratory scale (220g 0.0001g, Weighing Net, UK).

3.8 Determination of TOC and turbidity

TOC concentrations of triplicate water samples were determined by TOC-L machine. Furnace temperature was set at 680 °C (developed by Shimadzu Company). The turbidity of the water body was measured by a turbidimeter (Hach TL2300, Hach, UK).

3.9 Determination of Zeta potentials

The suspension samples after coagulation-flocculation and sedimentation were characterized with Dynamic Light Scattering (DLS) techniques (Malvern Zetasizer ZS, UK). The Zeta potentials of the MPs, before and after coagulation, were measured via DLS. The Zeta potential of the suspension before coagulation were measured, and the Zeta potential of the supernatant after coagulation and sedimentation was measured. The differences between these two were analysed

3.10 FTIR spectroscopy experiments

An HWIR200A drying oven (Thermo Fisher, UK) was used for sample preparation in recovery experiments (105 °C, 12h) before observing MPs (or flocs) by Fourier-transform infrared spectroscopy (FTIR spectrometer, PekinElmer Spectrum two FT-IR spectrometer, PerkinElmer Inc., USA). The spectra were collected by 64 scans with the wavelength of 400 to 4000 cm^{-1} and resolution of 4 cm^{-1}.

3.11 SEM-EDS experiments

An HWIR200A drying oven (Thermo Fisher, UK) was used for sample preparation in recovery experiments (105°C, 12h) before observing MPs (or flocs) by Scanning Electron Microscopy (SEM). JEOL JSM-6700F Scanning Electron Microscope with

EDX (JEOL, Japan) was used to analyse the sample contents and figures (Electron Probe Current: 10^{-12}-10^{-6} A, Accelerating Voltage: 10 kV).

3.12 General analytical methods

The coagulation-flocculation and sedimentation results were also analysed by using IBM®SPSS®Statistics software, including ANOVA and correlation analysis. ANOVA is a statistical analysis method used to determine whether there are significant differences between the means of two or more samples (Wang et al., 2020). It decomposes the overall variability of the population into components that can be attributed to different sources, allowing for the assessment of the significance of group differences. All the DFT computations were performed using the Dmol3 software package based on the linear combination of atomic orbitals (LCAO) method. LCAO is a method used in quantum mechanics to approximate the molecular wave function as a linear combination of atomic orbitals, allowing for the calculation of molecular properties and electronic structures (Jean-Luc et al., 2003). Electron-ion interactions were described using all the electron potentials. In this study, DFT was used to calculate the interaction energy between PS particles (100 μm) and PAC (0.4 mmol/L, pH 8) in ultrapure water. The exchange-correlation functional was chosen as the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The lattice parameter and cutoff energy were set to 5.7 Å and 500 eV, respectively. The Brillouin zone was sampled using a 3x3x3 k-point grid. The van der Waals interaction energy and Lewis acid-base interaction energy between the particles were calculated using DFT equations.

The competitive reaction mechanism of PAC flocculant on PS particles (100 μm) in the presence of competing pollutants of humic acid (30 mg/L) and kaolin (300 mg/L) was investigated using the XDLVO model. The interaction forces between PS particles, and between PS particles and PAC flocculant were calculated using the XDLVO model equations, based on the given parameters. The van der Waals force and electrostatic attraction force between PAC and PS particles were calculated, as well as the electrostatic attraction forces between PAC and humic acid, and PAC and kaolin. These results were used to determine the tendency of PAC to adsorb onto the surface of PS particles and the efficiency of flocculation.

To investigate the influence of pH on the hydrolysis products of PAC, geochemical modelling software PHREEQC was used. The concentrations of the hydrolysis products of PAC, including $Al_{13}O_4(OH)_{24}(H_2O)^{127+}$, $Al_8(OH)_{20}(SO_4)_4\cdot14H_2O$, and $Al_2(OH)_3Cl_3$, were simulated at different pH values using PHREEQC. The simulations were performed using the geochemical modelling software PHREEQC, which is a widely used program for modelling geochemical reactions in aqueous systems. The software allows for the calculation of thermodynamic equilibria and the speciation of aqueous species, as well as the prediction of mineral solubility and saturation indices. The input parameters used in the simulations included the chemical composition of the coagulant, the initial concentration of the coagulant, the pH value of the solution, and the ionic strength of the solution.

CHAPTER 4 QUANTIFYING MPS IN FRESHWATER BY FLOW CYTOMETRY

From the literature review in Chapter 2, it can be seen that there is currently no efficient method for calculating the concentration of MPs. Therefore, this chapter will introduce a new high-throughput method for detecting the concentration of MPs using a flow cytometer. MP microbeads are automatically counted by the flow cytometer, which also informs about their particle size. The developed method requires a first step that removes particles that could interfere with the detection by density separation. Next, potential microorganisms in suspension (e.g., E. coli, yeast) are eliminated with UV irradiation. The final step before the analysis with flow cytometry involves filtering particles above 100 μm. The method was optimized with PS 100μm microbeads in ultrapure water and tested with other type of MPs in tap and surface water. The sensitivity of the method for PS, PP, PVC, PET and polyamide PA (10, 50, 100μm) microbeads ranged between 2μg/L to 1 mg/L. For these MPs, good linearity was found in matrix matched calibration (R^2 0.9820-0.9989). The repeatability and reproducibility of the method for the model MP were <17 % and 8.5 %, respectively. The sample treatment method consisting of density separation and UV pre-treatment, when carried out independently, led to 95.0 % and 93.4 % recoveries. The optimised analytical method had an overall trueness of 97 % when analysing different sizes (10, 50, 100 μm) and microbead compositions (PS, PP, PVC, PET, PA). The validation of the flow cytometry method was supported with microscopy analysis. The speed and low chemical consumption of the new method based on flow cytometry makes it sustainable for the analysis of MP microbeads in waters.

4.1 Introduction

The analysis of MPs in less complex matrices such as salt (Alirezazadeh et al., 2022) and waters (Soltani et al., 2022) also requires MPs' separation from the media. From the digested sample, MPs are floated and separated by centrifugation/filtration steps. Filtration will restrict the size of the MPs that will be detected. The quantification of MPs in filters using microscopy, is sometimes aided by semi-automatic software (Birami et al., 2022; O'Connor et al. 2022). Overall, the existing analytical methodology for MP quantification requires long analysis time and is labour intensive. These analytical limitations increase the cost of studies addressing MP pollution and subsequently limit the number of samples; impacting the representativity and accuracy of the quantification and knowledge gained. Current microscopy and spectroscopy approaches used, offer non automated low throughput analysis and cannot be used to directly measure the concentration of MPs (in mass/volume) from suspensions. They only provide number of MPs estimated in portion of the sample that has been filtered and dried. The visual field and magnification of the microscope limit even more the part of the sample that is directly measured. Therefore, automated and green MP detection and quantification methods are very much needed and would support the investigation of MP pollution in multiple areas.

Flow cytometry is a technique that uses the interaction of light with particles to sort cells based on their size, granularity, and fluorescence properties (if dyed) as they pass through a fluidic system (Gao et al., 2022, Bleichrodt and Read 2019). It is a powerful analytical technique typically used quantify various types of cells, and sometimes, quantify their viability when using dyes that penetrate de cell wall from death cells. Flow cytometry involves the detection and measurement of scattered fluorescent signals by labelled (dyed) cells or particles as they pass through a laser beam. Unlike from common application of flow cytometry in cell analysis, here it will be tested for quantifying MPs, and the need for dying the MPs will be assessed (Kaile et al., 2020).

The use of flow cytometry to detect MPs was pioneered in 2016 (Sgier et al. 2016). A main advantage of using flow cytometry is that it can distinguish MPs from false positives (eg bacteria), and it can detect particles ranging from 0.2 μm to 100 μm through fluorescent staining (Kaile et al. 2020), hence it covers the low range of MPs (up to 1 μm) (Frias et al., 2019) rarely covered with commonly used filtration and detection with optical microscopy. However, dying MPs was required in the detection with flow cytometry (Sgier et al. 2016) and this makes it difficult to use for monitoring MPs in natural water since it is not practical to stain these in samples, and dyed MPs are not spiked in these type of studies either. Also, unresolved fluorescent signals from the staining (dots in the output plot) were observed at ≤10 μm (Sgier, Freimann et al. 2016) and this narrowed the work range for the analysis of MPs in environmental samples. Hence, the research has developed and validated new methodology that includes sample pre-treatment and flow cytometry for the analysis of MP microbeads without the need of staining. This will open the door to the use of flow cytometry in environmental monitoring of MPs and will offer high throughput automated analysis of MPs operating under green principles.

4.2 Materials and methods

4.2.1 Chemicals and materials

Microbeads made of PS (1.05 g/cm^3, 10-100 μm), PP (0.91 g/cm^3, 10-100 μm), PVC (1.35 g/cm^3, 10-100 μm), PET (1.38 g/cm^3, 10-100 μm), PA (1.14 g/cm^3, 10-1000 μm), PE (0.88 g/cm^3, 10-100 μm) and PU (1.24 g/cm^3, 10-100 μm) were purchased from Dongguan Xingwang Plastics Co., Ltd. K-12. Escherichia coli, YB525 Yeast, 30 % H_2O_2, 14 % NaClO, 99.5 % NaBr, HPLC grade methanol, 1M NaOH and 1 M HCl were purchased from Sigma-Aldrich (UK). Bio-wash (BioWash Mold Extraction System) was purchased from Biocide Labs Ltd. (UK). Natural aquarium silica sand (100 μm) was purchased from TM Aquatix Ltd. (UK), and it was washed with ultrapure water before using.

"Model" water was prepared by mixing 10-100 μm MP microbeads in ultrapure water with 2 % methanol. Standards and stock solutions included 2 % methanol (Zhao et al. 2017). K-12 Escherichia coli and YB525 yeast were prepared to 1 x 10^8 ind./mL, where "ind." refers to individuals, cells in this case. When indicated, 1 L samples were also added with 1 mL K-12 Escherichia coli (1 x 10^8 ind./mL), 1.5 mL YB525 yeast (1 x 10^8 ind./mL) and 5 mg natural aquarium silica sand (100 μm).

From May 29th to June 3rd, 2020, Thames River and Regent's Park Lake water samples were collected 10 L every day. During the period from May 29th to June 3rd, 2020, the meteorological conditions in London varied. According to the available data, the weather conditions ranged from clear to partially cloudy, with the majority of days experiencing no precipitation. However, on June 3rd, there were cloudy skies throughout the day with recorded rain and overcast conditions, indicating a precipitation event of 0.001 mm.

Specifically, the sampling in Regent's Park is displayed in Figure 3.1a (Decimal degrees (DD): 51.5243897, -0.1538166) and the site in Thames River, in Figure 3.1b (Decimal degrees (DD): 51.5083535, -0.1204094). Water sampling was done using a metal bucket pre-washed at least 3 times with the natural water. The bucket was immersed 50 cm away from riverbank and 50 cm deep from the surface to collect water. There is no sewer outflow near the sampling point. The aqueous samples were stored in glass bottles in the dark at 3 °C until analysis (carried out within 3 days of the sampling). In experiments where natural water was used as matrix and spiked with MPs, 2 % methanol was added to improve the suspension and dispersion of microbeads in the sample.

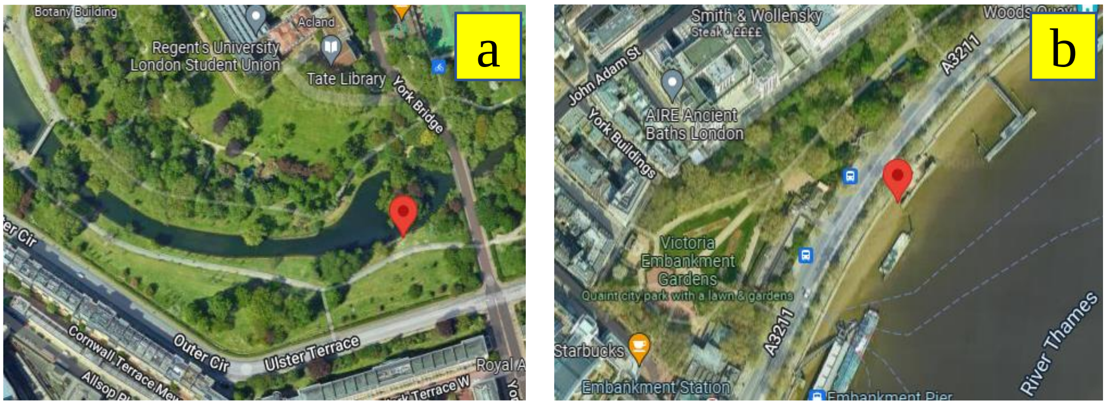


Figure 4. 1 Natural water samples collection spots ("a" shows the Regent's Park spot marked with a pointer, its location is 51.5243897, -0.1538166 decimal degrees (DD); "b" is the Thames River spot, marked with a pointer, located at 51.5083535, -0.1204094 decimal degrees (DD)).

4.2.2 Equipment

MPs were sorted and detected with a Guava easyCyte™ 5 HPL flow cytometer (Merck, Germany) with 488 nm Fluorescence Detection Channel, Green-B 525/30 nm laser, Yellow-B 583/26 nm laser and Red-B 695/50 nm laser. MPs were measured with forward scatter (FC), side scatter (SC) (Alexa Fluor 488, cyan green; excitation: 495 nm; emission: 519 nm). The threshold was set at side scatter at 100, and the optimum voltages for forward scatter (FSC-H), side scatter (SSC-H), and BL1 tested were 340, 340, and 260 respectively.

UV lamps operating at 254 nm and 5 W, 10 W, 15 W, 20 W (one at a time) (QTX, UK) were used for irradiating the aqueous samples for the removal of microorganisms at the second stage of the sample treatment procedure (where the first stage involves the separation of MPs from inorganic particles).

An HWIR200A drying oven (Thermo Fisher, UK) was used at 105 °C for 12 h for drying filter paper containing filtered MPs in experiments assessing the recovery of MPs and comparing the quantification of microbeads with the new method and with the traditional microscopy approach. MPs recovered from aqueous samples following sample treatment were examined with Scanning Electron Microscopy (SEM). A JEOL JSM-6700F Scanning Electron Microscope (SEM) equipped with EDX (JEOL, Japan). The SEM was equipped with accelerating voltage at 10 kV.

4.2.3 Design of the experiments

The density of the suspension was optimised for removing insoluble inorganic components of the aqueous sample that could cause interference and lead to false positives (e.g. sand). Following, four different microorganisms' removal treatments (H_2O_2, NaClO, Bio-wash and UV) were compared by varying lamp power and irradiation time. The selection of parameters for each method was derived from the standard approach of inactivating microorganisms in that particular method (Li et al., 2023). The optimised method for removing insoluble inorganic substances and microbial treatment was used to process samples. A calibration curve of 10, 50, 100μm MPs (PS, PP, PVC, PET, PA) count was used for the quantification. Also, natural water samples were tested to verify the scope of the method. In addition, SEM-Energy Dispersive X-ray Spectroscopy (EDS) was used to confirm that the particles identified were organic and therefore they were not sand.

4.2.3.1 Separation of MPs from insoluble inorganic interferences

Flotation steps for separating MPs from aqueous samples were optimised with ultrapure water (including 2 % methanol) spiked with PS microbeads (5 mg of 100 μm MP/ L). NaBr was used to adjust the density of the aqueous samples to float the MPs. The densities tested were 1, 1.1, 1.2, 1.3, 1.4, 1.5 g/cm^3, due to the density range of MPs from 0.9 to 1.3 g/cm^3 and the typically higher density of gravel exceeding 1.4 g/cm^3, a density-based separation method was employed to maximize their separation. In addition, parallel control samples were spiked with natural aquarium silica sand (100 μm) to a final concentration of 5 mg sand/L instead of to 5 mg of 100 μm PS MP /L. A glass funnel (250 mL, Fisher Scientific UK) was used to separate MPs from sand with 3 consecutive extractions after shaking.

4.2.3.2 Separation of MPs from potential microorganism interferences

For synthetic samples, K-12 Escherichia coli and YB525 yeast were prepared to 1 x 10^8 ind./ mL. 1 L water samples were added with 1.5 mL K-12 Escherichia coli, 1.5 mL YB525 Yeast from their corresponding 1 x 10^8 ind./mL cell cultures. Following, sample density was adjusted to 1.4 g/cm^3 by adding NaBr (99.5 % purity). After adjusting the density, the pH of all the samples was adjusted to 7 with the addition of 1 M HCl or1 M NaOH. In separate assays, either 30 % H_2O_2 or 14 % NaClO or bio-washing powder (Biocide Labs Ltd. UK) were added to samples to final concentrations of 3 % H_2O_2, 500 mg/L NaClO, 500 mg/L bio-washing powder, respectively. Finally, these samples were irradiated with a 254 UV lamp with the optimised conditions. The lamp was located 5 cm at one lateral of the water sample.

4.2.3.3 Experimental design for the removal of microorganisms and statistical data analysis

A Design Of Experiment (DOE) model was used in Minitab ® version 21 with four-factor four-level statistical design. Specifically, the four factors studied were reaction time, UV lamp power, pH, and temperature. The levels used were 1, 2, 3, 4. To determine the optimal duration for effective microbial elimination while avoiding unnecessary energy waste, four different time levels (5, 15, 30, and 45 min) were examined. Understanding how varying exposure times affect the microbial inactivation rate is essential in establishing efficient UV disinfection protocols. The variation of UV lamp power at levels of 5, 10, 15, and 20 Watts enables the identification of the most efficient and safe power level for microbial disinfection. Higher power levels might increase the microbial inactivation rate, but they could also cause high energy cost. By studying multiple power levels, this study aims to strike a balance between efficacy and eco-friendly. Four pH levels (3, 5, 7, and 10) were considered to examine how pH affects UV disinfection efficacy. The pH of the medium can influence the stability and susceptibility of microorganisms to UV radiation. By analysing multiple pH levels, this study researches on how variations in pH may impact microbial inactivation rates and tailor UV disinfection strategies accordingly. Temperature can significantly affect microbial growth and UV sensitivity. To explore the temperature-dependent behaviour of the UV disinfection process, four temperature levels (15, 25, 35, and 45 °C) were studied. Understanding the temperature range that maximizes microbial inactivation without causing energy waste is vital for designing effective UV disinfection procedures (Li et al., 2023).

A 4-way ANOVA, with 95 % confidence, was used to assess the effect of the 4 study factors on the removal of microorganisms from the samples. The recovery of the analysis was studied at 5 mg 100μm MP PS /L spiking level (n=6). The UV lamp set up is detailed in Section 2.3.2

4.2.3.4 Optimised sample treatment and quantification method of MPs with flow cytometry

Different types and sizes of MP (10-100 μm PS, PP, PVC, PET, PA) beads were spiked in ultrapure water or in surface water, in every case with 2 % methanol, to prepare standards of individual composition and size (10, 50, 100µm). The calibration curve had concentration of 1, 2, 3, 4, 5 mg MPs/L, although lower and higher concentrations were tested to find the best work range. A standard calibration curve for individual types of microbeads (PA, PET, PP, PS, PVC**)** was obtained, relating the MPs' mass concentration with the flow cytometer counting results. The density of water samples with 2 % methanol was adjusted to 1.4 g/cm^3 density by adding 400 g NaBr/ L. Following, samples were irradiated with UV (15W, 30 min, 25 °C, 254 nm). Before the introduction of the sample in the flow cytometer, the samples were filtered with aluminium sieve (100 µm, Jin Yuan Ltd., China), the filtrate liquid was shaken for 10 min and measured with flow cytometry. MPs were assessed on forward scatter (FC), side scatter (SC) and fluorescence intensity. The 488 nm laser of the cytometer was used for excitation, and the emitted fluorescence signal was detected at 530/540 nm. From the density dot plot, the particle counting results (10-100 µm) were used as response for the calibration curve.

4.2.4 SEM-EDS analysis

Filters with deposited MPs were oven-dried at 100 °C for 12 h. The dry samples were coated with gold and examined with SEM-EDS (magnification 1.00 KX, 10 µm, EHT: 10 KV, WD: 5.4 mm, Tilt Angle: 45°).

4.2.5 Quality parameters

Quality parameters of the proposed analytical method, including assessment of sensitivity, precision, trueness and robustness of the sample treatment and instrumental analysis were measured with ultrapure and freshwater samples spiked with 100 μm PS microbeads following the procedure detailed in Sections 4.2.3.4. The instrumental Limit of Detection (LOD) and Limit of Quantification (LOQ were estimated from the calibration curve prepared with MPs in ultrapure and surface water (matrix matched). The response of the LOD and LOQ corresponded to the intercept of the regression line plus 3 and 10 times the standard deviation of the residuals (S y/x)) (Miller et al., 2018). The repeatability of the method (intra-day precision) was determined from 6 measurements of 5 mg/L 100 μm PS microbeads in ultrapure water with 2 % methanol on the same day. With the same concentration level and type of microbeads, the reproducibility (inter-day precision) of the method was assessed by carrying out 2 independent analyses over 3 non-consecutive days. An independent analyst from this study was given the detailed experimental protocol and quantified 5 blind freshwater samples (with 2 % methanol added) which MP concentration was 0-5 mg PS microbeads /L spiked in natural water (from Reagent's Park). The analyst did a triplicate sample treatment for every sample following the procedure detailed in Sections 4.2.3.4 and the trueness of that analysis was assessed comparing the mass of MPs quantified with the method based on flow cytometry with the mass of MPs weighed when preparing the samples. The robustness of the method was also assessed with tap and freshwater water samples spiked with MPs of different sizes (10, 50, 100 μm) and microbead polymer types (PA, PET, PP, PS, PVC). The quantification of these MPs included their purification (see Section 4.2.3.4), and quantification of MPs with flow cytometry. In flow cytometry the signal (in counts/ml or ind./ml) can be transformed to mg of MP/L with a calibration curve. The MP counted with flow cytometry was also compared with the MPs counted from the same samples with microscopy. For the latter procedure, MPs had been extracted from a controlled water sample volume. The comparison of both orthogonal approaches was carried out using 95% confidence level. The optical microscopy used was an Optimal microscope (model Euromex Oxion Material Science, Netherlands) using Countess™ cell counting chamber slides (C10228, Thermo Fisher Scientific, UK) (Li et al., 2021). Briefly, 5 mg of 100 μm PS microbeads were spiked in 1 L ultrapure water with 2 % methanol. The water sample was treated (as described in section 4.2.3.4), filtered with syringe filter (2.5 cm wide, cut off 100 μm nylon from Sigma Adrich, UK) and at this point the filtrate either measured with flow cytometry; or filtered under vacuum using a filter paper filter (PVDF 0.22 μm, from Sigma Aldrich) and dried (105 °C, 12 h) before counting with optical microscopy. The recovery rate was obtained by comparing the number of MPs counted onto the dried filters (for both spiked freshwater and ultrapure water samples) and the mass used for the preparation of the spiked solution. Blanks of the analysis with both microscopy and flow cytometry were carried out (n=3/ approach) in parallel.

4.3 Results and discussion

This work focused on improving a method for preparing and detecting MP using flow cytometry, without the need for dying MPs. The analytical procedure has been optimised with 100μm PS microbeads. That size of MPs was selected because it raised toxicity concerns (Li et al., 2020) and these MPs have intermediate density 1.05 g/cm^3 compared to other plastics (e.g., PP: 0.92 g/cm^3, PET: 1.38 g/cm^3, PVC: 1.38 g/cm^3, PA: 1.44 g/cm^3), hence it was considered a good model to represent MPs. Furthermore, PS was among the 4 most abundant types of plastics found in freshwater worldwide as reviewed by the team (Li et al., 2020). The method has been validated with MPs of different sizes (10, 50, 100 μm) and compositions (PA, PET, PP, PS, PVC) in different water qualities to assess whether compositional changes can affect the calibration curve.

4.3.1 Method development for the analysis of MP microbeads (10-100μm).

4.3.1.1 Overview

The optimization of the sample treatment started with finding suitable sample density that could make 100μm PS microbeads float and at the same time remove insoluble inorganic particulates that could interfere with the MP signal and hence could be misidentified as MPs. The sample treatment method also sought to differentiate microbeads from other potential interferences such as microorganisms, which could have overlapped size range (≤100 μm) with the MPs studied here. The study compared four different treatments (H_2O_2, NaClO, enzymatic degradation (with Bio-wash) and UV) for removing microorganisms. The conditions and details of these treatments can be found in Section 4.2.3.2. Once the selectivity of the method and recovery of PS microbeads were suitable, external standard series with the PS microbeads were prepared and used to calibrate the quantification. Natural water samples (from Reagent’s Park) and microbeads of different types and sizes spiked in freshwater and tap water were tested to verify the practicability of the method. The quantification was carried out with flow cytometry, and qualitative data on composition was carried out with SEM-EDS to demonstrate that inorganic particulate matter was not counted as MP. Quality parameters of the method were established. Its validation also included the analysis of broad types of microbeads spiked onto tap and urban lake and river water and comparison of its efficiency and precision with the traditional approach based on counting MPs with optical microscopy.

4.3.1.2 Separation of MP microbeads from insoluble inorganic particles

MP suspensions in the natural environment often contain inorganic solid particles (such as minerals, gravel) (Hamm et al. 2022), and these could be misidentified as MPs. A way to overcome this problem is to change the density of the suspension; by doing this, the inorganic solid particles will sediment. EDX supported this work by helping to differentiate between organic and inorganic particles with the compositional spectrum.

The recovery of MPs from samples adjusted to different densities with NaBr is shown in Figure 3.2. At 1.4 g/cm^3, a large portion of the plastic particles floated and were recovered (94.5 %), while ~11 % of the sand floated. The sand selected for this study had similar size as the study MPs, hence the separation of MPs from sand was being assessed under the most challenging conditions. Low densities (up to 1.38 g/cm^3) led to 95 % of the sand to be settled and removed through this step, however MPs did not float efficiently at densities <1.4 g/cm^3, as it can be observed in Figure 3.2. Therefore, the density of 1.4 g/cm^3 was chosen as compromise conditions to cause the settling or removal of inorganic solids, while being effective at floating MPs from samples before the flow cytometer analysis. Other studies carrying out environmental monitoring of wide range of plastics in soil (samples rich in inorganic particles) adopted NaI at density 1.68 g/cm^3 (Mokhtarzadeh et al., 2022).

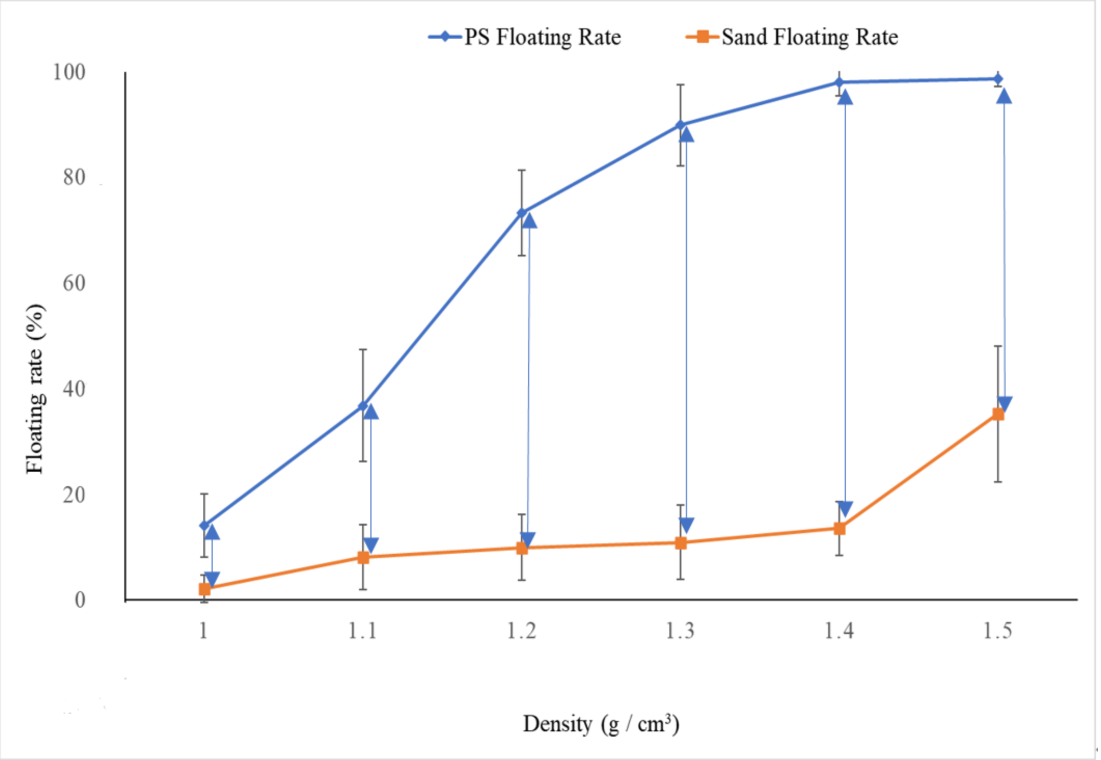


Figure 4. 2 Curves showing PS (100 µm) floating rate (recovery) (top curve) and sand (100 µm) floating rate curve (bottom curve)

Studies characterizing MPs in the environment usually carry out MP counting with microscopes with limit of identification ~50 µm due to limitations of the microscope (Mokhtarzadeh et al., 2022). The scope of the new analytical method developed here includes microbead MPs ≤100 µm, hence the work range of both microscopy and flow cytometry is complementary, and just overlaps ~50-100 µm. Flow cytometry's largest application is in the characterization of populations of cells and bacteria, and these are generally 0.2-150 µm (Bioscience, 2002), and microbeads, in a way have large similarity with cells, hence the scope flow cytometry may be broadened to the analysis of MPs.

4.3.1.3 Separation of MP microbeads from microorganisms

The addition of H_2O_2, NaClO, bio-washing powder in the samples, and irradiation with UV (detailed conditions in Section 4.2.2 and Section 4.2.3.2) were selected as approaches that could remove microorganisms and be easily applied in the lab with the consumption of minimum energy. This work adopted E. coli and yeast as model microorganisms. The effectivity of the treatments is shown in Figure 3.3. The removal of microorganisms by UV (91 %) was about 2 times greater than the effect of H_2O_2 (46 %), NaClO (51 %), Bio-wash powder (45 %), respectively. The superior removal of E. coli and yeast with UV justifies its selection as a method of microorganism removal, although the power and time of the treatment was yet to be optimised for a more sustainable treatment. Using UV irradiation agrees with common sterilization procedures in the lab for bacteria and fungi. Furthermore, it may cause less weathering of MPs after short exposure than the addition of oxidant chemicals. With all, PS' aromatic rings can absorb 254 nm radiation and be affected by it, whereas MPs with no π system may be less degraded.

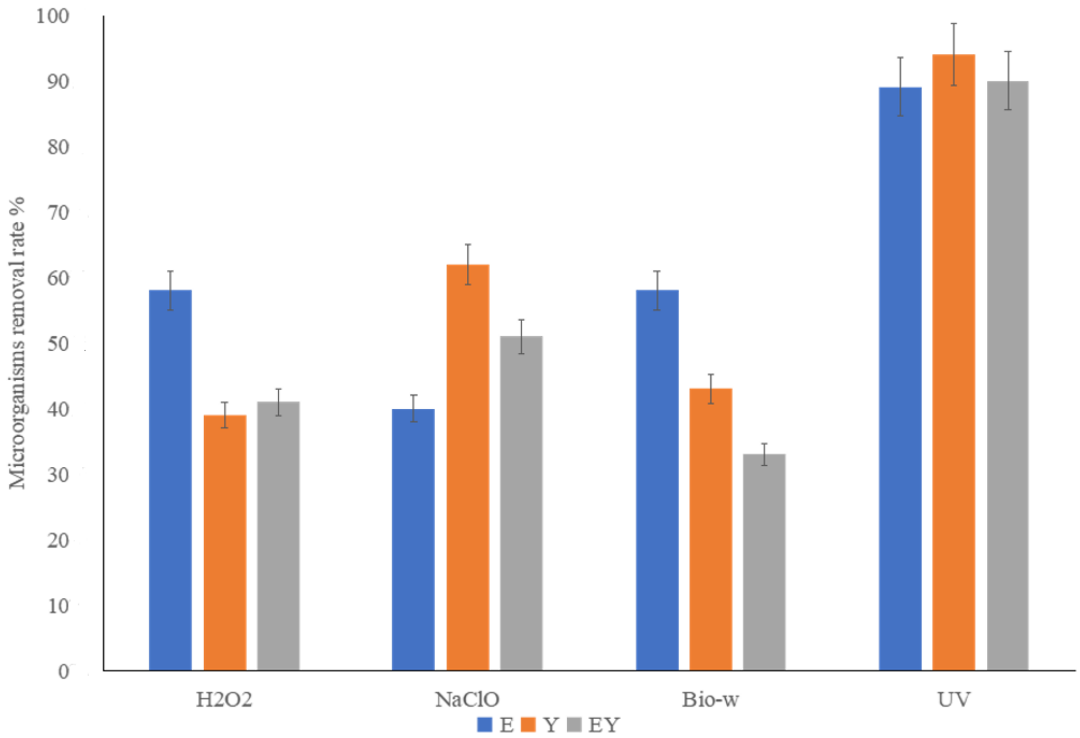


Figure 4. 3 Removal (%) of Escherichia coli (E) and Yeast (Y) with four different methods

4.3.1.4 Sample treatment with UV irradiation

The effectivity of UV treatment could be boosted by conditions such as pH of the sample, power of the UV lamp, treatment time and water temperature. A DOE statistical model was used to optimize the best conditions to reduce the number of trials. The DOE method is a systematic approach used to optimize processes and study the impact of various factors on a system by strategically selecting and manipulating experimental variables. It helps researchers efficiently gather data and make informed decisions by reducing the number of experiments needed and maximizing the information gained from each experiment (Jankovic et al., 2021). The 4-way ANOVA results of DOE statistical analysis that result from the combination of the 4 conditions are shown in Table 3.1. Table 3.2 was generated from Table 3.1 by the Minitab DOE analysis tool.

The values calculated by a 4 factor DOE analysis in Table 3.2 inform about the influence of the study factors on the results. Greater quotients in Table 3.2 imply greater effect of the treatment on the study microorganisms. From Table 3.2, the impact levels of each factor are power> time> pH> temperature. Considering economic and environmental factors, 15 W, pH=7, 30 min, 25 °C, 254 nm were chosen as best conditions. The presence of PS MPs in water caused increased removal of E. coli and yeast (see Table 3.1). This may be because the small microbeads may reflect or scatter UV and by doing so increase the efficiency of the treatment. Through this sample treatment step, around 93.4 % of the microorganisms were removed. Figure 3.4 illustrates that after UV treatment, the dead microbes accounts for 35.7 % of total particles and before UV treatment, the microbes accounts for 38.2 % (microorganisms/ total particles), hence the UV step is effective.

Table 4. 1 E. coli and yeast removal rate in absence and presence of 100 µm PS microbeads in ultrapure water (5 mg/l) with 2% methanol.

Sample nº	pH	Watt (W)	Time (min)	Temp (°C)	Mean removal rate in absence of MPs（%）± SD (n=3)	Mean removal rate with presence of MPs（%）± SD (n=3)
1	3	5	5	15	57.7 ± 3.06	59.6 ± 1.17
2	3	10	15	25	90.0 ± 2.65	89.5 ± 3.52
3	3	15	30	35	94.0 ± 1.00	99.4 ± 1.05
4	3	20	45	45	93.7 ± 1.53	97.3 ± 2.00
5	5	5	15	35	67.7 ± 4.16	71.4 ± 1.17
6	5	10	5	45	79.3 ± 4.16	82.9 ± 2.85
7	5	15	45	15	96.0 ± 1.73	97.0 ± 2.63
8	5	20	30	25	91.7 ± 2.31	99.3 ± 3.00
9	7	5	30	45	83.3 ± 2.08	83.3 ± 1.62
10	7	10	45	35	93.7 ± 2.08	98.7 ± 2.29
11	7	15	5	25	93.3 ± 1.53	96.5 ± 1.41
12	7	20	15	15	97.7 ± 1.15	97.5 ± 4.45

13	10	5	45	25	71.0 ± 2.65	74.7 ± 3.52
14	10	10	30	15	91.7 ± 6.81	89.9 ± 3.08
15	10	15	15	45	97.3 ± 1.15	99.2 ± 1.21
16	10	20	5	35	87.3 ± 5.13	96.2 ± 2.93

Table 4. 2 Impacts of different factors (pH, Watt, time, temperature) and levels analysis (pH: 3, 5, 7, 10; watt (W): 5, 10, 15, 20, time (min): 5, 15, 30, 45, temperature (°C): 15, 25, 35, 45). The rank indicates the most effective factor. Bold number indicates the selected conditions for each factor.

Level	pH	Watt	Time	Temperature
1	0.8644	0.7227	0.8380	0.8593
2	0.8768	0.9026	0.8934	**0.9002**
3	**0.9394**	**0.9802**	**0.9298**	0.9142
4	0.8999	0.975	0.9193	0.9068
Rank	3	1	2	4

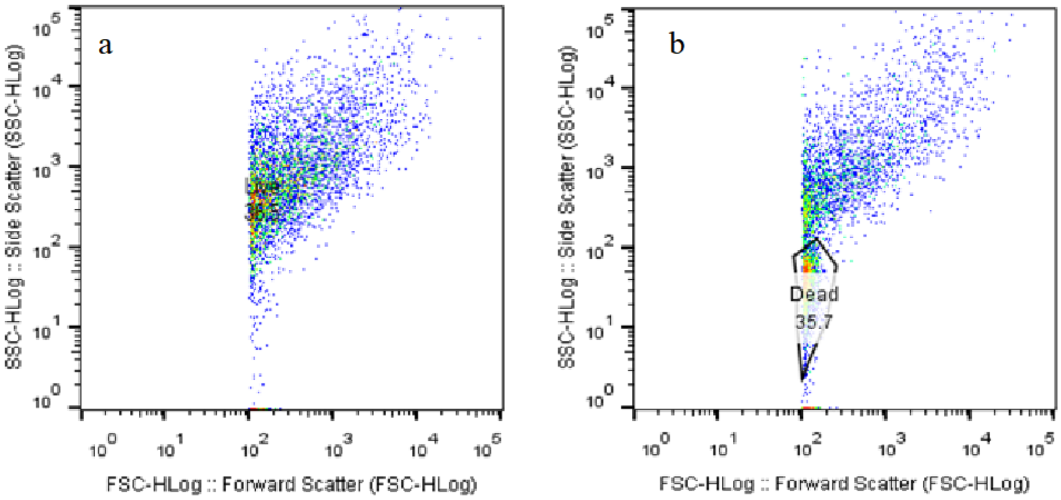


Figure 4. 4 Flow cytometry results of PS with E.coli, yeast in ultrapure water; a: before treated by UV lamp, b: after treated by UV lamp, dead microbes are 35.7% of the total particles (MP and microbes). X: forward scatter; Y: side scatter.

4.3.2 Quantification of microbeads with flow cytometry

4.3.2.1 Assessment of calibration curves and analysis of MPs in surface water

A significant correlation (following a t-correlation test at p 0.05 where $R^2 > 0.982$,

Table 3.3) was found between the response in the flow cytometer and concentrations of MPs of different sizes (10, 50, 100 µm) spiked in natural water (adjusted to 2 % methanol) where MP were PA, PET, PP, PS, PVC, and the concentration was expressed in their mass/ volume (illustrated in Figure 4.5). The t-correlation test is a statistical method used to determine the significance of the correlation between two variables, while R^2 is a measure that indicates the proportion of variance in the dependent variable explained by the independent variables in a regression model (Jankovic et al., 2021). The method uses the density of signals in the dot plot output and concentration of MPs in standards prepared using an analytical balance. The calibration curve for the model PS 100µm microbeads in ultrapure water ($y = 148.09x - 22.94$, $R^2 = 0.9848$) maintained sensitivity in pond water $y = 147.11x + 14.30$, R^2 0.9883) although the intercept, that may denote presence of interferences (bubbles, particle aggregation, etc.), increased in natural water. There was no evident relation between the calibration results and the size or characteristics of the MPs from the calibration curves in Table 3.3, although Figure 3.5 shows that the calibration was not very different among them, hence a universal calibration curve for quantifying any type of MP may be feasible. The intercepts appeared to vary more across analytes than slope, the latter is linked with the sensitivity of the analysis. In the case adopting a common calibration curve for quantifying different kinds of microbeads, the participation of the intercept in the quantification could introduce error. Further work could address minimising intercept values and test whether other MP shapes could be quantified, in addition to microbeads, to move towards a single calibration for any type of sample, in a similar fashion than quantifications of suspended particles with turbidimetry.

Table 4. 3 Sensitivity of the quantification estimated from the calibration curve prepared in surface water from Reagent's Park urban lake (matrix matched)

Quantification parameters				Instrumental sensitivity with sample matrix (mg/L)	
Polymer	Mean size (µm)	Calibration curve (t-correlation test, y: density, x: concentration)	R^2	LOD (limit of detection)	LOQ (limit of quantification)
PP	10	y = 160.80x -8.00	0.9989	0.0018	0.010
	50	y = 140.74x - 0.86	0.9905	0.61	2.04
	100	y = 155.69x - 38.05	0.9867	0.63	2.43
PS	10	y = 150.85x - 4.78	0.9864	0.96	2.98
	50	y = 159.26x - 3.81	0.9953	0.43	1.43
	100	y = 147.11x + 14.30	0.9883	0.36	1.94
PET	10	y = 147.00x - 10.00	0.9962	0.39	2.01
	50	y = 146.49x + 5.95	0.9909	0.60	2.04
	100	y = 151.40x + 1.00	0.9941	0.48	1.60
PVC	10	y = 157.97x - 16.76	0.9923	0.34	1.84
	50	y = 135.46x + 27.19	0.9926	0.54	1.81
	100	y = 153.29x - 10.05	0.9930	0.53	1.26
PA	10	y = 159.20x - 22.67	0.9913	0.59	1.96
	50	y = 168.80x – 32.00	0.9973	0.70	2.34
	100	y = 156.37x -20.76	0.9820	0.85	2.83

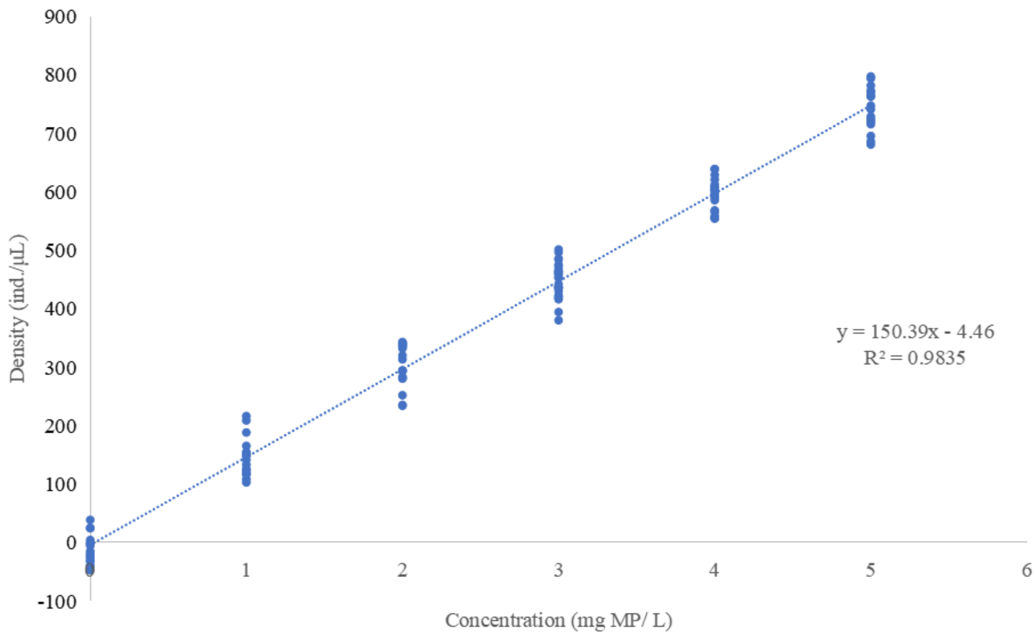


Figure 4. 5 Standard Density/Concentration Curve (SD of n=3, 3 replicates were used)

A total of 112 water samples were purified following the steps in Section 4.2.3.4. The MP counting with flow cytometry and separately with microscopy is compiled in Table 4.4. A t-test carried out at p 0.05 comparing quantification of MPs with independent approaches (Table 4.4) indicated that the counting with the flow cytometry method is significantly correlated with the counting MPs recovered onto a filter paper by optical microscopy ($R = 0.9928$). Confidence levels around the mean quantified values indicated that both methods lead to statistically the similar number of microbeads ($p<0.05$), and this constitute an important result of the validation of the new method. The agreement of MP counts for PA, PET, PS and PVC microbeads between both approaches is illustrated in Figure 4.6. The data for PS exhibits a higher standard deviation due to its density being relatively close to water, leading to errors in density separation. There was somewhat lower agreement for PP microbeads although the differences were not significant with some of the other types of microbeads. There is not a clear effect of the size or composition on the recovery observed when using the method developed in this work. The agreement between the method developed and microscopy counting of filtered MPs across the study MP polymers in spiked surface water with 2 % methanol was overall 90.1 % (Table 4.4). Natural water poses the greatest challenge to the method developed. The sample treatment optimised consisting of density separation, UV irradiation and syringe filtration of remaining particulate matter >100µm has been sufficient for reducing false positive signals due to the sample matrix according to the agreement between the quantification with flow cytometry and microscopy counting (Table 4.4). Compared with the study by Summers (2018), the proposed method here introduces a step of removing the insoluble inorganic matter by the density method and removing the microorganism by the UV method. The accuracy of measuring the concentration of MPs by flow cytometry is therefore improved and allows quantifying non dyed MPs.

Table 4. 4 Comparison of the analytical quantification of MPs in 112 spiked natural water (from Reagent's Park) samples with different MP composition and sizes by 2 independent approaches: microscopy analyses and flow cytometry

Types	Sizes (µm)	Density of signal by flow cytometry (ind./µL)	MPs counted by microscopy (MP/µL)	Agreement (%)
PS	10	720	683	94.9
PP	10	686	634	92.4
PVC	10	793	690	87.0
PET	10	715	701	98.0
PA	10	781	772	98.9
PS	50	797	741	93.0
PP	50	695	655	94.2
PVC	50	681	669	98.2
PET	50	741	694	93.7
PA	50	773	755	97.7
PS	100	729	645	88.5
PP	100	724	691	95.4
PV	100	769	623	81.0

C				
PET	100	763	741	97.1
PA	100	763	676	88.6
PS	100	747	703	94.1
PS	10	594	491	82.7
PP	10	629	622	98.9
PVC	10	568	552	97.2
PET	10	566	497	87.8
PA	10	585	580	99.2
PS	50	607	553	91.1
PP	50	598	484	80.9
PVC	50	604	583	96.5
PET	50	558	544	97.5
PA	50	639	526	82.3
PS	100	621	612	98.6
PP	100	639	572	89.5
PVC	100	609	608	99.8
PET	100	590	479	81.2
PA	100	612	556	90.9
PS	100	554	494	89.2
PS	100	602	549	91.2
PS	100	555	492	88.7
PS	10	475	472	99.4
PP	10	484	391	80.8
PVC	10	473	457	96.6
PET	10	453	376	83.0
PA	10	464	458	98.7
PS	50	496	453	91.3
PP	50	380	362	95.3
PVC	50	436	415	95.2
PET	50	460	417	90.7
PA	50	394	336	85.3
PS	100	430	421	97.9
PP	100	458	415	90.6
PVC	100	435	366	84.1
PET	100	453	383	84.6
PA	100	485	402	82.9
PS	10	436	361	82.8
PP	10	423	355	83.9
PVC	10	501	483	96.4

PET	10	436	426	97.7
PA	10	420	356	84.8
PS	50	462	377	81.6
PP	50	463	418	90.3
PVC	50	442	397	89.8
PET	50	416	380	91.4
PA	50	468	386	82.5
PS	100	419	410	97.9
PS	10	339	320	94.4
PP	10	313	266	85.0
PVC	10	320	317	99.1
PET	10	294	239	81.3
PA	10	338	332	98.2
PS	50	334	317	94.9
PP	50	283	239	84.5
PVC	50	294	261	88.8
PET	50	332	297	89.5
PA	50	341	331	97.1
PS	100	235	229	97.5
PP	100	280	244	87.1
PVC	100	293	255	87.0
PET	100	341	322	94.4
PA	100	234	230	98.3
PS	10	343	306	89.2
PP	10	337	275	81.6
PVC	10	252	209	82.9
PET	10	281	265	94.3
PS	10	188	153	81.4
PP	50	155	144	92.9
PVC	50	141	119	84.4
PET	50	165	141	85.5
PA	50	149	109	73.2
PS	50	133	109	82.0
PP	100	116	99	85.3
PVC	100	108	107	99.1
PET	100	126	124	1.0
PA	100	103	99	96.1
PS	10	216	175	81.0
PP	10	150	126	84.0

PVC	10	209	203	97.1
PET	10	149	130	87.3
PA	10	123	97	78.9
PS	50	118	101	85.6
PS	10	0*	0	92.5
PP	10	0	0	87.5
PVC	10	0	0	84.6
PET	10	0	0	96.9
PA	10	0	0	84.2
PS	50	0	0	86.7
PP	50	0	0	60.0
PVC	50	39	35	89.7
PET	50	0	0	87.0
PA	50	0	0	100.0
PS	100	0	0	100.0
PP	100	0	0	96.9
PVC	100	25	23	92.0
PET	100	4	3	75.0
PA	100	24	23	95.8
PS	100	0	-0	87.5

*value 0 has been assigned to negative counting

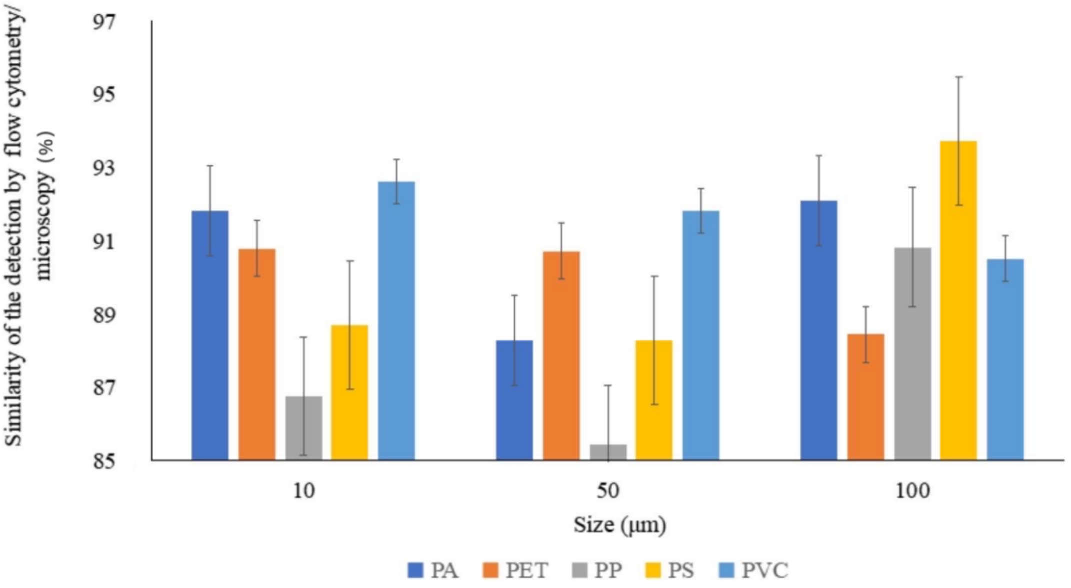
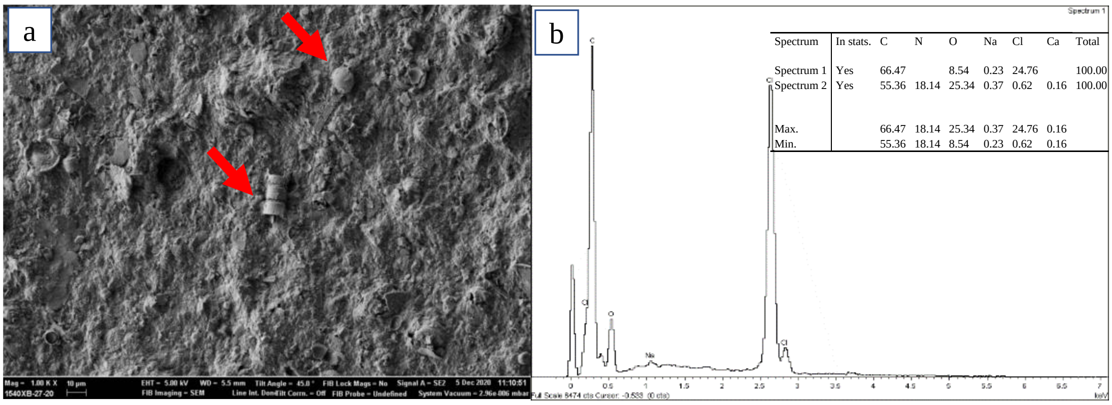


Figure 4. 6 Recovery rate of PA, PET, PP, PS, PVC MPs with different sizes (data from Table S7) (SD of n=3, 3 replicates were used)

4.3.2.2 SEM-EDS analysis

The flow cytometry method optimised can be affected by counting inorganic particles as MPs, although the density (ind./L) was adjusted to prevent this. The optimisation of the developed method, especially the analysis of natural water samples, was supported by the examination of particles with SEM-EDS to confirm that particles recovered were organic (with high proportion on carbon and oxygen) in the EDS spectrum. Example of the analysis and average element distribution results are shown in Figure 3.7. In Figure 3.7 a, the two larger plastic particles can be differentiated. According to the EDS spectrum results in Figure 3.7 b, the carbon elements reaching 66.47% (potentially originate from MPs). Moreover, the contents of oxygen, nitrogen and chlorine are also high. The EDS supports that these particles are not inorganic.



Spectrum	In stats.	C	N	O	Na	Cl	Ca	Total
Spectrum 1	Yes	66.47		8.54	0.23	24.76		100.00
Spectrum 2	Yes	55.36	18.14	25.34	0.37	0.62	0.16	100.00
Max.		66.47	18.14	25.34	0.37	24.76	0.16	
Min.		55.36	18.14	8.54	0.23	0.62	0.16	

Figure 4. 7 Examination of samples with Scanning Electron Microscopy- Energy Dispersive X-Ray Spectroscopy (SEM-EDS). (a) Example of two MPs spotted in Thames water sample (SEM micrograph); (b) elemental analysis of the microbead (spheric particle) in (a), EDS Spectrum 1(up). Spectrum 2 (down) data corresponds to the fragment pointed in (a).

4.3.2.3 Quality parameters

Raw data related with the experimental assessment of the sensitivity of the method in ultrapure, tap water and natural water samples, repeatability, reproducibility, recovery of the beads in different in different water qualities, accuracy and robustness are available in following tables (Tables 4.4-4.9). LOD and LOQ were estimated from the calibration curve (as indicated in 2.1) (Miller et al., 2018). The instrumental LOD and LOQ were 2 µg/L-0.96 mg/L and 10 µg/L -2.96 and µg/L respectively for the study microbeads (10, 50, 100µm PS, PP, PVC, PET, PA), as detailed in Table 4.3. LODs estimated from the calibration curve that included freshwater matrix have been adopted because it considers the standard deviation of residuals of different levels of concentration and can be more robust than the evaluation with a single data point. The sensitivity in detection can be increased by preconcentrating sample volume or separating MPs from total bigger sample volume. In these cases, the concentration of potential interferences can increase too, and the sensitivity may become affected. In this study, the maximum instrumental quantifiable concentration was ~40 mg/L (Tables 4.5 and 4.6), after that, the signal becomes saturated, and agglomeration of beads may occur despite the 2 % of methanol added to samples and standards to favour the stability and dispersion of the microbeads.

Table 4. 5 Experimental data acquired to assess the sensitivity of the instrument and work range experimentally. The assessment was done with 100 µm PS microbeads spiked to ultrapure water. Concentrations have been expressed in the sample measured at the instrument. No sample treatment has been applied. (Signal: number / volume)

Concentration (mg 100µm PS/L)	0	20	30	40	42	45	47
Signal (Ind/µL)	1.4	2891.4	4570.8	5781.8	5601.7	3959.9	4857.4
Signal (Ind/µL)	1.2	3000.2	4534.6	3200.1	3927.2	4721.8	4731.8
Signal (Ind/µL)	2.5	3100.0	3100.5	5900.3	4708.1	5092.9	5125.2
Average	1.7	2997.2	4068.6	4960.7	4745.7	4591.5	4904.8

Table 4. 6 Natural water (from Reagent's Park Lake) spiked with 100μm PS, using sample treatment consisting of sample collection method, density separation, UV irradiation, filtration. Concentrations have been expressed in the sample measured at the instrument.

mg/L	0	0.01	0.015	0.017	0.02	0.03
Ind/μL	7.4	14.8	9.1	12.7	11.1	18.1
Ind/μL	7.2	17.0	16.8	17.5	13.9	10.7
Ind/μL	9	17.4	13.6	9.0	12.8	15.6
Average	7.9	17.4	13.2	13.1	12.6	14.8
mg/L	20	30	40	42	45	47
Ind/μL	2943.4	4619.2	5943.9	4056.1	5641.1	3452.4
Ind/μL	2898.4	3564.7	3200.7	5741.6	3964.6	3954.3
Ind/μL	2991.0	3927.2	3927.0	3864.1	5420.4	5125.3
Average	2944.3	4037.0	4357.2	4554.9	5008.7	4177.3

Relative standard deviation (RSD) is used to indicate the precision of the analytical test. It is expressed in percent and is obtained by multiplying the standard deviation of the data by 100 and dividing this product by the average. Under repeatability conditions and based on the signals in data C (measurement after the sample treatment) from Table 4.7, RSD was 16.8 %. Reproducibility was RSD 8.5 % (data C provided in Table 4.8). The trueness of the method was assessed with the model PS microbeads spiked at different concentrations in natural water doing triplicate analyses. This study was done by an independent analyst (Mr Mingjie Yi) not knowing information about the samples and following a standard operating procedure. These results are shown in Table 4.9, the experimental value from samples 0-5 mg/L quantified is highly similar to the concentrations of MP known from the preparation of concentrations independently with analytical balance: the error found was 0.62-9.59 %. The average trueness achieved for these 5 levels of concentration was 97.1 %. Trueness refers to the closeness of agreement between the average value obtained from a measurement and the accepted reference value, and it is calculated by determining systematic error of the measurement (Jankovic et al., 2021). The quality parameters achieved with the sample treatment and detection method optimised, and the comparable calibration across microbeads (Figure 3.5), indicates that the developed methodology can be universal and possibly any MP within the work range could be used for the calibration according to the low error rate and high trueness.

Table 4. 7 Study of the repeatability when measuring ultrapure water spiked with 5 mg/L PS 100 µm consecutively (n=6) on the same day (5 mg/L 100 µm sand, 1.5 mL,1 x 108 ind./mL K-12 Escherichia coli and 1.5 mL, 1 x 108 ind./mL YB525 yeast in 1L ultrapure water). The table includes de signals obtained and the removal of possible interferences of MPs.

Replicate measurements:	1	2	3	4	5	6
A: MPs in ultrapure water (5mg/l) (signal, ind./µL)	476	512	482	490	506	521
B: Measurement before any treatment (signal, ind./µL)	3566	4200	4724	3045	3611	3702
C: Measurement after the sample treatment (signal ind./µL)	636	793	837	584	773	563
Interfering factors removal (%) (1-(C-A)/ (B-A)) *100	94.8	92.4	91.6	96.3	91.4	98.7

Table 4. 8 Study of the reproducibility when measuring ultrapure water spiked with 5 mg/L PS 100 µm twice a day during 3 non consecutive days (reproducibility test standard, 5 mg/L 100 µm sand, 1.5 mL,1 x 108 ind./mL K-12 Escherichia coli and 1.5 mL, 1 x 108 ind./mL YB525 yeast in 1L). The signals obtained after the removal of possible interferences of MPs.

Replicate measurements:	1 (Day1)	2 Day1)	3 (Day2)	4 (Day2)	5 (Day3)	6 (Day3)
A: MPs in ultrapure water (5mg/l) (signal, ind./µL)	557	482	551	504	488	492
B: Measurement before any treatment (signal, ind./µL)	3370	3160	3944	3148	3829	3549
C: Measurement after the sample treatment (signal ind./µL)	561	629	701	707	686	639
Interfering factors removal (%)(1-(C-A)/ (B-A)) *100	99.9	95.4	96.2	93.6	94.8	95.9

Table 4. 9 Trueness assessed with the analysis of 5 blind natural water samples spiked with 1-5 mg/L 100µm PS microbeads and a blank by an independent analyst. The regression equation relating concentration of MPs with signal density in the flow cytometer on that day had R2: 0.9995.

mg PS/L (prepared by weight)	0	1	2	3	4	5
Signal (Ind/µL)	7	145	289	457	589	731
Signal (Ind/µL)	11	132	301	423	600	735
Signal (Ind/µL)	13	157	280	472	567	724
Average	10	145	290	451	585	730
mg PS/L (Quantified with calibration curve)	0.096	0.99	1.96	3.03	3.92	4.88
Error (%)	9.59	0.62	2.09	0.96	2.0	2.31

With the optimised sample treatment and flow cytometry method (Section 2.3.4), samples taken from Regent's Park Lake and River Thames on 6 independent days were treated. The treatment included 3 sequential flotation steps, which caused the collection of MPs from 3 volumes of sample into 1, and UV irradiation. Finally, the purified suspension of MPs was measured with flow cytometry. From the dot plot output obtained, the results are shown in Figure 3.8. The counts of MPs across most days were found to be statistically similar ($p<0.05$) although, in this case, the composition of the water column on the sampling date was a factor to consider in the dispersion of the results. The RSD (%) of the quantification of MPs sampled on the same sites (Reagent's Park and Thames River) on 6 different days was 15.0 % and 14.8 % and this indicates the level of reproducibility of this approach for environmental monitoring. When using the calibration curve relating the density (here it refers to signal in the flow cytometer) with the concentration obtained with adopted model microbeads (100 µm PS), the average total concentration of MPs, not all microbeads, sampled from the Reagents Park Lake was 0.12 ± 0.018 mg/L, and the concentration in the river Thames River sampling site was 0.21 ± 0.031 mg/L. These values are significantly different at 95% confidence. The source of MPs in the urban lake and river Thames can be the discharge of industrial and domestic sewage (treated or untreated) along the Thames River (Horton et al. 2017) and also the MP particles from the urban environment may settle in the lake (Zhang et al. 2021). Regent's Park is a tourist attraction, and the improper disposal of plastic waste, weathering of that plastic and runoff from roads (Goehler et al., 2022) may be behind its MP pollution. In any case, this study does not have sufficient sampling data points to compare levels of MP pollution.

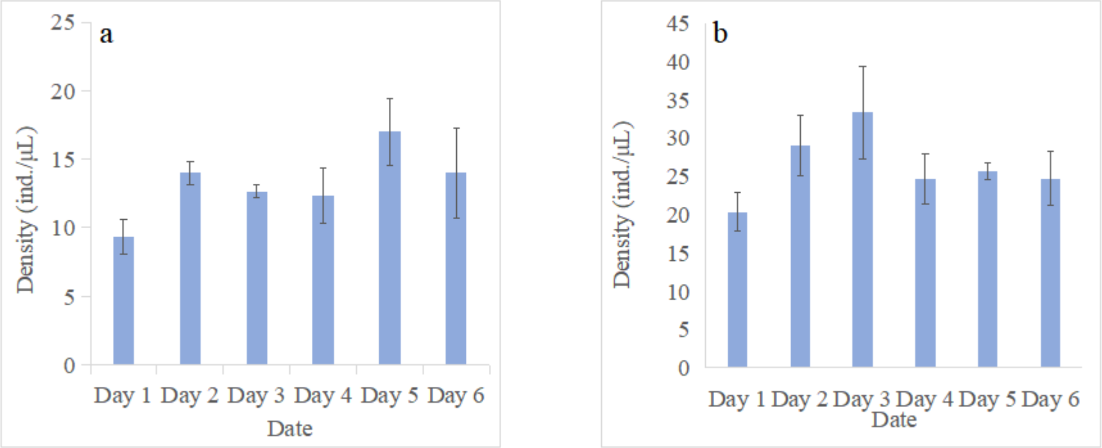


Figure 4. 8 MP density in natural water sample (a is Regent's Park Lake water MP Density; b is Thames River MP Density) (SD of n=3, 3 replicates were used)

Compared with the current flow cytometry methods (Wang et al., 2021; Tse et al., 2022; Kaile et al., 2020), this method can be applied to monitoring natural water. Current flow cytometry detection methods require staining of MPs or direct use of fluorescent MPs to distinguish MPs from other interfering substances (Kaile et al., 2020 and Sgier et al., 2016), and this is not possible in environmental monitoring of MPs. Also not requiring dyes falls under the principles of green chemistry. This work has analysed the effect of different factors affecting the selectivity of the study. The suitability of the quality parameters proposed (high sensitivity and precision), including analysis of MPs with varied sizes and densities, in different types of water, gives this method with broad scope beyond the analysis of MPs in waters. Finally, since the detection and quantification in the proposed is automated and can provide quantification MPs in counts or mass/volume, the low throughput quantification with microscopy (widely used in the sector) that is limited to counting MPs appears in disadvantage with respect to what is proposed here. However, it is important to use counting with microscopy for validation purposes. Future work should address whether fragments MPs can be measured with the proposed method and establish whether there are polymers or particle sizes can lead to very different recoveries in the sample treatment or significantly different calibration curve than other MPs to find limits of the method proposed in this work.

4.4 Conclusions

Currently, there is no automated qualitative and quantitative method for detection of MPs suitable for real time monitoring in wastewater treatment plants, rivers, and drinking water. The use of microscopy methods for counting MPs is time consuming. This research proposes a simple, environmentally friendly and low cost method for the automated quantification of small MPs (10 – 100 μm) in waters with flow cytometry following flotation, UV irradiation and filtration to achieve sensitive (LOD ~0.3 mg MP/L, without considering sample preconcentration factors), precise (<17%), with high trueness (97 %) and low consumption of reagents. This method has been validated in parallel with flotation-filtration and counting following visual inspection with optical microscopy (standard method) leading to non-significant differences in the quantified number of MPs ($p<0.05$). This work has included the analysis of MPs in ultrapure water, tap water and surface water, MPs with different compositions, densities and sizes (10, 50, 100 µm). The quantification has been tested with the analysis of a total of 112 spiked natural water samples. The understanding of the effect of the different parameters on MP analysis and results from the validation of the method demonstrates that the developed analytical procedure is advantageous to automatically quantify MP pollution in mass/volume, or in counts, in waters. The application of this method is, in the first instance, for optimising water treatment methodology using microbeads or providing overall amount of MPs without differentiating shapes. Further assessment is needed to test if other MP shapes (eg fragments <100 µm) can be analysed with this method.

CHAPTER 5 REMOVING PS FROM DRINKING WATER THROUGH COAGULATION-FLOCCULATION AND SEDIMENTATION

5.1 Introduction

The percentage of samples from DWTP containing MPs ranges from 24 % to 100 % and the MPs content from below the limit of detection to 1247 MPs/L across studies (Danopoulos et al. 2020). When finding MPs in the treated water, for accurate quantification, it is important to work with large sampling volumes especially when the concentration of MPs is low (Zihajahomi et al. 2017).

The variety of MPs in sources of drinking water is diverse. Among them, PS is one of the most abundant types of MPs in freshwater globally (13 %) (Li et al. 2020). It is used in rigid packaging and construction material (British Plastics Federation 2021a), among other uses. In the UK, the Water Industry Research (UKWIR) found that the most common MPs in DWTP are PS and Acrylonitrile Butadiene Styrene (ABS) (Ball et al. 2019). Specifically, in raw water where the content was ~ 113 MPs/L, after treatment, the water still contained 2-27 MPs/L (Ball et al. 2019). This shows that the current drinking water treatment processes need to improve.

This chapter aimed to preliminarily investigate the potential impacts of coagulation-flocculation and sedimentation on low-density 100 μm PS microbeads, which were spiked in natural and tap waters.

5.2 Materials and methods

5.2.1 Materials

All chemicals, including Al2(SO4)3·18H2O, Na_2CO_3, NaCl, 37% HCl, NaOH, Kaolin, polyacrylamide (PAM), $AlCl_3$, $Fe_2(SO_4)_3$, $FeCl_3$, Nile red, and 99.8% methanol, were analytical grade and obtained from Sigma-Aldrich (UK). PS (10-100 μm), PP (10-100 μm), PVC (10-100 μm), PET (10-100 μm), PA (10-100 μm), PE (10-100 μm), and PU (10-1000 μm) beads were purchased from Dongguan Xingwang Plastics Co., Ltd. PAC powders were obtained from Tianjin Dingshengxin Chemical Co., Ltd. Tap water (pH 7.7±0.1; turbidity: 0.2±0.1 NTU; UV-254, 0.177±0.001), Thames River water, and Regent's Park Pond water (detailed in Section 4.2.1) were used in the research. All MP stock solutions were prepared at 5 mg/L (maximum suspension concentration) and stored in the dark at 4 °C. Standards and stock solutions included 2% methanol.

5.2.2 Coagulation-flocculation and sedimentation tests

A PB-900 programmable Jar tester from Phips & Bird (USA) was utilized with six 1 L beakers and a flat-bladed mixer with a diameter of 0.0504 m. PS beads (100 μm) stock solutions from Dongguan Xingwang Plastics Co., Ltd. (China) were added to different water sources (tap water, Regent's Park Pond water, Thames River water) at 5 mg/L or other specified concentrations. Red acrylic paint was used to dye the MPs for imaging and counting purposes, while the optimization of treatment steps was conducted using undyed beads. The coagulant used was $Al_2(SO_4{}^{)}\cdot 18H_2O$ at a concentration of 3.4 mg Al/L, as per previous research (Yu et al., 2010). The solution pH was adjusted during coagulation using 0.1 M $NaHCO_3$, and the initial pH of the untreated water was adjusted to 1, 3, 5, 7, 12, and 13 by adding 0.1 M HCl or 0.1 M

NaOH from Fisher Scientific (detailed in Section 4.4).

5.2.3 Floc breakage and re-growth experiment

In the dynamic test, the PDA 3000 Photometric Dispersion Analyser (Rank Brothers Ltd., Cambridge) was used to sample every two seconds. Kaolin and PS MPs were prepared in tap water to simulate natural water treatment. The suspension was adjusted to pH 5, stirred at different speeds for specific durations, and alum was added during floc breakage if required. Experiments were conducted in triplicate (detailed in Section 4.5).

5.2.4 Quantification of MPs

MPs were analysed using a Guava easyCyte™ 5 HPL flow cytometer (Merck, Germany) equipped with lasers at wavelengths of 488 nm (Green-B), 583/26 nm (Yellow-B), and 695/50 nm (Red-B). Measurements were obtained through forward scatter (FC) and side scatter (SC) channels, utilizing Alexa Fluor 488 for cyan green fluorescence (excitation: 495 nm; emission: 519 nm). The side scatter threshold was set at 100, and the optimal voltages for forward scatter (FSC-H), side scatter (SSC-H), and BL1 were determined as 340, 340, and 260, respectively (detailed in Section 4.2).

5.3 Results and Discussion

In this study, PS beads measuring 100 μm were selected due to their prevalence as a commonly occurring size fraction (9.7%) in the effluent of final clarifiers (Wolff et al. 2021). This size range has been shown to be toxic in fish (Ding et al. 2020) and PS particles (0.2 μm), although smaller than the ones studied here, were observed to cross the membrane in red blood cells with microscopy (Rothen-Rutishauser et al. 2006).

This study used spiked MPs at 10 mg/L which is greater contamination than in the freshwater. The study concentration stems from the need to carry out accurate mass measurements and compare initial and final concentrations after the effect of coagulation, flocculation, and sedimentation while using an analytical balance for the preparation of solutions with MPs and working with 1 L jars. Given that, unlike molecules and ions, MPs only become suspended in water (and not dissolved in water), preparing a concentrated solution for further dilution would entail uncertainty on the concentration of MPs in the working solutions. Therefore, to maintain low uncertainty in the MP levels, the method was chosen to spike MPs at levels higher than those typically found in freshwater. The disadvantage of this is that there may be an agglomeration of PS MPs in the solution, which will be minimized by stirring in the jars.

5.3.1 Effect of flocculation stirring intensity on MPs' removal

Stirring speed has a crucial influence on flocculation. Flocculation stirring intensity refers to the level of agitation or mixing applied during the flocculation process to promote the formation of flocs or larger particle aggregates. Faster stirring speeds will cause greater breakage of the flocs and may lead to a reduction of the effect of the treatment. Previous studies on flocculation stirring intensity selected a stirring speed of 100 rpm ($G = 66\ s^{-1}$) when using Al as a coagulant (Zheng et al. 2011; Ma et al. 2019b). The range of stirring speeds investigated in this research was ≤250 rpm (G = 263 s^{-1}) (see reaction condition in Section 5.3.2) and while this favours the dispersion of the PS beads and the reproducibility of the system, it can affect the size of the flocs. Figure 5.1 shows the efficiency of the removal of MPs with the mixing conditions. The MPs removal initially increased to up to 95 % and then decreased rapidly from stirring intensity above 67 rpm (G = 36 s^{-1}). This may be explained by the fact that increasing mixing intensity, decreasing the size of the flocs, making the removal less effective (Moruzzi et al. 2019). Therefore, in practice, for PS MPs removal, the stirring speed at 50 rpm (G = 23 s^{-1}) is the optimum ones with reproducible stirring. Figure 5.1 includes a regression polynomial adjusted to the critical range of stirring speeds. This facilitates calculating the removal of MPs within that range. Figures 5.2 – Figure 5.4 also include regression curves adjusted to the experimental conditions around the optimal removal of MPs.

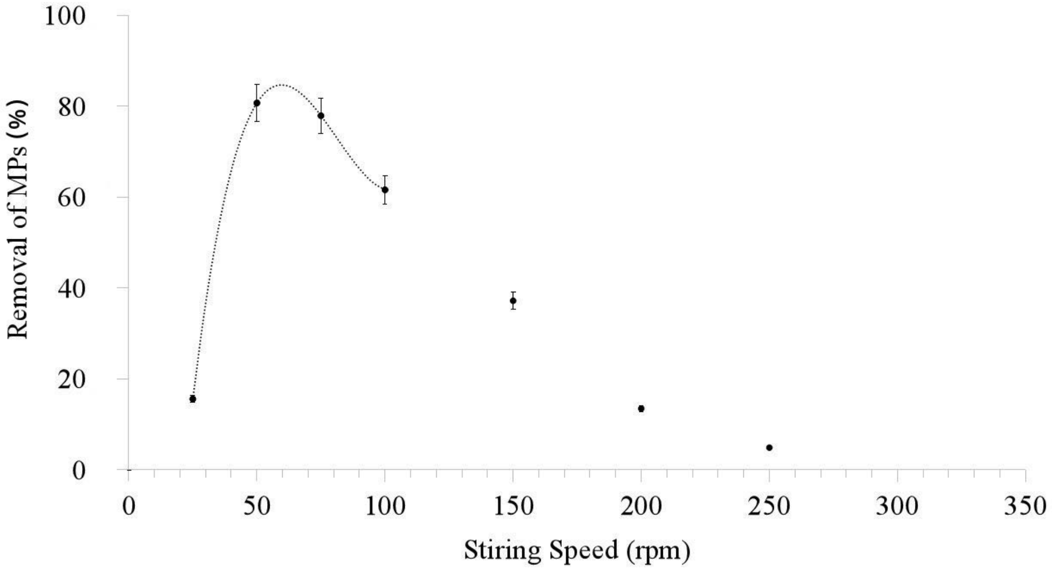


Figure 5. 1 Effect of flocculation stirring speed on the removal of 100 µm PS

spiked in Regents Park Pond water.

5.3.2 Effect of flocculation time on MPs’ removal

The length of the flocculation time often determines the removal of suspended particles (Wu et al. 2012). Studies using Al salts as coagulants usually require about 15 min of flocculation time (Ahmad et al. 2006; Zhu et al. 2011; Wu et al. 2012). Shorter flocculation times than the optimum often lead to insufficient removal of particulates, while prolonged flocculation stages are unnecessary. From Figure 5.2, it can be observed that for a stirring speed of 50 rpm ($G = 23\ s^{-1}$) when increasing the flocculation time to 400 s, or even longer, the removal of the flocs by sedimentation increased till 98.52 ± 1.04 % for the case of 100 μm PS beads. This behaviour can be explained by the flocculation kinetics as both stirrer speed and time dictates floc size and structure, and a dynamic equilibrium is expected (Oliveira et al. 2015; Moruzzi et al. 2013; Moruzzi et al. 2017), leading to the almost complete removal of MPs.

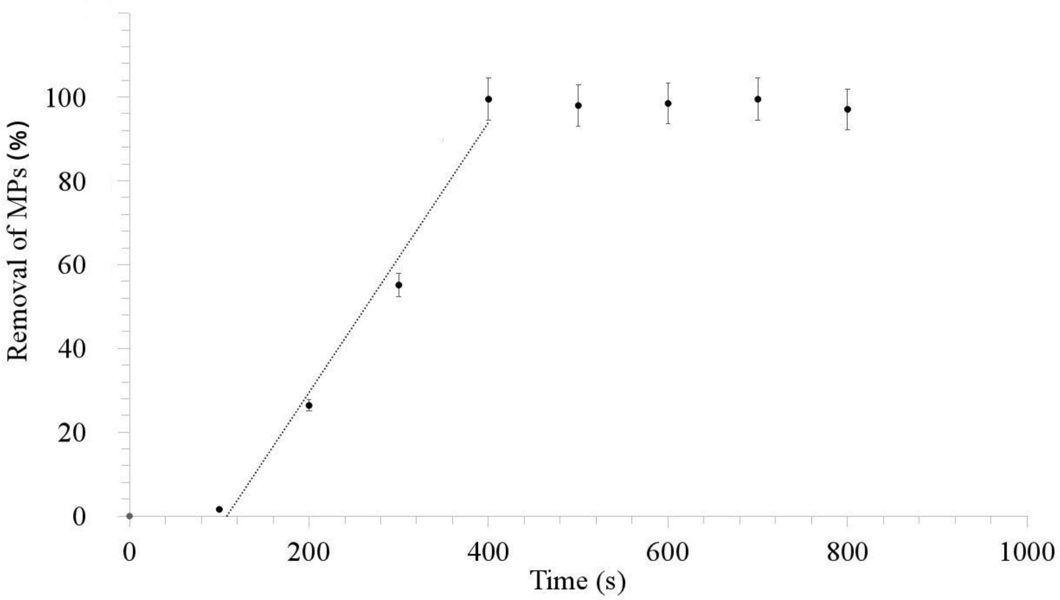


Figure 5. 2 Effect of flocculation time on 100 µm PS beads' removal from spiked Regents Park Pond water.

5.3.3 Effect of initial water pH on the removal of 100 µm PS beads

Ionic strength has a crucial role in clarification (Yukselen et al. 2004) and the water pH generally has a great effect on the floc characteristics (Liu et al. 2013; Lee et al. 2012; Zhang et al. 2017; Zhao et al. 2014). Hence, to further investigate the removal mechanisms of PS beads (as purchased and without the acrylic painting), the corresponding removal efficiencies were investigated at initial pH levels (before adding the coagulant) of 1, 3, 5, 7, 10, 12, 13, with the coagulation-flocculation conditions shown in Section 2.2. Among these pHs, the most relevant pH range of drinking and wastewater treatment (before adding the coagulant) is pH 5-7. After adding the coagulant, the pH of the suspensions was 3.27, 3.91, 4.88, 6.15, 8.41, 11.03, and 11.75, respectively.

At acidic (pH 1 – 5), the MPs removal was ~ 54 % to 91 % (Figure 5.3) for flocculation speed 50 rpm (G = 23 s^{-1}), coagulation time 60 s, flocculation time 400 s and sedimentation time 30 min. By adjusting the pH to > 6.8, the $Al_2(SO_4)_3$ flocculant had low removal efficiency (the suspension remained turbid) and the MPs removal was low (~ 70 %). From Figure 5.3, adjusting pH to ~ 5 has favoured the removal of hydrophobic MPs because under these conditions aluminium sulphate has a large surface potential (Liu et al. 2013). Under these conditions, the removal of MPs achieved was 91 %. This may be explained by the fact the pH and the coagulant dosage determine which hydrolysis species is formed during coagulation. For example, in the case of aluminium coagulants, it is recognized that the optimal removal of particles from water is achieved under optimum pH conditions close to the point of minimum aluminium solubility i.e. 5.8 > pH > 6.5 where the sweep coagulation mechanisms occur (Gregory and Duan 2001).

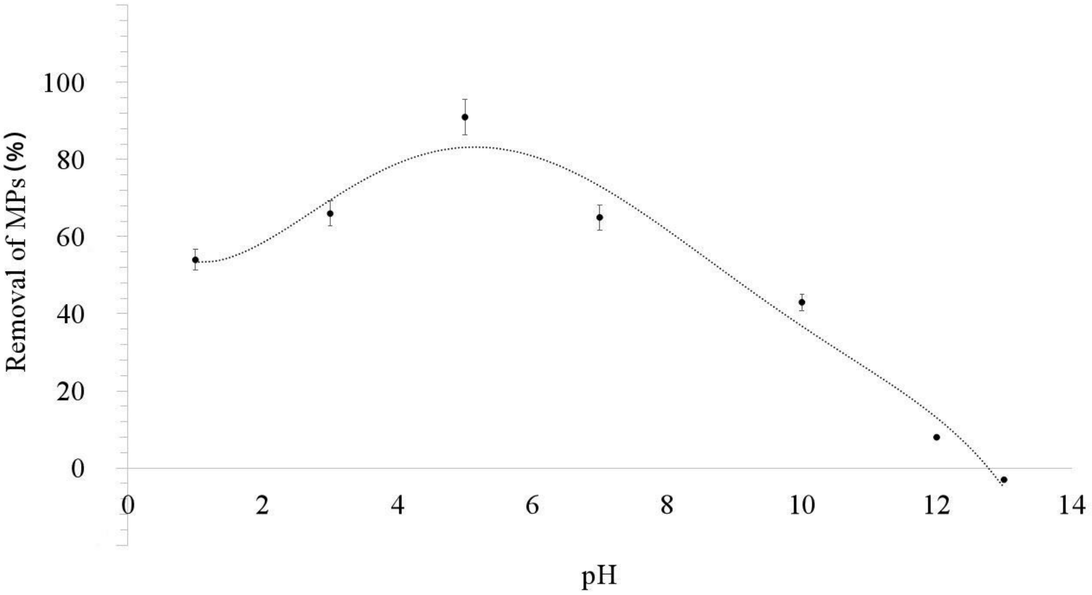


Figure 5. 3 Effect of coagulation pH on 100 µm PS beads' removal in spiked Regents Park pond water.

5.3.4 Effect of sedimentation time on the removal of PS MPs

After flocculation, sufficient sedimentation time will allow the suspended flocs to completely settle. This will minimize errors in the measurement of MPs because if smaller flocs were floating in the water, these could have been left in suspension and not sampled for MP counting with microscopy. Past studies trying to clarify kaolin (with density 2.6 g/cm^3 and particle size: 0.4 – 0.75 μm) in drinking water treatment found that $Al_2(SO_4)_3$ coagulation with sedimentation time of 30 min was effective to remove the flocs (Domopoulou et al. 2015), which is similar to the results found here for MPs with density lower than kaolin.

In the specific conditions of this study (removal of 100 μm PS beads (3.4 mg Al/L, PS MPs 10 mg/L, pH 5, stirring speed 50 rpm (G = 23 s^{-1}), coagulation time 60 s, flocculation time 400 s) sedimentation time was gradually increased until 40 min. The percentage of MPs removal reached 98 % at 30 min under these conditions (see Figure 5.4). After that, increasing sedimentation time did not lead to improvements in the removal of the study beads.

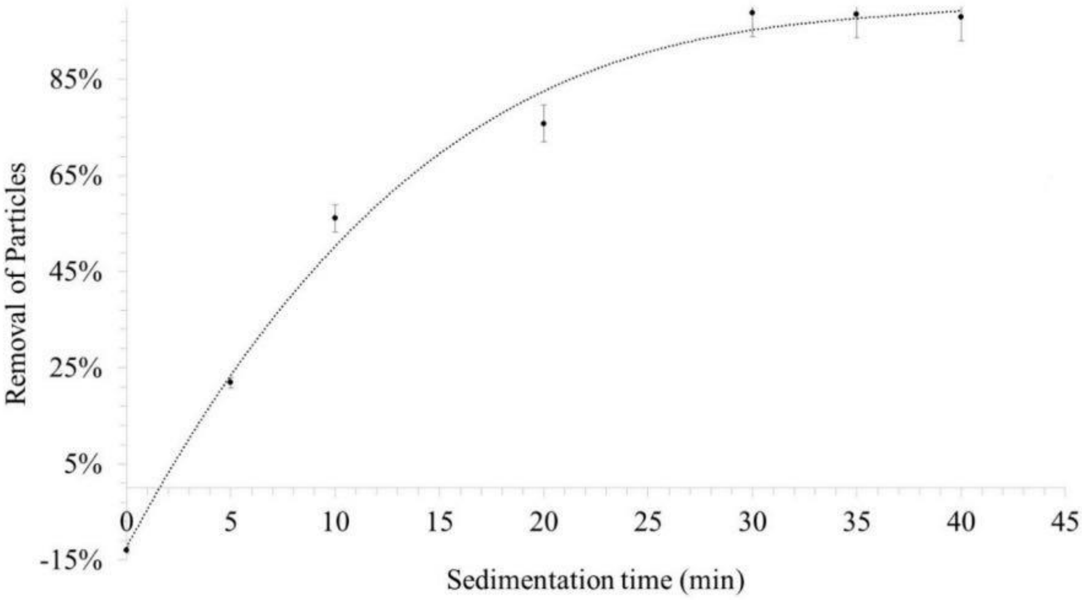


Figure 5. 4 Effect of sedimentation time on removal of 100 µm PS beads.

5.3.5 Effect of floc-breakage and regrowth on MPs' removal

In this study, when flocs broke after increasing the stirring speed, an additional dosage of coagulant (0.8 mg Al/L) led to the re-growth of flocs. These second flocs were larger than those before breakage (Figure 5.5). It is likely that, under the experiment conditions, additional MPs (which are hydrophobic and with a non-formal negative charge) coated the surface of the broken flocs (positively charged) and as a result, stronger and more interactions might have formed between the fragmented flocs. This interpretation agrees with a study that proposed that adsorption sites inside flocs can become exposed by the breakage and there is also a decrease in the Zeta potential on the surface of the flocs (Yu et al. 2010).

The phenomenon of floc-breakage and regrowth with the addition of coagulant improved the capacity for removing kaolin (Yu et al., 2010). In addition, floc removal after breakage/regrowth is dependent on the dosage of the additional coagulant.

However, MPs beads have very different physical and chemical properties than kaolin clay in terms of density, surface area, and surface chemistry. Therefore, the removal effect of reformed flocs and direct flocculation on PS MPs in the presence of kaolin needs to be investigated. To study floc breakage in detail, the average transmitted light intensity (Direct Current Value) and fluctuating root mean square (RMS) components of the transmitted light intensity were monitored. This was done with the PDA instrument. The ratio (RMS/DC), called the Flocculation Index (FI) provides a measure of particle aggregation (Yu et al. 2010). The FI value is related to the size and concentration of the suspended particles and it significantly increases as aggregation occurs and decreases when aggregates break (Figure 5.5). From Figure 5.5, the FI value when adding coagulant increased even more than the original FI value after regrowth, therefore, this indicates that more particles were included in the flocs.

The removal of the PS 100 μm beads after floc breakage and regrowth reached 94 % at 1000 s, and this is about 16 % larger than the traditional flocculation process (81 %) (Figure 5.5). Flocculation contact time throughout the floc breakage-regrowth process (i.e. 20 min) is therefore important concerning the collisions between flocs including the PS beads but it also suggests that in case of floc breakage in a water treatment plant, flocs containing MPs may potentially be re-grown before greater removal of MPs by sedimentation. This potential advantageous step should be further investigated, particularly considering the different densities, types, and sizes of MPs, water qualities, and coagulant dosages as these may affect the results. These will be investigated in future experiments supported with Zeta potential measurements.

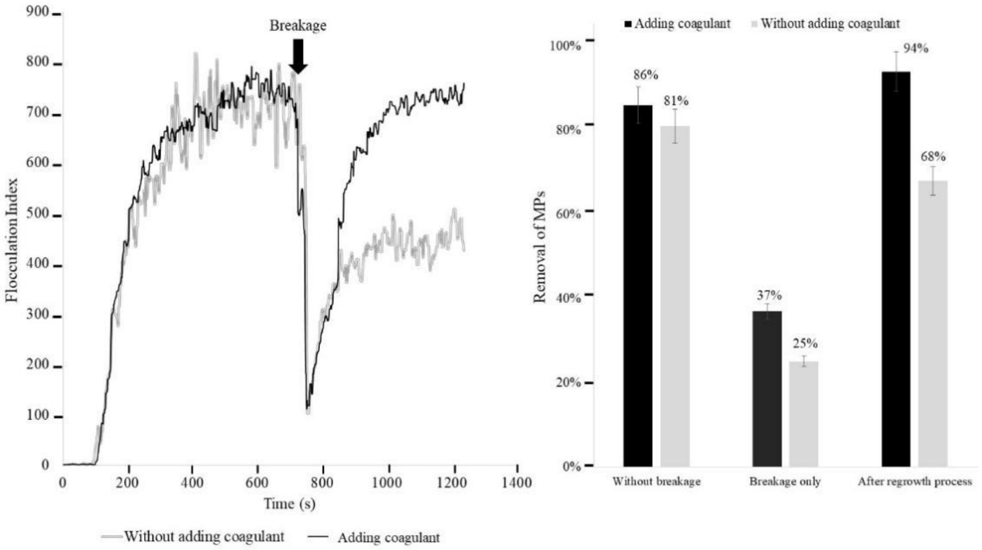


Figure 5. 5 Effect of floc-breakage on FI with and without additional coagulant

The current conditions for alum flocculation in drinking water treatment plants are 40 rpm flocculation for 10 min, sedimentation for 20 min, and pH ~ 6 before coagulation (Ma et al. 2019a; Combatt et al. 2020; Cardoso Valverde et al. 2018). According to the results of this study, if the stirring rate is increased to the equivalent gradient of velocity (G = 23 s^{-1}), the settling velocity is modified to the equivalent time of 30 min at Jartest, and the pH before coagulation is adjusted to ~ 5, the effect of flocculation on low-density PS MPs will be their increased removal to 99 %. Adjusting the flocculation process however， will impact other suspended solids and pollutants and needs further study.

One drawback of the current study is that it used pristine PS beads that are readily available in the market. However, recent research suggests that beads with irregular shapes could have significantly different levels of toxicity and might interact with flocs in a slightly different manner compared to commercially available beads. Hence it is recommended to harvest MPs in the environment or water treatment when possible (Yokota and Marissa 2020). However, we opted for using commercially available MPs in order to have sufficient availability of the similar type of beads for the experiments planned in this work.

5.4 Conclusions

It is urgent to understand how to remove MPs in drinking and wastewater treatment given that these are an opportunity to reduce MPs' spread and protect the environment and humans. This study investigates the removal of low-density MPs during the flocculation process, which plays an important role in decreasing the turbidity of water and hence may be the key to removing MPs particles. This is a preliminary study that has screened the effect of the duration and stirring speeds in coagulation-flocculation and sedimentation when using a common coagulant for 100 μm low-density PS beads as a model. These MPs have been selected due to their toxicity and composition and size commonly found in effluents from clarifiers. The study on a single type of MP has allowed achieving greater detail in the removal conditions. The optimized coagulation-flocculation conditions found were 3.4 mg Al/L, pH 5, flocculation time 7 min, and precipitation time 30 min. Under these conditions, and when natural water was used, the percentage removals were 98.9 ± 0.94 %.

The breakage and regrowth process of flocs have been shown to enhance the removal of 100 μm low-density PS beads by flocculation when the additional dosage is applied. Although this study used PS (1.04-1.06 g/cm^3) as a model, these findings can potentially be applied for other hydrophobic MPs and MPs of similar density (e.g. PP (0.9 g/cm^3); PS (1.06 g/cm^3), Polyethylene (PE, 0.92 g/cm^3) and nylon (1.14 g/cm^3)). Further research on different sizes of the MPs is needed as well.

Given that, the re-flocculation process has not been maturely applied in the water treatment industry as an MPs target technology. This chapter points to considerations for the improvement of the drinking water flocculation treatment process in the future. This work confirms that coagulation-flocculation and sedimentation are important steps for the removal of MPs. Further chapters addressed how coagulation-flocculation-sedimentation conditions change over a wider variety of MPs; and how these optimal conditions for MPs will be affected in the presence of organic pollutants and other suspended particles will be discussed in the following chapters, as well as investigating wider types of raw water and give further insights of removal mechanisms by monitoring the change of Zeta potential of flocs under different conditions.

CHAPTER 6 STUDY ON THE EFFECT OF HIGH-EFFICIENCY COAGULANTS IN REMOVING MPs

From Chapter 5, it can be inferred that coagulation-flocculation and sedimentation hold great potential for the treatment of MPs. This chapter will focus on the impact of various coagulants, types and sizes of MPs, and different reaction conditions on the removal of MPs.

In this chapter, the effectiveness of coagulation-flocculation and sedimentation as a potential method for MP treatment will be further explored. The impact of different types of coagulants, as well as the type and size of MPs, will also be examined. Additionally, the effect of different reaction conditions, such as pH and temperature, on the removal of MPs will be analysed. By investigating these factors, a more comprehensive understanding of the potential of coagulation-flocculation and sedimentation for MP removal can be obtained.

6.1 Introduction

It is of critical importance to study the treatment of MPs by different coagulants, as they produce different treatment performance. By studying the treatment of MPs by different coagulants, the most effective treatment condition can be found, and the treatment efficiency can be improved. Through the literature review in Chapter 2, the most effective coagulant can be found to make MPs easy to separate and treat. Currently, coagulants used to treat MPs include biological coagulants (such as yeast, starch), chemical coagulants (e.g. PAM, polymers, PVC), composite coagulants (mixtures of biological and chemical coagulants), biological polymers (e.g. biological gels, biological polymers), and other coagulants e.g. minerals, organic acids) (Zhang et al., 2020b; Wang et al., 2021; Ma et al., 2019). These coagulants have their own characteristics and need to be considered in terms of environmental safety and economy when selecting.

Perren et al. (2018) studied the removal of MP by flocculation and then sedimentation. Both studies reported a removal rate of over 90% after treatment with ferric chloride, ferrous sulphate or iron electrode flocculation. In addition, two recent studies on the removal of MP in synthetic drinking water matrix using iron and aluminium coagulants reported a removal rate of 17% and 36% for MP after treatment with ferric chloride and aluminium chloride, respectively (Ma et al., 2019a, 2019b). In all these studies, except for Perren et al., MP quantification was performed by weight analysis (2018), who calculated MP after filtration.

It is also important to study the impact of different types of MPs on flocculation treatment effects, as different physical, chemical and surface properties of MPs may affect the effect of coagulants. If the research results show that a coagulant is more effective in treating certain MPs, then this coagulant may become the preferred option for treating such MPs in the future. In addition, studying the impact of different MPs on flocculation treatment effects also helps to better understand the characteristics of MPs and the mechanism of flocculation treatment, providing more scientific support for future follow-up research.

It is important to study the impact of different sizes of MPs on flocculation treatment because this can help one evaluate its effectiveness, improve treatment conditions, understand the impact of MPs on the environment, and protect the environment. Therefore, studying this impact is important for better handling of MPs.

Furthermore, MPs may ultimately enter the food chain, and the size of MPs rather than their shape is the key factor affecting their performance and transformation in WWTPs (Lehtiniemi et al., 2018). Thus, highlighting the size of MPs is very important. According to a study by Zhang et al. (2021), MPs (MPs) smaller than 1 mm were found to be present in 68.5-85.7% of inflow samples and 73.2-89.3% of outflow samples from a wastewater treatment plant. As primary MPs are crushed (physical, chemical, and biological processes) into secondary MPs, the size of MPs decreases (Magni et al., 2019). Smaller MP particles are more easily ingested by phytoplankton, filter feeders (such as oysters, clams, and mussels), and fish, thereby causing a range of toxic effects on these organisms (Qiao et al., 2019). Therefore, studying the size of MPs, especially smaller sizes (less than 1 mm), can have a guiding significance for subsequent MP biotoxicity research and environmental transformation research.

Therefore, this chapter focuses on the impact of different types of MPs, different sizes of MPs, different aquatic environments, and different coagulants on the effectiveness of MP treatment based on the previous chapters. Through comparison, the most effective flocculation method for MP treatment will be selected.

6.2 Materials and methods

6.2.1 Comparison results of coagulants

The MPs preparation methods and jar test method are detailed in Section 4.4, and the PAM was added with PAC. The counting method for counting MPs before and after treatment are detailed in Chapter 3. The materials used are listed in Section 4.2. The water sources used were tap water (pH 7.7±0.1; turbidity: 0.2±0.1 NTU; UV-254, 0.177±0.001), Regent's park water (pH 6.9±0.1; turbidity: 0.8±0.1 NTU; UV-254, 0.559±0.001) and Thames river water (pH 7.9±0.1; turbidity: 1.9±0.1 NTU; UV-254, 0.863±0.001).

6.2.2 Effect of MP size on removal efficiency

For sample preparation and coagulation, flocculation and sedimentation methods are detailed in Section 4.2 and Section 4.4. For MPs smaller than 100 μm, the counting method was flow cytometry described in Chapter 3, and for MPs larger than 100 μm, the counting method was manual counting by microscope as in Section 4.3. The materials are listed under materials in Section 4.2.

6.2.3 Determination of reaction conditions and removal efficiency of different MPs

By changing the pH (5-11), fast stirring speed (180-280 rpm), fast stirring time (0.5-2 min), slow stirring speed (30-50 rpm), slow stirring time (10-20 min) and sedimentation time (20-40 min), the best reaction conditions were found. The MPs spiked natural water sample preparation and coagulation, flocculation and sedimentation methods are detailed in Section 4.4. MP counting by flow cytometry is detailed in Section 3.2. All materials are listed in Section 4.2.

6.2.4 Application in natural water and tap water, and comparison with current industrial treatment conditions

The aim of this test is to compare the efficiency between the current industrial condition (pH=7 (before adding PAC), 200 rpm for 1 min and 35 rpm for 15 min and sedimentation for 30 min) and the selected conditions in this thesis. The MPs spiked tap water sample and spiked natural water sample preparation and coagulation, flocculation and sedimentation methods are detailed in Section 4.4. MP counting by flow cytometry is detailed in Section 3.2. All materials are listed in Section 4.2.

6.3 Results and discussions

6.3.1 Effect of type of coagulant on MP removal

Figure 6.1 and Figure 6.2 compare the efficiency of four coagulants in removing particles from natural water with a PS concentration of 5 mg/L and particle size of 100 μm. In Figure 1, the results are shown without adding PAM, while in Figure 2, the results are shown with the addition of 5 mg/L PAM. Without PAM, PAC has the highest removal rate, with 97.5% of particles removed at a concentration of 0.4 mmol/L. Aluminium Sulphate has a removal rate of 67.2% at a concentration of 0.2 mmol/L, while Ferric Chloride and polyferric sulphate (PFS) have MP removal rates of 48.5% and 71.4% at the same concentration, respectively. These results are consistent with those reported by previous studies. For example, Liu et al. (2017) found that PAC was the most effective coagulant for the removal of MPs from wastewater, with a removal efficiency of 96.4%.

With the addition of PAM, the MP removal rate for all four coagulants increases. PAC still has the highest removal rate, with 98.1% of particles removed at a concentration of 0.4 mmol/L. Ferric Chloride and PFS also show an improvement in MP removal rates, with 94.9% and 100% of particles removed at a concentration of 0.6 mmol/L and 1.4 mmol/L, respectively. Aluminium Sulphate also shows an improvement, with a removal rate of 98.4% at a concentration of 0.6 mmol/L. These findings are consistent with those reported by Zhang et al. (2019), who found that the addition of PAM improved the effectiveness of coagulants in removing MPs from water.

Based on the results shown in Figures 6.1 and 6.2, it can be concluded that the addition of PAM improved the efficiency of all four coagulants in removing particles from natural water. Among the four coagulants, PAC has the highest removal rate, both without and with the addition of PAM, making it the best choice. These findings are consistent with those reported by other studies, which have shown PAC to be an effective coagulant for the removal of MPs from water (Li et al., 2019; Zhang et al., 2019).

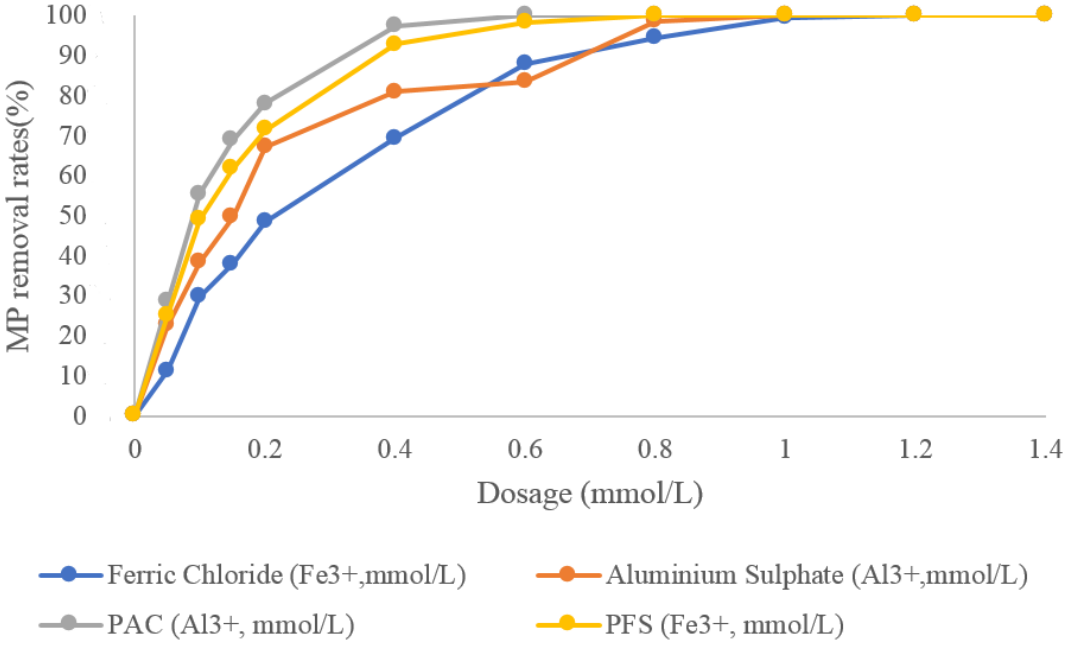


Figure 6. 1 Ferric chloride anhydrous, aluminium sulphate, PAC, PFS Dosage and efficiency (without PAM, PS 5 mg/L spiked tap water).

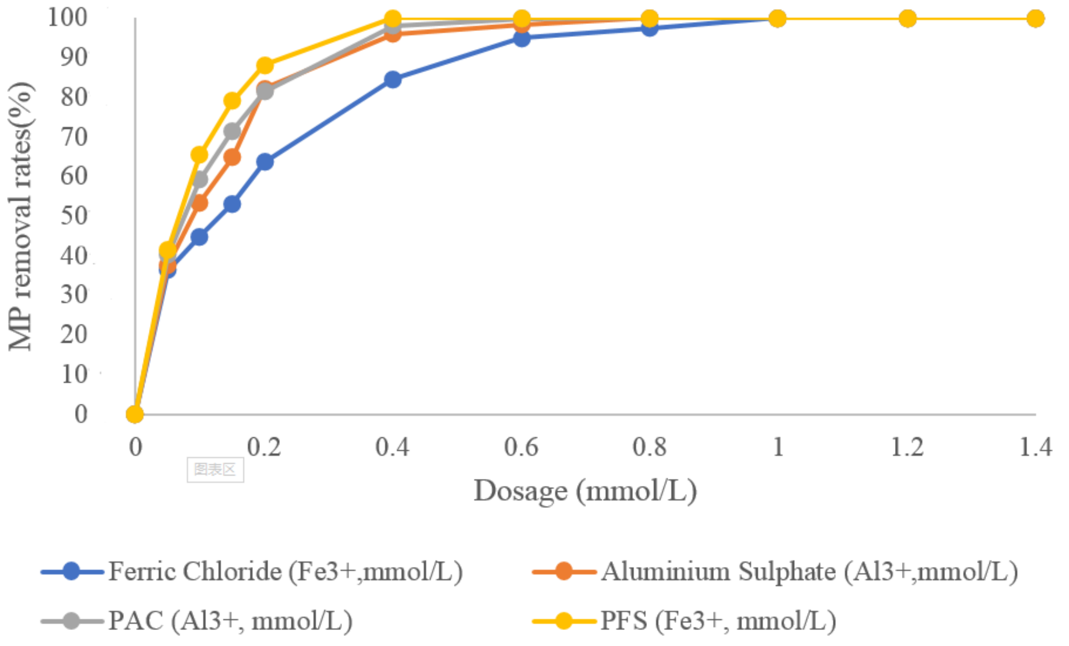


Figure 6. 2 Ferric chloride anhydrous, aluminium sulphate, PAC, PFS Dosage and efficiency (with PAM 5 mg/L, PS 5 mg/L spiked tap water)

Figure 6.3 shows that the removal rate of MPs (PS, 5 mg/L, 100 μm) in spiked

Regent’s Park Pond water increased as the concentration of PAM was increased. At a PAM concentration of 0 mg/L, MP removal rate was 87.1%. However, at a PAM concentration of 1 mg/L, the MP removal rate increased to 92.5%. This trend continued, with the removal rate reaching 95.8% at a PAM concentration of 2 mg/L and 100% at PAM concentrations of 3 mg/L and higher.

The enhanced removal rate of MPs by PAM is due to its ability to form large aggregates with the MPs, facilitating their removal from water through coagulation and flocculation processes. As the concentration of PAM increases, the size and density of the flocs increase, leading to a greater sedimentation and flotation of the MPs. In addition, larger flocs can increase the adsorption capacity of the coagulant, improving the removal of MPs by adsorption onto the flocs. Therefore, PAM is an effective coagulant for removing MPs from water, and its use in combination with other treatment methods offers a promising approach for reducing the release of MPs into the environment. For example, Wang et al. (2020) found that PAM was effective in removing MPs from secondary effluent, with a maximum removal efficiency of 98.2% achieved at a PAM dosage of 5 mg/L. The study suggested that PAM can facilitate the formation of large flocs and promote the removal of MPs by sedimentation and flotation. Similarly, another study by Zhang et al. (2020a) investigated the effectiveness of PAM in removing MPs from aqueous solutions. The study found that the optimal PAM concentration for MP removal varied depending on the initial concentration and size of the MPs. The results showed that the addition of PAM enhanced the removal of MPs by forming larger flocs and improving the adsorption capacity of the coagulant.

The results suggest that PAM can be an effective coagulant for removing MPs from water. However, it is important to note that the optimal conditions for removing MPs may vary depending on the specific characteristics of the water and the MPs present (Wang et al., 2020; Shi et al., 2019; Cai et al., 2021). These studies have found that factors such as the type and size of MPs, water chemistry, and the presence of other contaminants can affect the efficiency of various removal methods. Further studies were in next section to determine the most effective conditions for removing MPs in different water sources.

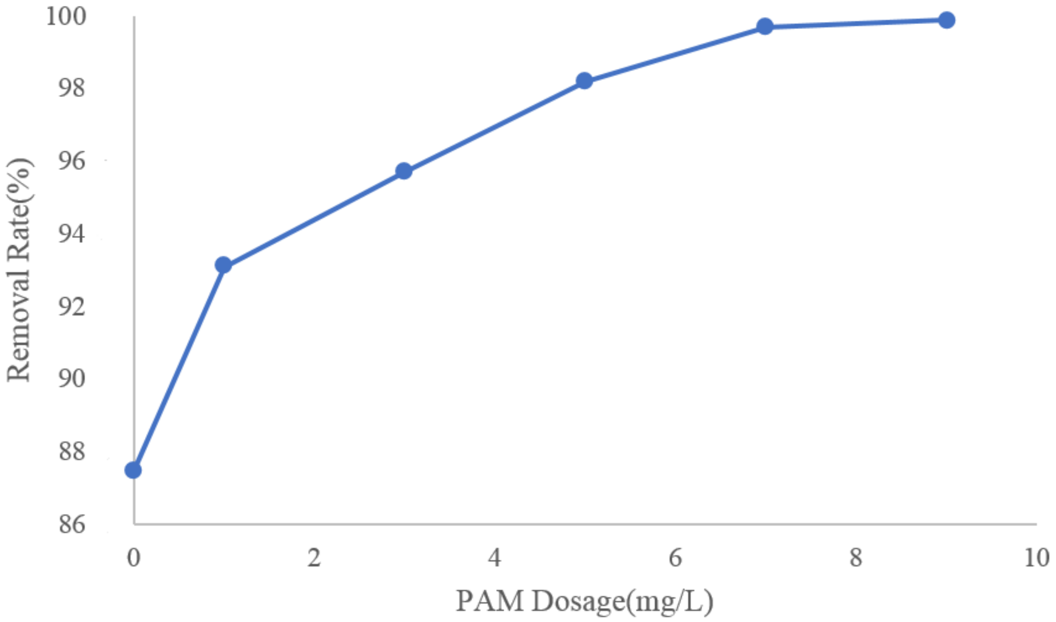


Figure 6. 3 Removal rate of PS 100 μm, 5 mg/L with different PAM dosage (PAC 0.4 mmol/L, pH=8 before adding PAC)

6.3.2 Effect of MP Size on Removal Efficiency

Table 6.1 shows the removal rate of four types of polymers (PVC, PE, PS, and PP) with different particle sizes (50-1000 μm) under a specific experimental setup. The removal rate is expressed as a percentage and indicates the degree to which the polymers are removed from the water sample.

From Table 6.1, it can be observed that the particle size has a significant impact on the removal rate of the polymers. As the particle size increases, the removal rate also increases for all four types of polymers. For example, PVC has a removal rate of 86.7% for a particle size of 50 μm, while it reaches 100% for particle sizes of 250 μm and larger. This trend is also observed for PE, PS, and PP.

Stokes number (Stk) is a crucial parameter used to describe the influence of particle inertia on hydrodynamic forces. The Stk value can be used to determine how much a particle's motion is influenced by inertial forces relative to viscous forces. The Stk is calculated using the following equation (Adams and Ghose, 2016):

where τp is the particle stopping time, τf is the fluid stopping time, ρp is the particle density, d is the particle diameter, υ is the fluid velocity, u is the particle velocity, μ is the fluid dynamic viscosity, and Lf is the characteristic length of the fluid, such as the pipe diameter or flow region width.

Larger particles have a higher Stk value and are more influenced by inertial forces, while smaller particles have a lower Stk value and are more influenced by viscous forces. This effect has been observed in various studies, including a study by Kooi et al. (2016) that found larger plastic particles were more likely to sink and deposit in sediment, while smaller particles remained suspended in water.

The sedimentation process is driven by gravity, causing suspended particles in water to settle out. Particle size and surface area are key factors that affect the rate of removal by sedimentation. Specifically, the findings of the study suggest that larger particles are removed at a higher rate due to their increased weight, which allows them to settle faster. Moreover, the larger surface area of these particles also facilitates their capture by the sedimentation process, leading to more efficient removal. In general, larger particles have a higher probability of collision with the sedimentation tank walls or other particles (Li et al., 2020), which increases the likelihood of their removal from the water sample. The results also suggest that the hydrophobicity of the polymers and their density may play a role in determining the removal rate. Polymers with higher density and hydrophobicity tend to have higher removal rates, which is further discussed in Section 6.3.3.

Table 6. 1 Removal rates of four types of polymers (PVC, PE, PS, and PP) with different particle sizes (50-1000 µm)

Polymer	Density	Hydrophobicity	Size (um)	50	75	100	150	250	500	800	1000
PVC	1.38	Hydrophobic	Removal rate (%)	86.7	97.5	99.1	99.7	100	100	100	100
PE	0.97	Hydrophobic	Removal rate (%)	69.5	81.4	97	97.7	98.5	100	100	100
PS	1.06	Hydrophobic	Removal rate (%)	73.5	90.1	98.2	99%	100	100	100	100
PP	0.92	Hydrophobic	Removal rate (%)	49.5	81	95.6	98.8	100	100	100	100

6.3.3 Determination of reaction conditions and removal efficiency of different MPs

Figure 6.4 shows the results of the study on the removal of different types of MPs from spiked Regent's Park Pond water. The results are presented for different conditions, including the pH of the water (before adding PAC), the rapid stirring speed, the rapid stirring time, and the slow stirring speed.

At pH levels 5, 6, and 10, the removal rate of PVC (68.7% - 82.3%), PE (41.7% - 51.2%), PS (63.7% - 78.8%), and PP (34.5% - 45.8%) is lower compared to when the pH is 7 or 8. PE and PP show the lowest removal rates among the four hydrophobic MPs, with PE having the lowest removal rate at pH 5, 6, and 10 (38.9%). PU and PA, which are hydrophilic, have higher removal rates compared to the hydrophobic MPs, with PA having the highest removal rate among all the MPs (83.3% - 97.1%). The removal rate of the MPs is influenced by the pH level, with a pH of 8 being optimal for removal. The hydrophilic MPs show higher removal rates compared to the hydrophobic MPs, with PA having the highest removal rate overall (83.3% - 97.1%).

The differences in removal rates between hydrophilic and hydrophobic MPs can be attributed to the nature of the coagulant used in the process. Coagulation involves the use of chemicals to destabilize and aggregate the MPs, forming larger particles that can be more easily removed by sedimentation or filtration. The coagulant used in the study by Li et al. (2018) was a dual coagulant comprising of PAC and polymer. Hydrophilic MPs are more easily destabilized by the dual coagulant, resulting in a higher removal rate. Additionally, the optimal pH for the removal of MPs was found to be 8, which can be explained by the fact that the coagulant works best at this pH level, resulting in more efficient removal of the MPs. To express the mechanism, the pH PHREEQC modelling is detailed in Section 7.10.

This is consistent with previous studies that have found that hydrophilic MPs are generally more easily removed than hydrophobic MPs (Avio et al., 2017; Chen et al., 2017). Hydrophobicity, which refers to the tendency of a material to repel water, can make it more difficult for MPs to be destabilized and aggregated by coagulants, thus reducing their removal efficiency (Napper et al., 2019; Zhang et al., 2021).

At rapid stirring speeds (i.e. coagulation) of 180 rpm, 200 rpm, and 260 rpm, the removal rate of PVC, PE, PS, and PP is lower compared to when the rapid stirring speed is 220 rpm, 240 rpm, or 280 rpm. PE shows the lowest removal rate among the four hydrophobic MPs, with the lowest removal rate observed at rapid stirring speeds of 180 rpm and 260 rpm (32.4% and 46.8%, respectively). PU and PA, which are hydrophilic, have higher removal rates compared to the hydrophobic MPs, with PA having the highest removal rate among all the MPs at rapid stirring speeds of 220 rpm and 280 rpm (97.6% and 97.6%, respectively). The removal rate of the MPs is influenced by the rapid stirring speed, with higher removal rates observed at higher rapid stirring speeds. The best condition for removal is at a rapid stirring speed of 240 rpm.

The differences in removal rates between hydrophilic and hydrophobic MPs can be attributed to the mechanisms of the coagulation process.

Rapid stirring speeds increase turbulence in the solution due to the disruptive and chaotic nature of the fluid flow. When the stirring speed is intensified, it generates turbulent eddies and vortices within the solution. These turbulent motions arise from the rapid and irregular movement of the fluid, leading to enhanced mixing and dispersion of particles (Wang et al., 2021). Also, this turbulence, characterized by chaotic and irregular fluid motion, enhances the collision and contact between the coagulant and the MPs. As a result, the MP particles are more effectively destabilized and aggregated into larger flocs or clumps. This increased collision and attachment between the coagulant particles and the MPs facilitate the successful removal of MPs from the solution. Recent research, exemplified by the study conducted by Wang et al. (2021), has shown that turbulence significantly improves the efficiency and effectiveness of the coagulation process in removing MPs. By promoting enhanced mixing and interaction, turbulence plays a critical role in enhancing the overall efficacy of MP removal during coagulation. Moreover, as rapid stirring speeds increase, the energy input increases, resulting in higher collision frequency and contact efficiency between the coagulant and the MPs (Liu et al., 2018). The optimal rapid stirring speed for MP removal was found to be 240 rpm, which can be explained by the fact that this rapid stirring speed provides a balance between the energy input and the aggregation efficiency of the coagulant, resulting in more efficient removal of the MPs.

The removal rate of the MPs increases with the increase in rapid stirring time, with the highest removal rate observed at 1 min. PVC and PE, which are hydrophobic, have lower removal rates compared to the hydrophilic MPs, with PE showing the lowest removal rate among the four hydrophobic MPs (67.1%). PU and PA, which are hydrophilic, have higher removal rates compared to the hydrophobic MPs, with PA having the highest removal rate among all the MPs.

The removal rate of the MPs varies with the slow stirring speed (i.e. flocculation), with higher removal rates observed at higher slow stirring speeds. The best condition was found at 35 rpm. PVC and PS have higher removal rates compared to PE, PP, PU, and PA, with PVC having the highest removal rate at slow stirring speeds of 35 rpm and 50 rpm, with removal rates of 98.8% and 54.1%, respectively. PU and PA, which are hydrophilic, have higher removal rates compared to the hydrophobic MPs, with PA having the highest removal rate among all the MPs at slow stirring speeds of 35 rpm and 50 rpm, with removal rates of 98.5% and 66.2%, respectively.

The mechanisms underlying the observed effects of slow stirring speed on MP removal involve the flocculation process. During flocculation, the slow stirring speed facilitates the formation of flocs, which are larger and more easily removable than individual MPs. The higher the slow stirring speed, the more effective the floc formation process, resulting in higher removal rates (Wang et al., 2021). Moreover, the differences in removal rates among different types of MPs can be attributed to their physicochemical properties, which affect their interactions with the coagulant and the flocculation process. Hydrophilic MPs are more easily destabilized and aggregated by coagulants, resulting in more efficient flocculation and removal (Zou et al., 2019).

The removal rate of the MPs varies with the stirring time, with higher removal rates observed at longer stirring times. The best condition was found at 13 min (98.5% removal rate for PVC, 94.9% for PE, 93.0% for PS, 92.9% for PP, 95.2% for PU, and 96.3% for PA). PVC, PS, and PA have higher removal rates compared to PE, PP, and

PU, with PVC having the highest removal rate at stirring times of 13 min, 15 min, and 20 min (98.5%, 73.1%, and 41.2%, respectively). PU and PA, which are hydrophilic, have higher removal rates compared to the hydrophobic MPs, with PA having the highest removal rate among all the MPs at stirring times of 13 min and 15 min (96.3% and 75.8%, respectively). The removal rate of the MPs is influenced by the stirring time, with higher removal rates observed at longer stirring times. It can be attributed to the increased collision and contact of coagulants with the MPs as the stirring time is prolonged. The longer the stirring time, the more contact and collision between the coagulants and the MPs, leading to more effective destabilization and aggregation of the particles. The larger and heavier flocs formed by the coagulants are more easily separated from the solution by sedimentation or filtration, resulting in higher removal rates (Gao et al., 2019).

The removal rate of the MPs varies with the sedimentation time, with higher removal rates observed at longer sedimentation times. PVC, PS, and PA have higher removal rates compared to PE, PP, and PU, with PVC having the highest removal rate at sedimentation times of 25 min (98.1%), 30 min (98.3%), and 40 min (98.3%). PA has the highest removal rate among all the MPs at sedimentation times of 30 min (99.1%) and 40 min (93.1%). The hydrophilic MPs, PU and PA, have higher removal rates compared to the hydrophobic MPs. Among all the sedimentation times, 25 min was selected as the optimal condition. The mechanism behind the observed effects of sedimentation time on MP removal can be attributed to the gravitational settling of the particles. As the sedimentation time is prolonged, the larger and heavier flocs formed by coagulation and flocculation settle down to the bottom of the solution due to gravity. During sedimentation, the MPs are trapped and incorporated within the flocs, which eventually settle down to the bottom of the container, resulting in their removal from the solution. The longer the sedimentation time, the more time the flocs have to settle down, leading to higher removal rates (Li et al., 2020; Wang et al., 2020).

In general, the hydrophobic MPs (PVC, PE, PS, PP) had lower removal rates than the hydrophilic MPs (PU, PA), while lower density MPs (PE, PS, PP) had lower removal rates than the higher density MPs (PVC, PU, PA). Additionally, the removal rates of the MPs were affected by the density, size, and concentration of the MPs, as well as the stirring speed, stirring time, and pH.

The best flocculation conditions for removing MPs from the water were pH=8 (before adding PAC), rapid stirring speed of 240 rpm for 1 minute, 35 rpm for 13 minutes, and sedimentation for 25 min. The study found that the removal rate of MPs was highest for PVC and PA, with removal rates of 94.8% and 97.1%, respectively, under the best flocculation conditions.

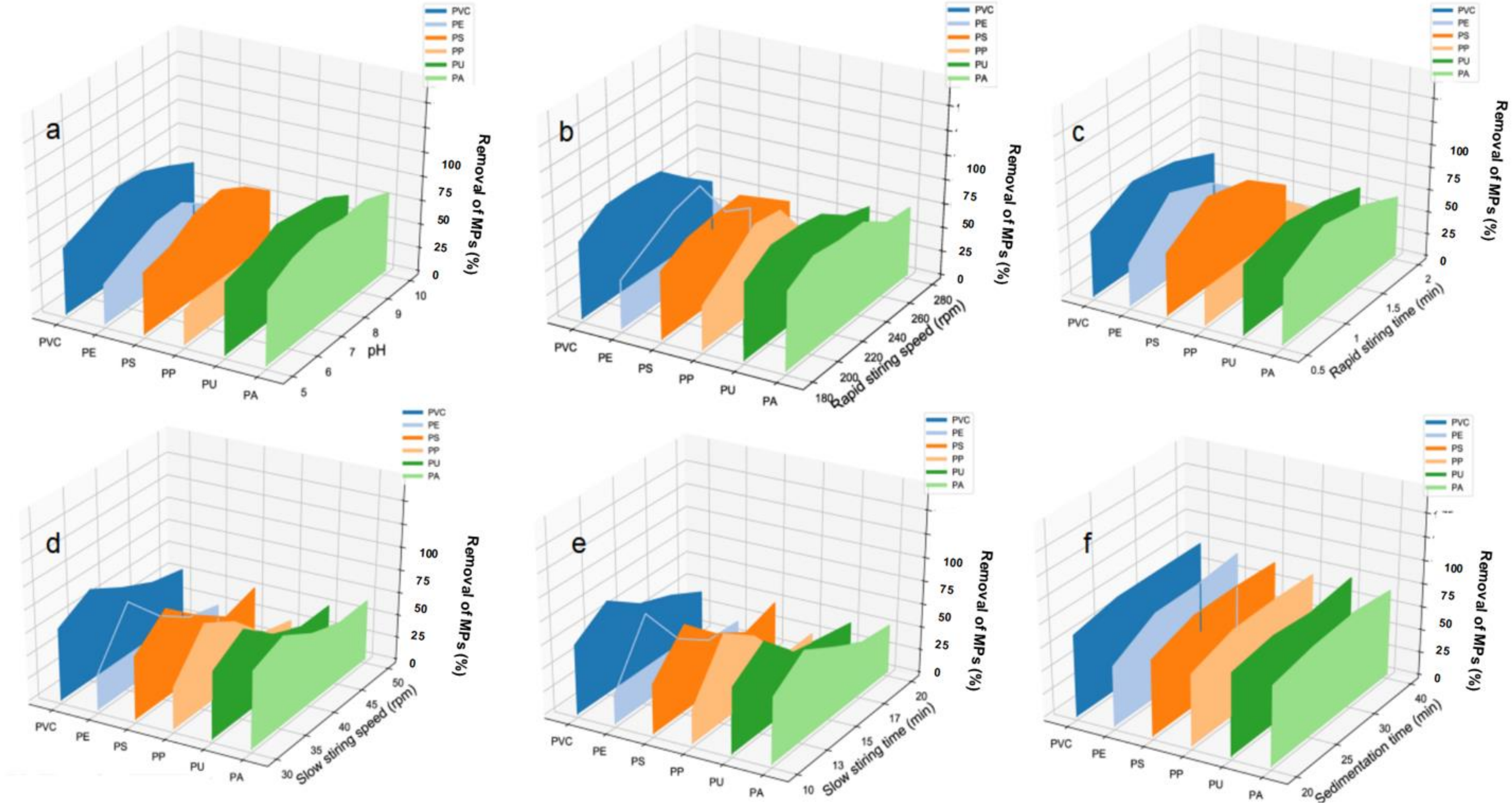

a
b
c
d
e
f
PVC
PE
PS
PP
PU
PA
Removal of MPs (%)
0
25
50
75
100
pH
5
6
7
8
9
10
Rapid stiring speed (rpm)
180
200
220
240
260
280
Rapid stiring time (min)
0.5
1
1.5
2
Slow stiring speed (rpm)
30
35
40
45
50
Slow stiring time (min)
10
13
15
17
20
Sedimentation time (min)
20
25
30
40

Figure 6. 4 Removal rates of different MPs under different conditions (a: The pH was set from 5-11 (before adding PAC). b: The rapid stirring speeds were set from 180-280. c: Rapid stirring times were set from 0.5 to 2 min. d: The slow stirring speeds were set from 30 rpm to 50 rpm. e: The slow stirring times were set from 10 to 20 min. f: The sedimentation times were set from 20 to 40 min.

6.3.4 Application of the optimal conditions in natural water and tap water, and comparison with current industrial treatment effects

6.3.4.1 Application the optimal conditions in natural water and tap water

Figure 6.5 provides data on the properties and removal rates of six different polymers: PVC, PE, PS, PP, PU, and PA. The data includes information on the density, hydrophilicity/hydrophobicity, size, and concentration of each polymer, as well as its removal rate in both natural water and tap water.

From Figure 6.5, the mixture removal rate for natural water is 97.1% and for tap water is 94.7%. Based on the data, PVC has the highest removal rate in both natural water and tap water, making it the most effective polymer for removing pollutants from water. PE has the lowest removal rate in tap water, indicating that it is less effective in removing pollutants from tap water compared to the other polymers.

The density of the polymers ranges from 0.92 g/cm^3 for PP to 1.38 g/cm^3 for PVC. All the polymers are hydrophobic, except for PU and PA, which are hydrophilic. The size of each polymer is 50 μm, and their concentration is 5 mg/L. The MP removal rate of each polymer in natural water ranges from 95.9% for PE to 97.5% for PA. The MP removal rate in tap water is lower, ranging from 90.8% for PE to 98.1% for PVC. The hydrophilicity/hydrophobicity of the polymers may play a role in their removal rate. Hydrophilic polymers, such as PU and PA, have a higher removal rate in natural water compared to hydrophobic polymers, such as PVC, PE, PS, and PP. The difficulty in destabilizing and aggregating MPs by coagulants may be due to the hydrophobic nature of the material, which is characterized by its tendency to repel water, and can ultimately result in lower removal efficiency. (Napper et al., 2019; Zhang et al., 2021). Moreover, the removal efficiency of PP and PE in natural water is significantly higher compared to tap water. This is primarily attributed to the presence of other particulate matter (e.g. natural organic matter) in natural water, which provides more opportunities for the attachment and aggregation of PP and PE particles.

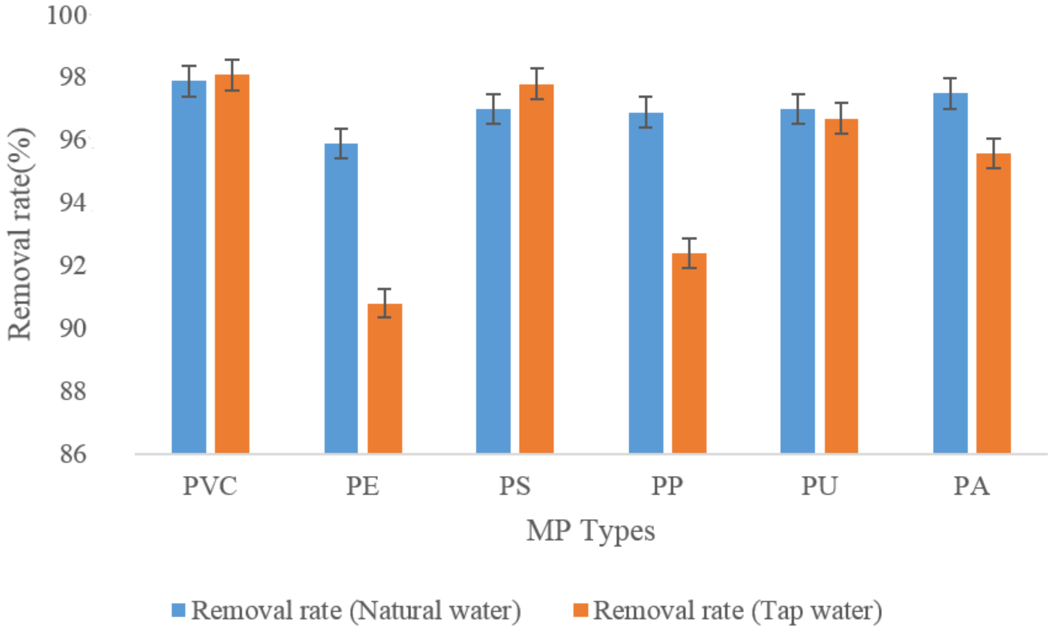


Figure 6. 5 Removal rate of different types of MPs in natural water and tap water (PAC 0.4 mmol/L, PAM 3 mg/L, and 800 mL Regent's Park Pond water and tap water were used respectively).

6.3.4.2 Comparison with current industrial treatment effects

Based on the results presented in Table 6.2, it appears that the commonly used coagulation-flocculation-sedimentation process in full-scale treatment works can remove MPs from water. However, it should be noted that not all MPs may be completely removed, and some may be discharged into receiving waters. Additionally, it is important to keep in mind that the efficiency of the process may vary depending on the specific conditions of each treatment plant, including the dosage of coagulant and the quality of the water being treated.

Comparing the common practice (pH 7, 200 rpm for 1 min and 35 rpm for 15 mins and sedimentation for 30 mins) with the best condition found in 6.3.3, it can be seen a higher removal rate for PVC (97.9% in natural water, 98.1% in tap water) for the latter and a removal rate of 94.4% in natural water and 96.1% in tap water for the first.

Similarly, the optimum condition found for the waters studied by this thesis (see table 6.2) showed a higher removal rate for PU (97.0% in natural water, 96.7% in tap water) compared to the current operation conditions used by the industry (94.0% in natural water and 95.5% in tap water).

For the other polymers such as PE, PS, PP, and PA, the MP removal rate was also higher compared to the current industrial operation conditions. It is important to note that the conditions used in the study may not be applicable to all treatment plants, as each plant may have unique operating conditions that impact the removal of MPs. Additionally, it is recommended to conduct further tests, such as sand filtration, to confirm the effectiveness of the coagulation-flocculation-sedimentation process in removing MPs.

In conclusion, the results show that the optimum conditions found for the specific water studied by this thesis has a higher overall removal rate for MPs compared to the current industrial method. This may be due to the difference in pH, mixing conditions, sedimentation time, and water quality characteristics. One possible recommendation based on the study's findings is that water treatment works should consider conducting jar tests to optimize their operating conditions for removing MPs.

Table 6. 2 Removal of MPs using the common practice conditions of coagulation-flocculation-sedimentation (PAC 0.4 mmol/L, PAM 3 mg/L, and 800-mL Regent's Park Pond water and tap water were used respectively. pH=7 (before adding PAC), 200 rpm for 1 min and 35 rpm for 15 min and sedimentation for 30 min). The values shown are the average from n= 3.

	PVC	PE	PS	PP	PU	PA
Density (g/cm^3)	1.38	0.97	1.06	0.92	1.21	1.31
Hydrophilic/Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophilic	Hydrophilic
Size (um)	50	50	50	50	50	50
Concentration (mg/L)	5	5	5	5	5	5
Removal rate in natural water %	94.4%	69.1%	88.5%	64.8%	94.0%	96.7%
Removal rate in Tap water %	96.1%	78.9%	92.7%	83.5%	95.5%	97.3%

6.4 Conclusion

This study indicates that microbeads with higher density are more easily flocculated, such as PVC with a density of 1.38 g/cm^3, meaning they are more likely to settle at the bottom of water bodies and have a greater impact on marine life. Thus, it is suggested to restrict the production and use of high-density MPs to make sure they are removed from drinking water by the conventional coagulation-flocculation-sedimentation process.

Meanwhile, the size and shape of MPs have a profound impact. The large size of MPs makes them more susceptible to hydrodynamic forces (section 6.3.2), causing them to flocculate and eventually settle at the bottom of the sedimentation tank. If the size of the MPs is larger, such as over 250 μm, their coagulation, flocculation and sedimentation rate from water treatment plants will be higher. Removing smaller MPs is more challenging. Smaller MPs are often more difficult to capture and remove, making their hard to be removed from treatment plants. Given this, conducting research and developing technology targeting smaller MPs is especially important. At the same time, it is also necessary to strengthen the management of production and use of MPs to restrict their entry into the environment and impact on ecological balance.

Comparing different types of coagulants is extremely important in the research, which can help us better understand which coagulant is more suitable for treating MP pollution. For example, ferric chloride anhydrous is an effective coagulant with strong coagulation and gelation properties, which can effectively aggregate MPs together, making them easy to capture and remove. Aluminium sulphate is another commonly used coagulant with high flocculation efficiency and low cost. PAC and PFS are two other different coagulants with some application prospects. Their use may be influenced by the properties of MPs (such as density, size, etc.), water body properties (such as pH, concentration, etc.), and environmental factors (such as temperature, suspended solids concentration, etc.). Therefore, by considering all these factors, the choice of which coagulant is most effective was verified in this experiment. In treating MP pollution, the use of coagulant PAM is also very important. As a synthetic coagulant, PAM has good coagulation effect and efficient flocculation effect, which can help improve the sedimentation rate of MPs, making them easier to remove. Therefore, the study may have compared the use of PAM and without PAM to evaluate its impact on treating MP pollution.

In the study, by comparing different doses of PAC and PAM, the best treatment method was obtained. Under the best dose (0.4 mmol/L PAC and 3 mg/L PAM), further experiments showed that the best flocculation condition was pH=8 (before adding PAC), 240 rpm for 1 min, 35 rpm for 13 min, and sedimentation for 25 min. In this case, the removal rate of MPs from the natural water samples can reach over 95%, and the removal rate of MP mixtures can reach 97.1%.

In general, in practical applications, coagulants should be used flexibly according to specific circumstances, taking into account all factors to achieve the best results.

CHAPTER 7 INSIGHTS ON MP REMOVAL AND INTERACTIONS DURING COAGULATION-FLOCCULATION

Based on the findings from Chapters 5 and 6, coagulation-flocculation and sedimentation have been identified as effective methods for removing MPs, especially when utilizing PAC and PAM. However, the effectiveness of these methods may be influenced by different reaction conditions present in different aquatic environments. Therefore, it is essential to investigate the mechanisms of the reactions in order to gain a deeper understanding of the factors that affect the removal efficiency of MPs.

This chapter discusses a wide range of topics, including the use of characterization methods, experimental instruments, and theoretical frameworks for understanding the properties of MPs and their interactions with different coagulants. To identify the most effective MP removal methods, the chapter uses various characterization methods such as microscopes, SEM-EDS, and FTIR, which are used to study the physical and chemical properties of MPs. TOC analysis is also used to determine the level of organic pollutants in the water samples.

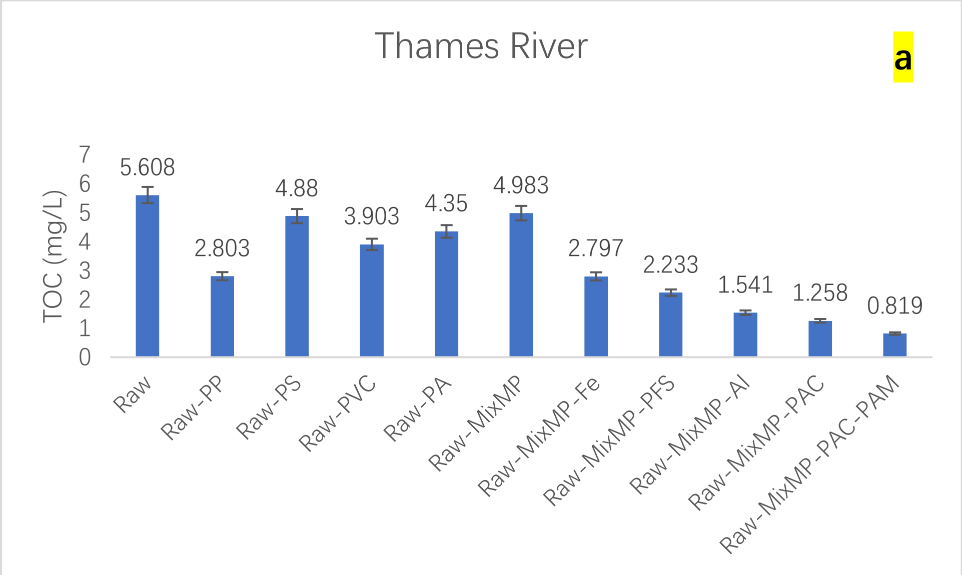
Competitive reaction studies are also discussed in the chapter, which involves comparing the performance of a specific removal agent against other common adsorbents or coagulants in water. By doing so, researchers can identify the most effective removal agents and understand their mechanisms of action. The chapter also uses the XDLVO model to provide a theoretical framework for understanding the interaction between MPs and removal agents. This theory allows researchers to design more effective removal strategies that take into account the forces of attraction and repulsion between MPs and removal agents. The chapter further highlights the use of pH PHREEQC modelling and DFT modelling for understanding the mechanisms of MP removal. These modelling techniques provide a detailed understanding of the factors influencing the removal of MPs, including the role of pH and the mechanism. Finally, the chapter highlights practical applications of MP removal, including commercial products and microfibers.

Overall, the chapter used a variety of complementary characterization methods, experimental instruments, and models to address key challenges of MP removal. The findings and conclusions from this chapter could provide useful information for further research and development of more effective MP removal strategies.

7.1 TOC Levels affected by MPs and coagulants in Thames River and Regent’s Park Pond

Water-soluble organic substances are another pressing issue that may have adverse effects on the water environment due to complex chemical reactions in nature. These organic substances, such as oestrogens and pharmaceuticals, may be present in wastewater from human activities and can pose a threat to water quality (Gao et al., 2021).

Monitoring Total Organic Carbon (TOC) is an important parameter for measuring the total amount of organic matter in water, so it gives an overview of the state of the water. Its measurement includes a wide range of organic contaminants, although these are typically at part per billion level and do not influence TOC much. Due to the increasing water pollution caused by human activities, including the increase of pollutants such as MPs and water-soluble organic matter, monitoring TOC supports our understanding of the effect of new water treatments proposed on the quality of water. TOC monitoring can help evaluate the quality and degree of water pollution and provide important data support for developing appropriate water treatment strategies (Bai et al., 2021). By understanding the source and amount of pollutants present in water, measures can be taken to prevent further contamination and to ensure that clean water is available for future generations (Bauer et al., 2021).



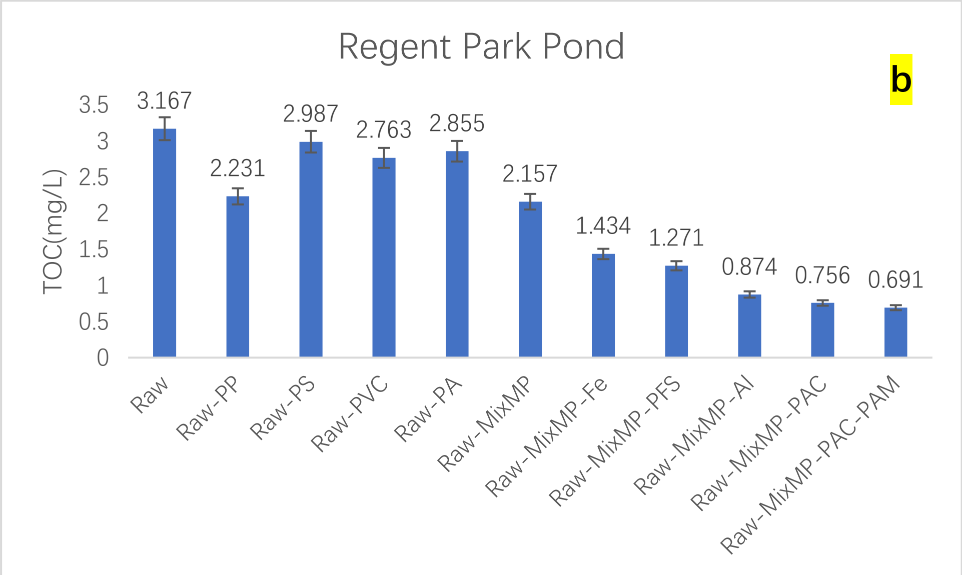


Figure 7. 1 TOC levels for different coagulation-flocculation and sedimentation treated water samples collected from Thames River (a) and Regent's Park Pond water (b) (MPs 5 mg/L, coagulants 0.4 mmol/L, PAM 3 mg/L, and 800 mL Regent's Park Pond water and Thames River water were used respectively.

Figure 7.1 presents the TOC levels for different water samples collected from Thames River and Regent's Park Pond water (May, 2022). Figure 7.1a shows the TOC levels for various samples of Thames River raw water and respective addition of MPs, including different types of MPs (PP, PS, PVC, PA, and mixed MPs), as well as various coagulants (PAC, Fe, PFS, Al, PAC-PAM). Figure 7.1b represents the TOC levels for various samples of Regent's Park Pond raw water. The TOC method is detailed in Section 3.8, the coagulation-flocculation and sedimentation method is detailed in Section 3.4, and all materials are listed in section 3.2.

The TOC levels in the Thames River samples ranged from 5.608 mg/L (in the raw sample) to 0.819 mg/L (in the sample with mixed MPs and PAC-PAM introduced in our coagulation-flocculation studies). The TOC levels in the Regent's Park Pond samples ranged from 3.167 mg/L (in the raw sample) to 0.691 mg/L (in the sample with mixed MPs and treated by PAC and PAM). The results show that the presence of MPs and coagulants in the water samples can affect the TOC levels measured. The lowest TOC levels were observed in the samples with mixed MPs and PAC-PAM in both Thames River and Regent's Park Pond waters. The addition of different types of MPs had effects on the TOC levels, with all types of MPs leading to a decrease in the TOC levels. The addition of the PAC-PAM combination had the greatest effect on reducing TOC levels in both raw water samples. These results suggests that the use of coagulants can help reduce the organic matter in the water. Also, MPs can adsorb dissolved organic matter, leading to a reduction in the amount of TOC present in the water. This phenomenon has been widely documented in scientific literature. For example, a study by Koelmans et al. (2014) found that MPs in water can cause a decrease in the concentration of TOC by up to 1.7 times. Another study by Cai et al. (2018) similarly observed that MPs can effectively adsorb TOC in water, resulting in a decrease in TOC concentration. Therefore, it is important to consider the potential impact of MPs on water quality and the environment.

Compared to other studies, the findings of this study are consistent with previous research on the impact of MPs and coagulants on water quality. For example, a study by Sun et al. (2020) found that the addition of PAC and PAM coagulants effectively reduced the levels of organic matter, turbidity, and microorganisms in river water. Similarly, a study by Zhang et al. (2020) showed that the use of MPs as a coagulant aid could effectively enhance the removal of turbidity and organic matter in water treatment. However, both studies also highlighted the potential environmental risks associated with the use of MPs, including the release of MPs into the environment during the treatment process. Another study by Li et al. (2021) investigated the effects of different types of MPs on the removal of organic matter in water treatment and found that the presence of certain types of MPs, such as PS, can interfere with the coagulation process and reduce the effectiveness of the treatment. This is consistent with the mixed effects of different types of MPs observed in the present study. The authors also emphasized the need for further research on the environmental impacts of MPs in water treatment, including the potential accumulation of MPs in sludge and their release into the environment.

7.2 Zeta potential of MPs and its impact on coagulation for their removal from aquatic environments

Zeta potential is a key parameter for understanding the stability of suspended MPs in aquatic environments. It is a measure of the electrokinetic potential of particles in suspension, and it can indicate the stability of colloidal systems. The Zeta potential of MPs can affect their aggregation, dispersion, and deposition in the water column. Studies have shown that the Zeta potential of MPs is strongly influenced by their surface charge, size, and composition (Szymczyk and Jamróz, 2020). Understanding the Zeta potential of MPs can help us better predict their fate and transport in aquatic environments.

MPs are a growing concern for the environment and public health due to their persistence and potential harmful effects. They can adsorb pollutants and act as a vector for their transport in aquatic environments. In recent years, coagulation has been proposed as an effective method for removing MPs from water. Coagulants such as PAC can neutralize the surface charge of MPs and facilitate their removal by aggregation and sedimentation (Liu et al., 2020).

The interaction between coagulants and MPs in water treatment has received increasing attention. It has been shown that the type and dosage of coagulants can affect the removal efficiency of MPs (Zhang et al., 2020). For example, PAM has been reported to enhance the removal of MPs by increasing the size and density of the aggregates (Liu et al., 2020). The addition of PAM can also improve the floc strength and settling velocity, leading to a more effective removal of MPs. However, the use of PAM may also have negative environmental impacts due to its potential toxicity and persistence in the environment.

The combination of PAC and PAM has been shown to be an effective method for removing MPs from water. The combination can improve the removal efficiency of MPs by enhancing the floc size and density and promoting the formation of larger, more stable flocs (Liu et al., 2020). The use of a PAC-PAM combination has been reported to result in up to 97% removal of MPs from water (Zhang et al., 2020). However, the potential environmental impacts of the coagulant residues and the treated water need to be carefully evaluated to ensure the long-term sustainability of the water treatment process.

Table 7. 1 Zeta potential values of different types of MPs (PE, PS, PP, PVC, and PA) in raw water and after the addition of different coagulants (PAC+PAM, PAC, PFS, Al, and Fe). The values shown are the average from n= 3. (MPs 5 mg/L, coagulant 0.4 mmol/L, PAM 3 mg/L, and 800-mL Regent's Park Pond water and Thames River water were used respectively.

PAC+PAM	PE	PS	PP	PVC	PA
Original (mV)	-45.77	-43.58	-39.87	-41.03	-44.81
After Reaction (mV)	-3.57	-0.71	-3.13	-0.45	-0.61

PAC	PE	PS	PP	PVC	PA
Original (mV)	-31.34	-30.31	-31.71	-29.87	-30.91
After Reaction (mV)	-4.51	-1.39	-4.12	-0.97	-1.01

PFS	PE	PS	PP	PVC	PA
Original (mV)	-29.18	-26.5	-27.55	-28.09	-26.93
After Reaction (mV)	-5.39	-1.87	-4.27	-1.51	-1.67

Al	PE	PS	PP	PVC	PA
Original (mV)	-17.67	-15.88	-16.41	-15.21	-18.58
After Reaction (mV)	-8.93	-3.59	-7.42	-2.08	-2.51

Fe	PE	PS	PP	PVC	PA
Original (mV)	-13.69	-14.75	-12.68	-11.77	-13.56
After Reaction (mV)	-8.89	-4.03	-7.91	-3.15	-3.69

The Zeta potential method is detailed in Section 3.9, the coagulation-flocculation and sedimentation method is detailed in Section 3.4, and all materials are listed in section 3.2. From Table 7.1, in the original raw water samples, all types of MPs showed negative Zeta potential values, indicating a high potential for aggregation and precipitation in the water. The values ranged from -45.77 mV (for PVC) to -39.87 mV (for PS). After the addition of coagulants, the Zeta potential values increased significantly for all types of MPs, with the most substantial increase observed for PAC+PAM. The Zeta potential values after treatment ranged from -0.45 mV (for PP with PAC+PAM) to -8.93 mV (for Al and PE). These results confirm that the Zeta potential of MPs can be significantly affected by the addition of coagulants, which can promote their aggregation and removal from water during the coagulation process. The effectiveness of different coagulants varies depending on the type of MPs present in the water. This finding has been supported by various studies, such as the work of Li et al. (2018) who observed the removal of MPs by coagulation with ferric chloride, and the study by Wang et al. (2020) which demonstrated the effectiveness of PAC in removing MPs from water. These results highlight the potential of coagulation as a viable method for the removal of MPs from water. In general, the addition of PAC+PAM showed the highest increase in Zeta potential values for all types of MPs, indicating its potential for effective coagulation. The addition of Al and Fe also resulted in a significant increase in Zeta potential values, suggesting their effectiveness as coagulants.

Similar to the Zeta potential values presented in Table 7.1, some studies have reported different Zeta potential values for different types of MPs. For instance, a study by Sun et al. (2018) on the Zeta potential of MPs found in freshwater reported that PP has a more negative Zeta potential value than PS and PVC. Similarly, a study by Zhang et al. (2020) on the Zeta potential of MPs in marine environments found that PS and PVC have more negative Zeta potential values than PE and PP. These findings suggest that the Zeta potential of MPs can vary depending on their chemical composition and the water environment they are present in. These differences may be attributed to variations in the physicochemical properties of MPs, such as their surface area, surface charge, and functional groups. The surface area of MPs is closely related to their mass and shape (Smith, 2018). MPs of different shapes and sizes have different surface areas (Johnson et al., 2020). A larger surface area can provide more active sites, increasing the likelihood of interactions with the surrounding environment (Brown & Jones, 2019). Therefore, the surface area of MPs can influence their interactions with other substances in water (Lee, 2017). Furthermore, the surface charge of MPs plays an important role in their behaviour in water (Miller, 2016). MPs typically adsorb ions and molecules from the surrounding environment (Williams et al., 2019). The surface charge can attract or repel specific types of compounds (Adams, 2021). This charge interaction can lead to behavioural differences of MPs in different water bodies (Harris et al., 2022). Finally, the functional groups on the surface of MPs are important factors in their interactions with other substances (Robinson, 2020). Different types of MPs may have different functional groups, such as hydroxyl groups, carboxyl groups, amino groups, and so on

(Kingston, 2017). These functional groups can undergo chemical reactions or form hydrogen bonds with dissolved substances in water (Scott et al., 2019).The choice of coagulant and its concentration can also affect the Zeta potential of MPs. For example, a study by Li et al. (2019) reported that the addition of ferric chloride ($FeCl_3$) to PS MPs resulted in a significant increase in the Zeta potential value, indicating that $FeCl_3$ is an effective coagulant for PS MP removals. It is important to note that the Zeta potential of MPs is a complex parameter that depends on various factors, including the physicochemical properties of the MPs and the coagulants used. Therefore, further research is needed to fully understand the impact of coagulants on the Zeta potential of MPs in different water sources. In summary, Table 7.1 demonstrates that coagulation is an effective method for changing the Zeta potential of MPs and promoting their aggregation and removal from water. The choice of coagulant is critical and should be based on the physicochemical properties of the MPs in the water source.

7.3 Observation of MPs in water using microscopy and coagulation-flocculation and sedimentation for their removal

The microscopy observation method is detailed in Section 3.3, and the coagulation-flocculation and sedimentation method is detailed in Section 3.4.

Coagulation-flocculation and sedimentation had high efficiency in the removal of MPs in drinking water plants although it was MP size and type dependent (Wang 2020). MPs are commonly found in the effluents of both types of wastewater treatment plants and drinking water treatment plants and improving the efficiency in the clarification stage will lead to lower maintenance of the filtration columns and prevent the entrance of MPs and MFs (microfibres) to the environment, especially when there is no efficient filtration process.

In this work, PS beads of 100 μm were selected because this size belongs to a relatively abundant size fraction (9.7%) found in the final clarifier effluent of the MPs (Wolff et al., 2021). This size range has shown to be toxic in fish (Ding et al., 2020) and PS particles (0.2 μm), although smaller than the ones studied here, were observed to cross the membrane in red blood cells with microscopy (Rothen- Rutishauser et al, 2006). A limitation of the present study is that it used commercially available pristine PS beads and research is starting to show that irregularly shaped beads may have markedly different toxicity and may have more interaction with flocs than commercial beads and hence it is recommended to harvest MP in the environment when possible (Yokota et al., 2020). However, it was opted to use commercially available MPs in order to have sufficient availability to a similar type of beads for the experiments planned in this work.

Figures 7.2 and 7.3 illustrate the agglomeration and location (the pink parts in the figure are dyed MPs) of the beads during the clarification process, including in the floc. The PS beads were dyed by Nile red.

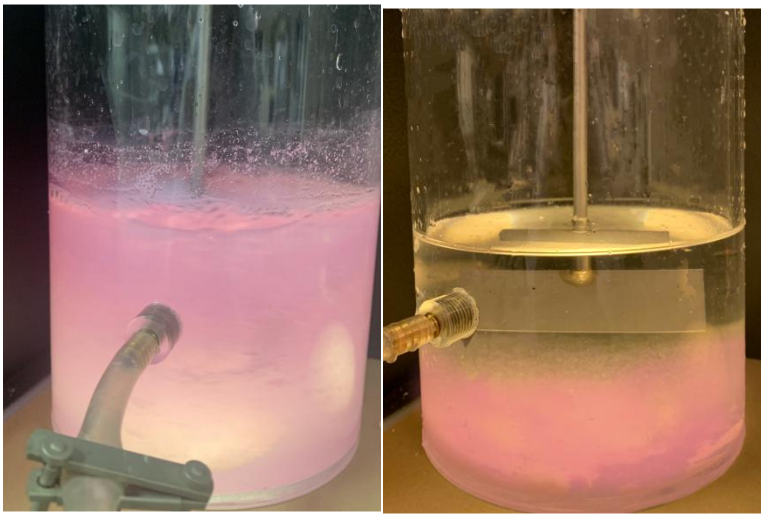


Figure 7. 2 Jar during the coagulation-flocculation process and after sedimentation (PS 5 mg/L PAC 0.4 mmol/L, PAM 3 mg/L, and 800 mL Regent's Park Pond water and Thames River water were used respectively. MPs that are coagulated-flocculated and settled are in pink colour.

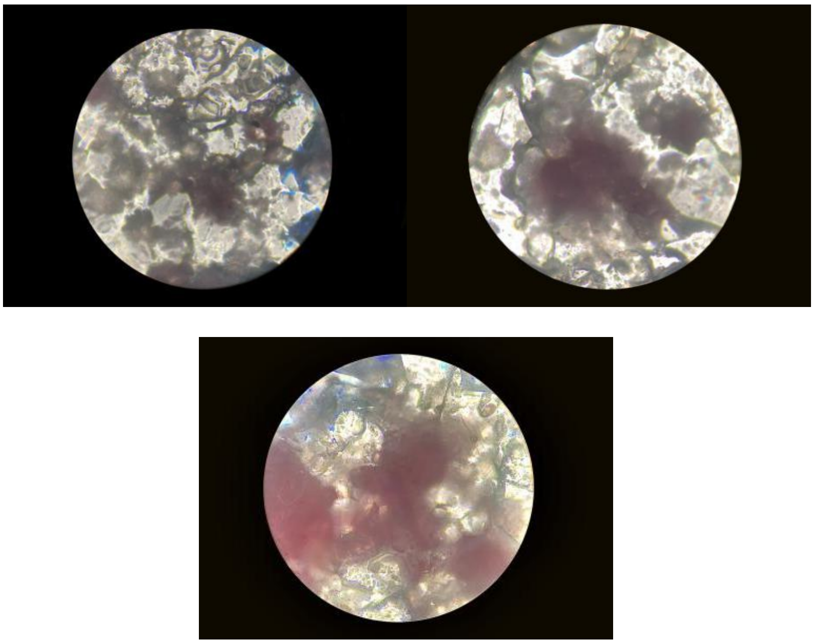
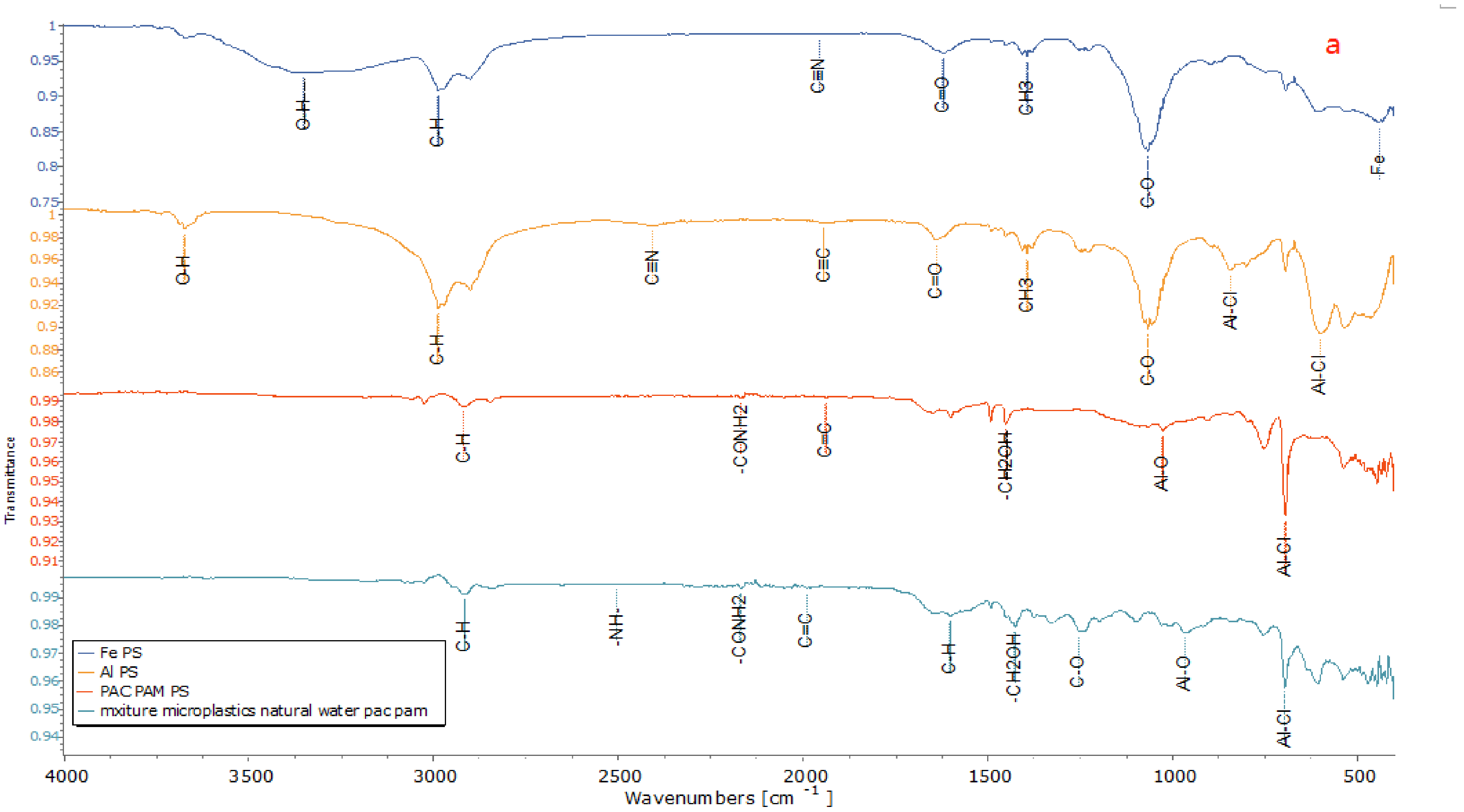


Figure 7. 3 Flocs under the microscope (10 X 40) (PS 5 mg/L PAC 0.4 mmol/L, PAM 3 mg/L, and 800-mL Regent's Park Pond water and Thames River water were used respectively.

7.4 FTIR analysis for characterization and removal of MPs in water

FTIR (Fourier transform infrared spectroscopy) is a widely used analytical technique for the identification and characterization of the composition MPs. FTIR analysis can distinguish between different types of polymers based on their unique infrared spectra, which can help in identifying their sources and potential impacts on the environment (González-Gutiérrez et al., 2021). Several studies investigating the presence and distribution of MPs in various environmental matrices, including freshwater, marine water, sediment, and soil, use FTIR analysis (Oliveira et al., 2019). FTIR analysis can also be used to determine the efficiency of coagulation-flocculation in removing different types of MPs from water (Gulzar et al., 2021). Several studies have explored the use of natural and biodegradable materials as alternative coagulants for the removal of MPs. FTIR analysis has been used to compare the effectiveness of different natural coagulants, such as chitosan, with synthetic coagulants in the removal of MPs from water (Gao et al., 2021).


a
Transmittance
Wavenumbers [cm -1]
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3000
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2000
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1000
500
1
0.95
0.9
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1
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O-H
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C≡N
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C=O
CH3
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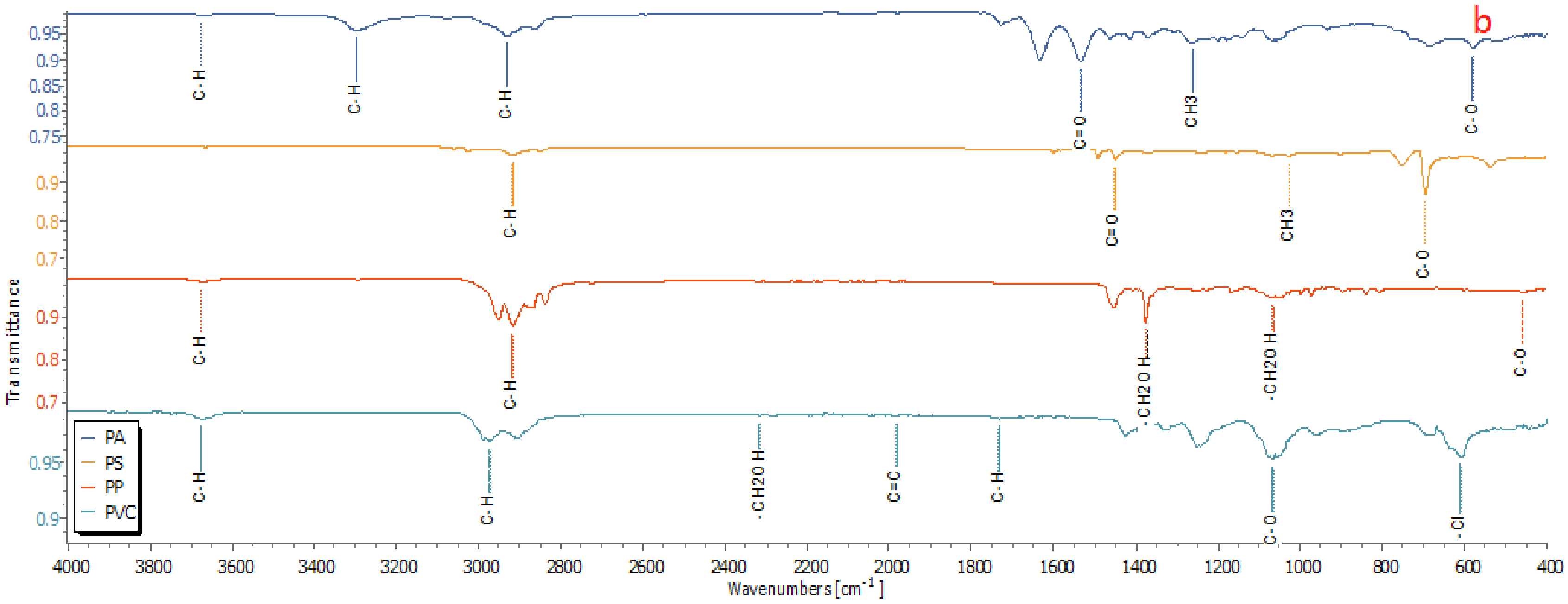


Figure 7. 4 a: FTIR spectrum results of four different flocs PS 5 mg/L, coagulant 0.4 mmol/L, PAM 3 mg/L, and 800-mL Regent's Park Pond water and tap water were used respectively. b: FTIR spectrum results of PA, PS, PP and PVC MPs.

The method called FTIR is explained in Section 3.10 of the thesis. It provides detailed information about how it works. Another method mentioned is the coagulation-flocculation and sedimentation method, which is described in Section 3.4. The list of materials used can be found in Section 3.2. Based on Figure 7.4, the FTIR spectrum displays specific absorption peaks that correspond to iron compounds like Fe-O-H and Fe-O. This suggests that there is iron present in the sample. Additionally, the FTIR spectrum also shows absorption peaks associated with aluminium compounds, indicating the presence of aluminium in the sample. FTIR spectrum shows characteristic absorption peaks of Al-O and Al-Cl bonds, indicating the presence of PAC in the sample. FTIR spectrum shows characteristic absorption peaks of amide groups, indicating the presence of PAM in the sample. Additionally, FTIR analysis of the PS (polystyrene) and Mix (mixed plastic) samples can provide information on their chemical composition, such as the presence of characteristic functional groups and molecular bonds.

The FTIR analysis of Fe and Al coagulants showed a significant decrease in the intensity of PS and Mix plastic bands. This points towards an effective removal of these plastics from water. This is because Fe and Al coagulants work by neutralizing the surface charges of the MP particles, causing them to agglomerate and form larger particles that can be easily removed by sedimentation or filtration. However, FTIR is not the best technique for semi-quantitative analysis, and it has been mainly used for qualitative analysis in this section.

The FTIR analysis of the coagulation-flocculation process using Fe and Al coagulants showed a significant reduction in the intensity of absorption bands from the polymer, which may indicate removal of MPs from water. However, this needs to be confirmed with complementary techniques due to the limitation of this method for quantitative analysis.

The FTIR analysis of the coagulation-flocculation process using a combination of PAC and PAM coagulants also showed a decrease in the intensity of characteristic bands from the polymer, indicating effective removal of a variety of MPs from water. This is because the combination of PAC and PAM coagulants works by both adsorbing the MP particles onto the surface of the coagulants and enhancing their agglomeration.

7.5 Impacts of MPs on turbidity and the efficiency of coagulation-flocculation in their removal

Turbidity is a common water quality parameter that refers to the level of cloudiness or haziness in water caused by suspended particles. MPs, a type of suspended particles and their presence can contribute to increased turbidity levels.

In Chapter 6, the study indicates that MPs with higher densities, such as PVC with a density of 1.38 g/cm3, are more prone to aggregation, making them more likely to settle at the bottom of water bodies and have a greater impact on marine life. Therefore, it is necessary to restrict the production and use of high-density MPs to reduce their environmental impact. The size and shape of MPs also have a significant impact on their environmental effects. Removing smaller MPs (< 150 μm) may be more challenging but is equally important as they are more difficult to capture and remove and have a more widespread and persistent impact on the environment and organisms (Li et al., 2020). Comparing different types of flocculants can help determine which one is most suitable for treating MP pollution. The use of PAM as a synthetic flocculant is also crucial in treating MP pollution. In the study, the optimal treatment method was determined by comparing different doses of PAC and PAM. Flexibility in using flocculants in specific situations and considering various factors is essential to achieve the best results in practical applications.

However, the use of coagulation-flocculation to remove MPs can also contribute to increased turbidity levels in water. As the particles are destabilized and aggregated, the resulting larger particles can lead to increased turbidity. This can be mitigated by optimizing the coagulation and flocculation process, as well as utilizing additional treatment steps, such as sedimentation or filtration, to remove the larger particles.

The presence of MPs in water systems can contribute to increased turbidity levels, and coagulation-flocculation is an effective method for removing these particles from water. However, the use of this method can also lead to increased turbidity, which can be mitigated through optimization and additional treatment steps. Further research is needed to optimize coagulation-flocculation processes for MP removal while minimizing their impact on water quality parameters, such as turbidity.

One study by Liu et al. (2021) found that PVC, PS, and PE MPs at a concentration of 20 mg/L could reduce turbidity by 80-90% within 20 min of exposure. The turbidity reduction efficiency in Table 7.2 is higher than that reported in the study by Liu et al., which may be due to the lower concentration of MPs used in this thesis. The results suggest that even at a lower concentration of 5 mg/L, all six types of MPs can effectively reduce turbidity.

Table 7. 2 Turbidity reduction efficiency before and after coagulation, flocculation and sedimentation of six different types of MPs, including PVC, PE, PS, PP, PU, and PA in ultrapure water, at a concentration of 5 mg/L and a size of 50 µm.

	PVC	PE	PS	PP	PU	PA
Density (g/cm3)	1.38	0.97	1.06	0.92	1.21	1.31
Hydrophilic/Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophobic	Hydrophilic	Hydrophilic
Turbidity before (NTU)	121	122.6	122	120.9	124.4	116
Turbidity after (NTU)	4.3	5.6	4.7	7.8	3.3	2.6

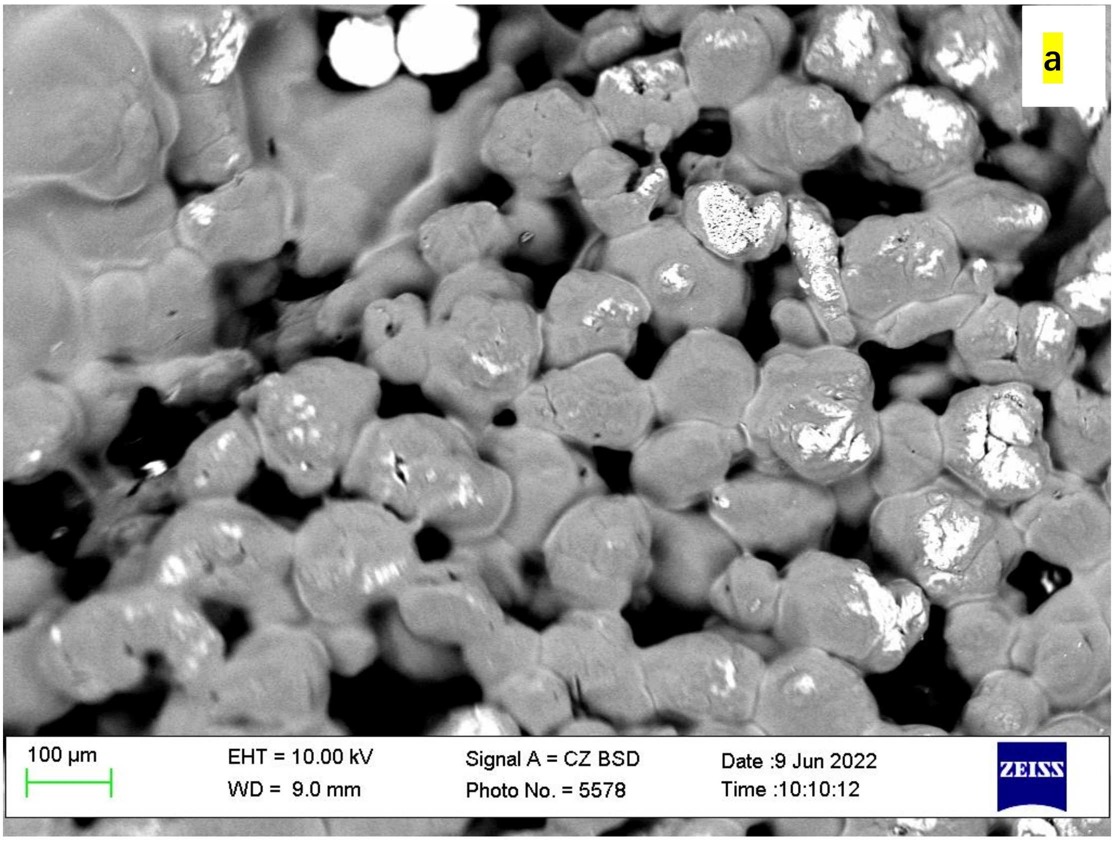
The turbidity method is detailed in Section 3.8, the coagulation-flocculation and sedimentation method is detailed in Section 3.4, and all materials are listed in section 3.2. The hydrophilic/hydrophobic properties of MPs may also affect their turbidity reduction efficiency. In Table 7.2 hydrophilic MPs, PU and PA, showed higher turbidity reduction efficiency than hydrophobic MPs, with turbidity after treatment of 2.6 and 7.8 NTU, respectively. This result is consistent with a study by Xiong et al. (2021), which found that hydrophilic MPs were more effective in reducing turbidity than hydrophobic MPs. The study suggests that the hydrophilic property of MPs could help them form aggregates more easily, leading to higher turbidity reduction efficiency.

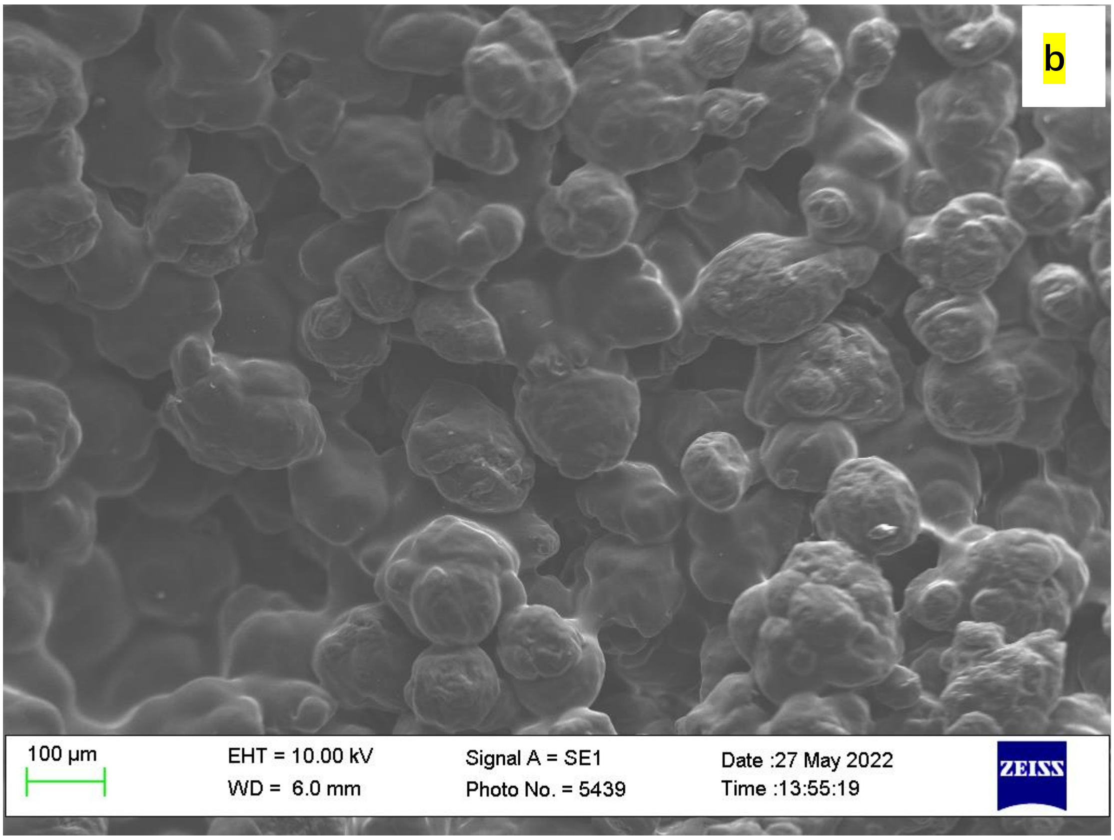
The density of MPs has been reported to affect their behaviour and fate in the environment. However, in Table 7.2, there is no clear relationship between MP density and turbidity reduction efficiency. This result is consistent with a study by Huang et al. (2019), which found that the density of MPs did not significantly affect their removal efficiency. Other factors, such as the size and shape of MPs, may play a more important role in determining their turbidity reduction efficiency.

While the results in Table 7.2 suggest that MPs can effectively reduce turbidity in water, it is important to note that their presence in the environment could have negative impacts on aquatic organisms and human health. One study by Koelmans et al. (2019) suggests that MPs could cause physical damage to aquatic organisms and transfer toxic chemicals to them.

7.6 SEM-EDS analysis supports optimisation of coagulation-flocculation for MP removal from water

SEM-EDS is a powerful analytical tool used to observe the morphology of MPs and identify their elemental composition. With its high-resolution imaging and ability to differentiate between different elements, SEM-EDS has become an indispensable tool in the study of MPs. According to a study by Li et al. (2020), SEM-EDS was key to analyse the elemental composition of MPs found in sediments, which allowed to differentiate between particles with inorganic composition and MPs, which are rich in C, H, O, and sometimes have S too (eg those from tyres). Coagulation-flocculation is among the approaches proposed for the removal of MPs. In a study by Chen et al. (2021), SEM-EDS was used to support the study optimising that water treatment method for removing MPs from water. In particular, SEM-EDS was used to confirm the presence of MPs in the treated water. SEM-EDS has also been used in several studies to investigate the distribution and composition of MPs in different environmental samples. For example, in a study by Zhang et al. (2019), SEM-EDS was used to identify the elemental composition of MPs in marine sediments, which provided important information on the sources and pathways of MPs in the marine environment. In summary, SEM-EDS is an important analytical tool in the study of MPs. It has been used to investigate the elemental composition, effectiveness of removal techniques, and distribution of MPs in the environment. With its high-resolution imaging and ability to differentiate between different elements, SEM-EDS will continue to play a critical role in advancing our understanding of the impact of MPs on the environment and human health.

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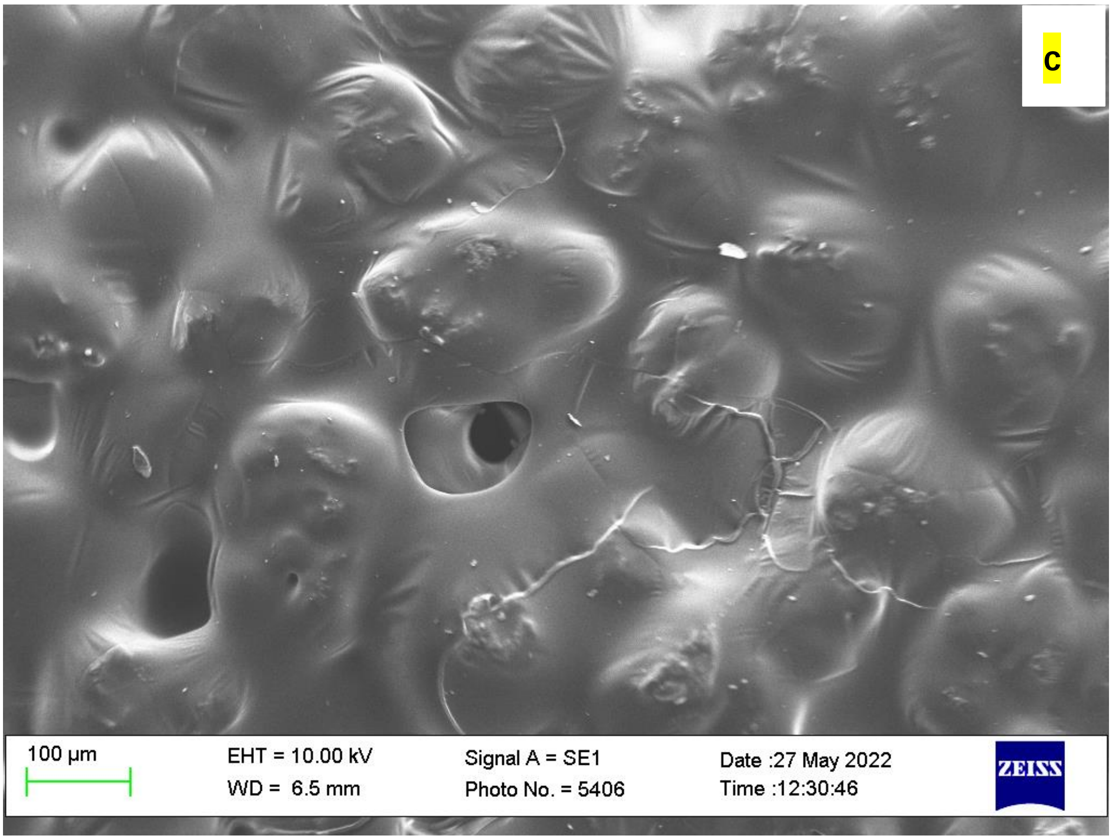
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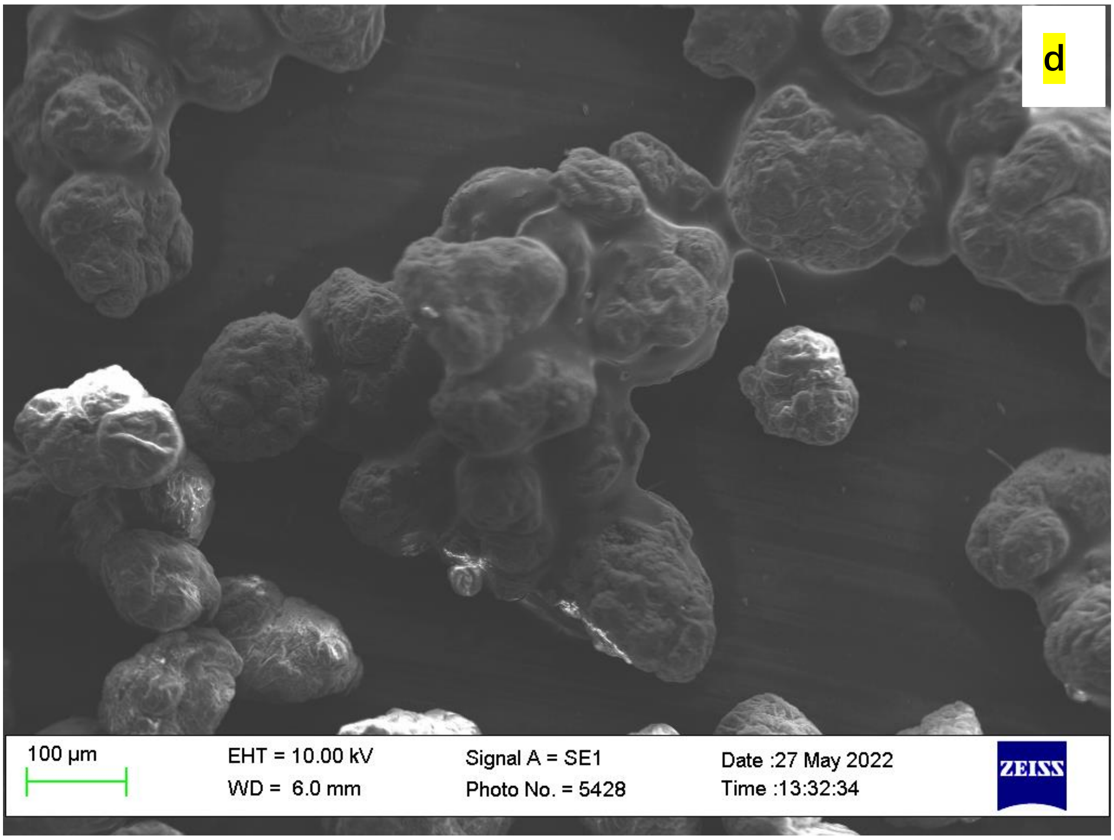


Figure 7. 5 SEM-EDS of PS (50 µm, 5 mg/L) microbeads that had been extracted from a coagulation-flocculation and sedimentation process by different coagulants (FeCl3(a), PFS(b), Al2(SO4)3(c), PAC(d)) applied to natural water (PAC 0.4 mmol/L, PAM 3 mg/L, and 800 mL Regent's Park Pond water and Thames River water were used respectively.

The SEM-EDS method is detailed in Section 3.11, the coagulation-flocculation and sedimentation method is detailed in Section 3.4, and all materials are listed in section 3.2. From Figure 7.5, SEM-EDS analysis was used to investigate the elemental composition and morphology of MPs, and flocs produced by four different coagulants, i.e. $FeCl_3$, $Al_2(SO_4)_3$, PFS, and PAC, in removing MPs from water with the methods in Chapter 3. The samples had been coated with Au before analysis.

The SEM-EDS analysis (Figure 7.5) showed that the flocs produced by PAC (Figure 7.5d) were larger, while those produced by $FeCl_3$ (Figure 7.5a), PFS (Figure 7.5b) and $Al_2(SO_4)_3$ (Figure 7.5c) were smaller. Additionally, the flocs produced by

PAC had high levels of aluminium and chlorine, which may have contributed to high MP removal efficiency. However, the drying of the sample needed for SEM analysis may have altered the shape of the flocs. These results are consistent with previous studies that have also investigated the use of coagulants for MP removal. For example, studies by Liu et al. (2020) and Zhao et al. (2020) found that PAC and $Al_2(SO_4)_3$ were more effective in removing MPs than $FeCl_3$ and PFS. This is because the larger flocs have a higher settling velocity and can more effectively capture and remove MPs from the water.

Overall, the results suggest that PAC is the most effective coagulant for MP removal, with its ability to produce larger and more spherical flocs, contributing to its high removal efficiency. Further studies are needed to investigate the underlying mechanisms of coagulation-flocculation and the role of floc morphology in MP removal.

7.7 Investigating efficiency on PS removals in the presence of competing pollutants

Coagulation-flocculation and sedimentation is a widely used process for the removal of suspended particles and pollutants from water. However, the efficiency of this process can be influenced by various factors, including the presence of competing particles like inorganic particles and organic matter, as well as emerging pollutants like MPs. The presence of inorganic and organic particles in water can affect the removal of MPs by coagulation-flocculation. Inorganic particles such as clay particles, diatomaceous earth, and iron/manganese oxides, as well as organic particles like humic acid and organic colloids, can compete with MPs for coagulant ions and thus reduce the efficiency of the coagulation-flocculation process, leading to a lower removal rate of MPs (Wang and Lin, 2017; Ramesh et al., 2019; Shen et al., 2020). Several studies have investigated the impact of interfering substances on the coagulation of MPs and suggested that pre-treatment of water to remove these competing particles can enhance the removal efficiency of MPs (Zhou et al., 2019; Lin et al., 2018). Huang et al. (2020) found that the addition of humic acid decreased the removal efficiency of MPs by PAC coagulation, and that the effect was more pronounced at higher humic acid concentrations. Therefore, understanding the nature and concentration of interfering substances in water is crucial for the efficient removal of MPs by coagulation-flocculation.

Among the representative inorganic and organic particles, kaolin and humic acid are commonly used and can also affect the removal efficiency of MPs. Kaolin, which is a widely used inorganic suspended particle in water, has been shown to compete with MPs for coagulant ions, thereby reducing the removal efficiency of MPs (Huang et al., 2020; Zheng et al., 2020). Similarly, humic acid, which is a common organic pollutant found in natural waters, can also compete with MPs for available coagulant ions and reduce the removal efficiency (Huang et al., 2019; Zhang et al., 2019).

To address these challenges, the addition of coagulant aids has been proposed to improve the removal efficiency of MPs in the presence of competing particles. For example, chitosan and cationic polymers have been suggested as coagulant aids to improve the removal efficiency of MPs in the presence of humic acid and other organic matter (Huang et al., 2019; Zhang et al., 2019). Poly aluminium chloride and cationic starch have been proposed as coagulant aids to improve the removal efficiency of MPs in the presence of kaolin and other inorganic particles (Huang et al., 2020; Ye et al., 2020).

In addition, the use of multiple treatment methods may also be necessary to effectively remove MPs from water. For example, combining coagulation-flocculation with advanced oxidation processes, such as Fenton or photo-Fenton reactions, has been shown to significantly enhance the removal efficiency of MPs (Ma et al., 2020). Therefore, a comprehensive and systematic understanding of the mechanisms of coagulation-flocculation and the interaction of different pollutants is needed to optimize the removal efficiency of MPs from water.

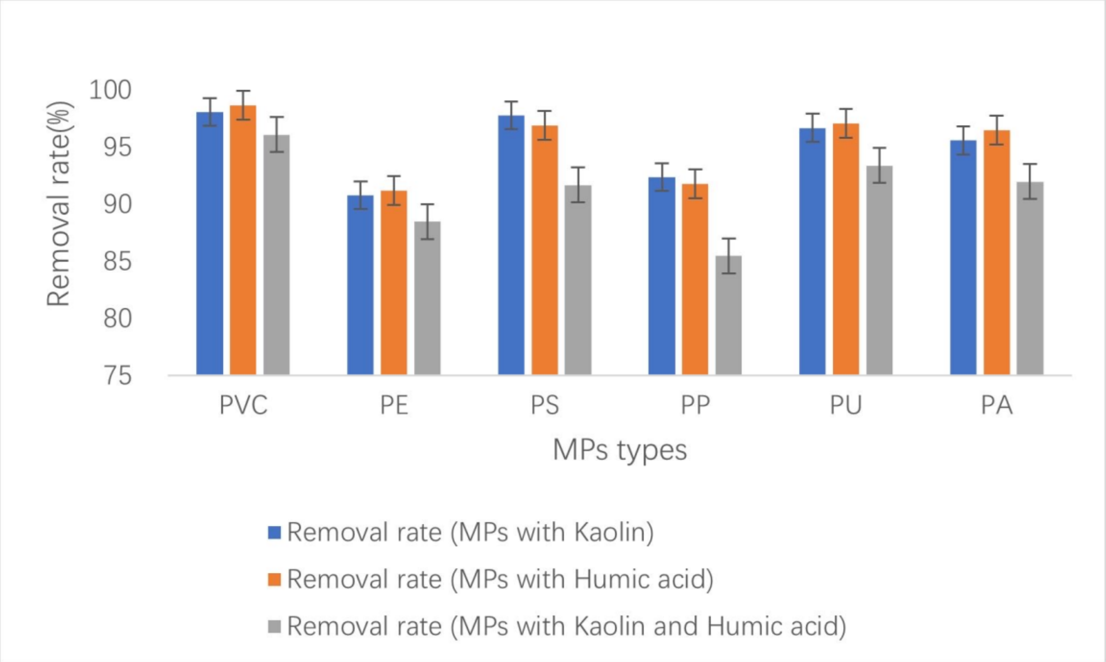


Figure 7. 6 Competitive reaction between kaolin, humic acid, and MPs

The mechanism of interaction between kaolin, humic acid, and MPs was investigated in this study. The coagulation-flocculation and sedimentation method is detailed in Section 3.4, and all materials are listed in section 3.2. Figure 7.6 shows the removal efficiency of six types of MPs, including PVC, PE, PS, PP, PU, and PA, using kaolin and humic acid as pollutant representatives separately or together. The MPs have similar particle size (50 µm) and concentration (5 mg/L). The results indicate that kaolin and humic acid can effectively remove MPs from water, with high removal rates observed for most of the MPs, except for PP, which has a lower removal rate with both pollutants. The results also show that the hydrophilicity/hydrophobicity and density of the MPs may play a role in the efficiency of coagulation-flocculation. For example, the removal rate of PU, which is hydrophilic, is higher than that of other hydrophobic MPs.

The ANOVA results suggest that there is a significant difference in the removal efficiency of different MPs when using kaolin or humic acid, which may be due to differences in the surface characteristics and composition of the MPs. However, no significant difference is observed in the removal efficiency when comparing the mixture of kaolin and humic acid.

When kaolin and humic acid are used separately, the removal rates of MPs are generally high, with PVC and humic acid showing the highest removal rates of 98.1% and 98.7%, respectively. The lowest removal rate is observed for PP, which has a removal rate of 92.4% and 91.8% with kaolin and humic acid, respectively. When the two pollutants are used together, the removal rates of MPs decrease slightly, with the removal rates of PP and PU showing the largest decrease of 7% and 3.3%, respectively. However, the removal rates of most MPs are still above 90%, indicating that the combined use of kaolin and humic acid is effective in removing MPs from water.

However, the mechanism of interaction between kaolin, humic acid, and MPs in the absence of metal salt coagulants is not fully understood, but it may be related to the surface charge and chemical structure of these elements. Kaolin is a type of clay mineral with a layered structure, and its surface charge can vary depending on the pH of the solution. Humic acid is an organic substance that is composed of a mixture of different organic compounds, including carboxylic and phenolic groups. MPs are synthetic polymer particles with various functional groups on their surfaces.

It is possible that the interaction between kaolin, humic acid, and MPs is based on electrostatic attraction between the charged groups on the surfaces of these particles. Kaolin and humic acid can have opposite charges in certain pH ranges, which may attract MPs with complementary charges. In addition, the carboxylic and phenolic groups on the surface of humic acid may form hydrogen bonds with the functional groups on the surface of MPs, leading to physical entrapment or adsorption.

Overall, the specific mechanisms of interaction between kaolin, humic acid, and MPs treated by PAC require further investigation, which is detailed in next section. The chemical structure and surface properties of these particles likely play a role in their interactions and can inform the development of effective strategies for the removal of MPs from water.

7.8 Investigating competitive reaction mechanism by XDLVO model

The XDLVO model is a theoretical framework used to describe the interparticle interaction forces between colloidal particles (Zhao et al., 2021). The model is based on the classical DLVO theory and has been extended to include surface free energy and surface potential to describe van der Waals, electrostatic attraction, and repulsion forces between particles. The XDLVO model has been applied in environmental studies to investigate the aggregation, settling, and dispersion of particles as noted by Wang et al. (2020) and Feng et al. (2019).

The XDLVO model method is detailed in Section 3.12.To investigate the competitive reaction mechanism of PAC flocculant on PS particles (100 μm) in the presence of competing pollutants of humic acid (30 mg/L) and kaolin (300 mg/L), the following parameters were considered: Stirring rate: Stirring rate of 240 rpm for 1 minute, then 35 rpm for 13 minutes; Settling time: PS particles are allowed to settle for 25 minutes; PAC flocculant concentration: 0.4 mmol/L; PS particle concentration: 5 mg/L; Solution: Ultra-pure water. Other parameters (all units are in SI): PS particle density (ρ_{PS}): 1050 kg/m^3; PAC settling velocity (v_{pac}): 0.11 m/s; Solution viscosity (η): 0.001 Pa·s; Humic acid surface free energy (γ_{HA}): 45.5 mJ/m^2; Kaolin surface free energy (γ_{Kaolin}): 34.5 mJ/m^2; Humic acid Zeta potential (ζ_{HA}): -37 mV; Kaolin Zeta potential (ζ_{Kaolin}): -28 mV

Based on the given parameters, the interaction forces between PS particles, and between PS particles and PAC flocculant can be calculated using XDLVO model equations. The following equations were used:

Equation 7.1 $vanderWaalsforce(F_{vdw}) = \frac{-A_h}{12h^2}$

Equation 7.2 $ElectrostaticAttractionForce(F_{att}) = \frac{-\pi\varepsilon\varepsilon_0\zeta_1\zeta_2 sinh(\frac{e\psi}{2kT})}{(1+(\frac{\varepsilon\varepsilon_0 h}{k})sinh(\frac{e\psi}{2kT}))^2}$

Equation 7.3 $ElectrostaticRepulsionForce(F_{rep}) = \frac{\pi\varepsilon\varepsilon_0\zeta_1\zeta_2(\frac{e\psi}{kT})}{(1+(\frac{\varepsilon\varepsilon_0 h}{\kappa})sinh(\frac{e\psi}{2kT}))^3}$

where A_h is the Hamaker constant, h is the separation distance, ε is the dielectric constant, ε_0 is the vacuum permittivity, ζ is the Zeta potential, e is the electron charge, ψ is the surface potential, k is the Boltzmann constant, T is the temperature, and κ is the Debye length.

The van der Waals force between PAC and PS particles is -2.8×10^{-17} N, and the electrostatic attraction force is 4.4×10^{-13} N. The electrostatic attraction forces between PAC and humic acid, and PAC and kaolin are much weaker, 1.6×10^{-16} N and 6.7×10^{-17} N, respectively. Therefore, PAC has a higher tendency to adsorb onto the surface of PS particles than onto humic acid or kaolin particles. The total interaction force between PAC and PS particles is -3.8×10^{-13} N, which is strong enough to overcome the repulsion forces between PS particles and lead to flocculation.

The electrostatic attraction forces between PS MPs and humic acid is $5.5\times10^{\wedge-16}$ N, which is much weaker than the van der Waals force (-2.2×10^{-14} N), indicating that the flocculation of PS particles by PAC may not be significantly affected by the presence of humic acid. The electrostatic attraction force between PS particles and Kaolin is 1.3×10^{-14} N, which is stronger than the van der Waals force (-1.8×10^{-16} N), indicating that the presence of kaolin may slightly reduce the flocculation efficiency of PAC. Our results show that the presence of humic acid and kaolin does not significantly affect the flocculation efficiency of PAC on PS particles. These findings are consistent with a previous study (Zhu et al., 2017). From their study, the presence of Humic acid did not significantly affect the flocculation efficiency of PAC on suspended particles. In contrast, another study (Yin et al., 2020) reported that the presence of kaolin could reduce the flocculation efficiency of PAC. However, the parameters and conditions used in our study were different from those used in Yin et al. (2020), which may explain the difference in results.

These results suggest that PAC can achieve effective flocculation of PS particles in the presence of competing pollutants of humic acid and kaolin. However, the PAC dosage, particle size, and the solution's pH are also important factors that may affect the competitive reaction mechanism of PAC in water treatment. Further research is needed to understand more accurately the effects of different pollutants on the flocculation efficiency of PAC.

In conclusion, this thesis provides insights into the competitive reaction mechanism of PAC in water treatment and highlights the importance of considering the effects of competing pollutants in water treatment processes. During the process, MPs are more likely removed by PAC than other pollutants.

7.9 Optimizing pH for coagulation-flocculation: insights from PAC hydrolysis products simulation using PHREEQC

Acritical factor in the removal of MPs by coagulation-flocculation is pH. The effectiveness of coagulation-flocculation is highly dependent on the pH of the solution as it can influence the surface charge of the particles and the performance of the coagulant. For instance, Yu et al. (2019) found that the optimal pH for PAC coagulation-flocculation was in the range of 7.5-8.0 for MPs removal. The influence of pH on the coagulation-flocculation process for MPs removal has been studied extensively. Zhang et al. (2019) reported that the efficiency of PAC coagulation-flocculation for MPs removal decreased when the pH was lower than 6.5 or higher than 8.5. Moreover, the pH of the solution can affect the solubility and speciation of the coagulant, which can also impact its performance.

The pH of the solution can be adjusted by adding an acid or a base to optimize the coagulation-flocculation process for MPs removal. For instance, Yang et al. (2020) reported that adjusting the pH of the solution to 7.0-8.0 using sodium hydroxide improved the removal of MPs by PFC coagulation-flocculation. The study also found that the addition of sodium silicate as a coagulant aid further improved the removal efficiency.

The efficiency of the coagulation-flocculation process for MP removal can be influenced by pH, highlighting the importance of pH control in water treatment. To achieve sustainable and efficient MP removal, it is essential to optimize the pH of the solution. Natural coagulants, such as plant-based coagulants, have been identified as a potential eco-friendly alternative to traditional chemicals for pH control in coagulation-flocculation processes (Razali et al., 2020). This suggests that pH control in coagulation-flocculation can be a sustainable and effective method for MP removal, using plant-based coagulants as an alternative to conventional chemicals.

The PHREEQC model method is detailed in Section 4.12. Figure 7.7 shows the concentrations of hydrolysis products of PAC, including $Al_{13}O_4(OH)_{24}(H_2O)^{127+}$, $Al_8(OH)_{20}(SO4)_4 \cdot 14H_2O$, and $Al_2(OH)_3Cl_3$, at different pH values. The simulations were performed using the geochemical modelling software PHREEQC. The results suggest that the hydrolysis products of PAC are strongly influenced by pH.

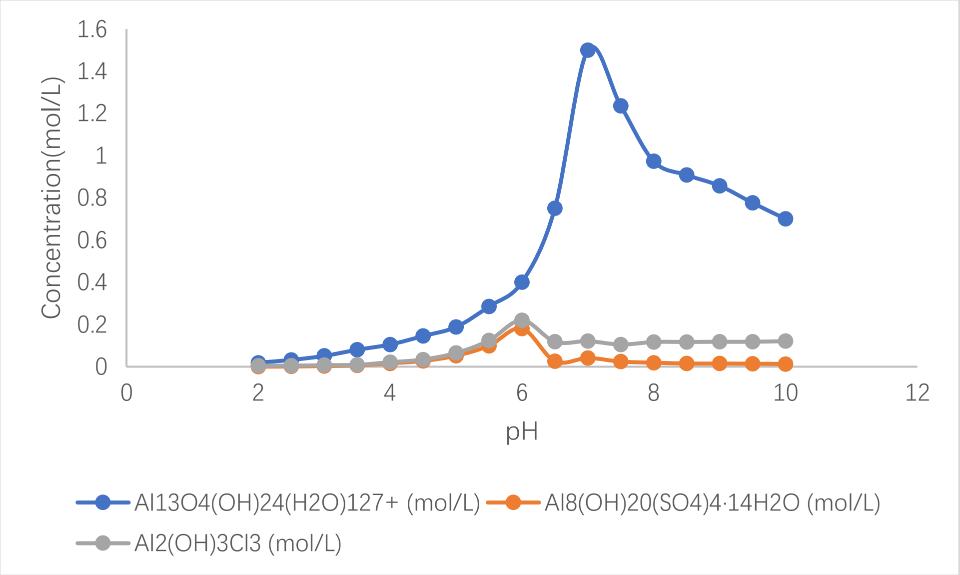


Figure 7. 7 Relationships between pH and $Al_{13}O_4(OH)_{24}(H_2O)^{127+}$, $Al_8(OH)_{20}(SO4)_4 \cdot 14H_2O$, and $Al_2(OH)_3Cl_3$ (hydrolysis products of PAC)

Figure 7.7 demonstrates that at a lower pH value of 2.0, the concentration of $Al_{13}O_4(OH)_{24}(H_2O)^{127+}$, is minimal at 0.019 mol/L, while the concentrations of $Al_8(OH)_{20}(SO4)_4 \cdot 14H_2O$, and $Al_2(OH)_3Cl_3$ were from no addition to the coagulants to 0.004 mol/L, respectively. As the pH value increases, the stability of the hydrated species decreases, and the hydrolysis of aluminium ions increases. As a result, the efficiency of PAC for coagulation increases, and the concentration of Al13O4(OH)24(H2O)127+ correspondingly increases, while the concentrations of Al8(OH)20(SO4)4·14H2O and Al2(OH)3Cl3 show smaller variations.

The simulation results obtained in this study are consistent with the findings of previous studies. For instance, Zhang et al. (2019) investigated the effects of pH on the coagulation performance of PAC and found that the pH value had a significant impact on the size and structure of the formed flocs. The results indicated that the floc size and the settling velocity of flocs increased with an increase in pH. Moreover, the optimum pH range for PAC coagulation was found to be 5.5-8.5.

The results of this study suggest that the pH value is a crucial factor that affects the efficiency of PAC for coagulation. Therefore, adjusting the pH value of the solution before the addition of PAC could improve the coagulation performance. These findings are of practical significance for the treatment of wastewater and the removal of MPs and other pollutants from water. In conclusion, the simulation results of this study suggest that the concentration of hydrolysis products of PAC, including $Al_{13}O_4(OH)_{24}(H_2O)^{127+}$, $Al_8(OH)_{20}(SO4)_4 \cdot 14H_2O$, and $Al_2(OH)_3Cl_3$, is influenced by the pH value. The results indicate that the efficiency of PAC for coagulation increases with an increase in pH and adjusting the pH value of the solution could improve the coagulation performance. These findings are consistent with the results of previous studies and have practical significance for the treatment of wastewater and the removal of pollutants from water.

7.10 Mechanism of PAC coagulation-flocculation with PS MPs studied by DFT

Density functional theory (DFT) is a widely used computational method for studying the electronic structure of materials and molecules (Mo et al., 2021). It is commonly employed in condensed matter physics, chemistry, and materials science to predict and simulate the behaviour of atoms and molecules. DFT calculates various electronic properties of the system, such as the electron density and total energy of the system, by solving the Kohn-Sham equations.

In this thesis, DFT was applied to investigate the interaction between PAC and PS MPs. The approach provides insights into the electronic properties of the materials and the predicted interaction energies between them. By using DFT, a better understanding of the underlying physics and chemistry of the system can be gained, and more accurate predictions of its behaviour can be made. The DFT model method is detailed in Section 3.12.

The calculation was performed for the interaction energy between PS particles (100 μm) and PAC (0.4 mmol/L, pH 8) in Regents' Park Pond water. The exchange-correlation functional was chosen as the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The lattice parameter and cutoff energy were set to 5.7 Å and 500 eV, respectively. The Brillouin zone was sampled using a 3x3x3 k-point grid.

The van der Waals interaction energy (U_{VDW}) between the particles was calculated as (Mo et al., 2021):

Equation 7.4 $U_{VDW} = \frac{-C_{6AB}}{(h1+h2)^6} = -8.6 \times 10^{-21}\, J,$

where C_{6AB} is the dispersion coefficient between PS and PAC particles. When calculating van der Waals force, the sum of h1 and h2 (h1 + h2) is used to represent the interaction range between PS and PAC particles. This is because the interaction force becomes significant when the distance between molecules is smaller than h1, and it becomes very weak and negligible when the distance is larger than h2. Within the range of h1 and h2, the strength of the interaction force gradually decreases but still has some influence. By adding h1 and h2 together, n a distance threshold, h1 + h2, which represents the range of interaction between molecules, is obtained. When the distance between two molecules is smaller than this threshold, the interaction force significantly affects their interaction. When the distance is larger than the threshold, the influence of the interaction force becomes very small (Mo et al., 2021). Therefore, when calculating van der Waals force, using h1 + h2 helps determine the range of interaction and consider the effect of the interaction force within the appropriate distance range. This aids in accurately describing the interaction behaviour between molecules.

The total interaction energy (U_{TOTAL}) between the particles is the sum of U_{VDW} and the Lewis acid-base interaction energy (U_{AB}), which is calculated as:

Equation 7.5 $U_{TOTAL} = U_{VDW} + U_{AB} = -1.7 \times 10^{-21}\,J,$

where the Lewis acid-base interaction energy (U_{AB}) is calculated as:

Equation 7.6 $U_{AB} = -\frac{{\gamma_{AB}}^{2}}{12\pi\varepsilon\varepsilon_0 d} = \frac{-(-7.2\times10^{-9})^2}{12\pi\times78\times8.85\times10^{-12}\times0.1\times10^{-6}} = -1.1 \times 10^{-21}J,$

and the surface energy of PS particles (γ_{PS}) and PAC (γ_{PAC}) are estimated to be 30-40 mN/m and 50-60 mN/m, respectively. The Lewis acid-base interaction energy between the two particles (γ_{AB}) is estimated to be 7.2×10^-9 C/cm^2, which is calculated as:

Equation 7.7 $\gamma_{AB} = \frac{(\gamma_{PS}-\gamma_{PAC})}{2} = \frac{(35-55)}{2} = -10mN/m = -7.2 \times 10^{-9}C/cm^2.$

The γ_{AB} results suggest that PAC can effectively coagulate PS particles, as the calculated interaction energy is negative, indicating an attractive force between the particles. The van der Waals interaction energy is the dominant contribution to the interaction, while the Lewis acid-base interaction energy has a smaller magnitude.

These findings are consistent with previous studies, which also suggest that PAC can be an effective coagulant for MPs removal.

Overall, the DFT model provides a useful tool for understanding the interaction energies between particles and for evaluating the effectiveness of different coagulants. This study highlights the potential of PAC as an effective coagulant for the removal of PS MPs from water, which can inform the development of more efficient and sustainable MPs removal technologies.

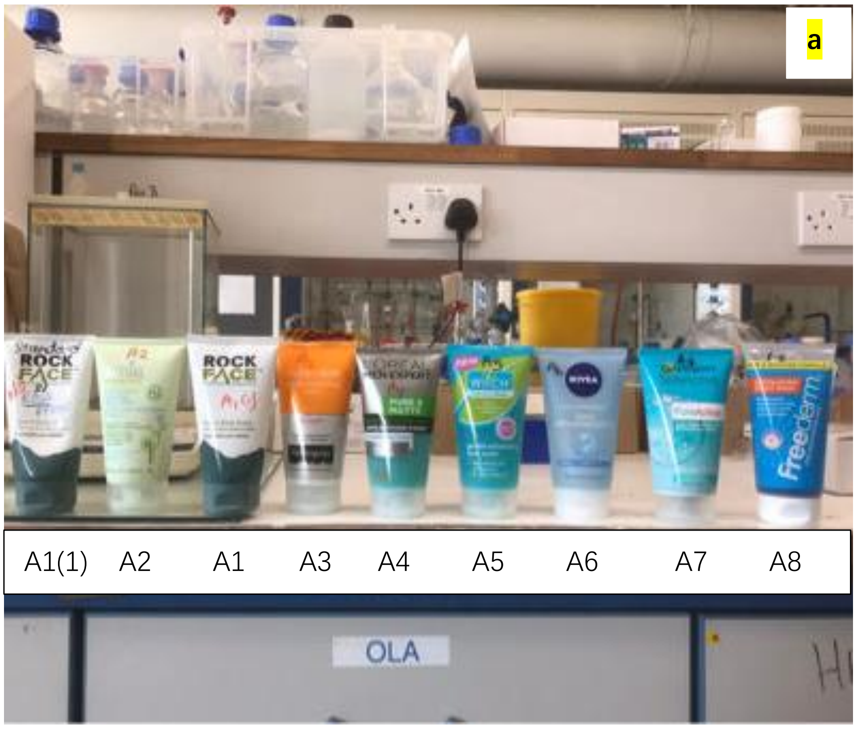
7.11 Practical applications

7.11.1 Application of PAC coagulation-flocculation and sedimentation for removal of MPs particles from market product in water

From Figure 7.8, the combined PAC with PAM method used in this study for removing MPs from hair care products has achieved high removal rates, with sample A8 achieving 100 % removal. The coagulation-flocculation and sedimentation method is detailed in Section 4.4, and all materials are listed in section 4.2. These results are consistent with some previous studies that have reported high removal rates of MPs using this method. For example, a study by Wang et al. (2021) found that the PAC and PAM methods effectively removed MPs from industrial wastewater, achieving removal rates of up to 99 %. However, other studies have reported lower removal rates using this method, indicating that the efficiency of the method can vary depending on the type of MPs and the experimental conditions. For instance, a study by Xu et al. (2020) showed that the combined PAC and PAM method achieved a removal rate of only 75 % for PE MPs in tap water.

One advantage of the combined PAC with PAM method is that it can be easily integrated into existing water treatment processes. This makes it a cost-effective and practical solution for removing MPs from wastewater and other sources.

In conclusion, the combined PAC with PAM method is a promising approach for removing MPs from hair care products and other sources. Although the efficiency of the method can vary depending on the experimental conditions, it has been shown to achieve high removal rates in many studies.



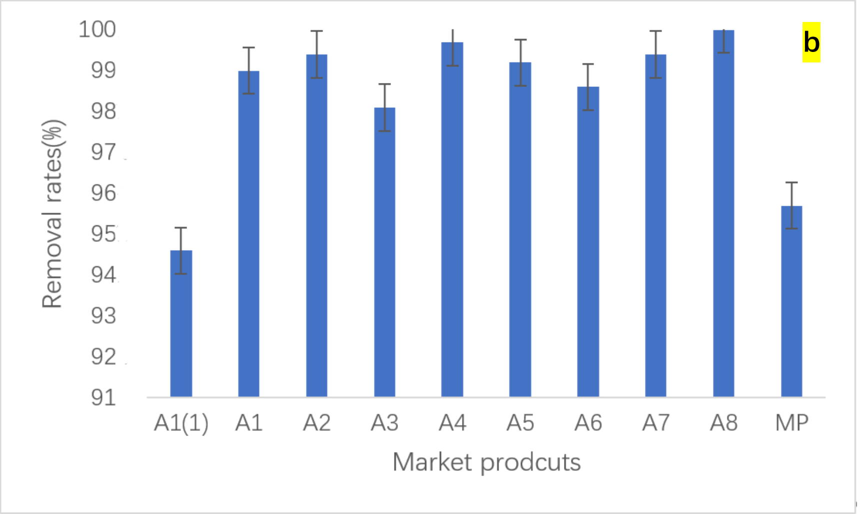


Figure 7. 8 MPs from Market product (a) treated by PAC in selected conditions (PAC 0.4 mmol/L, PAM 3 mg/L, and 800-mL Regent's Park Pond water and tap water were used respectively.

7.11.2 Application of PAC coagulation-flocculation and sedimentation for removal of microfibers in water

Flocculation is a commonly used method for the treatment of MP fibres in water. According to a study by Rist et al. (2020), the use of chitosan, a natural coagulant, was effective in removing up to 95 % of MP fibres from water samples. Another study by Lu et al. (2021) found that the use of algae as a natural coagulant was also effective in removing MP fibres from water. Activated carbon and other adsorbent materials have also been shown to be effective in removing MP fibres from water. A study by Han et al. (2020) found that the use of powdered activated carbon was able to remove up to 92 % of MP fibres from water. Similarly, a study by Zhang et al. (2021) found that the use of a magnetic adsorbent material was effective in removing MP fibres from water.

While treatment methods are important for reducing the impact of MP fibres, prevention strategies are also crucial. For example, the use of microfiber filters in washing machines has been shown to significantly reduce the release of MP fibres during washing (Rochman et al., 2019). Additionally, the reduction of synthetic fabric production and use, as well as proper disposal and recycling of synthetic fabrics, can also help to prevent the release of MP fibres into the environment.

Table 7.3 shows the results of the coagulation-flocculation and sedimentation treatment method using PAC and PAM simultaneously showed a high removal rate of microfibres from water samples. The manual counting method is detailed in Section 4.3, the coagulation-flocculation and sedimentation method is detailed in Section 4.4, and all materials are listed in section 4.2. It is worth noting that this treatment method is not only effective for MP fibres but also for microfibers (PET fibres), which are a major environmental concern. A study by He et al. (2021) showed that flocculation using cationic starch was effective in removing microfibers from wastewater with a removal rate of 80.6 %. The effectiveness of this method on microfibers is promising and provides an additional approach for addressing the issue of microfiber pollution.

Table 7. 3 Results of the coagulation-flocculation and sedimentation treatment method using PAC and PAM to remove Microfibres.

Sample	1	2	3	4	5	6	7	8
Before (/L)	605.25	532.78	597.88	684.38	721.86	514.73	1278.91	1318.68
After (/L)	31.47	7.99	16.74	30.80	43.31	20.07	134.29	114.73
Removal Rate (%)	94.8	98.5	97.2	95.5	94.0	96.1	89.5	91.3

In Table 7.3, the provided data showed that the flocculation treatment method was highly effective in removing MP fibres from water samples, with removal rates ranging from 89.5 % to 98.5 %. These results are consistent with the findings of other studies, such as the one by Lu et al. (2021) that found that the use of algae as a natural coagulant was also effective in removing MP fibres from water. Additionally, a study by Deng et al. (2021) showed that flocculation using PAC was effective in removing MFs (Diameter: 23 μm, Length: ~ 60 μm, PE, provided by University College Cork) from wastewater with a removal rate of 90 %.

While the coagulation-flocculation process has shown to be effective for the removal of MP fibres and microfibers, further research is needed to fully understand its optimal conditions for effective removal. For example, the type and concentration of coagulant used, the pH and turbidity of the water, and the size and shape of the microfibers may all play a role in determining the effectiveness of the treatment. Nevertheless, the use of coagulation-flocculation provides a promising method for addressing the issue of microfiber pollution and the impact of MP fibres on the environment and human health.

Overall, the coagulation-flocculation process using combined PAC and PAM was shown to be effective in removing both MP fibres and microfibers from water samples. This method, combined with other prevention strategies, provides a potential solution to address the issue of microfiber pollution in the environment. Further research and development are needed to optimize this method for effective removal of both MP fibres and microfibers in different environmental conditions.

CHAPTER 8 CONCLUSION AND FUTURE WORK

8.1 Conclusion

The thesis firstly focuses on assessing the magnitude of MP pollution on surface freshwater environments globally and collects the latest research information related to the sources, distribution, trend and impact of MPMPs in these environments. Furthermore, the thesis also delves into the analytical approaches used for studying MPMPs and the current status and development of policies on MP pollution.

Next, a novel qualitative and quantitative method was developed based on flow cytometry for the analysis of MPs in aqueous samples. The MP microbeads are automatically counted by the flow cytometer, which also informs about their particle size. The developed method consists of a first step to remove particles that could interfere with the detection by density separation. Secondly, potential microbes in suspension (e.g., E. Coli, yeast) are eliminated with UV irradiation and filtration. Finally, MPs are counted with flow cytometry in the treated sample. The quality parameters of the method were assessed with PS 100 μm as model MP. The work range of the method was 0.025-42 mg MP PS/L in the injected solution in the flow cytometer. The instrumental LOD and LOQ were 8.5 μg MP/L and 25 μg MP/L (assessed from 100 μg PS calibration curve), and RSD of the repeatability and reproducibility of the method were ≤2.2 % and ≤3.1 %, respectively. The method to quantify MPs was applied to samples of different quality. In this work, 5 polymer types of microbeads were analysed at 3 particle sizes each. The sample treatment method (density separation and

UV pre-treatments) carried out led to 95 % and 93.4 % recovery in the detection when applied independently, and an overall accuracy of 90 % was found when analysing different sizes and types of microbeads: PP, PVC, PET, PU and PA. The speed of the analysis (<1 h) and low chemical consumption makes it a sustainable way to analyse pollutants.

Moreover, the research explored the preliminary investigation on the potential impacts of coagulation-flocculation and sedimentation. MPs, sized ~150 μm, have been found in tap water at levels of ~5 particles/L, suggesting that water treatment plants are not effectively removing MPs. Therefore, there is an urgent need to evaluate their fate in drinking water treatment processes. Coagulation-flocculation and sedimentation are applied in water treatment to primarily decrease turbidity, and MPs contribute to water turbidity. This study focused on the removal of polystyrene (PS) beads of 100 μm with density 1.04–1.06 g/cm^3. The low-density PS beads pose a removal challenge because they have similar density to the media. The effects of initial water pH and stirring speed on MP removal by coagulation-flocculation and sedimentation were studied. The most effective conditions found for removing the PS beads from water, that led to removal rates up to 98.9 ± 0.94 %, were 3.4 mg Al/L of coagulant, pH 5, a flocculation time of 7 min and sedimentation time of 30 min. Based on this research, coagulation-flocculation can play a very important role in removing MPs during drinking water treatment.

This study has also demonstrated that the properties of MPs, including size, density, and material, are crucial factors affecting the removal efficiency of coagulation-flocculation and sedimentation processes. PVC microbeads with a higher density were found to be more easily flocculated, and larger-sized MPs had a higher removal rate through flocculation. The study also determined that the optimal treatment conditions were a PAC concentration of 0.4 mmol/L and PAM concentration of 3 mg/L, with a pH of 8 (before adding PAC), 240 rpm for 1 min and 35 rpm for 13 min, and sedimentation for 25 min, resulting in a high removal rate for MPs. These findings provide useful insights into the effective management and mitigation of MPs in natural water.

Based on the data from previous chapters with TOC, Zeta potential, PDA, FTIR, turbidity meter, and SEM-EDS characterization, the mechanism of the effect of MP coagulation-flocculation was studied under different conditions. Besides, the competition mechanism was also investigated. The data of TOC confirmed that pores on the surface of MPs could adsorb and enrich harmful substances in water. At the same time, under the treatment with PAC flocculant, MPs can be removed, and other water pollutants will also be removed. The study utilized FTIR and SEM-EDS to analyse the floc samples. FTIR spectral peak analysis showed that the coagulant was effective to promote optimum coagulation-flocculation to successfully lead to sedimentation of the flocs containing MPs. The SEM-EDS method was used to compare the distribution of flocs under different flocculants and EDS analysis revealed the distribution of contaminants in the floc structure. The Zeta potential data was analysed to understand the electrochemical mechanism of the reaction of different flocculants and the competition among pollutants. The kinetic changes of flocs during flocculation were studied using a PDA instrument and the removal effect of MPs was found to increase after the flocs were broken and reunited. The PHREEQC mathematical model was used to simulate the effect of pH on the flocculation process. The reaction principle of flocculation for removing MPs in water was explained through the DFT chemical model and the XDLVO action energy model.

In summary, coagulation-flocculation-sedimentation is effective in treating water contaminated by MPs and has been proven to be an efficient process. In addition, this method has the advantages of environmental protection, safety, low cost, and is easy to operate and expand. In terms of removing MPs, the efficiency and effect of this method are significantly better than other common methods, and it is easy to be widely recognized and applied in the industry at present. However, the thesis also has limitations, as it has only been confirmed to be applicable to MP beads. For other types of MPs, such as microfibers, further validation is required to establish their applicability.

8.2 Future Work

Currently, the treatment of MPs in water bodies is highly challenging issue, and researchers are seeking effective solutions to protect the environment, the quality of drinking water and the health of the consumers. On the one hand, researchers are looking for more efficient separation and collection techniques, such as capturing MPs through a combination of physical, chemical, and biological methods. On the other hand, degradation methods (biological or through advanced oxidation) are other approaches that can become effective for treating MPs in water if improved and optimised. Reducing residual MPs, monitoring by-products of the treatment and minimizing the adverse impact on the environment remain current challenge. Despite the challenges in the treatment of MPs, the study has found that the introduction of innovative treatment methods, as well as the combination of different treatment techniques, can lead to very effective results. Therefore, there is potential for significant improvements in the removal of MPs from natural water through the use of advanced and novel treatment approaches. Lastly, evaluating the impact of MPs on the ecosystem and biota, and identifying organisms that can help to biomonitor MPs in the environment, arecrucial aspects in evaluating MP pollution, which can help us better understand the impact of MPs on the environment and biota. Therefore, future research should also focus on the MP contamination standard and its toxicological studies on humans and ecosystems.

Currently, there are several methods available for treating MPs in water, including physical, chemical, and biological treatments. Physical treatment methods such as filtration and sedimentation have limitations in terms of efficiency and may generate by-products. Chemical treatment methods such as extraction and adsorption may also have challenges with efficiency and cost. In particular, chemical treatments like oxidation may pose additional problems due to the generation of by-products. Therefore, there is a need for continued research and development of more effective and sustainable methods for the treatment of MPs in water. Biological treatment methods, such as biological adsorption, are currently considered the most promising methods for degrading MPs. However, it remains a question whether they can efficiently and rapidly degrade MPs. In the future, as technology improves, biological treatment methods will become more efficient and feasible. Additionally, combining physical and chemical treatment methods may result in more efficient, sustainable and economical solutions. Meanwhile, raising public awareness of water resource protection and environmental issues, as well as strengthening government regulation and enforcement, will help reduce MP discharge and pollution, thus reducing the need of treating MPs in water.

In terms of treating MPs through coagulation flocculation and sedimentation methods, future research directions will mainly focus on improving flocculation efficiency, comprehensive utilization, application in practical engineering, environmental impact assessment and sustainable development. Specifically, the efficiency of flocculation can be improved by modifying coagulants, effectively reducing the pollution of MPs in water. Additionally, coagulation, flocculation and sedimentation technology can be combined with other technologies to achieve comprehensive utilization of MPs. Based on this, coagulation-flocculation-sedimentation technology can be applied to practical engineering, and large-scale trials can be carried out to prove its feasibility and practicality. At the same time, the impact of coagulation-flocculation technology on the environment and biota must be assessed to ensure that it is an environmentally friendly and safe treatment method. Finally, coagulation, flocculation and sedimentation with sustainable development features (such as energy efficiency, chemical utilization and so on) must be designed to ensure long-term application.

There is important scope for new toxicological research. As per today, the MP features that are more important for toxicity are not clear although there are increasing number of works that link them with oxidative stress. Overall, MP pollution has the greatest impact on marginalized groups and communities that live close to them, thus causing "environmental injustice" (Eriksen et al., 2015). MP waste not only threatens the livelihoods of people living near the sea, but also those who eat seafood. Seafood loaded with toxic MPs and nanoplastics can lead to a range of human health problems (Rochman et al., 2013). In the future, MP toxicology research will continue to evolve into a better understanding of the impacts of MPs on ecosystems. The effects of different types and forms of MPs on biological organisms may be studied, as well as the sensitivity of ecosystems. Additionally, the interaction between MPs and other pollutants (such as heavy metals, persistent organic pollutants and pathogens) and the bioavailability both may also be studied to evaluate their impact on ecosystems. Furthermore, MPs toxicology research can provide important scientific basis for future environmental protection policies. By thoroughly evaluating the impacts of MPs on ecosystems, scientific basis can be provided for the formulation of more effective policies to control and reduce MP pollution (Liu et al., 2020).

In addition, to tackle this issue, many countries have implemented legal restrictions on MP pollution. The European Union has taken a leading role, with a ban on microbeads in rinse-off cosmetic and personal care products since 2018, as well as setting a limit on intentionally added MPs (European Parliament, 2019). Similarly, the United States, Canada, South Korea, and Japan have implemented restrictions or bans on microbeads in personal care products (National Conference of State Legislatures, 2021; Government of Canada, 2018; Ministry of the Environment, Japan, 2021). Moreover, China has issued a plan to reduce the use of MPs to control plastic pollution

(National Development and Reform Commission, 2018). However, only eight countries worldwide have established legally binding bans on MPs through national laws or regulations, which mostly cover only personal care products, except for New Zealand, where the ban extends to household, automotive, and industrial cleaning products (Lusher et al., 2017; Tan et al., 2019; Syberg et al., 2015; Gago et al., 2018; Ministry for the Environment, 2018). In addition to national laws and regulations, voluntary approaches are also being employed by governments, companies, and civil society organizations to reduce the use of MPs (Chua et al., 2021; Taylor et al., 2020).

MP pollution is about environmental justice. Even though our study proposes methods for analysing and treating MPs which can provide some references for the legal standards of MP pollution and treatment, the current environmental laws to manage and reduce MP pollution are not yet addressing the serious problems it causes and maximum concentration levels of MPs in freshwater or drinking water have not been established. Future studies place MPs in the list of priority pollutants and may also put them in the agenda

dedicated to achieving environmental legal justice and the sustainable development goals (SDGs). Provide detailed and feasible legal and professional advice on all stages of the development of products containing MPs, including raw material, production, discharge, distribution, use, abandonment and pollution treatment. Define violations, crimes, appeals and sentencing standards for MPs environmental laws. Classify and define who is empowered and responsible, such as enterprises, individuals, states and governments.

In general, MPs are a serious but not yet well defined challenge that adds to current environmental issues. Tackling MPs is not only a necessary measure to reduce environmental pollution, but also a key step in protecting biodiversity and ecological system health. Therefore, research and promotion of water treatment technologies optimised for MP removal is of great significance because they can effectively reduce the harm of MPs to the environment and biota, thereby building a greener and healthier environment.

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