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Electrochemical removal of PET and PE microplastics for wastewater treatment

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The presence of microplastics (MPs) in most ecosystems is a major problem globally, and effective strategies to avoid their release are not still established. In this work an electrochemical process to remove microplastics from wastewater is proposed. The removal of polyethylene (PE) and polyethylene terephthalate (PET) microplastics by electrolysis with mixed metal oxide anodes was studied. The weight loss of MPs, generation of by-products and surface transformation induced by the treatment were assessed. The effect of active chlorine species electrogenerated was also studied. Starting from MP suspensions of 1 g dm^{-3}, removal of about 70% of MPs (as weight loss) was achieved. A kinetic model based on a surface degradation process was used to quantify the performance of the process: degradation rates of 1.10 10^4 μm y^{-1} for PE and 1.32 10^4 μm y^{-1} for PET were obtained for electrolysis at 20 mA cm^{-2}.

Water impact

The presence of microplastics in most ecosystems is a major problem globally, and effective strategies to avoid their release are not still established. A possible approach to limit the release and the dispersion of MPs in the environment is the implementation of new processes in the existing water and wastewater treatment plants that are not designed specifically to remove microplastics. Advanced electro-oxidation processes mediated by strong oxidising chlorine-based agents, already established for the efficient removal of various organic micropollutants, may also be applied in wastewater treatment plants to effectively eliminate microplastics.

1. Introduction

Microplastics (MPs) have been recognised as significant water pollutants with considerable potential for exerting adverse impacts on human health and wildlife. Although it is not possible to know the exact extent of contamination, MPs have been detected in seawater, freshwater, food, air, and soil.[1]

Based on the source they are generated from, microplastics in the environment can be primary or secondary.[2] Primary microplastics are directly released into the environment with the products they are added to, such as shower gels and creams, but can also come from processes of abrasion of large plastic objects including tires while driving and from washing of synthetic textiles.[3] Secondary microplastics originate mostly from the degradation of plastic bags, fishing nets or other large plastic objects into smaller particles in the environment. Agricultural wastewater, industrial wastewater, litter, and sewage treatment plants are well recognised sources of microplastics, where they are often in low concentrations,[4,5] but MPs can also be released in high concentrations, reaching several thousands of particles per litre. Concentrations up to 12 800 particles per litre are reported for laundries,[6,7] up to 18 000 particles per litre for plastic waste recycling plants,[8] and up to 200 000 particles per litre in ships' grey water.[9,10]

Very few studies have been focused on the removal of microplastics, mostly with processes based on physical separation, namely coagulation–flocculation, flotation, and membrane processes.[11] Other studies have reported the use of chemical or biological treatment, including biodegradation, wet oxidation, and advanced oxidation processes (AOPs).[12–14] A possible approach to limit the release and the dispersion of MPs in the environment is the implementation of new processes in the existing water and wastewater treatment plants that are not designed specifically to remove microplastics.[8,15,16] Despite the removal efficiency of plastic wastes in the existing treatment processes that can reach values higher than 99%,[17,18] large amounts are still discharged in the environment.[19]

Among the possible solutions, advanced oxidation processes could be implemented in wastewater treatment plants to effectively eliminate microplastics as the action of

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strong oxidising agents can be exploited to decompose long-chain polymers to smaller molecules up to complete mineralisation to H_2O and CO_2.[20,21]

The application of AOPs has been proposed for the treatment of wastewaters with a high content of microplastics such as those derived from household washing machines and laundries.[22–24]

Among the AOPs, electrochemical treatment can produce different oxidising species such as OH radicals, ozone, and hydrogen peroxide as well as chlorine and hypochlorous acid, which are able to oxidise the pollutants.

Only a few studies are present in the literature regarding the electrochemical treatment of MPs. Kiendrebeogo *et al.* reported that the electrochemical oxidation process with BDD anodes is effective for the treatment of water contaminated by polystyrene. The authors reported a degradation efficiency of 89 ± 8% with 6 h of treatment of a suspension of 100 mg dm^{-3} in 0.03 M Na_2SO_4.[25] The role of main reactive oxygen species (ROSs) in the electrooxidation (EO) and electro-peroxidation (EO-H_2O_2) of polystyrene nanoparticles in water was also investigated. The EO-H_2O_2 process was about 2.6 times more effective than the EO process, and the result was attributed to the formation of $SO_4^{\bullet-}$ *via* H_2O_2.[26,27]

Electrochemical technology has been also applied to washing machine effluents at pre-pilot plant scale using active and non-active anodes. In this case, COD removal of 88% has been obtained and a degree of mineralisation of more than 85% was reported in the presence of sulphate with the BDD anode; a contribution of the active chlorine electrogenerated from the oxidation of chloride present in real wastewater (200 mg dm^{-3}) was highlighted.[24]

Also, combined treatment such as the electro-hybrid ozonation–coagulation process has been tested for laundry wastewater containing surfactants and microplastics ranging from 4400 to 10 800 particles per litre.[6]

However, most of the aspects related to the application of electrochemical processes to MP-contaminated waters are still to be studied and a quantitative interpretation of the process is not present in the literature. Moreover, considering that the waters polluted by microplastics are suspensions of organic particles rather than homogenous solutions, bulk degradation mediated by oxidising species electrogenerated at the anode may represent a suitable choice.

The electro-generation of active chlorine was largely investigated for the disinfection of water and wastewater but not for MP removal, although active chlorine is very effective and widely used for wastewater treatment.[28–30]

The aim of this study was to assess the effectiveness of an electrochemical treatment on the removal of polyethylene terephthalate (PET) and polyethylene (PE), which are the major MPs present in the environment.

Synthetic suspensions of microplastics were used with a content of MPs, typical of laundries, plastic waste recycling plants and ships' grey water.[6–10] Indirect oxidation mediated by active chlorine species (ACS) generated from the oxidation of chloride ions with a commercial mixed oxide anode was studied. A cell configuration was used with the anode close to the free surface of the water, where MPs tend to accumulate. A quantitative interpretation of the data with a model previously used to quantify the ageing of plastics in the environment was done, and the acceleration of ageing due to the electrochemical treatment was assessed.

2. Materials and methods

Electrolysis tests were performed in a 500 cm^3 cylindrical single compartment cell with two parallel electrodes, both composed of titanium grids coated with Pt (cathode) or mixed Ti/Ru/Ir oxides (anode); the composition of the anode coating was not indicated by the supplier (Magneto). The geometrical area of both the anode and the cathode was 20 cm^2. The electrodes were arranged parallel to the free surface of the solutions, with the anode close to the surface. The inter-electrode gap was 2 cm.

The cell was inserted in a thermostatic bath to maintain the temperature at 25 °C. The experimental apparatus and details of the cell are shown in Fig. 1.

Galvanostatic electrolysis tests were carried out with current densities of 10 and 20 mA cm^{-2}. High density polyethylene beads (Merck) with an average particle size of 150 μm and polyethylene terephthalate beads (GoodFellow) with an average particle size of 250 μm were used.

300 mg of PE or PET were dispersed in 300 cm^3 of a synthetic solution containing 0.1 M $NaClO_4$ as supporting electrolyte. NaCl was added to the suspension to obtain an initial concentration of chloride ions of 1000 mg dm^{-3}. Every 24 h the concentration of chloride ions was restored to the initial value with 10 mL of concentrated NaCl solution. For comparison, electrolysis tests of MP-free solution were also performed.

The process was monitored by analysing both the solid and the liquid phases. During the experiments liquid

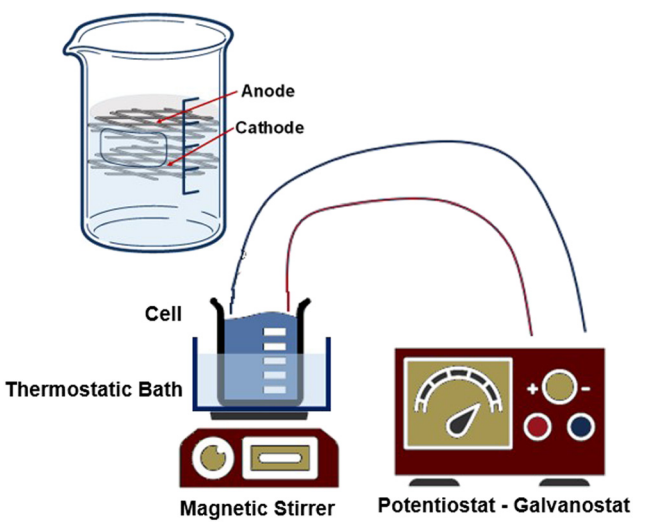

Fig. 1 Experimental apparatus with details of the electrochemical cell.

samples were withdrawn at prefixed times and analysed for the concentrations of oxidants, chloride ions and total organic carbon (TOC). The oxidant concentrations expressed as mg dm^{-3} of active chlorine were measured using the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) colorimetric standard method.[20] DPD is oxidised to form a red-violet product, the concentration of which is determined using a UV-vis spectrophotometer (Agilent, Cary 60 UV-vis) at a wavelength of 515 nm. The DPD method gave a measure of the active chlorine species (ACS) as the global concentration of oxidising species contained in the sample. The concentration of chloride ions was measured using an ion chromatograph (Metrohm 761, conductivity detector, Metrosep Anion supp. 4 column, mobile phase 2 mM $NaHCO_3$/1.3 mM Na_2CO_3, flow rate 1.5 cm^3 min^{-1}). TOC was analysed using a total organic carbon analyser (Shimadzu TOC-L).

The degradation efficiency of MPs was evaluated by the weight loss of PE and PET during the electrolysis. To measure the variations in weight loss of MPs, the electrolysis tests were stopped, and the dispersion was filtered with a nitrocellulose filter (0.22 μm pore size); the filters were then dried in an oven at 70 °C for 48 h. The mass loss of MPs was calculated using eqn (1):

$$\text{Weight loss}\ (\%) = \frac{W_0 - W_t}{W_0} \times 100 \qquad (1)$$

where W_0 and W_t are the initial and the residual mass of MPs, respectively. After the measurement, the MPs were then resuspended in the electrolyte, and the electrolysis was restarted.

The MPs were also analysed using an FTIR spectrometer (Jasco FTIR 6700) equipped with an ATR diamond crystal module in the range between 400 and 4000 cm^{-1}, acquiring 64 scans with a resolution of 4 cm^{-1}. The obtained spectra were compared with the reference spectrum recorded with pristine particles. The size and shape of MPs before and after anodic oxidation were analysed by SEM (ZEISS EVO 50).

3. Results and discussion

The production of chlorine-based oxidants in the cell was assessed first by measuring the concentration of active chlorine species formed and chloride ions with time. Fig. 2a and b show the concentration of active chlorine species generated during the electrolysis of water and water with PE under different applied current densities. As shown, in aqueous solutions with the supporting electrolyte and 1000 mg dm^{-3} chloride ions, at 10 mA cm^{-2} the amount of ACS increases with time during the initial 5 hours of electrolysis and then reaches a pseudo steady state. At a current density of 20 mA cm^{-2}, the concentration of ACS increases sharply to a maximum and then decreases.

The observed trend of ACS can be explained considering the different chemical and electrochemical reactions that may occur during electrolysis with mixed-metal oxide

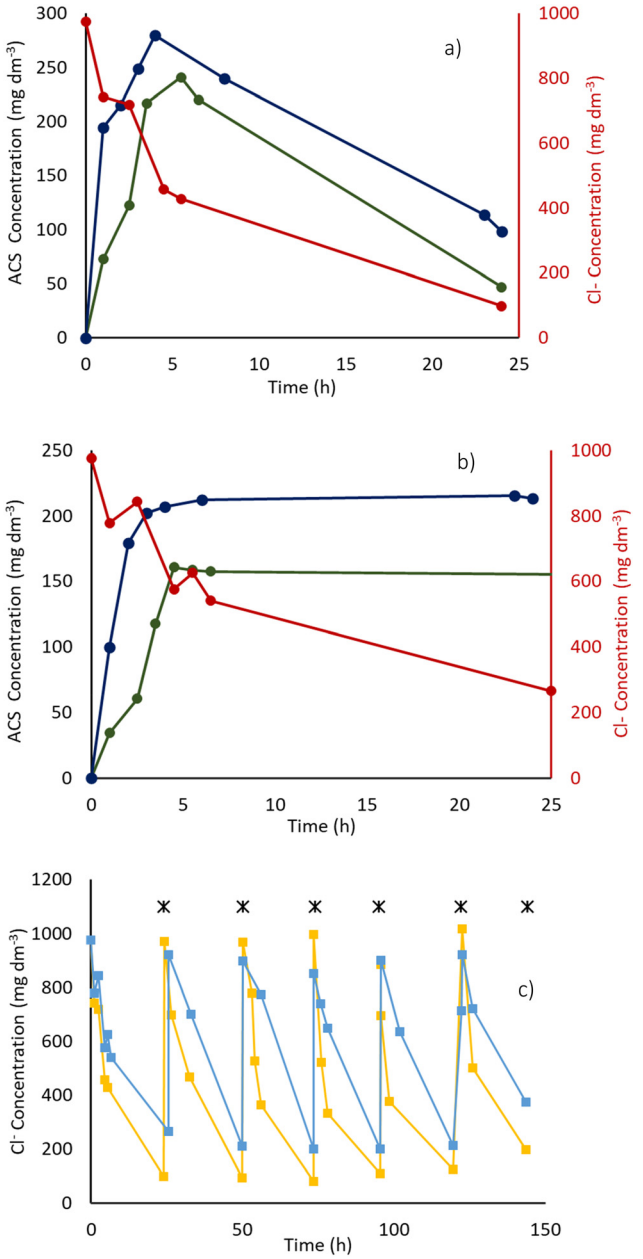

Fig. 2 Trend with time of the concentration of active chlorine species formed during electrolysis in the presence of PE (green) and in PE-free solution (blue). The secondary axis reports the trend of chloride ions (red). (a) Applied current density = 20 mA cm^{-2}; (b) applied current density = 10 mA cm^{-2}. (c) Trend with time of the concentration of chloride ions during electrolysis at 10 mA cm^{-2} (blue symbols) and at 20 mA cm^{-2} (yellow symbols). Black stars indicate the addition of concentrated NaCl.

anodes.[31,32] Chloride ions react in a complex manner at active Ru sites to give adsorbed and dissolved chlorine:[33]

$$2Cl^- \rightarrow Cl_{2(ads)} + 2e^- \qquad (2)$$

$$Cl_{2(ads)} \rightleftarrows Cl_{2(aq)} \rightleftarrows Cl_{2(g)} \qquad (3)$$

Under the conditions adopted in this work the oxidation of Cl^- is likely a migration-controlled process that depends on the applied current density.[34]

Dissolved chlorine, formed by the electrochemical reaction eqn (2), reacts with water to give hypochlorous acid and hypochlorite ions:

$$Cl_{2(aq)} + H_2O \rightarrow HClO + H^+ + Cl^- \quad (4)$$

$$HClO \rightleftarrows ClO^- + H^+ \quad (5)$$

The distribution of the three forms of active chlorine depends on the pH, and at neutral or weakly alkaline pH the reaction of disproportionation eqn (4) will be shifted towards HClO. In undivided cells cathodic reduction of active chlorine may also occur along with the hydrogen evolution reaction:

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \quad (6)$$

This electrochemical reaction is known to be fast, so that the kinetics of active chlorine reduction is often controlled by the mass transfer.[35]

Moreover, part of the gaseous chlorine produced at the anode may be stripped out, and the overall balance of chlorine (Fig. 2) results in a decrease of chlorides of about 70% at 10 mA cm^{-2}, and over 90% at 20 mA cm^{-2}.

The plateau of the ACS concentration observed at low current density results from the balance between the formation and the consumption of oxidants, where the relevant reaction rates are reasonably equal within the first 24 hours of treatment. With 20 mA cm^{-2} applied current density, the faster increase of concentration and the presence of a maximum can be ascribed to the faster consumption of chlorides in the batch system.

Under both conditions, the generation of ACS is higher in the absence of MPs, and the concentration of chlorine-based oxidants measured during electrolysis with 1 g dm^{-3} PE dispersions is lower than that obtained with PE-free water by almost 30%. This result may be due to the reaction of active chlorine with MPs and, as will be discussed later, is confirmed by the detection of organic compounds in the solution.

However, after 24 h no weight loss of MPs was observed, so the electrolysis tests were extended up to 800 h, where the concentration of chlorides was returned to the initial value every 24 h in a fed batch mode. The trend with time of the chloride concentration during the first six days of treatment is reported in Fig. 2c; black stars mark the addition of 10 ml of concentrated NaCl solution.

The weight loss of MPs with time was measured to assess the degradation of PE and PET beads during the electrochemical treatment, as it is the simplest and most direct way to quantify the extent of degradation of polymers.[36] Fig. 3 reports the weight loss measured during the treatment of suspensions containing PE and PET under different applied current densities.

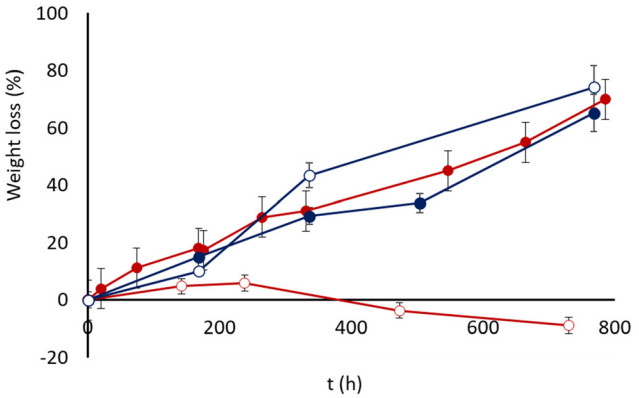

Fig. 3 Trend with time of the weight loss percentage measured during the electrochemical treatment of suspensions of PE (red) and PET (blue) performed at 10 mA cm^{-2} (empty symbols) and 20 mA cm^{-2} (full symbols).

As shown, a significant effect of the applied current density can be observed in the case of PE: at 20 mA cm^{-2} the weight loss percentage increases gradually, reaching 67% after 750 h of anodic oxidation, while at 10 mA cm^{-2} it shows low variation, with an increase after 400 h of treatment. Conversely, the weight loss of PET is measured after 200 h of treatment at both 10 and 20 mA cm^{-2} and increases up to about 75% after about 750 h of treatment.

The results can be related to the different chemical structures and wetting properties of PE and PET. PET is obtained by a polymerisation process that occurs with formation of ester functionalities, which in turn may constitute the starting point of its degradation due to its intrinsic reactivity (Fig. 4a). As already highlighted in the literature,[37] most of the degradation/depolymerisation processes including hydrolysis, alcoholysis or glycolysis take advantage of this reactivity.

On the other hand, PE is derived from polymerisation of ethylene, giving a saturated carbon chain backbone with no functional groups, meaning that a direct C–H functionalisation of the alkylic chain is necessary to start its degradation (Fig. 4b). PE is then expected to be a substrate harder to oxidise, and different short-chain oxidised by-products might be generally envisaged from its degradation (*i.e.* acetic, propionic or butyric acids, oxalic acid *etc.*).

To better understand the oxidation process, FT-IR analyses of the electrochemically treated PE and PET have been carried out (see Fig. 5). As can be observed, no changes in the PET surface were detected during the electrochemical treatment, suggesting fragmentation of PET during the process with formation of the oxidation by-products generally observed during PET degradation, including terephthalic acid (PTA), ethylene glycol (EG), and smaller fragments (dimers, trimers, tetramers) as well as compounds derived from the oxidation of such by-products.[38,39]

In the case of PE, some differences between treated and untreated MPs are observed. In particular, the formation of hydroxyl functionalities (signal at *ca.* 3300 cm^{-1}) and the

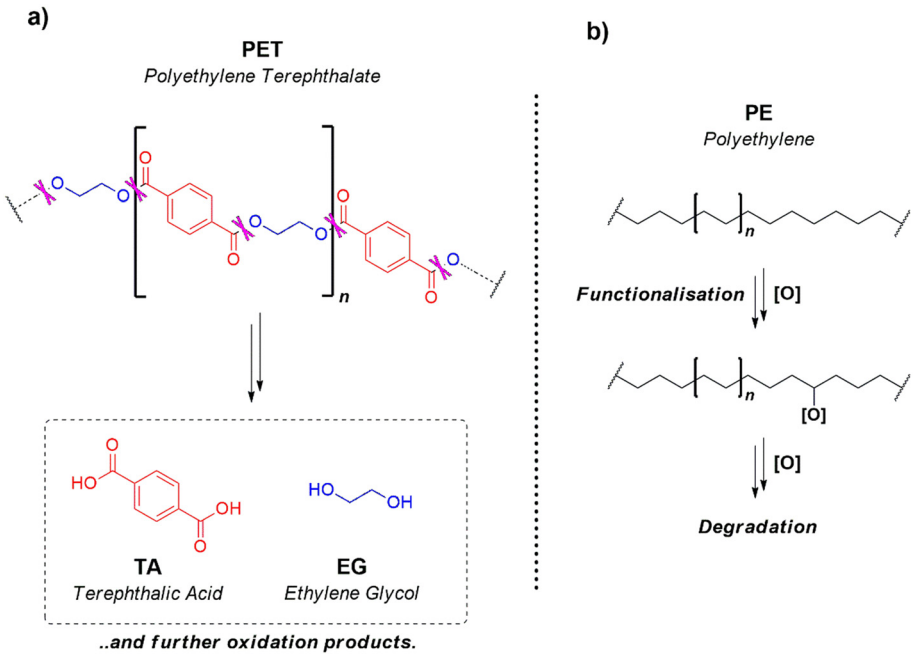

Fig. 4 Scheme of degradation mechanism for PET (a) and PE (b).

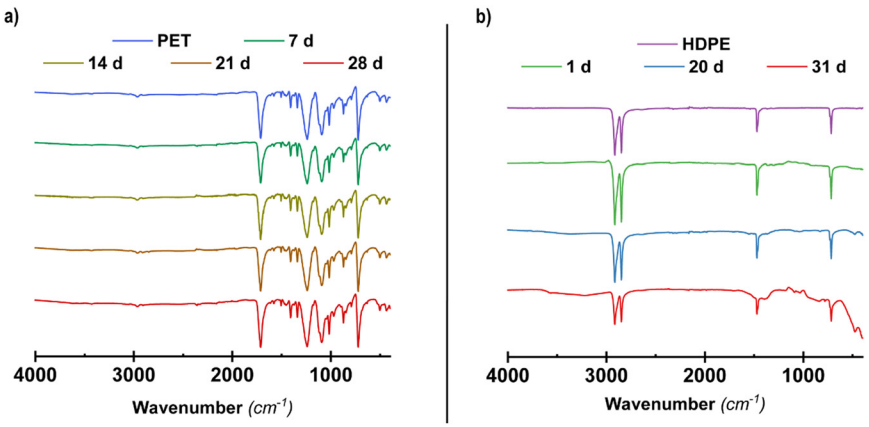

Fig. 5 FT-IR measurements of electrochemically treated PET (a) and PE (b) at 10 mA cm^{-2}.

reduction in intensity of the characteristic peaks of PE indicate structural changes in the molecular skeleton. This change in the surface of PE microparticles, obtained under mild oxidising conditions (10 mA cm^{-2}), was also observed during the aging of MPs in the environment, where little or no mass loss as well as an increase has been already measured[40,41] and correlated to the incorporation of oxygen on the surface of MPs. The observed increase in weight of the MPs is then due to this chemical modification of the surface of PE.

To investigate the formation of soluble intermediates, samples were collected at prefixed intervals of time during electrolysis and analysed for TOC. Fig. 6 shows the trend with time of TOC during electrolysis with PE and PET.

TOC trends of PE and PET at 10 and 20 mA cm^{-2} show similar results with both the applied current densities, suggesting that the formation of intermediates is scarcely influenced by the current density, as the possible reaction of the intermediates with ACS and their direct oxidation at the anode surface should be considered. The reactivity of organics is considerably higher than that of MPs, and the organics formed may be rapidly mineralised, so strong oxidising conditions do not necessarily result in high concentrations of organic intermediates. Moreover, lower values of TOC were observed for PET compared to PE, which is consistent with the formation of more oxidisable intermediates from PET.

Possible changes in size and shape induced by the electrochemical treatment were also investigated with SEM analyses. Fig. 7 shows the comparison between the SEM images of PE and PET before and after 800 h of electrolysis at 10 mA cm^{-2}: PE shows slight variations in size, barely

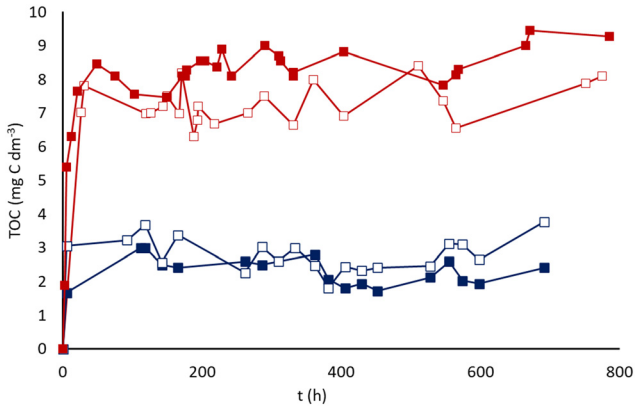

Fig. 6 Trend with time of the total organic carbon (TOC) measured in the solution during the electrochemical treatment of suspensions containing PE (red) and PET (blue) under batch conditions at 10 mA cm^{-2} (empty symbols) and 20 mA cm^{-2} (full symbols).

appreciable in the SEM images, while higher variation in size could be observed with PET. This result agrees with the trends of weight loss already discussed: the weight reduction of PET was 67% at the end of the treatment; considering spherical particles and a PET density of 1.38 g cm^{-3}, it roughly corresponds to an average reduction of 25% of the diameter of the particles, which is not negligible and can be observed in the SEM images.

To quantify the rate of degradation of PE and PET during the electrochemical treatment, the specific surface degradation rate (SSDR) k_d has been used. The parameter was defined by Chamas and co-workers to quantify the degradation of MPs in different natural environments, assuming a shrinking core model:

$$-\frac{dm}{dt} = k_d \rho SA \tag{7}$$

where m is the mass of the particles, ρ is the density of the polymer, SA is the surface area of the particle[36] and k_d is the rate of particle size reduction. With spherical beads of MPs of radius r and constant density, eqn (7) can be integrated and rearranged to give the mass as a function of the degradation time t as follows:[36]

$$m_t = \left[(m_0)^{\frac{1}{3}} - \frac{6^{\frac{2}{3}}}{3} k_d (\pi\rho)^{\frac{1}{3}} t \right]^3 \tag{8}$$

This equation can be used to evaluate k_d: in marine environments k_d values of 9.5 μm y^{-1} and 110 μm y^{-1} for PE and PET, respectively, have been reported.[36]

k_d was calculated for PE and PET during the electrochemical treatment, using values of density of 0.95 and 1.38 g cm^{-3} for PE and PET, respectively. Fig. 8 shows the comparison between the experimental data and the

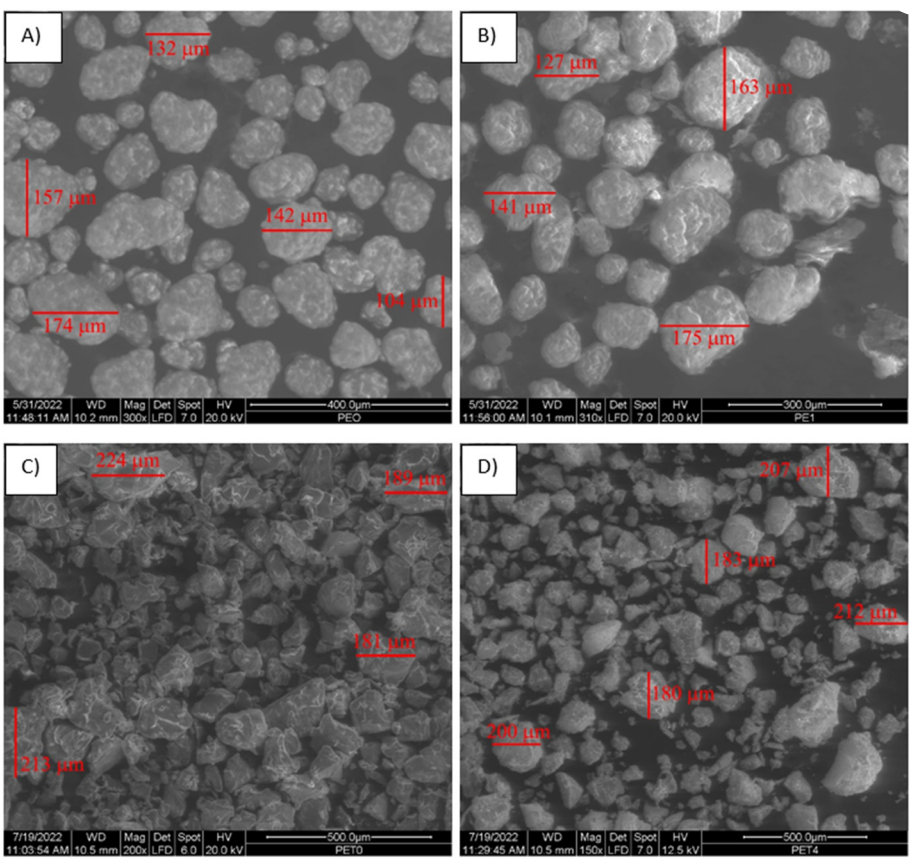

Fig. 7 SEM images of PE (A and B) and PET (C and D) before (A and C) and after (B and D) 800 h of electrolysis at 10 mA cm^{-2}.

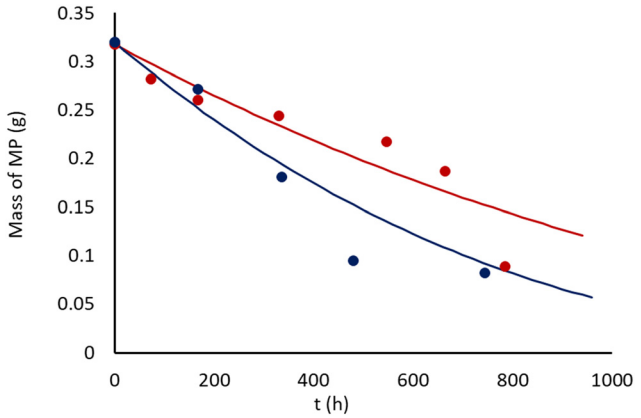

Fig. 8 Comparison between experimental decrease of mass measured during the electrolysis of suspensions of PE (red) and PET (blue) MPs obtained at 20 mA cm^{-2} and predicted decrease of mass with eqn (8).

values calculated with eqn (8): the good agreement that can be observed was obtained with k_d equal to 1.10 10^4 μm y^{-1} for PE and 1.32 10^4 μm y^{-1} for PET.

Conclusions

The results are promising, and the weight loss obtained confirms the effectiveness of electrochemical treatment in the removal of MPs from highly contaminated wastewater, with a content of MPs comparable to those in laundries or derived from ships' grey water. No alteration of the surface for PET or slight modification for PE was observed during the process, so the possible interactions of treated MPs with other contaminants are limited, avoiding their transport in the environment. Moreover, the TOC measured in the solution quickly reaches a constant value rather than a progressive accumulation, indicating that the intermediates of polymer degradation are mineralised by the process, limiting the risk of formation of hazardous compounds. The overall results of the process show the feasibility of an electrochemical process to remove MPs, and values of k_d were obtained that are two (PET) or three (PE) orders of magnitude higher than the corresponding degradation rates in the environment.[36] However, the removal rates are still low for direct implementation at plant scale, so that further investigations are required to optimise the design of the reactor and operative conditions.

Author contributions

Laura Mais: investigation, writing – original draft preparation. Nicola Melis: investigation, visualization, writing – original draft preparation. Annalisa Vacca: conceptualisation, writing – review & editing. Michele Mascia: conceptualisation, writing – review & editing.

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