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Pretreatment methods for the isolation of microplastics from wastewater and sludge samples: Part 1

Metody wstępnego przygotowania próbek ścieków i osadów do analizy zawartości mikroplastików: Część 1

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Słowa kluczowe: *ścieki komunalne, osady ściekowe, mikroplastik, polimery, oczyszczalnia ścieków*

Streszczenie

Mikroplastiki stanowią rosnące zagrożenie dla środowiska, a ścieki komunalne są jednym z ich istotnych źródeł. Oczyszczalnie ścieków to miejsca, gdzie mikroplastiki są usuwane ze ścieków i akumulowane osadach ściekowych. Wiedza na tematy zawartości mikroplastików w ściekach, ich wielkości, kształtu i innych właściwości fizycznych i chemicznych jest konieczna do opracowania technologii ich usuwania ze ścieków. W tym celu próbki ścieków i osadów ściekowych muszą być odpowiednio przygotowane do oznaczania zawartości mikroplastików. W artykule omówiono formy mikroplastików w ściekach, przedstawiono wpływ poszczególnych procesów technologicznych na usuwanie mikroplastików oraz stosowane sposoby obróbki próbek w celu identyfikacji i analizy ilościowej mikroplastików.

Keywords: *municipal wastewater, sewage sludge, microplastic, polymers, wastewater treatment plant*

Abstract

Microplastics are a growing threat to the environment, and municipal wastewater is one significant source of them. Wastewater treatment plants are sites where microplastics are removed from wastewater and accumulate in sewage sludge. Knowledge of the content of microplastics in wastewater, their size, shape and other physical and chemical properties is necessary to develop technologies for their removal from wastewater. To this end, wastewater and sludge samples need to be properly prepared for the determination of microplastics. This article discusses the forms of microplastics in wastewater, presents the influence of individual technological processes on microplastic removal and the sample treatment methods used to identify and quantify microplastics.

1. Introduction

Nowadays, the wide use of plastics together with an improper waste management and disposal led to the concerning presence of microplastics (MPs) in the environment. These synthetic polymers with a size less than 5 mm reached rivers, lakes, estuaries, ocean, air, and soil, causing several problems to living organisms due to their persistence and accumulation. MPs are characterized by accumulation and persistence in the environment, and their ingestion can cause toxicity to humans and living organisms like zooplankton, mollusks, and fishes (Alvim et al., 2020). The toxicological threat of MPs pollution is related to their capability to accumulate and transport toxic metals, pharmaceuticals, persistent organic pollution, and products of personal care. Even if MPs do not lead to acute fatal effect on living organisms, they may be responsible of chronic toxicity during long term exposure. Polymer materials such as polystyrene, which is widely used for protecting packaging and bottles, can cause direct toxic effects due to their capability of entering in blood circulation. Also, the ingestion of small size and sharp ends MPs was observed to be cause of malnutrition and reproduction problems for some organisms. Moreover, microparticles smaller than 10 µm could move from the gut into circulatory system of aquatic organisms (Sun et al., 2018). Other negative physical impacts that MPs can cause to living organisms are debilitation and difficulties in predator avoidance (Rodrigues et al., 2018). Lubricants, antioxidants, corrosion inhibitor, adhesives, flame retardants or heat stabilizers can be added to plastics for improving their properties, and wastewater treatment plants (WWTPs) can contribute with the dispersion of these chemicals into the environment. These additives can escape from plastic to the environment during the production, use, and disposal. MPs can also sorb persistent organic pollutants (POPs) and act as a vector for the pollution of environments and animals (Alvim et al., 2020).

WWTPs are designed for removing organic matter and nutrients from wastewater, not for other contaminants such as MPs (Magni et al., 2018). However, depending on the treatments, 80-95% of the MPs contained in the sewage are trapped in the sludge of WWTPs

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(Zeri et al., 2021). Despite a conventional wastewater system can remove more than 90% of MPs, these systems remain also the major source of MPs pollution of aquatic environment due to the large volume of effluent discharged (Alvim et al., 2020). Influent samples contain from 1 to >7000 particles/L and effluent ones from 0.0009 to 81 particles/L. Industrial wastewater has been discovered to contain a bigger quantity of MPs than the domestic wastewater (Hamidian et al., 2021). Not only inland water, but also terrestrial pollution can be caused starting from WWTPs, since a high percentage of MPs (>90%) settle at the bottom of the systems and is accumulated in the sludge, which is widely reused as fertilizer in agriculture (50% of total sludge production in Europe). This kind of use is currently banned by legislation just in case it contains high concentration of toxic pollutants, such as heavy metals (Magni et al., 2018).

Part 1 of the article discusses the problem of the presence of MPs in the environment in general and the role of the WWTPs as well as analyzes the methods of collection, pretreatment and MPs characterization of a sample from WWTPs. Part 2 will describe materials and methods applied during the experimental works and will discuss the obtained results.

2. Role of WWTP in microplastic reduction

WWTPs can be composed by preliminary, primary, secondary, and tertiary stages. Preliminary treatment consists in physical removal of materials that can damage further processes such as grit, rags, and sticks. Primary treatment relies on physical and chemical removal of settleable and floating pollutants, while the secondary treatment is mainly based on biological methods for the removal of nutrients and suspended and dissolved organic substances. Wastewater can be then disinfected by different methods such as UV radiation, chlorination, or ozone, during the tertiary treatment. Among the other pollutants, also plastics are removed through all these stages (Fig. 1) (Hamidian et al., 2021).

MPs are present in the effluents of WWTPs with a concentration which depends on the operational conditions, treatment processes, and population served. The majority of the MPs are removed at the beginning of WWTPs, during the mechanical and chemical pretreatments, skimming of solids and settling processes (Lares et al., 2018). According to the literature, primary treatment can remove about 78%-98%, and secondary treatment 7%-20% (Alvim et al., 2020). Primary sedimentation reduces MPs presence by 92.8% and scum removal by 88.4%. More than 60% of microfibers can be removed by screens and sieves and aerated grit chamber. The outflowing sewage of WWTPs with only primary and secondary treatment has been demonstrated to have higher concentration of MPs compared to the ones with also tertiary treatment (0.0009-447 particles/L and 0-51 particles/L respectively). In the tertiary treatment, technologies like sand filters, sequential biological reactor (SBR), biologically active filter (BAF), and membrane bioreactor (MBR) are used. Tertiary treatment decreases the number of MPs in the wastewater effluent to <2%. Sand filters remove almost 50% of MPs, starting from a content of 0.9 ± 0.3 MPs/L after the settler and ending up with 0.4 ± 0.3 MPs/L in the outlet. Referring always to tertiary treatments, the use of Al-based coagulant for the coagulation process has been shown to be good at removing MPs, but excess in the dosage above the optimal quantity results in a negative impact given by the charge reversal. Membrane bioreactor (MBR) seems to be the most efficient technology for the removal of MPs (99.4%), if compared to the conventional processes based on activate sludge (Hamidian et al., 2021).

3. Types of microplastics in WWTPs

The shape of MPs found at the effluent of WWTPs includes fibers, foam, pellets/beads, and fragments (Hamidian et al., 2021). Magni et al. (2019) differentiated MP particles (MPPs) and MP fibers (MPFs) and, according to their shape, they recognized lines, films, and fragments among the MPPs, and microfibers (Fig. 2).

Among the polymer species of MPs found at WWTPs there are polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polypropylene (PP), polyurethane (PU), polyvinylchloride (PVC), polyacrylates (PAR) (Xuemin et al., 2019). PS fibers represented the 96.3% of the MP fibers, and consequently the 79.1% of the total MPs of the sample. Regarding the MP particles, PE was the most found polymer (63.9% of MPPs and 11.4% of total MPS). About the predominant sizes of MPs present in WWTPs, 40% of MPs are >500 μm followed by 29% between 62.5 and 125 μm. Fibers are the most common type of MP in the range of 1 mm (large particles) and 125 μm (small particles). Pretreatment can efficiently remove classes of ≥300 and 100-300 μm. MPs size in the solid fraction is usually bigger than in the liquid fraction because smaller particles can stay in suspension (Hamidian et al., 2021).

Fibers are the dominant form in both influent and effluent of WWTPs, and they are followed by fragments and pellets/beads.

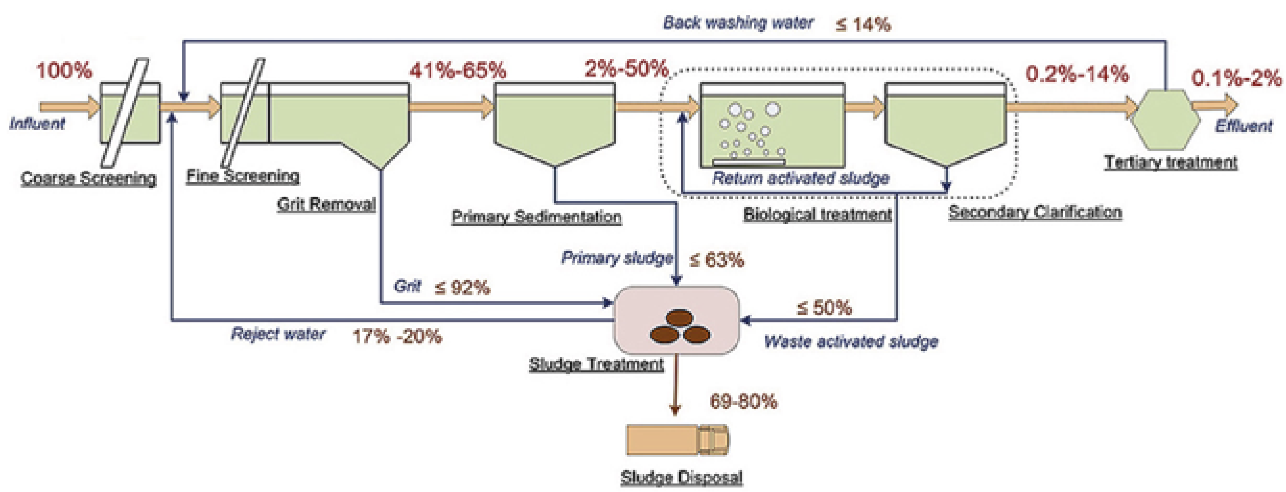

Fig. 1. Estimated microplastic flow in a WWTP with primary, secondary, and tertiary treatments (Sun et al., 2018)

Rys. 1. Szacowany przepływ mikroplastiku w oczyszczalni ścieków z oczyszczaniem wstępnym, wtórnym i doczyszczaniem ścieków (Sun et al., 2018)

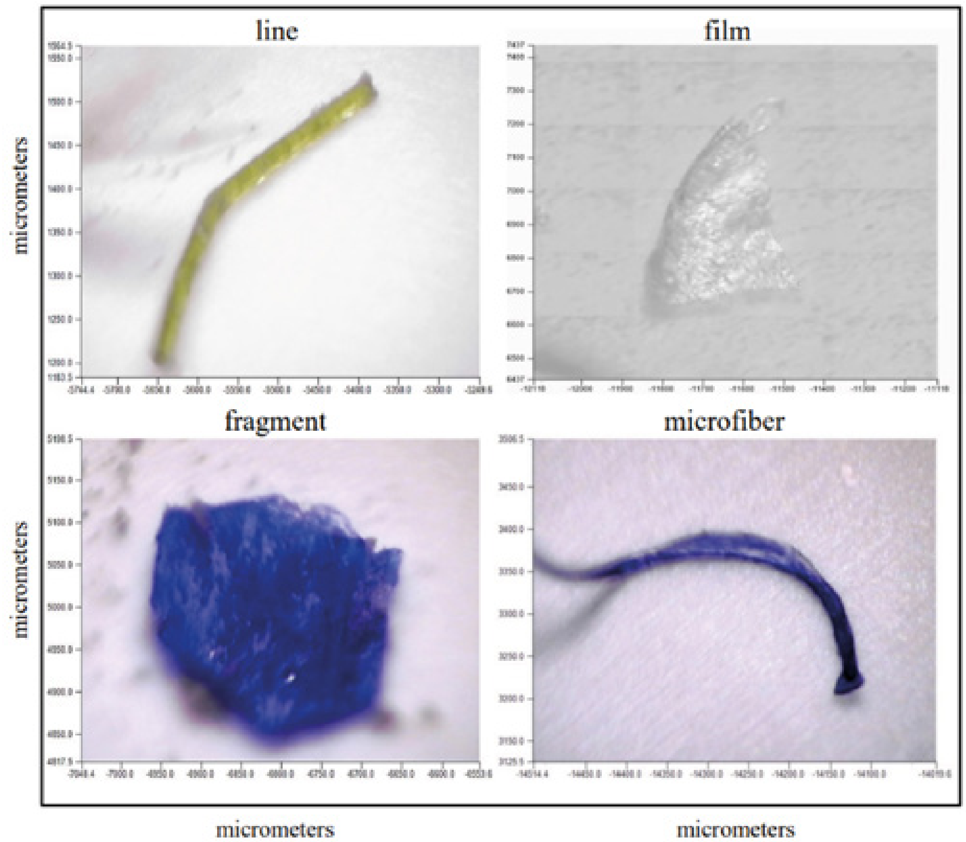

Fig. 2. MPPs and MPFs extracted from both sludge and wastewater (Magni et al., 2019)

Rys. 2. MPP i MPF zidentyfikowane w ściekach i osadzie (Magni et al., 2019)

The strong presence of plastic fibers in the effluent highlights the impact of laundry on MPs release (Hamidian et al., 2021). In fact, synthetic clothes, when washed, can release more than 1900 PET fiber and one garment fleece can release 110,000 fibers (Alvim et al., 2020). Moreover, WWTPs can more easily remove fragments (91.3%) than pellets (82.8%) and fibers (78.9%) (Hamidian et al., 2021). Zeri et al. (2021), comparing the samples from both effluents of secondary treatment and pilot biological membrane (MBR) of two WWTPs located in the metropolitan area of Athens, discovered that MBR treatments seems to be more effective on filaments than conventional secondary treatments. An increase of the presence of fragments can occur in combined sewers and the concentration of foam particles may grow with the run-off of stormwater. Microbeads derive from cosmetic and personal care products, and their shape is generally irregular. Since their size can range from 8 µm to 2 mm, they can also bypass filtration in WWT facilities. A concerning characteristics of microbeads is their low specific area, which results in a small degradation rate. Moreover, the smooth surface of microbeads makes their adsorption by other substances difficult. Foams can derive from the corrosion of packaging products and plastic bags (Hamidian et al., 2021).

4. The presence of microplastic in the sewage sludge

During primary and secondary treatments, many MPs settle with the sludge during the sedimentation process. It is important to well manage the sewage sludge to avoid terrestrial pollution. In Norway, for example, more than 500 billion of MPs are discharged every year into the environment due to sewage sludge application. MP average concentration was found to be 169,000 particles/g in dewatered sludge, which correspond to 4.5 mg/g (0.7% of the dewatered sludge). Percentage like 98% of the MPs in influent can be trapped in the sewage sludge (Hamidian et al., 2021). Lares et al. (2018), in their studies, demonstrated that MPFs occurred more than MPPs in the sludge fractions, with a percentage of 94%. This makes fibers the prevalent form of MPs present in the sludge (75.8%), but also microbeads and foams can be found, suggesting that also the smaller size tends to be transferred to the sludge. Studies show that 81% of MPs extracted from the sludge were below 1 mm, and medium size particles (200-300 µm) can be totally removed by the liquid thanks to the absorption onto the sludge. About the chemical composition, PE particles are more prevalent (30.5%) than PET (26.7%) and PP (20.3%). PP is more persistent than other plastic polymers. The treatment operated to the sludge can impact the characteristics of MPs, negatively or positively. Lime stabilization, for example, could cause fragmentation of fibers in smaller particles, resulting in an increase of risks for humans and biota. On the other hand, mesophilic anaerobic digestion (AD) and composting can reduce the number of fibers (Hamidian et al., 2021).

5. Methods of detecting microplastics in WWTPs

MPs detection in WWTPs is composed of three steps: sample collection, sample pretreatment and MPs characterization and quantification. The applied techniques can differ based on the sample, considering that MPs are found in both wastewater and sewage sludge (Sun et al., 2018).

5.1. Sample collection

The collection of MPs from wastewater can be done by container collectors, autosampler collection, separate pumping and filtration, and surface filtration. Even if it is easy, the use of container or autosampler allows to collect only few liters of wastewater per event. For this reason, containers and autosamplers are mostly used for the collection of MPs at the influent of WWTPs since it is characterized by high content of organic matters and solids. With separate pumping and filtration (Fig. 3a), the volume of the sample can be increased up to hundreds of liters or cubic meters.

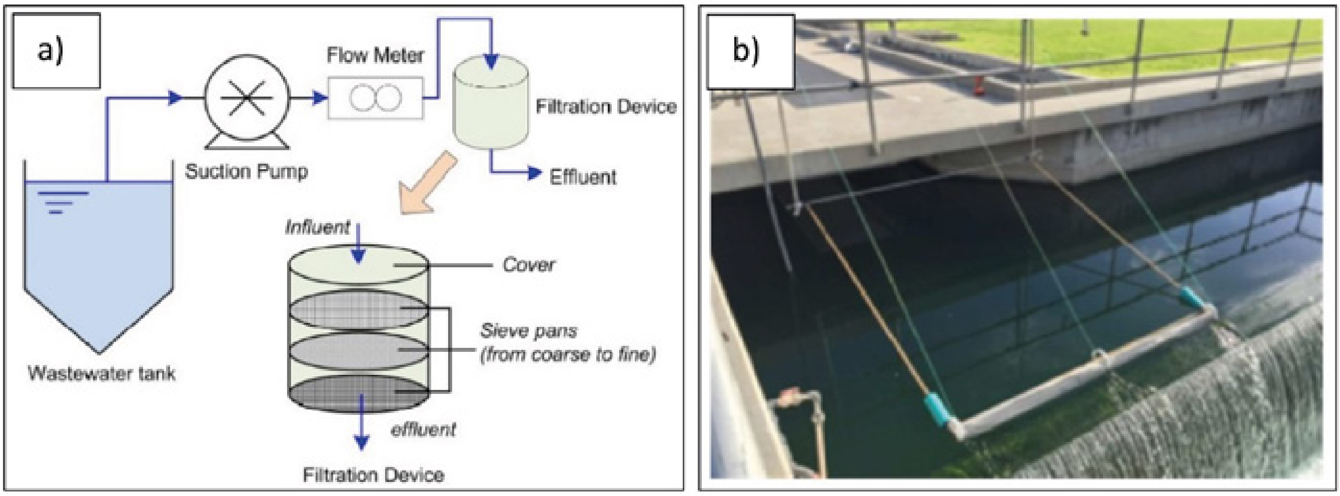

Fig. 3. Collection of MPs through separate pumping and filtration (a) and surface filtration (b) (Sun et al., 2018)
Rys. 3. Pobór próbek MP przez oddzielne pompowanie i filtrację (a) oraz filtrację powierzchniową (b) (Sun et al., 2018)

Wastewater is extracted with a pump from the water stream into a filtration device in which MPs are intercepted. This method is usually adopted for collecting MPs at the effluent of WWTPs. Surface filtration (Fig. 3b) is a method which allows to further increase the sampling volume, reaching thousands of cubic meters. However, water surface can only be skimmed at the final fall location in WWTPs, and the fugitive airborne contamination is difficult to avoid. Moreover, this method results in an underestimation of MPs because it only intercepts those with low density (Sun et al., 2018).

Since the representativeness of the sample is an important fact, 24-hour composite samples may be considered (Sun et al., 2018). Lares et al. (2018), in their studies of the presence of MPs in a WWTP located in Finland, which treats 10000 m^3 of municipal wastewater daily, were collecting samples every two weeks for 3 months. They demonstrate that the concentration of MPs varies substantially in both wastewater and sludge. In addition, also seasonal and diurnal variation are important. Collected wastewater samples are usually filtered for concentrating MPs. Unfortunately, a standard for the mesh/pore size applied is still missing and it can vary from 1 µm to 500 µm (Sun et al., 2018). If the effluents are characterized by a high organic load, the sieves tend to be blocked and for this reason a constant monitoring is necessary (Alvim et al., 2020). It must be remembered that the categorization of the size done with the mesh cannot be considered very accurate because some particles small enough may still do not pass through the sieve due to their irregular shapes or, on the other hand, some fibers may pass longitudinally through smaller meshes. The separation with filtration is not applied for sewage sludge samples due to the higher fraction of solids and organic matter. Usually, a quantity of sludge between 5-20 g is collected in a glass container and maintained in the dark at a temperature of 4 °C before further processing in the laboratory (Sun et al., 2018).

5.2. Organic matter removal

The removal of organic matter is of fundamental importance for simplifying the quantification and the identification of MPs. Organic matter removal can be carried out with different methods, such as wet peroxide oxidation, enzymatic degradation and acid and alkaline techniques (Sun et al., 2018).

5.2.1.Wet peroxide oxidation

In (catalytic) wet peroxidation (WPO), chemicals like H_2O_2 , NaClO solution, and Fenton reagents are applied (Sun et al., 2018). The use of WPO does not lead to a change of plastic debris except for PE and PP, which can record a slight change in their size. The exposition of the samples to H_2O_2 (30%) for one week can remove 83% of organic matters maintaining the same spectra of MPs. The limits of the adoption of this method can be related to the longer time needed in case of a sample volume larger than 1 L and the increase of the presence of organic detritus (Sun et al., 2018). Zeri et al. (2021), in their study, performed the removal of the organic matter with the use of 40 mL of hydrogen peroxide H_2O_2 (15%) per 3 g of dry sample and heating the mixture at 40 °C on a hot plate until complete digestion (24 hours). Fenton's reagent consists of a combination of 20 mL of 30% H_2O_2 solution with 20 mL of 0.05 M Fe (II) catalyst (Hamidian et al., 2021). The presence of Fe (II) allows the activation of peroxide and leads to the formation of hydroxyl radicals, strong oxidants for organic materials which have an oxidation potential of 2.8 V. The suggested reaction for Fenton is given (Rodrigues et al., 2018):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \dot{O}H + OH^-$$
$$\dot{O}H + organic\ material \rightarrow H_2O + CO_2 + final\ product\ from\ organic\ material$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \dot{O}OH + H^+$$
$$Fe^{3+} + \dot{O}OH \rightarrow Fe^{2+} + H^+ + \dot{O}O^-$$
$$Fe^{3+} + \dot{O}O^- \rightarrow Fe^{2+} + O_2$$

Usually the sample is left for 5 minutes after the addition of Fenton's reagent and then heated at 75 °C (Rodrigues et al., 2018). Heating the sample in a range of 60-70 °C could accelerate the reaction (Hamidian et al., 2021). However, it must be considered that temperatures above 60 °C can lead to an underestimation of the numbers of MPs because some microbeads can be melted. This process does not require neither long time nor any external energy. The pH 3 is considered as the ideal condition and it can be achieved with the use of sulphuric acid. With Fenton's reagent it is possible to reach more than 86% in organic matter removal in a sample of sludge, while with the use of NaOH just 67% (Alvim et al., 2020).

5.2.2. Enzymatic degradation

Enzymatic degradation is another kind of process in which MPs are purified from organic matter by submerging the samples in a mixture of technical enzymes such as proteinase, lipase, chitinase, amylase and cellulase. MPs are not ruined, while lipids, proteins and carbohydrates are removed selectively (Sun et al., 2018). Rodriguez et al. (2018) applied the digestion of the organic matter of an artificial sample starting with the addition of 2.5 g/L of sodium dodecyl sulfate (SDS), which has a pH in the range 8-8.2. The mixture was then stirred for 10 minutes and put in the oven to dry all night. After it cooled at room temperature, the sample was incubated with 20 mL of enzymatic solution for 3 days with constant oxidation and pH between 7 and 8. Regarding the removal of organic matter, enzymatic degradation does not allow removal greater than 80% and for this reason it is less efficient than WPO. Moreover, it is a long procedure to be performed (5 days) (Rodriguez et al., 2018). Nowadays, there is not much knowledge about the application of enzymatic digestion in samples taken from WWTPs (Alvim et al., 2020).

5.2.3. Acid and alkaline treatments

Alkaline and acid treatments are alternative methods for removing organic matters from both wastewater and sludge samples (Sun et al., 2018). Regarding acid treatments, over 80% of organic material removal can be achieved using 1 M of HCl. The use of NaOH alkaline solution was demonstrated to not be able to reach removal efficiency of 70%, and for this reason it cannot be considered appropriate for removing organic material (Alvim et al., 2020). The problem with both acid and alkaline processes is the harsh condition which could damage the MPs (Sun et al., 2018). Alvim et al. (2020) mentioned a sample containing different kind of MPs, which was treated with a mixture of HNO_3 and $HClO_4$ in a proportion 4:1, and digested for 5 hours at room temperature before being heated for 20 minutes at 80 °C. Under these conditions, polyamide (PA) and PU, together with a black tire rubber elastomer, were completely dissolved, while other polymers such as polycarbonate (PC), PET, and expanded solid polystyrene (EPS, PS), even if not completely dissolved, suffer from some degree of loss in color. To limit this problem, low concentration of acid solution should be used, but this compromises the efficacy of the digestion process. In addition to the reagents, the damage of polymers can be also attributed to the heating applied after the digestion (Alvim et al., 2020). For example, acid treatment can be performed at temperatures of 110-120 °C, but some MPs were observed to melt at 90 °C (Sun et al., 2018). When acid or alkaline treatments are applied, it is important to evaluate the resistance of polymers to these methods of digestion in each study (Alvim et al., 2020).

5.3. Inorganic matter removal

The density of the polymers without any additives incorporated varies from 0.90 to 1.6 g/cm^3, while the density of sand and other sediments is typically around 2.6 g/ cm^3 (Alvim et al., 2020). Due to these facts, the removal of inorganic material usually occurs by density separation using brine solutions (Sun et al., 2018). In this kind of separation, the sample containing different density materials is mixed in a liquid which has an intermediate density, and this leads to the flotation of less dense material and the settling of the denser ones. The change of the liquid density allows the floating of particles with different densities. The MPs on the surface can be caught by vacuum suction, using a glass tube connected to a vacuum system by a tube in rubber which can be moved around the surface allowing to collect the MPs into a three necked flask. After this, the solution containing MPs can be filtered through a filter paper, washed, and dried in the oven for 10 min at 70 °C before being weighted for calculating the MPs recovery (Quinn et al., 2016). The solutions most frequently operated for density separation in wastewater samples are NaCl, $ZnCl_2$, and NaI (Hamidian et al., 2021).

Among these solutions, saturated sodium chloride NaCl (density of 1.2 kg/L) is widely applied because it is not toxic, it is easily available, and it has a low cost. However, it needs to be considered that MPs like PVC (density of 1.14-1.56 kg/L) and PET (density of 1.32-1.41 kg/L) can settle in this brine solution, and this can lead to an underestimation of the total counts. To address this issue, denser solutions such as NaI or ZnCl can be used (density respectively of 1.6-1.8 kg/L and 1.5-1.7 kg/L) (Sun et al., 2018). With denser polymers like high-density PE, NaI and $ZnBr_2$ (density of 1.7 kg/L) allow higher recovery and smaller error bars in comparison to the use of NaCl and NaBr (density of 1.4 kg/L). The recoveries achieved using NaI and $ZnBr_2$ can reach 99%, while the ones with NaCl and NaBr are under 90% (Hamidian et al., 2021).

However, it must be remembered that the recovery rate is also related to the size of MPs (recovery rates can reduce to 40% for MPs with a size between 40 and 309 μm), and these higher density solutions are usually toxic to the environment and very expensive (Quinn et al., 2016). Elutriation technique has also been performed for achieving the isolation of MPs using water flow and aeration (Sun et al., 2018).

5.4. Microplastics characterization

In order to analyze MPs, either physical or chemical characterization can be adopted. During physical characterization the size distribution, color, shape, and other physical parameters are determined. Chemical characterization is more focused on the composition of MPs (Sun et al., 2018).

5.4.1. Physical characterization

The most applied equipment for physical characterization is stereomicroscope. With this device it is possible to measure the size, stabilize the number of MPs and characterize their morphology. It must be considered, however, that the stereomicroscope does not have a high magnification factor and the result is strongly dependent on the operator. Moreover, natural fibers such as cotton ones can be exchanged for synthetic ones, and when the color of the items is similar to the background one, some particles could be overlooked. For facilitating the counting of the particles, instead of normal Petri dish, the ones with numbered grids can be used. Regarding the possibility of mistakenly consider a natural fiber as a synthetic one, it should be remembered that the synthetic fibers have the same thickness along their length, they are not entirely straight, and if some cellular or organic structure is visible, it means that they are not MP. Fibers which appear transparent and green needs to be examined with high magnification to confirm their nature. Moreover, if alcohol is applied, natural fibers stays while plastics melts. Another method consists in applying the Rose-Bengal solution. In this way, particles which are not MPs are stained pink, allowing an easier visual separation of MPs (Sun et al., 2018).

5.4.2. Chemical characterization

Among the chemical analysis methods, there are both destructive and non-destructive ones. Destructive methods include liquid chromatography (LC), pyrolysis-GC-MS, and thermal extraction desorption-GC-MS. Spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy belong to non-destructive methods. These methods are largely used for analyzing MPs in the environmental samples (Sun et al., 2018). Lares et al. (2018) adopted spectroscopy methods for ensuring to avoid considering false MPs in their study. The nature of all the particles and fibers that could not be visually considered organic or non-plastic materials, were confirmed by spectroscopy methods. Thanks to the application of these techniques, from 42 groups analyzed at the start, 22 were excluded because of the content of organic compounds. The appearance of different polymers identified by FTIR and Raman spectroscopy is shown in Fig. 4 (Lares et al., 2018).

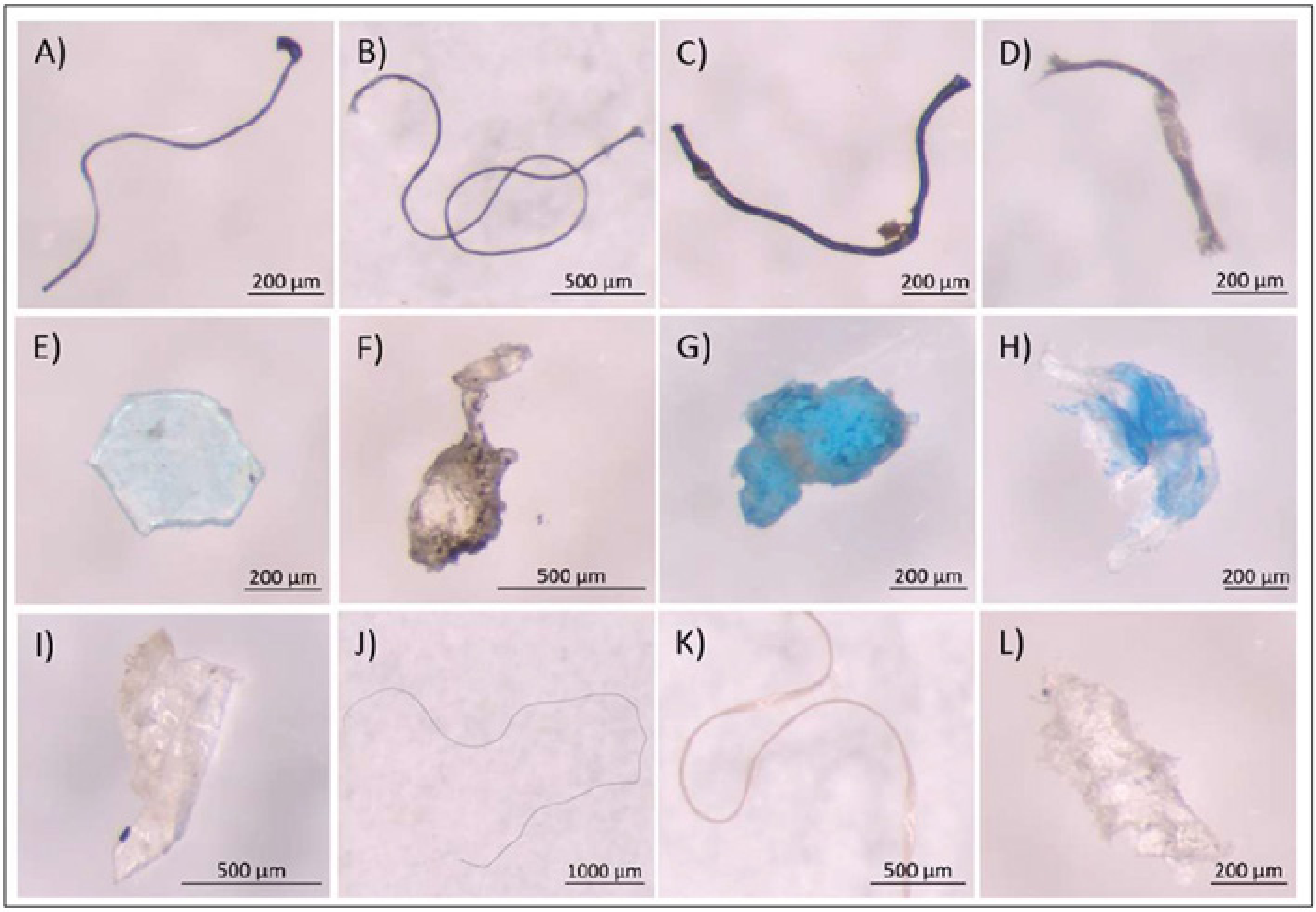

Fig. 4. Different kinds of polymer detected in environmental samples and identified with the use of FTIR and Raman spectroscopy technologies (Lares et al., 2018)
Rys. 4. Różne rodzaje polimerów wykrywane w próbkach środowiskowych i identyfikowane za pomocą technologii spektroskopii FTIR i Ramana (Lares et al., 2018)

Fourier transform infrared spectroscopy (FTIR)

FTIR is especially applied for characterizing MPs contained in WWTPs samples. This technique consists of applying an infrared radiation to the MPs and they respond with a spectrum in which each chemical bonds between atoms has a characteristic peak, giving the possibility to identify the sample composition thanks to the comparison between the obtained spectra and the ones in the library (Sun et al., 2018). It must be taken into consideration that usually the analysis does not provide a complete match with reference, and this could be due to the presence of attached organic material, the additives applied sometimes in plastics, or the treatment (thermal and chemical) adopted during the preparation of the samples (Lares et al., 2018). MPs are first selected under the light microscopy and afterwards their spectra are analyzed individually for each particle. Recently, the focal plane array based micro-FTIR was developed, giving the possibility of enhancing the MPs analysis in the sample thanks to a better evaluation of the spectra. However, it must be remembered that its lateral resolution is limited and samples with a size of 10-20 µm can be hardly analyzed (Sun et al., 2018).

Raman spectroscopy

Raman spectroscopy uses a vibrational spectroscopy technique which relies on the inelastic scattering of the light. It gives a vibrational spectrum which represents the molecular vibration of the system and allows to identify the species contained in the sample. This technique has a better spatial resolution than FTIR, since it allows to also analyze particles of 1 µm. However, Raman spectroscopy can suffer from fluorescence interference due to the presence in the sample of organic, inorganic, and microbiological items. For this reason, it is important to carefully purify the samples (Sun et al., 2018).

GC-MS and LC based techniques

GC-MS and LC based techniques can be used for a rapid identification of MPs in the sample. The GC-MS methods can identify MPs with the analysis of the mass spectrometry of the products of thermal degradation. The LC methods rely on the separation between dissolved analytes and their hydrodynamic volume based on the effective size of molecules (size exclusion chromatography). Both these methods give the type of polymers and, with proper calibration, quantitative results can also be obtained (Sun et al., 2018).

6. Conclusions

The presence of MPs in the aquatic environment represents a concerning issue, and WWTPs play an important role in MP pollution due to the large volume of treated wastewater discharged. Municipal wastewater contains significant amounts of MPs varying in size, shape, polymer type and other properties. When they remain in treated wastewater and end up in sewage sludge, they become a significant source of environmental pollution. The development of effective technology to remove MPs from wastewater requires a thorough understanding of their physical and chemical properties. Therefore, the identification of MPs requires proper sample preparation by removing organic material, inorganic contaminants and using an appropriate method to identify the substance forming the MP particle.

The removal of organic material from the sample can be carried out by various methods, however, the most effective is considered oxidation using H_2O_2 and Fenton's reagent at elevated temperature. The removal of inorganic substances can be carried out by density separation using saturated sodium chloride NaCl or, better, denser solutions such as NaI and $ZnBr_2$ (99% recovery). Physical characterization is most often performed under a microscope and allows determining the size, color, shape and other physical parameters of the MP particle. Chemical characterization is more focused on the composition of the MP and is performed using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy or GC-MS and LC based techniques. Each of these techniques has its limitations and their effectiveness depends on the specific case.

Part 2 of the article will describe the experimental studies on the validation of individual methods for preparing wastewater and sludge samples for the identification of microplastics.The article is based on a Master's thesis developed as part of the dual degree programme between the Cracow University of Technology and Università degli Studi di Cagliari (Blumenthal, 2022).

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