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Application of X-ray fluorescence spectrometry-based techniques in studies dealing with metal adsorption onto microplastics[☆]

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ABSTRACT

At present, water pollution by microplastics (MPs) is a significant environmental issue, affecting aquatic ecosystems and human health. One of the main concerns about MPs is the possible adsorption of pollutants due to their large specific surface area and chemical properties. In particular, the role of MPs as vector and carrier for trace metals in the environment is still poorly understood.

In this contribution, a novel analytical approach based on the combined use of X-ray fluorescence spectrometry techniques is proposed for investigating metal adsorption onto MPs. Quantitative analysis of supernatants before and after batch adsorption experiments was performed by total reflection X-ray fluorescence spectrometry (TXRF). Comparable results were obtained using inductively coupled plasma optical emission spectrometry (ICP-OES), a technique widely used for trace metal analysis in this type of microplastic studies. In parallel, MPs collected on filters after the adsorption process were directly qualitatively analysed, without any sample pretreatment, by energy-dispersive X-ray fluorescence spectrometry (EDXRF), enabling direct verification of metal adsorption and providing complementary information to TXRF results.

The applicability of the methodology was assessed through the evaluation of Zn adsorption onto unaged and UV aged "true-to-life" polyethylene (PE), polystyrene (PS), and polypropylene (PP) MPs with different particle sizes (<63 μm and 63–80 μm). Surface modifications induced by the UV aging process were further characterized by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometry.

Results showed that metal adsorption depends on polymer type and is strongly influenced by aging processes, with aged MPs exhibiting higher adsorption capacity.

1. Introduction

The extensive and persistent use of plastics in everyday products and industrial processes has resulted in widespread microplastic (MP) pollution, which represents a serious concern for ecosystems and human health [1].

The distinctive surface properties of MPs including small size, high porosity, large specific surface area, and strong hydrophobicity- make them highly effective at adsorbing and accumulating chemical contaminants in aquatic environments. Among these, the adsorption of metals has garnered particular attention due to its environmental significance [2]. MPs readily adsorb metals via various adsorption mechanisms including physical adsorption, electrostatic interaction, hydrogen bonding, complexation and π-cation bonding interactions [3]. To better understand metal adsorption onto MPs usually laboratory batch adsorption experiments are used. Then, the metal adsorbed onto the MP is estimated from the difference between the metal concentration in the aqueous solution before and after the adsorption process using an atomic spectroscopic technique such as flame atomic absorption spectroscopy (FAAS) [4] or ICP-based instrumentation [5]. In this type of adsorption studies, commercial, pristine and spherical MPs prepared at specific sizes are usually considered [6]. However, some recent

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publications have shown the limitations of using these commercial materials as environmentally representative MPs. For that, more recent contributions dealing with metal adsorption onto MPs consider more "true-to-life" MPs prepared as micronized fragments of single-use plastics [7]. It is also interesting to mention that in the natural environment MPs can undergo aging processes that can lead to changes in the surface and physicochemical properties of MPs and their bioavailability and adsorption capacities [8]. Photodegradation due to UV exposure is one of the most significant pathways, as plastics in natural environments are often exposed to sunlight for extended periods of time [9].

In the present contribution, we have evaluated Zn adsorption behaviour onto unaged and UVaged "true-to-life" polyethylene (PE), polystyrene (PS) and polypropylene (PP) MPs with different particle sizes (<63 μm and 63–80 μm). Adsorption studies were performed in batch mode over a period of 7 days, and Zn was used as a metal model due to its widespread presence in different types of natural and wastewater samples [10]. It is relevant to mention that, for the first time, a novel analytical approach combining the use of total reflection X-ray fluorescence spectrometry (TXRF) and energy dispersive X-ray fluorescence spectrometry (EDXRF) was employed to monitor metal content adsorbed onto the MPs through batch adsorption studies.

On the one hand, the potential of TXRF was evaluated for the quantification of Zn in the aqueous media solution before and after the adsorption process, as a potential analytical alternative to FAAS or ICP-based techniques. TXRF is a multielemental spectroscopic technique that is less costly than other atomic spectroscopic techniques, as it does not require cooling media or gas consumption during measurements.

On the other hand, EDXRF was also evaluated as an analytical tool to track Zn accumulation at the surface of MPs after the adsorption process. Owing to its ability to analyse solid samples, the loaded MPs were collected on a suitable filter, between two adhesive foils to ensure proper preservation and handling and analysed without any additional chemical treatment. Recent studies have reported the use of both μ-EDXRF and portable EDXRF instrumentation for metal determination in millimetre-sized MP- fragments from shoreline sediments [12] and beach sands [13]. However, in the present contribution, the potential of EDXRF for monitoring metal adsorption onto micrometre-sized MPs is investigated for the first time.

Within the framework of this study, we aim to demonstrate the potential of XRF-based techniques for investigating metal adsorption onto MPs, as well as to contribute to a better understanding of metal interactions with these particulate contaminants.

2. Materials and methods

2.1. Reagents, materials and apparatus

Metal stock solutions (1000 mg·L^{-1}, ROMIL PrimAg, United Kingdom) were used for preparing aqueous solutions in batch adsorption studies. Tween 80 surfactant, acquired from Sigma-Aldrich (Germany), was used for preparing homogeneous MP suspensions. Batch adsorption experiments were performed using a rotary mixer Dinko (Barcelona, Spain). In TXRF analysis, quartz glass discs with a diameter of 30 mm and a thickness of 3.0 ± 0.1 mm were used as sample holders. The sample carriers were siliconized before sample deposition by silicone from Serva Electrophoresis GmbH (Heidelberg, Germany). Images of the studied MPs were obtained with a portable USB digital microscope with LED illumination (Resolution: 1600 × 1200 pixels, magnification: 1000×).

2.2. Microplastic (MP) samples

2.2.1. Commercial and "true-to-life" MPs

Commercial, pristine, and spherical polyethylene (PE) fluorescent MPs with a particle size range of 53–63 μm (UVPMS-BV-1.00) were acquired from Cospheric LLC (California, United States). To better simulate the MPs that can be found in real scenarios, PE, polypropylene (PP), and polystyrene (PS) MPs with different sizes (<63 μm, 63–80 μm) were also prepared from daily life utensils ("true-to-life" MPs) and used in laboratory experiments (transparent PE pipettes and white PS, and PP drink cups). The original plastic macropieces were fragmented through a mechanical process using an ultracentrifugal mill (Retsch ZM 200) equipped with a cyclone connected to a vacuum cleaner. Specific details on the preparation protocol are described in Ducoli et al. [7].

2.2.2. UV light aging process and characterization by IR analysis

As mentioned in the introduction section, MPs in the natural environment can undergo aging processes that can lead to changes in their surface and adsorption capacities. For that, the same "true-to-life" MPs were also submitted to an aging process with UVC light (8 weeks at 42 °C) to simulate the effect of sunlight on MPs once they have entered the aquatic environment. UVC light has higher energy than natural sunlight, which accelerates polymer degradation and surface oxidation. Therefore, experimental aging does not correspond directly to environmental time but rather simulates a longer-term environmental aging process within a shorter laboratory timescale. Specific details on the preparation protocol are described in Ducoli et al. [9].

First, the shape, morphology and overall appearance of the target MPs before and after UV aging, were examined. In **Fig. S1**, images of the studied MPs obtained with a portable USB digital microscope with LED illumination are displayed. As it is shown, a big difference in terms of shape and morphology can be identified within commercial and "true-to-life" MPs. MPs derived from micronized fragments of single-use plastics exhibit a heterogeneous distribution of irregular shapes, which more closely reflects environmentally relevant conditions compared to the homogeneous spherical particles of commercial PE MPs. Particle shape has been shown to influence key physical processes in the environment, such as settling velocity and aerodynamic behaviour, and may also play a significant role in the adsorption of metals onto MPs [15].

As mentioned in the introduction section, MP exposure to UV radiation may cause significant deterioration of these materials. UV radiation causes photooxidative degradation which results in breaking of the polymer chains, produces free radical and reduces the molecular weight. Visually, depending on the polymer type, also a change in the colour can be observed. As shown in **Fig. S1**, PS exposed to UV radiation exhibited slight yellowing, consistent with the initial stages of photodegradation [16].

To study more deeply the surface modifications caused by UV aging process, unaged and aged PE, PS, and PP "true-to-life" MPs were also characterized by a Perkin Elmer® Frontier Attenuated Total Reflection Fourier Transform InfraRed (ATR-FTIR) spectrometer. The ATR module is a UATR sample position plate which has a 7 mm chamber in the centre of the plate designed to position small samples directly over the UATR crystal which is a standard diamond crystal. It has a high-pressure clamp to ensure intimate contact for solid samples (the force was adjusted in order to ensure a reliable spectra) and a high-sensitivity DTGS detector. IR spectra were recorded at a resolution of 1 cm^{-1}, with 32 scans over a wavenumber range of 650–4000 cm^{-1}. Three replicates were made from each MP sample.

In **Fig. S2**, obtained IR spectra are displayed. First of all, the polymer type in the unaged "true-to-life" MPs was confirmed by comparing the obtained FTIR spectra with characteristic vibration modes reported in the literature [17]. As shown in **Fig. S2**, numerous C—H stretching vibrations are common to all the polymers studied. Nevertheless, each polymer exhibits distinctive spectral features, such as aromatic ring vibrations in PS and CH_3 stretching modes in PP, which facilitate the identification of the different polymers.

The variations of functional groups before and after UV exposure of the target MPs was also studied from the obtained IR spectra. In fact, IR has proven to be a useful and widely applied analytical technique for monitoring the oxidation process of different polymer types [18]. As it is shown in **Fig. S2**, the main changes in the IR spectra for all the studied

MPs after the photooxidation process are in the carbonyl absorption region. As reported in the literature, this spectral change is associated to the formation of ketones in the initial stages of oxidation, followed by the formation of carboxylic acids (1713 cm^{-1}), esters (1735 cm^{-1}), and lactones (1780 cm^{-1}) as secondary oxidation products [18]. In view of that, one of the most commonly used methods to evaluate and monitor oxidation reactions in polymers is the so called "Carbonyl Index" (CI). The CI is calculated as the ratio of the carbonyl absorption peak to a reference peak, providing a quantitative measure of oxidative degradation and the progression of polymer aging [19]. At present, there is no current universal method for determining CI. Indeed, when looking into the literature a multitude of different approaches are reported. In our case, CI was calculated from the ratio of the integrated band absorbance of the carbonyl (C=O) peak from 1650 to 1850 cm^{-1} to that of the methylene (CH_2) scissoring peak from 1420 to 1500 cm^{-1} as described by Almond and co-workers [20]. In this approach, the methylene group is chosen as the reference peak because it exhibits high stability and minimal variation in IR spectra. To estimate the CI, the spectra obtained for unaged and UV aged "true-to-life" MPs (63–80 μm) (**Fig. S2**) were processed by using Spectragryph 1.2. (Friedrich Menges, Oberstdorf, Germany) and the area was integrated setting the baseline as "0" and using the peak analysis tool. After that, the CI index was calculated according to the following expression:

$$Carbonyl\ index = \frac{Area\ under\ band\ from\ 1650 - 1850\ cm^{-1}}{Area\ under\ band\ from\ 1420 - 1500\ cm^{-1}}$$

The obtained CI values are reported in Table 1. As shown, significantly higher CI values were observed for UV aged MPs across all polymer types, confirming oxidative degradation of the MP surface. It is also interesting to remark that the obtained CI values for the aged MPs were slightly higher but comparable with those obtained in real MP samples collected in different environmental scenarios [21]. Therefore, they can be good candidates to be used in further metal adsorption studies.

2.3. *Batch adsorption studies*

To study in detail the time dependency of Zn adsorption process depending on the MP type, batch kinetic studies were carried out. For all the experiments 20 mL of aqueous solutions enriched with 1 mg/L Zn were put in contact with 20 mg of MPs. The tubes were then agitated at 30 rpm using a rotatory mixer. Sampling was performed at different time intervals with a maximum exposure time of 7 days. After the adsorption process, MP- suspensions were vacuum filtered using a 0.45 μm Nylon filter and rinsed with ultrapure water to eliminate any Zn not adsorbed onto the particles. Liquid extracts were analysed by ICP-OES and TXRF (section 2.3.1) and the loaded MPs collected onto the Nylon filter were also analysed by EDXRF (section 2.3.2).

In all cases, batch adsorption experiments were conducted using a mineral water sample as the aqueous medium. However, in one experiment, additional water types were considered to evaluate the influence of the aqueous matrix on Zn adsorption onto MPs. Specifically, three different reclaimed wastewater samples were used for such purpose: Reclaimed WW1, obtained from a conventional tertiary treatment (sand filtration followed by UV-sodium hypochlorite disinfection); Reclaimed WW2, produced by a nature-based system employing *D. magna* for pollutant removal; and Reclaimed WW3, derived from a nature-based system combining solar energy and biofilm technology. Physicochemical characteristics of all water samples used in the metal adsorption studies are presented in **Table S1**.

Table 1
Carbonyl Index values for "true-to-life" MPs before and after the UV aging process.

Polymer	**Particle size**	**UV aging process**	**Carbonyl Index**
PE	80-63 μm	No	0.11 ± 0.01
		Yes	1.03 ±0.12
PP	80-63 μm	No	0.39 ± 0.04
		Yes	1.37 ±0.12
PS	80-63 μm	No	0.69 ± 0.08
		Yes	2.11 ± 0.17

2.3.1. *Metal determination in liquid extracts by ICP-OES and TXRF analysis*

For ICP-OES analysis, a 4 mL aliquot of the filtered liquid extract was analysed. Calibration was performed using matrix-matched Zn standards covering a concentration range of 0.01–1.2 mg/L.

For TXRF analysis, a 1 mL aliquot of the filtered liquid extract was spiked with Rh as an internal standard to a final concentration of 0.5 mg/L. After vortex mixing for 20 s, 10 μL of the standardized solution were deposited onto a siliconized quartz reflector and dried at 60 °C prior to measurement.

Because the sample is deposited as a thin film, matrix effects are negligible, and elemental concentrations in TXRF analysis can be determined through internal standardization by adding a suitable internal standard to the sample and using the instrumental sensitivities of both the analyte and the internal standard (see Expression 1) [11]:

$$C_i = \frac{N_i C_{is} S_{is}}{N_{is} S_i}$$

where C_i and N_i are the concentration and net peak area of the analyte, C_{is} and N_{is} are the concentration and net peak area of the internal standard, and S_i and S_{is} represent the instrumental sensitivities for the analyte and the internal standard, respectively.

In all cases, Zn adsorption (%) onto MP samples was estimated using the following formula:

$$Zn\ adsorption\ onto\ MP\ (\%) = \frac{(C_i - C_f)}{C_i} x100$$

where C_i and C_f corresponds to the initial and final Zn concentrations in the aqueous media, respectively.

Instrumental characteristics and operating conditions for TXRF and ICP-OES measurements are summarized in Table 2.

2.3.2. *Study of metal adsorbed onto MPs by EDXRF analysis*

The loaded MPs collected onto the Nylon filter were dried at room temperature and then sandwiched between two adhesive 35 μm PP foils

Table 2
Instrument characteristics and measurement conditions.

Analytical technique	Measurement parameters
ICP-OES (Agilent 5100)	
Power	1200 W
Plasma flow	12 L/min
Nebulizer type	Concentric
Plasma view	Axial
Detector	Multichannel (CCD)
Replicates	3
Analytical wavelength	Zn: 213.857 nm
TXRF (S2 PICOFOX Bruker Nano)	
Anode X-ray tube	W
X-ray tube power	50 W (50 kV, 1 mA)
Atmosphere	Air
Measuring time	1000 s
Analytical line	Zn-K_{α}: 8.638 keV
EDXRF benchtop system (S2 Ranger, Bruker AXS)	
Anode X-ray tube	Pd
X-ray tube power	50 W (40 kV)
Primary filter	Al 500 μm
Irradiated area	30 mm
Atmosphere	Vacuum
Measuring time	150 s
Analytical line	Zn-K_{α}: 8.638 keV

to ensure proper preservation and handling prior to EDXRF analysis. After, the laminated filter was placed in a Teflon cup which incorporates snap-on ring at the end of the cell for attachments of thin-film supports and inserted into the instrument sample holder. To avoid instrumental blanks from the measurement chamber of the EDXRF system, a circular piece of Teflon with a thickness of 1.5 cm was used as a back-stopper. Teflon possesses a low transmittance at 20 kV that makes it a proper mask material to be used for such a purpose [14].

In Fig. 1 an image of the experimental setup used for the measurements is shown, together with an overview of the batch adsorption experiments and the procedures applied for metal determination using X-ray fluorescence-based techniques.

3. Results and discussion

3.1. *Comparison of TXRF and ICP-OES for Zn determination in liquid extracts*

In the present contribution, the feasibility of using TXRF for Zn concentration determination in the aqueous extracts from batch adsorption experiments was evaluated. As mentioned in the introduction section, TXRF is a multielemental spectroscopic technique which is more aligned with the green analytical chemistry principles than other commonly used techniques such as FAAS, ICP-OES and ICP-MS since it does not require cooling media or gas consumption during measurements and metal quantification can be achieved by internal standardization, eliminating the need for external calibration with aqueous metal standards. In Fig. 2, comparison of the Zn concentration obtained by TXRF and ICP-OES analysis of liquid extracts derived from kinetic adsorption studies using different types of polymers (PE, PP, and PS) with and without UV radiation exposure is displayed. As it is shown, no significant statistical differences were obtained among both experimental data sets, demonstrating that TXRF constitutes a cost-effective and environmentally friendly analytical tool to be used in this type of studies.

3.2. *Zinc adsorption studies onto MPs*

To gain deeper insight into Zn adsorption onto MPs, the effects of both MP physicochemical properties (polymer type and particle size), aging process and aqueous medium composition (water type and the presence of coexisting pollutants) were evaluated.

3.2.1. *Effect of polymer type*

MPs derived from micronized fragments of single-use PE, PS, and PP devices, with a particle size range of 63–80 μm, were selected to investigate Zn adsorption. Fig. 3 shows the Zn sorption kinetics for the different polymer types over a period of 7 days. In general, Zn uptake increased with time for all MP types until equilibrium was reached, occurring after approximately 48 h for PP, 96 h for PE, and 144 h for PS. These results indicate that interactions between Zn and the polymers were relatively rapid, in agreement with previous reports [22]. Notably, in the case of PP, a slow desorption of Zn was observed after the maximum adsorption was reached. This effect could be related to the stability of the metal-polymer interactions, which are not necessarily irreversible. In this sense, previous studies have reported that metals adsorbed onto MPs can be partially released over time depending on environmental conditions [23].

Fig. 3 also shows that, within the same particle size range, different polymer types exhibited distinct Zn adsorption percentages after 7 days: PS achieved the highest adsorption (~45%), followed by PE (~30%) and PP (~10%). Previous studies on Zn adsorption onto MPs reported a slightly different order (PE > PS > PP) [24]; however, differences in experimental duration (15 days) and conditions make direct comparisons difficult. Nonetheless, the results presented in the present study clearly demonstrate that polymer type has a significant impact on Zn adsorption.

3.2.2. *Effect of MP aging process with UV light*

As demonstrated in Section 2.2.2, UV aging of “true-to-life” PE, PS, and PP MPs modifies their surface chemistry by introducing oxygen-containing functional groups (mostly C=O), which can serve as specific binding sites for metal adsorption. In Fig. 4, Zn adsorption kinetics over a period of 7 days for both unaged and UV aged PE “true-to-life” MPs (63–80 μm) are displayed. For comparison purposes, Zn adsorption results for a commercial PE MPs of a similar size range are included as well. As it is shown, Zn adsorption percentage is substantially higher for the MP exposed to UV radiation (~60%) compared to the unaged ones (~30%), confirming the improvement of the Zn binding efficiency after the photooxidation process. From the results obtained is also interesting to mention that no significant differences were found on Zn adsorption percentage after 7 days between commercial and “true-to-life” PE MPs despite the differences in terms of shape and morphology previously mentioned (**Fig. S1**). Results obtained in Zn adsorption experimental tests for PS and PP “true-to-life” MPs (**Fig. S3**) also demonstrated that UV-induced aging enhance MP adsorption yield for Zn, above all for PP (from ~6.0% to 40%). This behaviour can be attributed to surface modifications induced by UV exposure, including the formation of oxygen-containing functional groups (e.g., carbonyl or hydroxyl groups), which increase the affinity of MPs for metal ions. In addition, UV aging may lead to surface roughening and microcrack formation, further promoting adsorption by increasing the number of available binding sites. These findings are consistent with previous studies reporting enhanced metal adsorption onto aged MPs [25] [26].

It seems that in the case of PE MPs, the UV aging process also affects the Zn adsorption rate. As shown in Fig. 4, Zn adsorption onto UV aged PE MPs proceeds rapidly, reaching an adsorption yield of approximately 30% with less than 2 h. In contrast, unaged PE MPs require a much longer contact time (around to 3 days) to achieve a comparable level of Zn adsorption. For other MPs types (PP and PS, **Fig. S3**), UV aging does

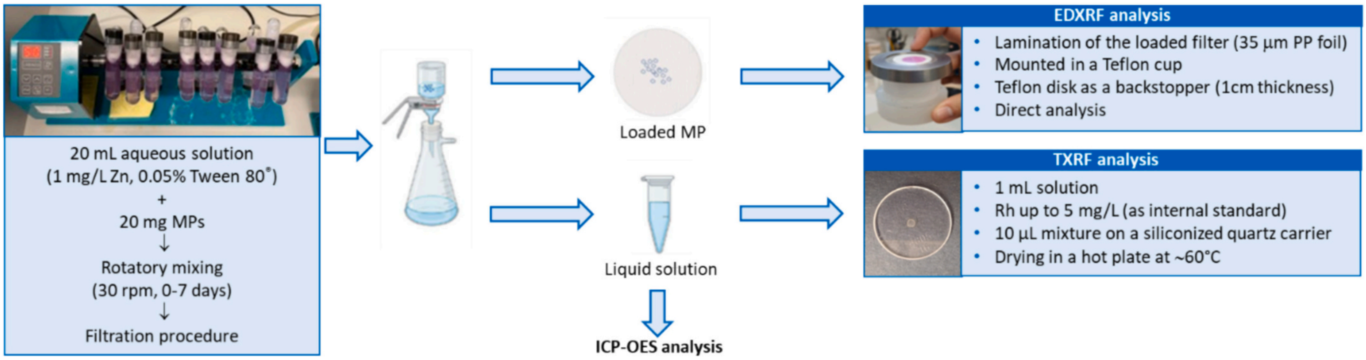

Fig. 1. Schematic view of metal adsorption studies onto MPs and experimental details for metal determination using X-ray fluorescence-based techniques.

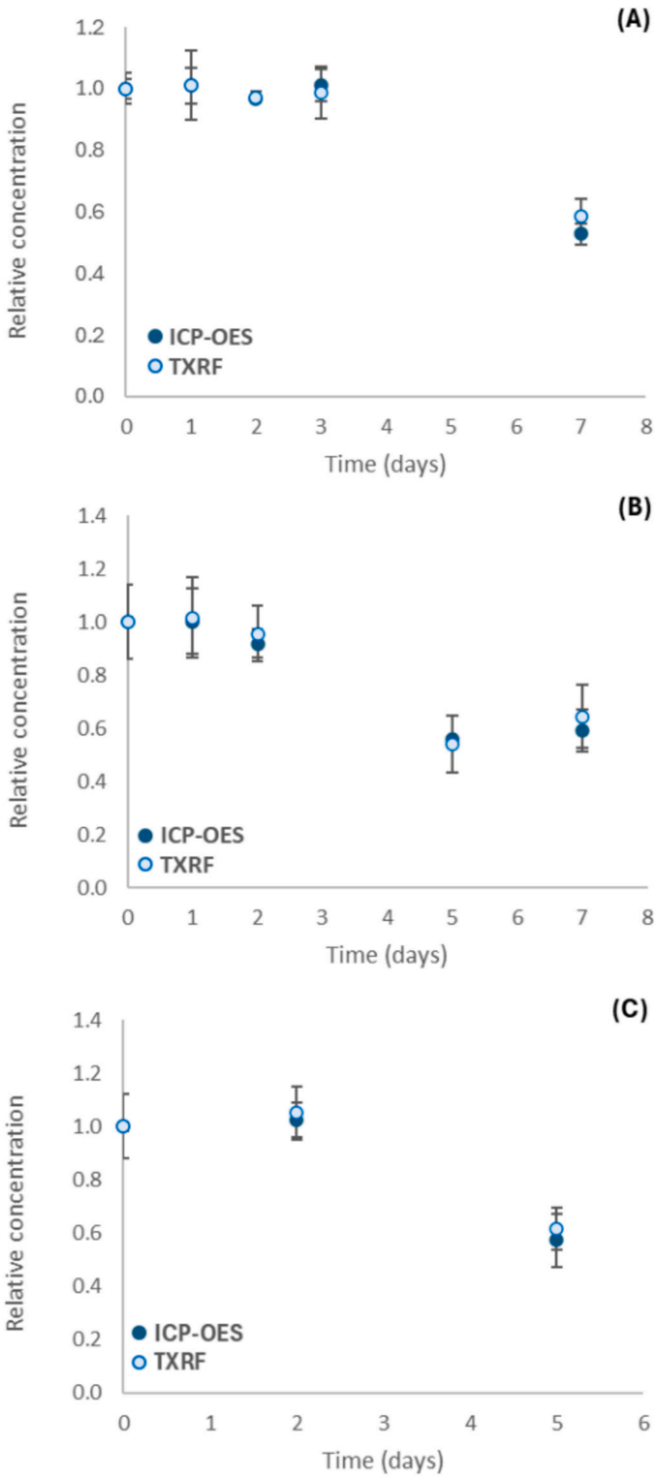

Fig. 2. Comparison of TXRF and ICP-OES for Zn determination in liquid extracts derived from kinetic adsorption studies: (A) PE commercial (53–63 μm), (B) PP "true-to-life" with UV aging (63–80 μm) and (C) PS "true-to-life" (63–80 μm). Relative concentration was estimated by dividing the Zn concentration of each point by the initial Zn concentration in solution. Error bars correspond to standard deviation of duplicates. Initial Zn concentration was set at 1 mg/L.

not lead to an increased adsorption rate.

In order to verify the obtained results, a qualitative EDXRF analysis of Zn on the loaded MPs was also carried out (specific details in section 2.3.2). Spectra obtained for specifically selected experimental points are displayed in Fig. 4 (PE MPs) and **Fig. S3** (PS and PP MPs). EDXRF results

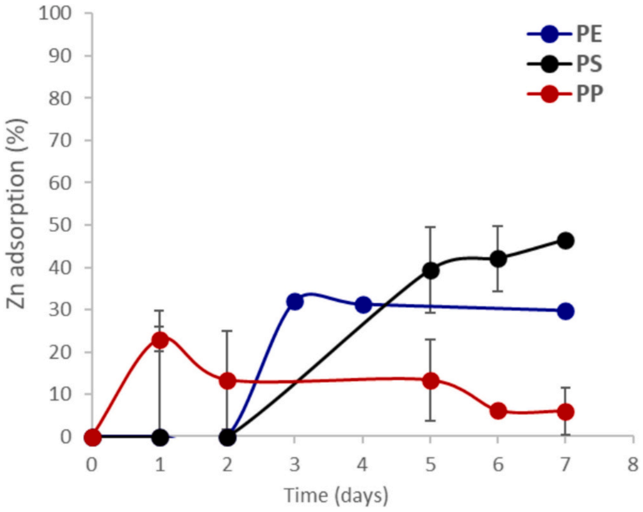

Fig. 3. Effect of polymer type on Zn adsorption kinetics. In all cases, "true-to-life" MPs with a particle size range of 63–80 μm were employed. Error bars correspond to standard deviation of duplicates. Initial Zn concentration was set at 1 mg/L.

confirmed the trends already observed when estimating Zn adsorption percentage from the difference between the initial and final Zn concentration in the aqueous media. Therefore, although EDXRF provides primarily qualitative information, the advantages of this rapid, low-cost and less time-consuming analytical approach make it an attractive option for monitoring metal adsorption onto MPs in this type of studies. Additionally, due to the simultaneous multielemental capability of the technique, it can be also used to get screening information of other elements present in the MP before the analyte adsorption process. Therefore, EDXRF analysis offer a reliable and efficient approach for tracking metal accumulation in raw and loaded MP samples.

3.2.3. *Effect of MP particle size*

The particle size of solid sorbents is a critical parameter that strongly influences metal adsorption processes. A reduction in particle size generally leads to an increase in specific surface area, thereby enhancing the availability of active adsorption sites. In the context of metal adsorption onto MPs, previous studies have demonstrated that smaller particle sizes exhibit significantly higher adsorption capacities for divalent metal ions such as Cu, Pb, and Cd compared to larger particles, highlighting the importance of particle size in governing adsorption efficiency [27] [28]. In the present study, the effect of MP particle size on Zn adsorption was evaluated using polyethylene (PE) "true-to-life" MPs within two particle size ranges: <63 μm and 63–80 μm. The obtained results are presented in Fig. 5. Although the final Zn adsorption percentage after 7 days does not show significant differences between the two particle size fractions considered, the adsorption kinetics during the first 48 h are clearly enhanced for PE "true-to-life" MPs with particle sizes <63 μm. This behaviour can be attributed to the reduced intraparticle diffusion distances in smaller particles, which facilitate faster mass transfer of Zn toward the available adsorption sites.

The influence of MP particle size on Zn adsorption was also investigated for PE "true-to-life" MPs subjected to UV aging. As shown in Fig. 5, smaller aged MPs not only exhibit faster Zn adsorption kinetics but also achieve significantly higher Zn adsorption after 7 days, reaching 90.6 ± 0.1%, compared to 67 ± 3% for the larger aged MPs.

This behaviour can be attributed to the combined effect of particle size reduction and UV-induced aging. On the one hand, smaller MPs provide a higher specific surface area, increasing the number of available adsorption sites. On the other hand, UV aging promotes surface oxidation, leading to the formation of oxygen-containing functional groups (e.g., carbonyl and hydroxyl groups) that enhance metal binding

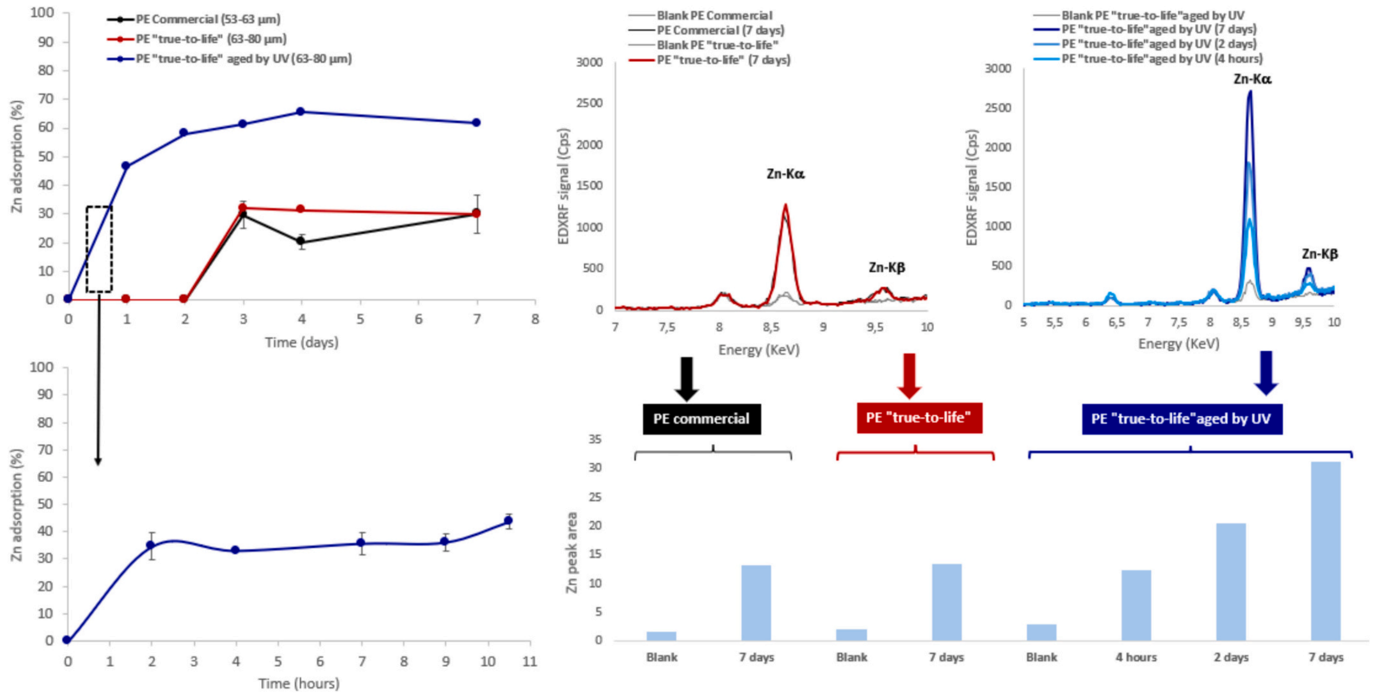

Fig. 4. Zn adsorption kinetics depending on the type of PE MPs: commercial and "true-to-life" (with and without UV aging). Error bars correspond to standard deviation of duplicates. The initial Zn concentration in the solution was 1 mg/L. On the right, spectra and integrated Zn peak areas obtained by EDXRF analysis of different types of PE MPs exposed to Zn. For comparison purposes, results for blank MP samples (without Zn exposure) are also shown.

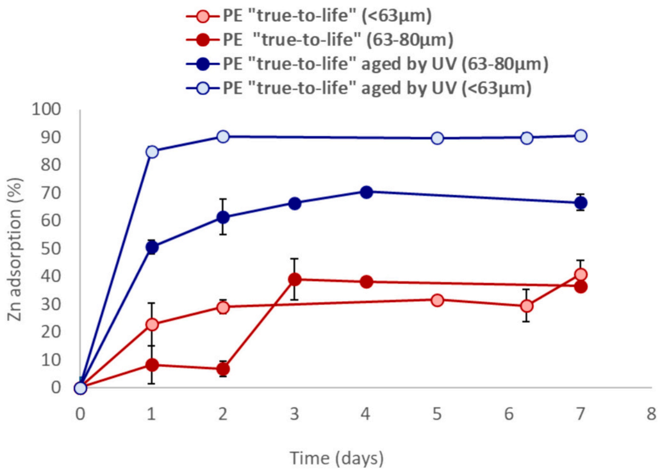

Fig. 5. Effect of MP particle size range (63–80 µm and < 63 µm) on Zn adsorption: (A) PE "true-to-life" MPs and (B) PE "true-to-life" MPs aged by UV. The initial Zn concentration in the solution was 1 mg/L.

through complexation mechanisms. The synergistic effect of these two factors results in both faster adsorption kinetics and higher adsorption capacity. These findings are consistent with recent studies reporting enhanced adsorption capacities of smaller and aged MPs relative to unaged MPs for divalent metals such as Pb and Cu [29].

3.2.4. *Effect of the aqueous media*

As demonstrated in the previous sections, the sorption behaviour of metals onto MPs is strongly governed by their physical and chemical properties. However, prolonged contact between MPs and the aqueous medium can induce also surface weathering or aging processes, which may further modify the surface characteristics of MPs and, consequently, influence their metal adsorption capacity [2]. In fact, in real aquatic environments, a large number of ecological macromolecules (i.e., natural organic matter, proteins) can adsorb onto the surface of MPs to form the so-called "environmental corona" which can alter the bioavailability and toxicity of MPs to aquatic organisms [30].

To assess the effect of aqueous-media aging on MPs, 20 mg of PE "true-to-life" MPs (63–80 µm) were suspended in 20 mL of mineral water (**Table S1**) and continuously stirred at 30 rpm for one month. After the aging process, an appropriate amount of a Zn solution was added to obtain a final concentration of 1 mg/L, and the suspension was agitated at 30 rpm for an additional 7 days. Zinc adsorption onto MPs was then evaluated. As shown in Table 3 (Effect 1), aqueous-aged MPs exhibited a significantly higher Zn adsorption after 7 days (80 ± 1%) compared with unaged MPs (30 ± 1%). Moreover, Zn adsorption onto aqueous-aged MPs was also significantly greater than that observed for MPs subjected to UV aging (62 ± 3%, Fig. 4). These results highlight the important role of weathering processes occurring in aqueous environments in enhancing the metal adsorption capacity of MPs.

This behaviour likely results from physicochemical changes induced during aqueous aging, such as surface oxidation, the formation of oxygen-containing functional groups, and the possible adsorption of dissolved organic matter or inorganic species present in the water, which can act as additional binding sites or modify surface charge. In this sense, the aqueous medium may promote more complex surface interactions than UV aging alone. Consistent with these findings, Holmes et al. (2014) reported that beach-sourced plastic pellets exhibited a substantially higher affinity for trace metals than virgin pellets in aquatic environments [31], which was attributed to environmental weathering processes that increase surface reactivity and metal-binding capacity.

Another effect investigated in this study was the influence of the aqueous medium on metal adsorption onto MPs. Recent studies have shown that the chemical characteristics of the aqueous medium (e.g., pH, salinity, and dissolved organic matter, DOM) can modify MP surface properties, such as roughness and surface charge, thereby affecting metal adsorption processes [26]. In the present work, the percentage of Zn adsorption onto PE "true-to-life" MPs, both unaged and UV aged, was evaluated using mineral water and different reclaimed wastewater

Table 3
Study of the effect of aqueous media parameters on Zn adsorption onto PE "true-to-life" MPs. Adsorption experiments were performed by rotatory mixing (30 rpm) of 20 mg of MP and 20 mL of spiked aqueous media at 1 mg/L Zn for 7 days. Results are expressed as mean percentage of Zn adsorption with the associated standard deviation ($n = 2$).[1, 2]

Parameter studied	Type of MP	Aqueous media[1]	% Zn adsorption
Effect-1: Water aging process	PE "true-to-life"	Mineral water	30 ± 1
	PE "true-to-life" with previous contact with mineral water (20 mg MP/20 mL) for 1 month	Mineral water	80 ± 1
Effect-2: Aqueous media type	PE "true-to-life"	Mineral water	30 ± 1
		Reclaimed WW 1	13.6 ± 0.3
		Reclaimed WW 2	37 ± 2
		Reclaimed WW 3	31 ± 2
	PE "true-to-life" aged by UV	Mineral water	62 ± 3
		Reclaimed WW 1	24 ± 2
		Reclaimed WW 2	60.1 ± 0.4
		Reclaimed WW 3	60 ± 10
Effect-3: Presence of other metals	PE "true-to-life"	Mineral water[2]	2.8 ± 0.1
	PE "true-to-life" aged by UV	Mineral water[2]	6.1 ± 0.5

[1] Physico-chemical information of Mineral water, Reclaimed WW1, Reclaimed WW2 and Reclaimed WW3 can be found in Table S1.

[2] Mineral water was also spiked at 1 mg/L Fe, 1 mg/L Cu, 0.1 mg/L Pb, 0.1 mg/L Cr and 0.1 mg/L Cd.

samples. The results are summarized in Table 3 (Effect 2). As shown, comparable Zn adsorption levels were observed after 7 days of exposure in mineral water, reclaimed WW2, and reclaimed WW3. In contrast, significantly lower Zn adsorption was measured in reclaimed WW1 for both aged and unaged MPs. As described in Section 2.3, reclaimed WW1 was obtained from a conventional tertiary treatment that includes sand filtration and disinfection by UV radiation and the addition of sodium hypochlorite. In view of the obtained results, it seems that the presence of sodium hypochlorite in this sample may negatively influence Zn adsorption onto MPs, since the other physicochemical parameters measured in the aqueous media were similar among the samples under study (**Table S1**). Based on these findings, future research will focus on further elucidating the role of aqueous media composition in controlling metal adsorption onto MPs.

Finally, the effect of the presence of other metals on Zn adsorption onto MPs was also investigated. For that, the mineral water used previously in adsorption studies, was spiked at 1 mg/L of Zn but also with 1 mg/L (Fe and Cu) and 0.1 mg/L (Pb, Cr and Cd). Obtained results for both UV aged and unaged PE "true-to-life" MPs are reported in Table 3 (Effect 3). A pronouncedly decrease (10 times) in Zn adsorption onto both types of MPs was found in the presence of other metals in the aqueous media. This fact can be related to the competitive effect of other metals due to their different adsorption capacities onto MPs. For instance, in a study dealing with the study of metal adsorption onto PET MP fibres, it was found that the highest levels of sorption were for $Pb^{2+} > Cd^{2+} > Cu^{2+} > Hg^{2+} > Zn^{2+}$ [5]. In the present study, percentage adsorption rates for other metals present in the target solution were also estimated (Cu: 54.5 ± 0.1% unaged MP and 75.6 ± 0.2% aged MP, Fe: 61 ± 4% unaged MP and 69 ± 3% aged MP, Pb: 59 ± 4% unaged MP and 77 ± 3% aged MP, Cd: 1.0 ± 0.3% unaged MP and 15.1 ± 0.1% aged MP and Cr: 2.9 ± 0.3% unaged MP and 7.4 ± 0.1% aged MP) showing a prevalence adsorption of other studied metals in comparison to Zn.

4. Conclusion

The proposed XRF-based strategies provide fast, cost-effective, and environmentally friendly alternatives for investigating metal adsorption onto MPs, thereby contributing to more sustainable analytical practices in environmental research. TXRF demonstrated strong potential for monitoring and estimating metal adsorption through the analysis of supernatants before and after batch adsorption experiments. Complementarily, qualitative EDXRF analysis of MP-loaded filters enabled the direct verification of metal adsorption onto MPs without any sample pretreatment. In view of the promising results obtained, future work will focus on the development of a robust quantification strategy, including the preparation of appropriate MP-based reference materials for EDXRF analysis.

The results of this study demonstrate that "true-to-life" PE, PS, and PP MPs exhibit a significant capacity to adsorb metals such as Zn, which is governed by polymer type, particle size, and aging state. Adsorption was strongly influenced by surface properties, with UV aged MPs showing markedly enhanced metal uptake, likely due to surface oxidation and the increased availability of binding sites. Furthermore, smaller particle sizes promoted higher metal accumulation, particularly after aging, highlighting the combined effect of particle size reduction and surface modification on adsorption behaviour.

These observations suggest that environmentally aged MPs may have an increased potential to act as vectors for metal contamination. This effect is expected to be further influenced by the presence of multiple metals and matrix characteristics. In this context, future studies based on design of experiments approaches would be valuable to systematically assess the interactions between the key variables involved.

CRediT authorship contribution statement

Mary Isabel Villacís: Writing – review & editing, Methodology. **Laura Torrent:** Writing – review & editing. **Mònica Iglesias:** Writing – review & editing. **Fabjola Bilo:** Writing – review & editing, Methodology. **Serena Ducoli:** Writing – review & editing, Methodology. **Òscar González-Fernández:** Writing – review & editing, Methodology. **Eva Marguí:** Writing – original draft, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization.

Ethics statement

This study does not involve human subjects, animals, or protected biological/chemical materials. No ethical approval or informed consent was required for the research.

Declaration of competing interest

The author is an Editorial Board Member/Editor-in-Chief/Associate Editor/Guest Editor for this journal and was not involved in the editorial review or the decision to publish this article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sab.2026.107533.

Data availability

The data from the experiments presented throughout this research paper may be obtained from the authors upon reasonable request.

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