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Insight into the physical and chemical attributes of polypropylene microplastics

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ABSTRACT

Microplastics (MPs) are increasingly recognised for their significant impact on the environment and human health. Understanding MPs is crucial to grasp their widespread presence in various environmental areas. The unique properties of MPs, such as their small size, durability, and potential to adsorb and transport environmental pollutants, underscore the necessity of studying their characteristics. This study aims to investigate the physical and chemical characteristics of polypropylene microplastics (PPMPs) and address the dispersion stability issues associated with them. The PPMPs were characterised using scanning electron microscopy (SEM), revealing a surface structure marked by cracks, fractures, and a rough texture. The PPMPs were observed as irregularly shaped, white particles. Their size distribution spans from 14 to 96 µm, with a mean size of 50.00 µm. Fourier Transform Infrared Spectroscopy (FTIR) confirmed the presence of polypropylene functional groups, specifically identifying characteristic peaks at 2952-2846 cm^{-1} and 1456 -1376 cm^{-1}, indicating C-H stretching and bending vibrations, respectively, with additional peaks suggesting degradation. The effect of different concentrations of sodium lauryl sulfate (SLS) on PPMPs dispersion indicated that 5% SLS led to superior dispersion of PPMPs, thereby addressing the stability issue. These findings provide comprehensive insights into the physical and chemical attributes of PPMPs and their dispersion stability, offering a foundation for informed environmental assessments and the development of effective mitigation strategies.

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1. INTRODUCTION

Plastic pollution in wastewater has emerged as a serious environmental concern in recent years. This plastic waste enters the wastewater systems and threatens human health and the environment. The annual global plastic production in 2017 exceeded 348 million tonnes and is expected to double by 2035 [1]. Approximately 13 million tons of plastic are reported to be discharged into water bodies annually, with 80-90% of this waste being microplastics (MPs) [2-3]. MPs, small plastic particles with a size less than 5 mm, have emerged as a pervasive environmental concern, particularly in aquatic ecosystems. The MPs are created by the degradation of larger plastic products or from the raw materials used in many personal care products. MPs are highly persistent and may exist in water for a long time. Governed by a high surface area-to-volume ratio and low density, MPs readily adsorb persistent organic pollutants, facilitating their transportation from heavily contaminated zones to less affected areas along the sea surface layer [4]. MPs can pose severe threats to aquatic organisms through ingestion, exposing them to harmful chemicals that may cause health problems, including reproductive disorders, immune system suppression, and impairment of vital functions such as respiration and reproduction [5-7]. This harmful effect may eventually transfer to humans through the food chain, leading to serious health issues.

Among the diverse types of MPs, polypropylene microplastics (PPMPs) hold significance due to their prevalent use in various consumer products and their resistance to degradation. As the global prevalence of PPMPs pollution escalates, understanding its key properties becomes important for developing effective water remediation strategies. Various removal methods such as chemical coagulation [5], [8-9], biodegradation [10-12], ferrofluid [13], photodegradation [14-18] and electrocoagulation [16], [19-21] have been explored to address this growing environmental challenge. However, each method possesses unique advantages and limitations, and their efficacy can vary depending on factors such as the type and characteristics of MPs and the properties of the wastewater.

Understanding the properties of PPMPs is crucial for designing effective removal strategies. MPs of varying sizes, shapes, and surface properties influence removal efficacy, transport dynamics, and pollutant adsorption. Additionally, the role of surfactants in wastewater, which can significantly affect MPs characteristics, is often overlooked. Surfactants alter MPs surface properties, impacting aggregation, sedimentation, and pollutant interactions [22-23]. They enhance MPs mobility by reducing surface tension, leading to increased dispersion, and modifying pollutant adsorption capacity.

This study aims to investigate both the physical and chemical properties of PPMPs and the effects of surfactants on their dispersion. By focusing on the interactions between surfactants and PPMPs, the research seeks to understand how these factors influence the stability and behaviour of PPMPs in water environments. The insights gained from this study will contribute to mitigating the environmental impact of plastic pollution, especially in water systems where surfactants and MPs coexist.

2. METHODOLOGY

2.1 Preparation of the polypropylene microplastic

In this study, polypropylene microplastics (PPMPs) sourced from degraded polypropylene (PP) storage boxes were utilised. The degraded PP box was cut into small pieces, and a thorough washing process was performed to eliminate any impurities, such as dirt and debris. The PP fragments were subsequently air-dried completely in a well-ventilated area and then finely ground into smaller particles using an industrial grinder. To obtain a refined consistency, the ground PP material was passed through a 63-micron sieve, yielding a finely powdered form of PPMPs. These prepared PPMPs were carefully stored in a container away from sunlight and moisture for further analysis. Fig. 1 presents a summary of the preparation process of PPMPs.

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Fig. 1. Preparation of PPMPs

2.2 Physical and chemical characterisation of the polypropylene microplastics

The physical attributes of the PPMPs were meticulously examined using a G1600 digital optical microscope, which facilitated the detailed characterisation of their shape, colour, and texture. For sizing the PPMP particles, ImageJ software was utilised. Moreover, an in-depth analysis of the PPMPs' morphological features was conducted using a Regulus 8200 scanning electron microscope (SEM). This provided a comprehensive view of the PPMPs' surface structure and topography, thereby offering crucial insights into their microscopic physical characteristics.

The chemical composition of the PPMPs was analysed using Fourier Transform Infrared Spectroscopy (FTIR) with a Nicolet 7600 spectrometer. This analysis focused on identifying the functional groups present in the PPMPs. The study also investigated the impact of surfactants on the dispersion of aged PPMPs in a solution. This was achieved by introducing sodium lauryl sulfate (SLS) in concentrations varying from 1% to 5%. A mixture of 15 mL of 1-5% SLS solution was added to 150 mL of a 500 ppm PPMPs solution to examine the resulting dispersion of the PPMPs. The extent of this dispersion was quantitatively assessed using a turbidity meter, which measured the relative turbidity (RT) as per Eq. 1.

$$RT = {}^{T_i}/_{T_0} \quad (1)$$

Where RT represents the relative turbidity, T_i reflects the turbidity at a specific time, and T_0 signifies the initial turbidity (turbidity at time 0).

3. RESULT AND DISCUSSION

3.1 SEM and optical image of PPMPs

To gain a deeper understanding of the structural characteristics and surface morphology of the PPMPs prepared in this study, SEM and optical microscope imaging were employed. Fig. 2(a) presents the SEM image of the PPMPs, which exhibit a distinctive surface texture characterised by cracks, fractures, and a notably rough surface. These observed surface features are attributed to polymer ageing and oxidative processes, which render the PPMPs fragile and prone to degradation [24]. Besides, the grinding process during sample preparation, as mentioned in Section 2.1, contributes to these morphological changes. These observed surface structures significantly influence their toxic properties in the environment, primarily due to the increased surface area that facilitates the adsorption of pollutants and enhanced leaching of additives [25]. Moreover, the rough surface and structural deformities enhance bioavailability, impacting ingestion dynamics and contributing to the overall ecological implications of MPs pollution [26].

The optical image of PPMPs is shown in Fig. 2(b), exhibiting an irregular, white flake-like morphology. These irregular-shaped flakes suggest variations in size and morphology within the MPs population. The physical properties of these MPs, such as size, shape, and colour, play a crucial role in their removal during wastewater treatment processes. Smaller particles, due to their reduced size, may escape filtration systems

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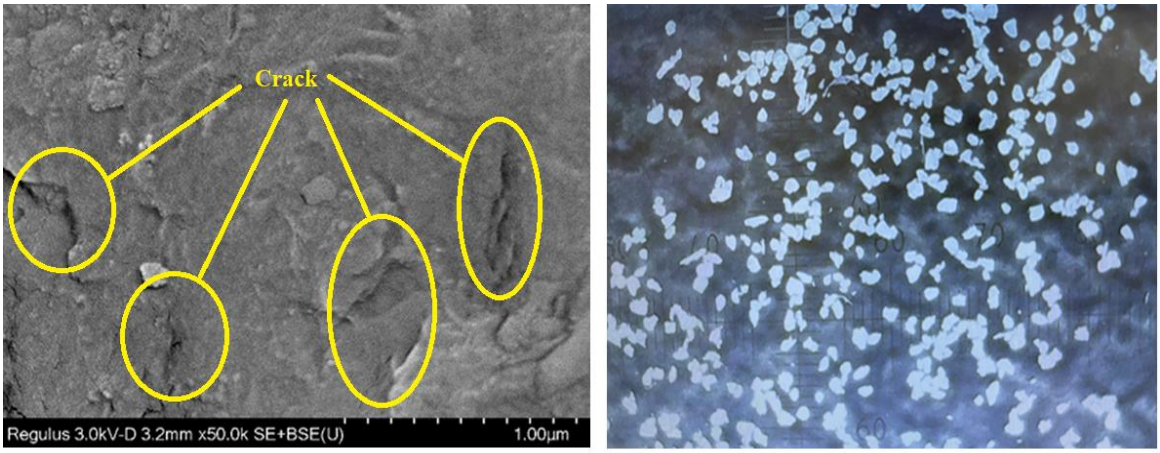
[27], while irregular shapes can affect the efficiency of mechanical screening methods [28]. Additionally, the colour of MPs, particularly if they blend with the wastewater, can make visual detection and subsequent removal challenging [29]. Understanding these physical properties is essential for developing more effective wastewater treatment strategies that can address the varying characteristics of MPs and enhance their removal efficiency.



(a) (b)

Fig. 2. (a) SEM image of PPMPs; (b) Optical image of PPMPs

3.2 Size analysis of PPMPs

The analysis of MPs size distribution provides valuable insights into the characteristics of the studied particles. The particle size distribution of PPMPs was statistically analysed and presented in Table 1. With a sample size of 334, the average size of PPMPs is approximately 50.00 µm. The median of 48 µm suggests a slightly left-skewed distribution. The standard deviation of 15.81 µm highlights a moderate level of size variability, with a range spanning from 14 to 96 µm. This diverse size range is crucial in understanding the potential impacts of MPs on the environment. The data follows a symmetric normal distribution, as shown in Fig. 3, with most particles clustered near the mean, creating a bell-shaped curve.

The particle size of MPs is vital in pollution research as it influences their environmental transport, bioavailability, and toxicity, with smaller particles potentially posing greater risks to ecosystems and organisms. The MPs size emerged as a crucial factor influencing their role as vectors and their overall environmental impact. In the aquatic environment, MPs with sizes smaller than 500 µm have been identified within various aquatic organisms, such as shrimp, mussels, and fish [30-32].

Understanding the size distribution of PPMPs is crucial for selecting the most effective removal method. Different removal techniques exhibit varying degrees of efficacy depending on the size of MPs. Larger MPs, typically those exceeding 1 mm, can be efficiently removed through physical filtration methods. The relatively larger size facilitates their capture or filtration, making these methods particularly effective, especially during the preliminary or primary treatment phase in a wastewater treatment plant (WWTP) [5], [7]. On the other hand, addressing smaller MPs requires the application of more sophisticated treatment methods, including advanced oxidation processes (AOPs), coagulation-flocculation, electrocoagulation, and biodegradation. MPs within the size of 27 -1000 µm have been reported to be effectively removed using these methods [6], [33-35]. These methods account for both the physical characteristics of the MPs and their chemical properties, such as surface chemistry, charge, polarity and

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hydrophobicity. By utilising the MPs chemical properties, these methods can selectively target and remove MPs within the specified size range, offering a comprehensive and effective approach to mitigating their presence in various environmental settings.

Table 1. Size particle analysis of PPMPs

N total	Mean (µm)	Standard Deviation (µm)	Min (µm)	Max (µm)	Median (µm)
334	50.00	15.81	14	96	48

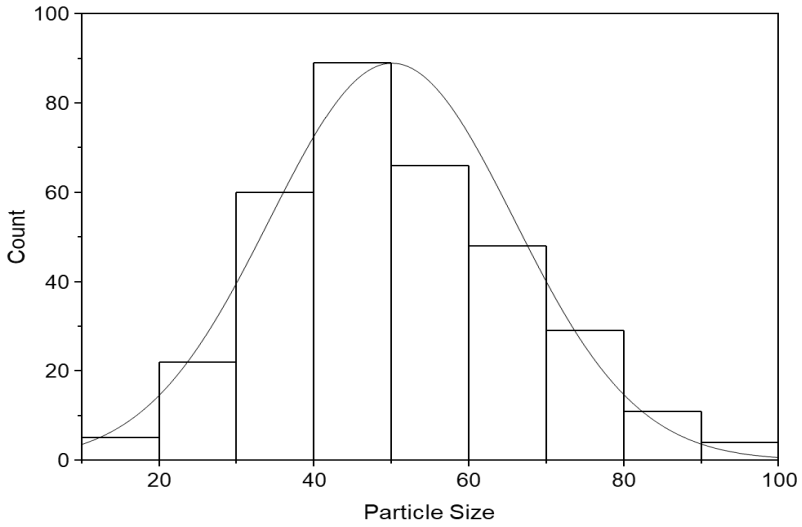

Fig. 3. Particle size distribution of PPMPs

3.3 FTIR analysis of PPMPs

To achieve a thorough characterisation of the PPMPs, Fourier Transform Infrared Spectroscopy (FTIR) plays an important role. The FTIR spectra of PPMPs, as shown in Fig. 4, provide a detailed analysis of the chemical bonds and functional groups of the PPMPs. This information is crucial for understanding their chemical properties and how they may interact with the environment. By examining the specific absorption bands, the presence of various chemical structures within the PPMPs can be deduced, providing insights into the effects of ageing and environmental exposure on their chemical integrity. The FTIR spectra of PPMPs showed characteristic peaks of PP located at 2952-2846 cm^{-1} and 1456 -1376 cm^{-1} were assigned to the C-H stretching vibration of methyl and methylene group respectively [36-37]. Several peaks at 1170. 970 and 873 cm^{-1} were assigned to the reference characteristic of PP [38], demonstrating that the MPs can be identified as PP.

The peaks observed at 1704 cm^{-1} and 3856 cm^{-1} in the FTIR spectrum indicate the stretching vibrations associated with the carbonyl group and hydroxyl group, respectively. These findings indicate oxidative degradation during the ageing process. The carbonyl peak shows the formation of carbonyl groups from oxidative reactions [39]. The hydroxyl peak suggests the addition of hydroxyl groups, confirming oxidative changes in the PP structure. This degradation occurs through environmental processes such as UV exposure (photo-oxidation), heat (thermal oxidation), and chemical interactions with pollutants. These processes create new functional groups like carbonyl (C=O) and hydroxyl (OH) groups. These groups can increase

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the chemical affinity of PPMPs for pollutants through hydrogen bonding. Understanding these changes is crucial for assessing the environmental impact and removal of PPMPs using electrocoagulation (EC).

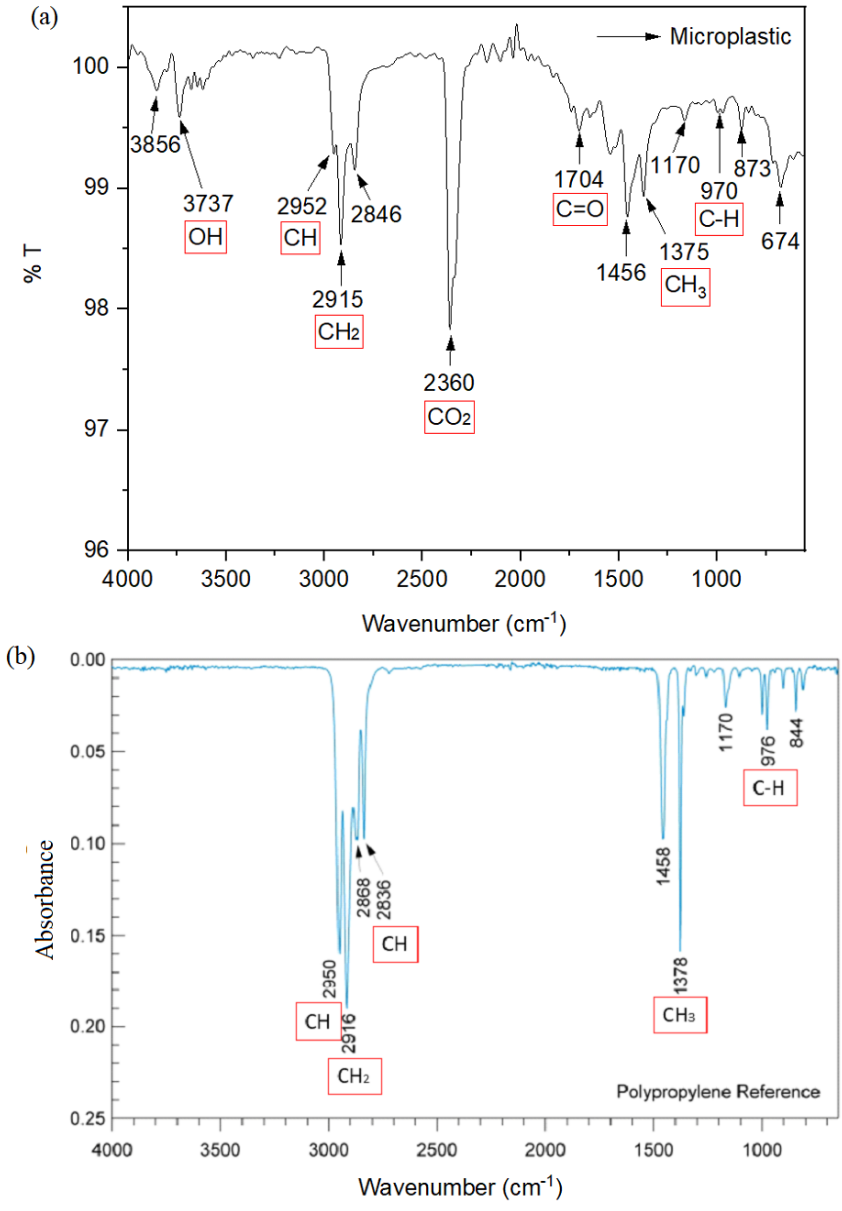

Fig. 4. FTIR spectra of PPMPs and PP reference

3.4 Dispersion of PPMPs in SLS

The study on the dispersion of PPMPs in aqueous solution is important to provide a standardised approach to investigate the behaviour of PPMPs in aquatic environments. The choice of dispersant plays an important role in simulating realistic scenarios and standardising experimental conditions. Different

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concentrations of sodium lauryl sulfate (SLS) were employed to examine its impact on the stability and dispersion behaviour of PPMPs. Relative turbidity is utilised as an indicator, providing valuable insights into the dynamics of MPs dispersion over time. Fig. 5 depicts the dispersion trends of PPMPs under varying SLS concentrations (2-5% SLS).

Relative turbidity, representing the degree of dispersion, is plotted over time. The control group without SLS serves as a reference. In this study, a notable trend in relative turbidity was observed concerning the varying concentrations of SLS. At a concentration of 5%, there was a modest increase in relative turbidity, followed by a period of stability over time. This persistent stability at 5% SLS concentration suggests an effective dispersion of PPMPs in the solution, implying that this concentration is optimal for maintaining a dispersed state. In contrast, the 4% and 3% SLS concentrations showed an initial spike in relative turbidity, followed by a slight decrease and then stabilisation. This pattern may suggest a temporary aggregation phase before reaching a more stable dispersion. The behaviour at 2% SLS concentration was more erratic, displaying a fluctuating trend without clear stabilisation, potentially indicating difficulties in achieving and maintaining an effective dispersion state. The control group, without any dispersant, demonstrated poor dispersion capabilities. Interestingly, the stabilised dispersion observed at 5% SLS concentration appears ideal for the removal processes, ensuring that PPMPs remain dispersed and are more effectively removed.

These findings align with previous studies that have emphasised the importance of surfactant concentration in stabilising MPs dispersions. For instance, a similar study found that higher surfactant concentrations led to better dispersion of MPs [40-41], echoing these observations. The selection of an appropriate SLS concentration is therefore crucial for optimal MPs dispersion, enhancing the efficiency of removal methods and aiding in the reduction of MPs pollution in aquatic environments.

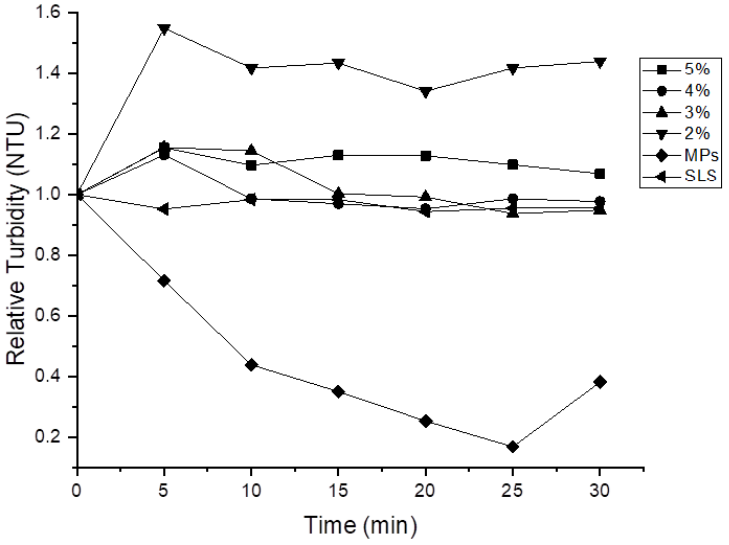

Fig. 5. Effect of SLS concentration on PPMPS dispersion

3.5 Comparison With Other Studies

This section discusses a comparative approach of the findings with existing research in the field to contribute to the collective understanding of the characteristics of MPs. The physical characteristics of MPs, as investigated by various studies, are presented in Table 2. The imaging methods employed in these studies have provided valuable insight into the surface structure of MPs and their associated characteristics. The observation revealed MPs with size ranges from 13 to 3000 µm depending on the purposes of the study,

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with irregular and flake shapes being common. The identification of MPs surface features showing fractures, cracks and rough textures aligns with similar findings from [38], [42-44]. [38] reported crack formation on the surface of MPs and emphasised the enhancement of polarity and surface negative charge on MPs. Additionally, [42] reported wrinkle and discolouration on the surface of MPs in the sea sediment, indicating potential environmental degradation effects that exhibited comparable surface characteristics to those observed in this study. Similarly, [43] noted crack formations, wrinkles and rough surface texture on MPs. The development of cracks, wrinkles, rough surfaces, and pits observed in these studies can be attributed to a combination of factors related to environmental exposure and the ageing process of the material. These diverse findings collectively contribute to a comprehensive understanding of the physical characteristics of PPMPs, emphasising the importance of careful considerations in environmental research and removal strategies.

Table 2. Physical Characteristics of MPs

Reference	Imaging method	Observed surface structure	Size (µm)	Shape characteristic	Additional findings
This study	SEM, optical microscope	Crack, fractures, rough	14-96	Irregular, flake	May enhance adsorption, bioavailability.
[45]	-	-	1000-2000	Microspheres	Up to 98.4% removal via electrocoagulation (EC).
[38]	SEM	Crack	2000-3000	Flake	Polarity & surface negative charge enhanced in aged PP.
[42]	SEM, optical microscope	Wrinkle and discolouration	255-1279	Irregular, fiber	The surface morphology changed due to degradation.
[43]	SEM	Crack, wrinkle and rough surface	13	-	The removal process is sensitive to microplastic surface physicochemical properties.
[44]	SEM	Crack and pit	-	-	Crack and pit due to MPs ageing.

Table 3 summarises findings regarding the influence of surfactants on the dispersion behaviour of MPs from previous studies. This study utilised SLS at concentrations ranging from 2% to 5%, with optimal dispersion observed at 5% SLS concentration. Contrastingly, most of the previous studies investigated the use of various types of surfactants in different categories, such as cationic, anionic, and non-ionic surfactants. Examples of surfactants used include cetyltrimethylammonium bromide (CTAB) [40], [46-47], hexadecylpyridinium bromide (HDPB) [48-49], benzyldodecyldimethylammonium bromide (BG) [47], polyquaternium-28 (PQ28) [47], benzyltriethylammonium bromide (BLB) [47], tetraethylammonium bromide (TLB) [47], sodium dodecyl sulphate (SDS) [11], [50], sodium lauryl diphenyl ether disulfonate (SLDED) [47], dodecyl sodium sulfonate (DSS) [47], sodium dodecylbenzene sulfonate (SDBS) [11], [50], polyoxyethylene stearate (POES) [47], tween-40 (T40) [47], tween-80 (T80) [47], Triton X-100 (Tx100) [11], [48], polyoxyethylene nonyl phenyl ether-20 (TX20) [47], and sodium dodecylbenzene sulfonate (SDBS) [50], [11]. The type and concentrations of surfactants play a significant role in improving the mobility of MPs with significantly greater mobilities of MPs. These findings highlight consistent evidence of the influential role of surfactant type and concentration on the dispersion characteristics. The findings emphasise the vital influence of surfactant type and concentration on MPs mobility, suggesting a need for more in-depth study, particularly on SLS, to understand its specific role and compare its efficacy with other surfactants for environmental impact assessment. Future research could explore comparative studies on different surfactant types and concentrations on various microplastic types and assess ecological implications.

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Table 3. Effect of Surfactant on the Properties of MPs

Reference	Surfactant	Concentration	Observed dispersion behaviour	Additional findings
This study	SLS	2-5%	Varied dispersion with optimal at 5%.	Stable dispersion at 5%.
[40]	CTAB, SDBS	20 mg L^{-1}	The mobilities of PE and PP under CTAB were much greater than those under SDBS.	Applying surfactants can greatly enhance the suspension and mobility of PP.
[46]	CTAB, SDBS	100, 500 mgL^{-1}	The mobility under high concentrations of surfactants was greater than that at low concentrations.	The presence of surfactants was effective in increasing the migration of microplastics.
[48]	Tx-100, , HDPD, SDBS,	0 to 5 CMC (critical micellization concentration)	The addition of surfactants changed the surface properties of microplastics, leading to improved adsorption capacity for Pb^{2+} on MPs.	The concentration of surfactant had a significant impact on the adsorption capacity of microplastics for Pb^{2+}, with higher concentrations leading to increased adsorption capacity.
[11]	SDBS, SDS, CTAB, DTAB, Tw20, and Tx100	0 to 100 ppm for SDBS and 30 ppm for the other surfactants	Surfactants can significantly enhance the capacity of microplastics to adsorb hydrophilic pollutants.	Suggests that electrostatic forces, van der Waals' forces, and steric hindrance influence the adsorption behaviour of ionic organic pollutants on surfactant-adsorbed microplastics.
[47]	Cationic surfactants: BG, PQ28, CTAB, BLB, TLB Anionic surfactants: SDS, SLDED, DSS, SL, SDBS Non-ionic surfactants: POES, T40, T80, Tx100, TX20	NM	The research found that both anionic and cationic surfactants had similar effects on the mobility of polyethylene microplastics in the sand column.	The surfactants were observed to interact with the microplastics through a hydrophobic effect, leading to an increase in the hydrophilicity of the microplastics and promoting their migration into the porous media.
[49]	HDPB	0.369 mmol g^{-1}	The introduction of HDPB into the aluminosilicate filter media significantly improved the removal of microplastics, particularly polyamide (PA) microplastics.	The use of a cationic surfactant (HDPB) to modify the surface of the aluminosilicate filter media transformed it into a hydrophobic surface.
[50]	SDBS, SDS, CTAB, CDAB, Tw20, and Tx100	0 to 100 ppm for SDBS and 30 ppm for the other surfactants	It was observed that surfactants can significantly enhance the capacity of microplastics to adsorb hydrophilic pollutants.	The study reveals how surfactants modify microplastics' surfaces, enhancing their adsorption of ionic pollutants.

NM : Not mentioned

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4. CONCLUSION

This research was conducted to discover the physico-chemical properties of PPMPs, focusing on their complex physical and chemical attributes. The study revealed their surface structure, size distribution, functional group characteristics, and the impact of surfactants on the dispersion of PPMPs, suggesting viable routes for future environmental mitigation. Crucial insights were gained into the intrinsic properties of PPMPs. SEM and optical microscopy identified a unique surface structure characterised by fractures and roughness. The average particle size, approximately 50 µm, along with their irregular, flake-like shapes and white colour, significantly influence their behaviour in aquatic settings, affecting both their removal during wastewater treatment and their ecological impact. Furthermore, FTIR analysis provided insight into the oxidative ageing of PPMPs, revealing specific functional groups that contribute to a deeper understanding of their chemical composition. This research discovers that effective dispersion of PPMPs is achieved at higher concentrations, specifically at 5%, offering a promising strategy for their removal from water systems. This research lays the groundwork for developing targeted strategies to address MPs pollution, highlighting the imperative for future studies to expand on these findings and explore innovative solutions to this pressing environmental issue.

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6. CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits or commercial or financial conflicts and declare the absence of conflicting interests with the funders.

7. AUTHORS' CONTRIBUTIONS

Nor Ku Nazatul Husna Mohd Jackariya: Experimental work; **Nor Aimi Abdul Wahab**: Experimental work and writing the original draft; **Norfaezatul Alysa Othman**: Experimental work and writing the original draft; **Nor Ayuni Zamri**: Experimental work; **Norain Isa**: Conceptualisation, supervision, editing, and validation; **Vicinisvarri Inderan**: Editing and supervision.

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