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Original Research Article

MICROSCOPIC METHOD TO VERIFY THE EFFICIENCY OF REMOVAL OF ORGANIC POLLUTANTS FROM MICROPLASTIC SURFACES

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A b s t r a c t

The purification of microplastic samples is a crucial step in environmental research, aiming to remove contaminants and ensure accurate analysis. This study explores various methods for purifying microplastics, focusing on the removal of organic contaminants, specifically fulvic acids. Comparative analysis using microscopic imaging techniques was conducted to evaluate the effectiveness of these methods. The results highlight the complexities involved in microplastic purification and the challenges associated with different approaches. While some methods showed promising outcomes, such as the sonification method, it was also observed that they could potentially alter the microplastic structure. Additionally, the limitations and potential interferences of other purification methods, such as Fenton's solution, were identified. This study underscores the importance of selecting purification methods that minimize negative impacts on microplastics and ensure reliable analysis. Further research is needed to optimize purification techniques and fully understand their effects on microplastic integrity. This research contributes to the broader goal of developing robust methodologies for microplastic analysis in environmental studies.

Keywords: microplastics, purification methods, fulvic acids, comparative analysis, microscopic imaging, environmental research

1. INTRODUCTION

Research into the search for methods to identify microplastic particles confirms that assessment based on visual analysis alone can be prone to error, so additional chemical verification is required [1–3]. Advanced chemical identification techniques for microplastic samples based on instrumental analysis enable precise detection and characterization of small plastic fragments. Fourier transform FT-IR microspectroscopy and Raman spectrum microspectroscopy techniques are particularly popular in microplastics research. However, both of these techniques can encounter issues when identifying plastic due to surface contamination with organic and inorganic matter. Spectroscopic techniques can be

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interfered with, especially by biofilm [4,5]. A prerequisite for reliable particle analysis of environmental microplastic samples is the removal of contaminants from the sample through a purification process that does not adversely affect the microplastic particles themselves [6].

The surface of microplastics offers favorable conditions for the deposition of contaminants, particularly those from external sources. This is attributed to several factors, including surface degradation that leads to the formation of kinks, cracks, and depressions on the polymer surface, providing ideal sites for the absorption of contaminants. Porous structures exhibit the highest affinity for adsorbing contaminants, and in the case of microplastics, this is particularly relevant to foamed forms due to the increased actual surface area of the microplastic particles.

Another significant factor that influences the deposition of contaminants on the surface of microplastics is the hygroscopicity of the plastic. Hygroscopicity refers to the ability of various polymers, plastics, and fibers to absorb water from the surrounding environment [7–9]. The hygroscopicity is directly associated with the diffusion of water molecules (along with micro-pollutants of diverse properties and origins) into the polymer structure. It depends on several factors, including the chemical structure of the polymer, the degree of crystallinity, the molecular structure (conformational forms), the level of cross-linking, the thickness and dimensions of the sample, the presence of gaps and cracks, the humidity level, and the temperature of the environment [10].

Among the impurities commonly found on the surface of microplastics, organic matter is quite prevalent. Fulvic acid (FA), owing to its high solubility in water, represents a mobile and significant fraction of natural organic matter (NOM) [11,12]. One of the primary methods proposed for the purification of plastic microplastics from NOM is the wet peroxide oxidation (WPO) method in the presence of an Fe(II) catalyst [13], also known as the Fenton reaction. Considering that the presence of fulvic acids can enhance the rate constant of the Fenton reaction [14], promising results were expected in terms of cleaning the microplastic surface. In addition to the Fenton reaction, hydrogen peroxide alone was employed, along with the use of sonification in water accompanied by a cooling system to prevent excessive deformation of the microplastic caused by ultrasound and the resultant heat generation during the process. The study carried out aims to evaluate the effectiveness of the removal of organic compounds from the surface of microplastic samples collected from the environment using the known above-mentioned methods proposed in the literature on the topic of microplastics.

2. MATERIALS AND METHODS

2.1. Material and sample preparation for testing

The material collected during fieldwork was utilized to conduct a comparative analysis study on methods for cleaning microplastics from organic pollutants. To ensure a consistent and uniformly distributed contamination on the surface of all tested samples, a mesoplastic fragment obtained through the selective method described in [15] from the coastal area of the Baltic Sea (sample site coordinates: 53°55.4120'N, 14°16.5960'E) was chosen for the study. The Nicolet™ iS50 FTIR spectrometer (SN: AUP1400379) equipped with an ATR attachment and OMNIC 9.2.106 software (driver version: 9.2, firmware version: 1.11) was used to determine the type of plastic in the uncontaminated region of the fragment. The identification result is presented in Figure 1. The same spectrometer was employed to identify the contamination itself. The contaminated portion was mechanically removed from the plastic piece and directly applied onto the diamond crystal of the ATR attachment. The measurement result is depicted in Figure 2. Spectragryph 1.2.14 software was utilized for data visualization.

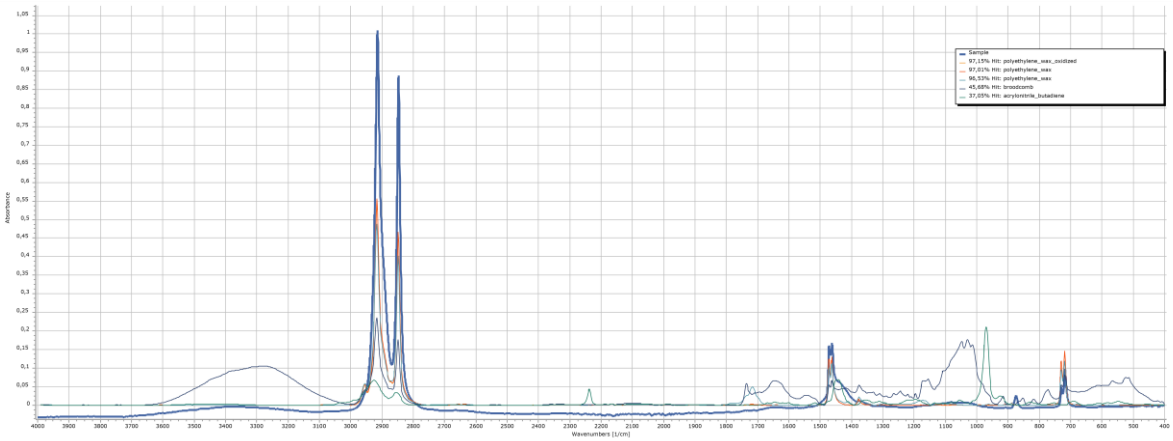


Fig. 1. FT-IR spectrum and spectral database fit factor indicating 94.17% similarity to Fulvic acids (Huleh peat; A. Nissenbaum)

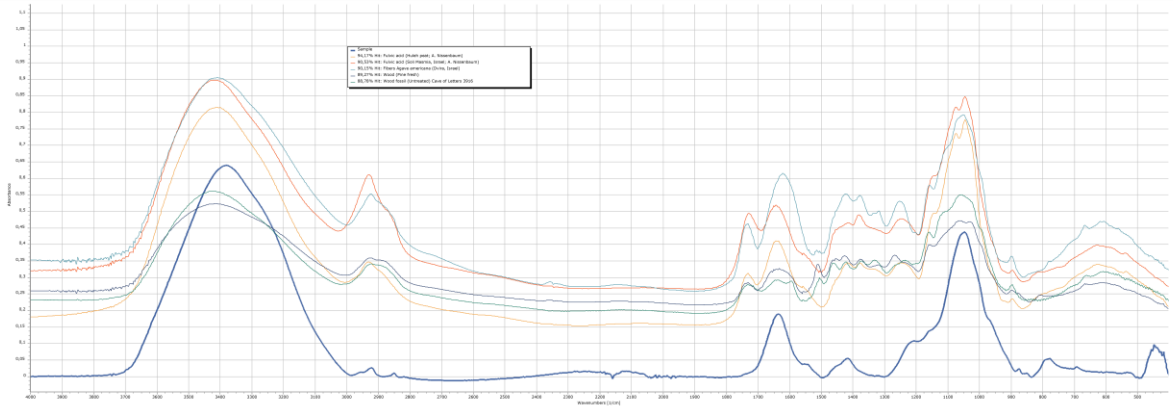


Fig. 2. FT-IR spectrum and spectral database fit factor indicating 97.15% similarity to polyethylene (Primpke 12)

2.2. Preparation of samples for testing

For the actual study, nine square-shaped samples, measuring approximately 5mm x 5mm, were prepared from the collected mesoplastic fragment. These samples were then affixed to microscope slides to facilitate further comparative analysis.

2.3. Conducting the experiment

The experiment was conducted on nine prepared samples. Specifically, samples labeled as PEFA_001 and PEFA_003 were immersed in hydrogen peroxide (30% H_2O_2) (Figure 3), while samples labeled as PEFA_002 and PEFA_004 were placed in Fenton's solution (the stable pH of the solution, measured with the VWR pHenomenal MU6100L, was 3.617) prepared following the procedure proposed by NOAA [13].

Fig. 3. Laboratory set-up for the slide stain experiment. On the left 30% H_2O_2, on the right Fenton's solution. Two slides each with samples applied in both containers

For the samples labeled as PEFA_006 and PEFA_007, the system was prepared using hydrogen peroxide with stirring. A magnetic stirrer (LLG Labware uniSTIRRER 3) was used at a speed of 500 rpm, with the heating function turned off. The samples were positioned on the outer sides of the stirrer, facing each other, to ensure that the solution would wash over both samples in the same manner. As for the samples designated as PEFA_008 and PEFA_009, the same setup as PEFA_006 and PEFA_007 was employed, but with the use of Fenton's solution (Figure 4).

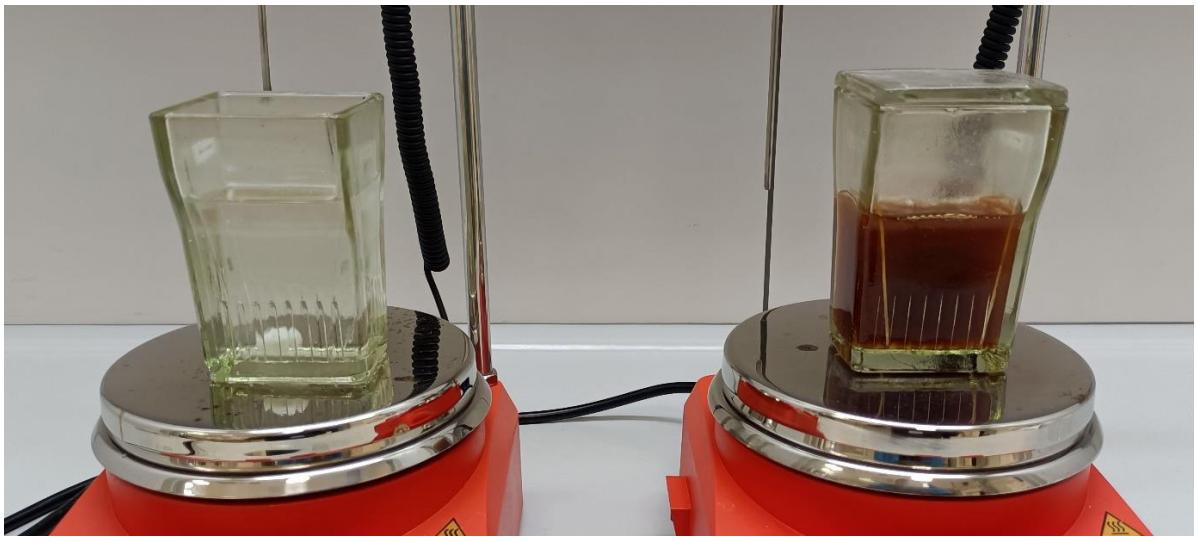


Fig. 4. Laboratory set-up for the slide stain experiment including mixing. On the left, there was 30% H_2O_2, and on the right, there was Fenton's solution. Two slides, each with applied samples, were placed in both containers

For the sample labeled as PEFA_005, a system utilizing sonification at 45kHz was set up. The sample was subjected to ultrasound cycling with an hourly cycle, and during each cycle, the water was cooled with ice. This cooling step was necessary to prevent the generation of excessive heat during the sonification process, which could potentially damage the thin microplastic piece. The initial assessment of surface changes on the sample, to maintain consistency with the rest of the study, was conducted after three hour-long sonification cycles. Subsequently, a second assessment was performed following an additional 21 hour-long sonification cycles.
The experimental times for each sample are summarised in Table 1.

Table 1. Summary of the samples tested in terms of process time in correlation with the purification method used

Sample ID	Purification method	Duration
PEFA_001	30% H_2O_2	3h
PEFA_002	Fenton solution	3h
PEFA_003	30% H_2O_2	24h
PEFA_004	Fenton solution	24h
PEFA_005	sonification with cooling	3h
PEFA_005	sonification with cooling	24h
PEFA_006	30% H_2O_2 + stirring	3h
PEFA_007	30% H_2O_2 + stirring	24h
PEFA_008	Fenton solution + stirring	3h
PEFA_009	Fenton solution + stirring	24h

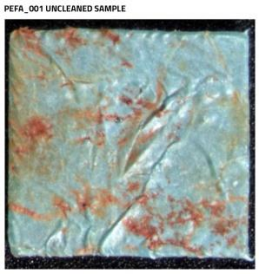
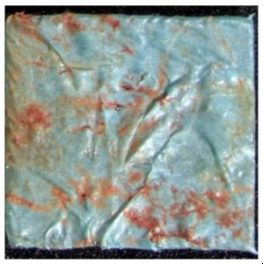
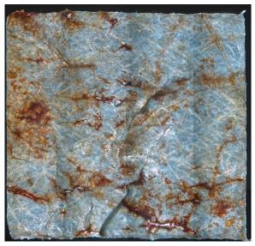
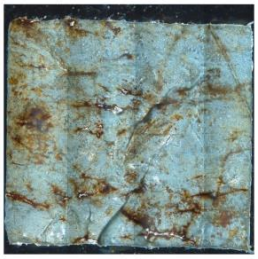
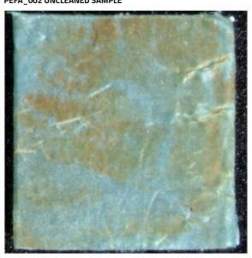
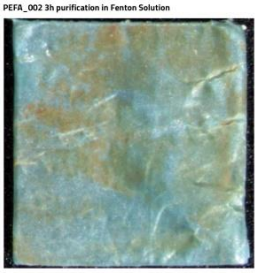
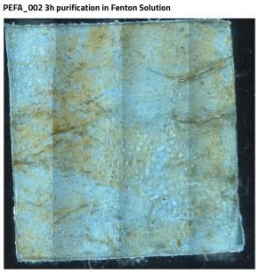
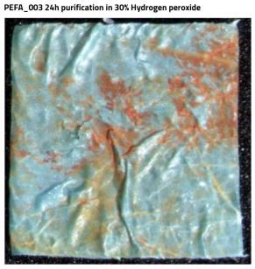
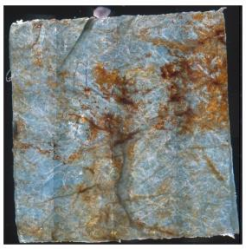
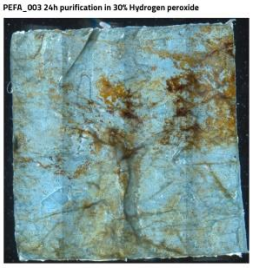
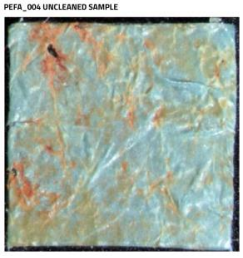
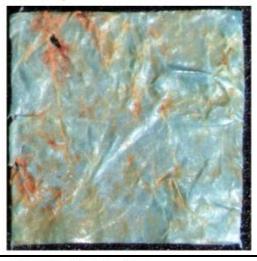
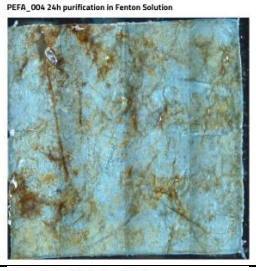
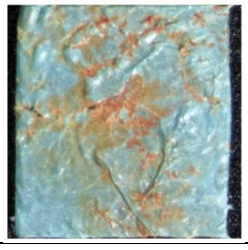
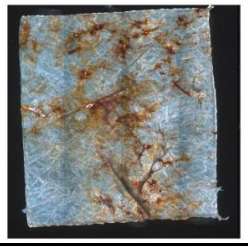
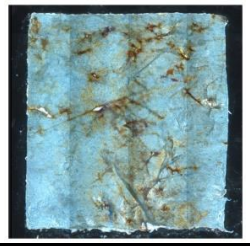
3. RESULTS AND DISCUSSION

The evaluation of the selected methods for cleaning the microplastic samples was conducted through a comparative analysis, which involved a detailed examination of the images' features and characteristics. The tested material exhibited a noticeable color contrast between the biofilm containing fulvic acids (rusty brown) and the plastic fragments with green-blue tones. This distinct differentiation allowed for clear and visible results without the need for additional confirmation.

The analysis of the microscopic images (Table 2) provided additional insights into the effectiveness of the microplastic cleaning process. The imaging was performed using two microscopes employing different sample illumination techniques. The Nikon SMZ 745T microscope captured images in reflected light (RL) mode, while the Carl Zeiss LSM 710 VIS AXIO Observer Z1 microscope utilized transmitted light (TL) mode, which was suitable for thin-film samples with a certain level of transparency.

Following the 3-hour cleaning process, only the sample labeled as PEFA_005, treated with ultrasound, exhibited noticeable cleaning effects. No significant changes were observed in the samples subjected to other purification methods. In the case of the sample labeled as PEFA_008 (treated with Fenton's solution and stirring), additional contamination was observed. This contamination intensified after the sample was exposed to the solution for an additional 21 hours. Purification for 24 hours was only effective for the sonication-treated sample, but surface changes in the microplastic structure itself were also observed. The sample began to lose its original form, with folds appearing at the edges and a slight shrinkage of the polymer, indicating potential internal structural changes in the material.

Table 2. Summary of the resulting microscopic images of the test samples before and after the purification process

Nikon SMZ 745T		Carl Zeiss LSM 710 VIS AXIO Observer Z1	
			
			
			
			
			

The analysis of the images yields valuable insights into the surface changes of microplastics resulting from the purification process. It is important to note that microplastic purification is a complex procedure, and the effectiveness of various methods can vary based on factors such as microplastic type, process conditions, and the chemical or physical agents employed. These factors are reflected in the experiment's results, emphasizing the variability and complexity associated with microplastic purification.

4. CONCLUSION

The results show that the sonification method proved to be the most effective in removing organic chemicals in the form of fulvic acids from the microplastic surface. However, this method, despite being the most effective, led to changes in the structure of the polymer surface as well as its shape. Fenton's solution and hydrogen peroxide proved ineffective in removing this contaminant from the microplastic. In the case of the Fenton solution, another additional feature could be observed, namely additional contamination of the sample. The effect of this contamination could be due to several important factors: variable or uncontrolled pH, which affects the reaction rate in different ways. At low pH values, Fe^{2+} complexation can occur, making the iron ions less available to produce reactive oxidative forms [16]. At high pH, the reaction can slow down due to the precipitation of $Fe(OH)_3$, thus lowering the concentration of Fe^{2+} in solution [17]. Not only the pH but also other factors such as reaction time, H_2O_2, dose, temperature, type of substance being oxidised [18] are important for efficiency when using Fenton's solution, and changing these parameters even slightly can result in undesirable contamination such as iron compounds or oxidation by-products. These contaminants can hinder the interpretation of microplastic analysis results or introduce additional interferences. For these reasons, Fenton's solution may be less suitable for purifying microplastic samples and, in this context, it is advisable to choose methods that minimise negative effects on microplastics and provide accurate and undistorted analytical results.

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