



Promoting removal of polystyrene microplastics from wastewater by electrochemical treatment

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ABSTRACT

Microplastics (MPs) are emerging contaminants with potential ecological and human health impacts, necessitating effective remediation technologies. Recently, electrochemical oxidation (EO) has garnered attention as a suitable method for treating water contaminated with MPs. However, research on EO's effectiveness remains limited. This study investigates the EO treatment of 1.0 μm polystyrene (PS) MPs in a lab-scale reactor using boron-doped diamond (BDD) electrodes. Various operational parameters, such as electrolyte composition and concentration, initial PS concentration, and applied current density, were examined for their impact on PS degradation efficiency. Optimal degradation was achieved using Na_2SO_4 (0.02 M) as a supporting electrolyte, an initial PS concentration of 60 mg L^{-1} , and an applied current density of 60 A/m^2 for 5 h. The degradation mechanism likely involved indirect EO through the formation of highly oxidizing radicals rather than direct EO between the anode and PS molecules. High current densities induced morphological changes in the PS micro-particles. Fourier transform infrared spectroscopy confirmed new functional groups on the PS surface, indicating oxidation. These findings suggest that EO using BDD electrodes is a promising approach for treating microplastic-polluted water. However, further studies are needed to optimize the process, particularly concerning power requirements, electrode costs, and reactor configuration.

1. Introduction

In the last decades, rapid population growth, industrialization, and continuous changes in consumption patterns have led to dramatic contamination and depletion of water resources [1,2]. The widespread presence of emerging and persistent pollutants, including pharmaceutical compounds, pesticides, *per*- and polyfluoroalkyl substances (PFASs), and plastic materials, has drastically increased in water bodies, causing damage to the ecological environment and human health [3,4]. Plastics are considered the revolutionary material of this century, with their production, consumption, and disposal increasing annually [5]. Due to their inert, corrosion-resistant, practical, and economical characteristics, they are widely used in various fields, including packaging, printing, chemical engineering, sports equipment, and electrical and electronic devices [6]. Global plastic production surged from 1.5 million metric tons in the 1950s to approximately 367 million in 2020. Improper plastic waste management has led to large amounts of plastic residues

being detected in various environmental compartments. [7–9]. Plastics exist in different shapes and sizes ranging from microfibers, films, foams, and fragments [10]. According to their sizes, plastic pollutants can be classified into nanoplastics ($< 1 \mu\text{m}$), MPs ($\geq 1 \mu\text{m}$ to $< 5 \text{mm}$), mesoplastics ($\geq 5 \text{mm}$ to 5cm), macroplastics (> 5 to 50cm) and megaplastics ($> 50 \text{cm}$) [11,12]. When plastics are released into the environment, they can undergo degradation through various environmental processes, such as photo-oxidation, biodegradation, and physical abrasion caused by stones, sand, or tides. These processes can lead to the formation of plastic fragments with dimensions lower than 5 mm, defined as secondary MPs [13]. However, MPs used as raw material in various products, such as soaps, scrubs, shampoos, toothpaste, and clothes, can enter directly into the environment as primary MPs [14]. MPs with different chemical compositions have been detected in the environment, including polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polystyrene (PS), polyurethane (PU) and polyamides (PA, nylon), among others [15,16].

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MPs were ubiquitously detected in aquatic and terrestrial ecosystems, and due to their small sizes, they can be easily ingested by aquatic organisms, affecting the growth rate, fertility and reproduction [17]. High hydrophobicity and high surface area make MPs carriers of many organic pollutants and heavy metals [18]. The interaction of MPs with plankton and algae affects the marine carbon cycle and carbon fixation, leading to climate change and global warming. Moreover, MPs bioaccumulate in the food chain and eventually reach humans. MPs were detected in blood, urine, human testis, semen, and placenta [19–22]. A recent study conducted by Marfella et al. [22] highlighted the harmful presence of microplastics (MPs), specifically PE and PVC, in human carotid plaques, which could have triggered non-fatal strokes, infarcts, and even death. Among others, wastewater and wastewater treatment plants (WWTPs) have been identified as the most significant sources of MPs release into the environment [23–26]. WWTP influents include a variety of impacted water with different chemical compositions [27]. Although the concentrations of MPs detected in the WWTPs effluents were considerably less than that of influents, the daily large volumes discharged in water bodies still provoke high levels of contamination. Enfrin et al. [28] showed that the WWTPs shred 80 % of MPs into nanoplastics, increasing the number of plastic particles by approximately 10 times. To frame the problem, a study performed by Conley and co-workers [29] reported that about 500–1000 million MP particles were daily discharged from only three WWTPs in the USA. Accordingly, the traditional treatments are ineffective in adequately removing MPs from impacted water, and the development of innovative and efficient technologies is highly required now.

Membrane filtration, adsorption, coagulation-flocculation-induced chemical sedimentation, bioremediation, and other methods have been tested for MP removal from water [30–33]. However, these processes have some disadvantages that make them inconvenient and impractical for large-scale applications. For instance, membrane filtration may become clogged leading to a reduction in filtration performance [34]. Adsorption processes may be impacted by low adsorbent capacity and the lengthy preparation of adsorbent materials [35,36]. Coagulation-flocculation-induced chemical sedimentation requires a high coagulant dose and can result in excessive levels of aluminum and iron in the effluent [34]. Meanwhile, bioremediation often exhibits low efficiencies [37]. Advanced oxidation processes (AOPs) are recently gaining much attention as effective technologies for removing refractory contaminants from impacted water [38,39]. AOPs are based on the efficient in-situ generation of reactive oxygen species (ROS) with high redox potential, including hydroxyl radicals ($\bullet\text{OH}$), superoxide radical ($\text{O}_2^{\bullet-}$), singlet oxygen ($^1\text{O}_2$), sulfate radical ($\text{SO}_4^{\bullet-}$), among others, which are capable of degrading pollutant molecules in solution. The main goal of applying AOPs is to completely mineralize the contaminant into CO_2 and H_2O .

Electrochemical oxidation (EO) is one of the most promising AOP widely applied for the degradation of persistent pollutants, such as pesticides, drugs, and PFASs [40–42]. EO consists of direct and indirect oxidation, both of which generally take place at the same time. Direct EO, also known as anodic oxidation, involves a direct electron transfer (DET) between the anode surface and the organic molecules (i.e. PS) via hydroxyl radicals produced during water electrolysis [43]. In contrast, indirect EO utilizes the formation of strong reactive species on the anode surface, including $\bullet\text{OH}$, sulfate radicals, $\text{CO}_3^{\bullet-}$, $\text{O}_2^{\bullet-}$, and reactive chlorine species (CRS), to further degrade contaminants in the bulk phase [44]. Among other parameters, the anode materials play a crucial role in the EO process thanks to their capacity to generate large amounts of $\bullet\text{OH}$ and other secondary oxidants [45,46]. Anodes are generally categorized into *active* and *non-active* types based on their capacity to bond with $\bullet\text{OH}$ on their surface. Active anodes, such as Ti/Pt, graphite and common dimensional stable anodes (DSA), bond strongly with $\bullet\text{OH}$, leading to partial degradation of contaminants, while non-active anodes, including BDD, PbO_2 , $\text{Ti}_n\text{O}_{2n-1}$, and SnO_2 , bond weakly with $\bullet\text{OH}$, enabling complete mineralization of the substrate [47]. In recent years, the use of

BDD anodes in EO processes has become increasingly widespread, thanks to their high capacity to generate $\bullet\text{OH}$ on the surface, in addition to their stability, durability and resistance in extremely acidic and basic environments [48]. Additionally, BDD anodes also favour the formation of other reactive species in solution, including CRS, ozone, persulfate, and hydrogen peroxide [48]. Therefore, using BDD anodes under appropriate experimental conditions (pH, type of electrolyte, electrolyte concentration, etc.), both direct and indirect EO are theoretically possible during the process.

Although several previous studies have employed AOPs for treating MPs-impacted wastewater, including UV photolysis, UV-induced photocatalysis, activated persulfate-based, and Fenton-based processes, among others [49,50] only a few efforts have been devoted to examining the potential of EO [51]. Kiendrebego et al. [52] explored the degradation of polystyrene microbeads with 26 μm size from water using anodic oxidation. They achieved 89 ± 8 % of PS degradation using a BDD anode electrode, Na_2SO_4 (0.03 M) as a supporting electrolyte and a current intensity of 9 A after 6 h of treatment. Moreover, they demonstrated that no smaller particles were formed during the process, confirming a direct mineralization of the MPs in gaseous products, such as CO_2 . Lu and co-workers [53] proposed a sodium dodecyl sulfate assisted EO process for PS (18.5 μm) degradation from water, achieving >40 % of MP degradation with a current density of 30 mA cm^{-2} and a very high MP concentration (2 g L^{-1}), but some transformation products were generated along the process. Ning et al. [54] investigated the degradation of PVC MPs via EO with a fabricated $\text{CeO}_2\text{-PbO}_2$ anode. The findings indicated that the EO process was a promising method for the degradation of MPs, but the weight loss rate of PVC at the end of the treatment (6 h) was of 38.67 ± 1.91 %. Moreover, the experimental results revealed that very high temperature (100 °C), high pH value of 11, and high Na_2SO_4 concentration (90 mM) were necessary operative conditions, pointing out that further investigation and process optimization are still required.

Given the very limited number of studies on MP removal by EO reported in the literature (Table S1), the current work aims to investigate the electro-removal of PS, chosen as target MPs, providing more knowledge to the scientific community. Since the previous investigations focused on MP sizes ranging between 18.5 and 200 μm , it was decided to examine the electrochemical degradation of a PS monodispersed aqueous phase containing 3.24×10^{10} particles mL^{-1} , with a diameter of 1.0 μm . As stated by Nugnes et al. [55], PS particles of this size, which lie on the borderline between nano- and microplastics, raise significant environmental concerns. Zooplankton cannot distinguish them from phytoplankton during normal feeding and swimming activities. The toxicity of PS has been also reported by previous authors [56–58].

Herein, an experimental approach was employed to identify the optimal operating conditions of the process (including electrolyte composition, initial concentration of polystyrene, electrolyte concentration, and applied current density) for degrading PS in water. To evaluate process performance, as well as possible changes in shape and MPs surface functional groups, specific samples collected before, during, and after the EO treatment were carefully analyzed using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and total organic carbon (TOC) analyses. Furthermore, assessments of the energy required for PS degradation and a cost analysis were conducted to provide comprehensive insights into the feasibility and efficiency of the process.

2. Materials and methods

2.1. Chemicals

PS monodispersed MP with an analytical standard size of 1.0 μm , a particle specific gravity of 1.05 g cm^{-3} , and a concentration of 21 g L^{-1} , 3.24×10^{10} particles mL^{-1} , was supplied by Sigma Aldrich (Milano,

Italy). According to the supplier's information, this analytical standard is an aqueous suspension of particles (0 % cross-linked) with a 2 % solid concentration [59]. Dilute polystyrene dispersions were prepared in Milli-Q ultrapure water from the standard and utilized for the EO experiments. Sodium chloride (NaCl, 99.5 %), sodium sulfate (Na₂SO₄, 99.2 %), and sodium nitrate (NaNO₃, 99.0 %) were used as received from various chemical suppliers and added to the dispersions. All experimental samples were prepared by diluting the PS stock with Milli-Q water (18.2 MΩ cm⁻¹ resistivity, 25 °C) supplied from an Elix ® Essential 10 UV water purification system (Merck, Darmstadt, Germany).

2.2. Experimental procedure

All electrochemical oxidation experiments were conducted in a batch reactor filled with 250 mL of polystyrene sample, operating at 25 °C for 300 min. The electrochemical cell comprised two boron-doped diamond (BDD) electrode plates (NeoCoat, Switzerland), each measuring 100 × 50 mm, with an active area of 50 cm² and an electrode gap of 1 cm. A bench-top direct current power supply BPS-305 (Lavolta, London, UK) was connected to the BDD electrodes, allowing it to operate under amperostatic conditions. A schematic of the electrochemical cell was provided in previous studies [60]. Tests were conducted by varying different operating parameters, such as electrolyte composition (NaCl, Na₂SO₄, or NaNO₃), initial PS concentration expressed as mg of TOC per L of water (ranging from 13.0 to 60.0 mg L⁻¹), electrolyte concentration (ranging from 0.02 to 0.06 M) and applied current density ($J = 20$ to 100 A m⁻²). Sampling was conducted at 60, 120, 180, 240, and 300-min intervals. The tests were triplicated to ensure the reproducibility of the results.

2.3. Analytical procedure

The EO of PS was evaluated by examining the evolution of TOC over the treatment. Since the experiments were performed using a synthetic liquid phase, PS constituted the sole source of organic carbon in the system [61]. In addition, FTIR and SEM analyses were carried out for selected experimental runs to investigate possible changes in the PS particle size and shape that occurred after the treatment.

2.3.1. PS degradation efficiency % analysis

At given time intervals, aliquots of water samples with PS were withdrawn from the electrochemical cell and analyzed by TOC [61]. In particular, a TOC-L CSH/CSN analyzer (Shimadzu, Tokyo, Japan) equipped with an infrared detector for CO₂ detection was used. The analyses were carried out according to the following instrumental conditions: furnace temperature = 720 °C; carrier gas = air (analytical grade); carrier gas flow = 150.0 mL min⁻¹; supply gas pressure = 285.0 kPa. Quantitative TOC analyses were assessed using an area-concentration calibration curve, which showed linearity in 0.5–100 mg L⁻¹ range. A standard solution of 10 mg L⁻¹ of diclofenac sodium (Alfa Aesar, Massachusetts, USA) was used to check the linearity of the instrument. The detection (LOD) and quantification (LOQ) limits were 0.372 mg L⁻¹ and 0.908 mg L⁻¹, respectively. On the basis that PS was the unique source of organic carbon present in the liquid phase, the evaluation of PS concentration and degradation was examined in terms of TOC:

$$PS \text{ degradation efficiency (\%)} = \frac{TOC(t=0) - TOC(t)}{TOC(t=0)} \times 100 \quad (1)$$

where TOC is the mg of TOC per L of water.

2.3.2. Recovery of PS microplastics

For each EO test, 20 mL of the water phase containing PS MPs were filtered through a 1 μm pore-size silicon filter (MakroPor, Thermo Fisher

Scientific). After that, filters were washed with ethanol and dried at room temperature for 24 h. For comparison, the water phase containing PS MPs before the EO test was processed with the same approach. The filters were then analyzed by using SEM and FTIR analyses.

2.3.2.1. SEM analysis. Scanning electron microscopy (SEM) was performed on silicon filters surface with PS microparticles using a FEI Quanta 200 FEG SEM (Eindhoven, The Netherlands) to evaluate the change in surface morphology of PS MPs due to EO processes. Silicon filters with PS MPs were mounted on aluminum stubs and coated with a thin layer (approximately 10 nm thick) of an Au–Pd alloy with a sputter coater (Emitech K575, Quorum Technologies LTD, UK). Observations were performed in high vacuum mode.

2.3.2.2. FTIR analysis. PS MPs recovered on silicon filters containing PS MPs were analyzed using a Fourier transform infrared micro spectrometer Nicolet iMX10 (Thermo Fisher Scientific). FTIR spectra were acquired using 64 scans and 4 cm⁻¹ resolution in the range 4000–650 cm⁻¹ using an aperture size of 20 × 20 μm².

2.3.3. Energy consumption and cost assessments

Specific energy consumption (SEC), defined as the energy consumed in kWh for the removal of 1 g of TOC, was estimated by Eq. (2) [62]:

$$SEC \text{ (kWh gTOC}_{removed}^{-1})} = \frac{P \cdot t \cdot 1000}{(TOC_0 - TOC_t) \cdot V \cdot 1000} \quad (2)$$

where P is the power applied during the process (W), t is the treatment time (h), TOC_0 and TOC_t are the TOC at time 0 and time t (mg L⁻¹), respectively, and V is the treated volume (L⁻¹). The electric treatment cost (ETC) was expressed in terms of € per g of TOC removed (Eq. (3)):

$$ETC \text{ (€ gTOC}_{removed}^{-1})} = SEC \cdot \text{Energy unit cost} \quad (3)$$

According to electricity prices for non-household consumers released by Eurostat, the Italian Energy unit cost in 2023 is 0.2031 (€ kWh⁻¹) [63].

2.3.4. Quality assurance and quality control

Stringent quality assurance and quality control protocols were adhered to throughout all laboratory procedures for treatment and analysis. All solvents were of analytical grade (>95 %). Glassware and metal items underwent meticulous cleaning with dichloromethane (DCM) before utilization to eliminate any organic impurities. Cotton laboratory coats were worn throughout all stages of analysis.

The electrochemical oxidation treatment took place within a fume cabinet to minimize the risk of contamination by airborne plastics. To guarantee the absence of contamination in the TOC system, 10 instrumental blanks (containing MilliQ water) were analyzed prior to chemical analyses. Furthermore, several procedural blanks, each comprising 250 mL of MilliQ water, underwent EO treatment using identical operational conditions as the PS samples. This method aimed to confirm the absence of cross-contamination, interference release by electrodes, background response, or potential system contamination. Subsequently, before any further data processing, blank subtraction was performed on all data.

3. Results and discussion

3.1. Effect of the electrolyte composition

To evaluate the effect of the electrolyte composition, a series of EO experiments were carried out using NaCl, Na₂SO₄, and NaNO₃, operating with a salt concentration of 0.06 M, an initial PS concentration of 60 mg L⁻¹, and a J of 100 A m⁻². The results are reported in Fig. 1.

As observed, a higher PS degradation efficiency of 59.5 % was achieved in the presence of Na₂SO₄ compared to those obtained with NaCl

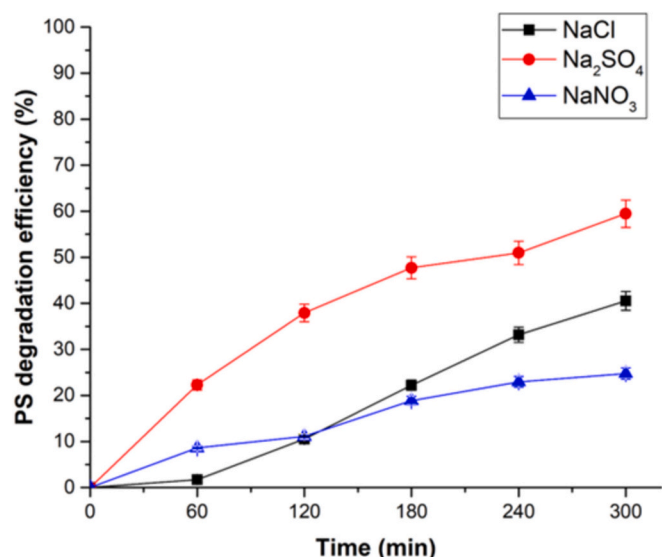
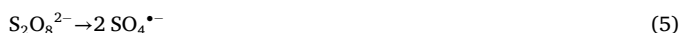


Fig. 1. Electrolyte composition effect on the PS degradation efficiency (%); salt concentration = 0.06 M; initial PS concentration = 60.0 mg L⁻¹; J = 100 A m⁻²; applied voltage = 24.5–25.3 V; T = 25 °C; initial pH = 5.8–6.2.

(40.5 %) and NaNO₃ (24.8 %) after 300 min of EO treatment. However, even after just 60 min, the benefits of adding Na₂SO₄ to the system were already apparent. These results can be attributed to the different nature of the electrolytes, which can influence the mechanism of contaminant degradation. As reported previously, the EO of PS can be attributed to two different pathways, namely direct and indirect oxidation [52,64]. In solution, Na₂SO₄ can dissociate into hydrogen sulphate (HSO₄⁻) and then form peroxy disulfate ions (S₂O₈²⁻) (Eq. (4)) (Khan et al., 2017). O—O bond cleavages of S₂O₈²⁻ generate sulphate radicals (SO₄^{•-}) (Eq. (5)) that are powerful reactive oxidizing species (ROS) capable of degrading persistent organic pollutants through indirect EO [67,68]. Moreover, SO₄^{•-} can react with H₂O generating •OH (Eq. (6)):



Therefore, when Na₂SO₄ is used as a supporting electrolyte, both direct EO, through DET reactions between the BDD anode surface and the PS molecules, and indirect EO by SO₄^{•-} and •OH in the bulk phase, occurred simultaneously, resulting in a higher contaminant degradation.

In the case of NaCl, chloride ions (Cl⁻) can oxidize to form chlorine gas (Cl₂) (Eq. (7)) at BDD anode. Then, Cl₂ can react with H₂O to generate hypochlorous acid (HClO) and hypochlorite (ClO⁻) according to the following reactions [69,70] (Eqs. (8) and (9)):



Cl₂, HClO, and ClO⁻, are well-known strong CRS which can indirectly degrade PS molecules [52]. The distribution of the CRS forms is affected by the solution pH. At the experimental initial pH of about 6.0 the predominant CRS is HClO, which is present in its undissociated form [71]. Very recently, Mais and co-workers [51] successfully treated MPs impacted wastewater by a chlorine assisted EO. Although the presence of NaCl as a supporting electrolyte can trigger both direct and indirect EO, similarly to Na₂SO₄, the lower PS degradation efficiency (%) can be attributed to the lower redox potential of chloride radicals (E⁰ =

2.0–2.47 V vs SHE) compared to SO₄^{•-} (E⁰ = 2.5–3.1 V vs SHE) [50,72]. Finally, when NaNO₃ was used, no oxidizing species were generated on the BDD anode, implying that the PS degradation process was based only on a direct EO mechanism.

It is worth mentioning that some side reactions, including the oxygen evolution reaction (OER), the generation of sulphate by-products, and the formation of undesired chlorine oxyanions, such as chlorate and perchlorate, can occur simultaneously, affecting the overall degradation efficiency of the system [73]. Regarding the higher PS degradation efficiency (%) observed after 60 min in the presence of NaNO₃, compared to NaCl, can be attributed to the formation of PS oxidation intermediates during the treatment, which may have influenced the degradation behavior, as reflected in the trends shown in Fig. 1. In fact, as reported by Lu et al. [53], the electrochemical generation of highly reactive radical species through indirect EO can lead to cleavage of benzene rings of the PS molecules, resulting in the generation of by-products, such as those with diphenyl rings, as well as esters, aldehydes, and alcohols, among others [74].

Overall, the results are in agreement with a previous study carried out by Kiendrebeogo et al. [52], in which higher polystyrene degradation performances were obtained in the presence of Na₂SO₄. Kang et al. [68] also reported superior degradation capabilities of sulfate radicals in removing MPs mainly composed of polyethylene in water. As stated by Du et al. [64] these generated active species can effectively decompose MPs, leading to chain breakage, chemical structure changes, or even full contaminant mineralization [75].

3.2. Effect of the initial PS concentration

Fig. 2 depicts the impact of different initial contaminant concentration on the degradation efficiency (%) of the system. The experiments were conducted by varying the PS concentration in the range of 13.0–60.0 mg L⁻¹, using Na₂SO₄ (0.06 M) as supporting electrolyte, at 100 A m⁻².

The higher the initial PS concentration, the higher the degradation efficiency (%). About 27.0, 37.0, and 59.0 % of PS degradation were achieved after 300 min of treatment, operating at 13.0, 26.7, and 60.0 mg L⁻¹ initial MP concentration, respectively. By increasing the initial contaminant concentration, the PS molecules have more opportunities to approach the anode surface and to react with SO₄^{•-} in the bulk phase, resulting in higher overall degradation performances [47,76].

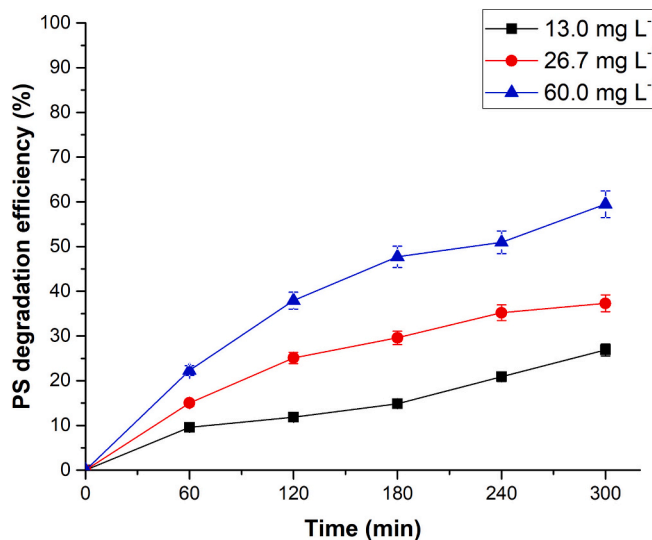


Fig. 2. Initial PS concentration effect on the system degradation efficiency (%); Na₂SO₄ concentration = 0.06 M; J = 100 A m⁻²; applied voltage = 21.6–25.3 V; T = 25 °C; initial PH = 5.9–6.1.

3.3. Effect of Na_2SO_4 concentration

The electrolyte concentration is a key parameter in the EO treatment since it affects the current transfer efficiency as well as the operating costs [77]. The impact of different initial Na_2SO_4 concentrations (0.02 to 0.06 M) was examined, and the outcomes were reported in Fig. 3.

Interestingly, no significant differences in terms of PS degradation efficiency (%) were obtained for all three salt concentrations investigated (0.02–0.06 M) at the end of the treatment. These findings are in contrast with previous EO studies in which higher degradation efficiencies were obtained by increasing the electrolyte concentration [78,79]. However, operating at high initial Na_2SO_4 concentrations, self-combination reactions among the electrogenerated $\text{SO}_4^{\bullet-}$ occurred in solution:



In addition, $\bullet\text{OH}$ can also react with $\text{SO}_4^{\bullet-}$ to generate HSO_5 , leading to a decrement in the process degradation efficiency [66,80,81]:



As stated by Saha et al. [82] high amounts of $\text{SO}_4^{\bullet-}$ can also chemically adsorb on the BDD anode surface, hampering the $\text{SO}_4^{\bullet-}$ formation. The reactions just described, along with the formation of PS oxidation by-products generated in the presence of Na_2SO_4 [53], and other undesired side reactions [74], have led to fluctuations in the concentration of sulphate species over time, potentially influencing the trends reported in Fig. 3 [66,81]. Based on the findings displayed in Fig. 3, the experiment carried out in the presence of Na_2SO_4 0.02 M allowed to achieve a significant PS degradation of 62.2 %, using the lower amount of supporting salt at the same time, resulting in chemicals cost-saving.

3.4. Effect of applied current density

Fig. 4 depicts the impact of the applied current density on the degradation performance of the system.

By increasing J from 20 to 60 A m^{-2} the PS degradation efficiency drastically increased from 28.4 to 65.5 %, after 300 min of treatment. A rise of applied current can lead to higher generation of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, resulting in better degradation efficiencies [83]. Kienrebeogo et al. [52] stated that a higher J allowed the oxidation of more H_2O molecules into $\bullet\text{OH}$ on the BDD anode surface, improving the PS oxidation.

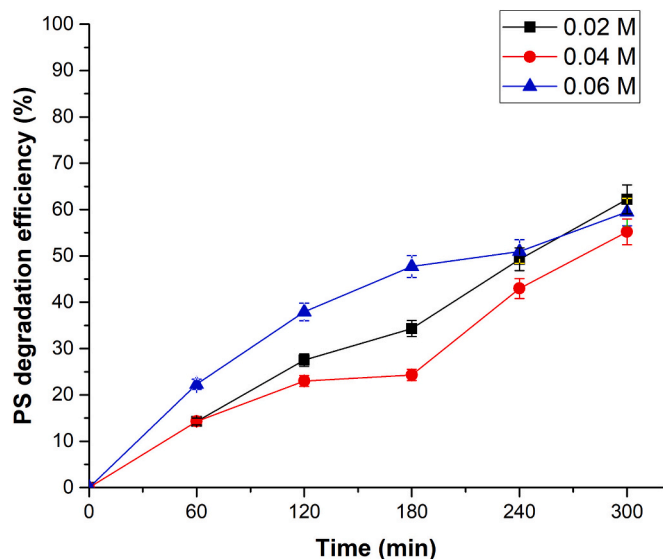


Fig. 3. Na_2SO_4 concentration effect on PS degradation efficiency (%); initial PS concentration = 60 mg L^{-1} ; J = 100 A m^{-2} ; applied voltage = 25.3–28.7 V; T = 25 °C; initial pH = 6.0–6.2.

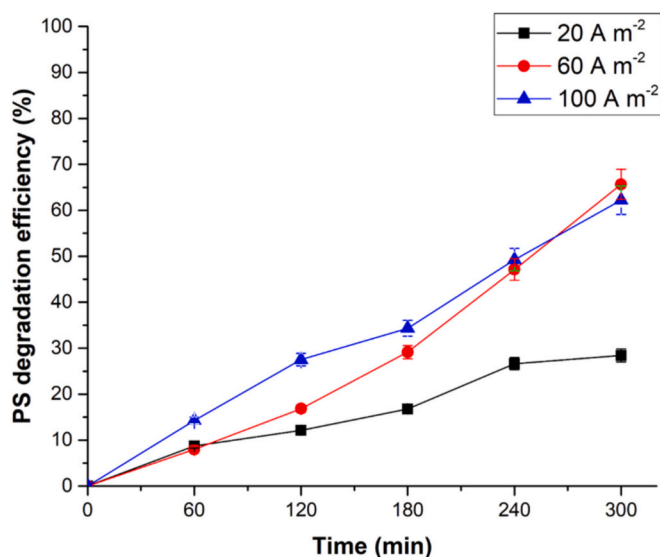


Fig. 4. Applied current density effect on PS degradation efficiency (%); Na_2SO_4 concentration 0.02 M; initial PS concentration = 60 mg L^{-1} ; applied voltage = 8.2–28.7 V; T = 25 °C; initial pH = 5.9–6.0.

But, as shown in Fig. 4, a further increase of J from 60 to 100 A m^{-2} did not favour the PS degradation, even provoking a slight drop in the PS removal efficiency to 62.2 %. The trend shown in Fig. 4 may have been influenced by the formation of PS oxidation intermediates and fluctuations in sulphate radical concentrations over the treatment period [81]. Furthermore, undesirable oxygen evolution reactions occurred in the solution, affecting the overall trends, especially at higher current densities (i.e., 60 and 100 A m^{-2}) [48,74].

3.5. SEM analysis

SEM analysis was performed to evaluate possible changes in the PS morphology due to the EO processes conducted under different operative conditions. Fig. 5 shows SEM micrographs, at two magnifications, of PS microparticles recovered on silico filters before and at the end of the EO test performed in the presence of different Na_2SO_4 concentrations (0.02 and 0.04 M) and applied current densities (20, 60 and 100 A m^{-2}).

The pristine PS MPs, see Fig. 5A and B, exhibited a well-defined spherical morphology and displayed a slightly rough surface, presumably stemming from the preparatory process. Furthermore, connections between the various microparticles were present (Fig. 5A), likely attributed to the dispersing agent utilized during the preparation phase of the neat PS dispersion.

The morphological analysis of the sample treated for 300 min in the presence of 0.04 M Na_2SO_4 and a current density (J) of 20 A m^{-2} (Fig. 5C and D) revealed the presence of a few deformed particles. In contrast, the sample treated with 0.02 M Na_2SO_4 and a J of 60 A m^{-2} (Fig. 5E and F) showed the presence of deformed PS particles along with spherical particles, suggesting an effect of the electrolytic process. Additionally, alongside the particles, structures resembling salts were clearly visible. A greater deformation was observed for the PS sample treated with Na_2SO_4 0.04 M and higher J of 100 A m^{-2} (Fig. 5G and H).

Similar findings were encountered for a different PS sample treated with the lower current density of 20 A m^{-2} and Na_2SO_4 0.02 M. Again, no deformed particles were observed at the end of the treatment (Fig. S1 A). An elemental analysis conducted on this sample (Fig. S1 B) showed the presence of sulfur and sodium, suggesting unreacted Na_2SO_4 , which does not influence the morphology of the PS microparticles but may explain the reduced PS degradation efficiency (28.4 %) achieved during this run. Finally, SEM analysis carried out on the sample treated with NaCl 0.06 M and a high J of 100 A m^{-2} revealed again visible deformed

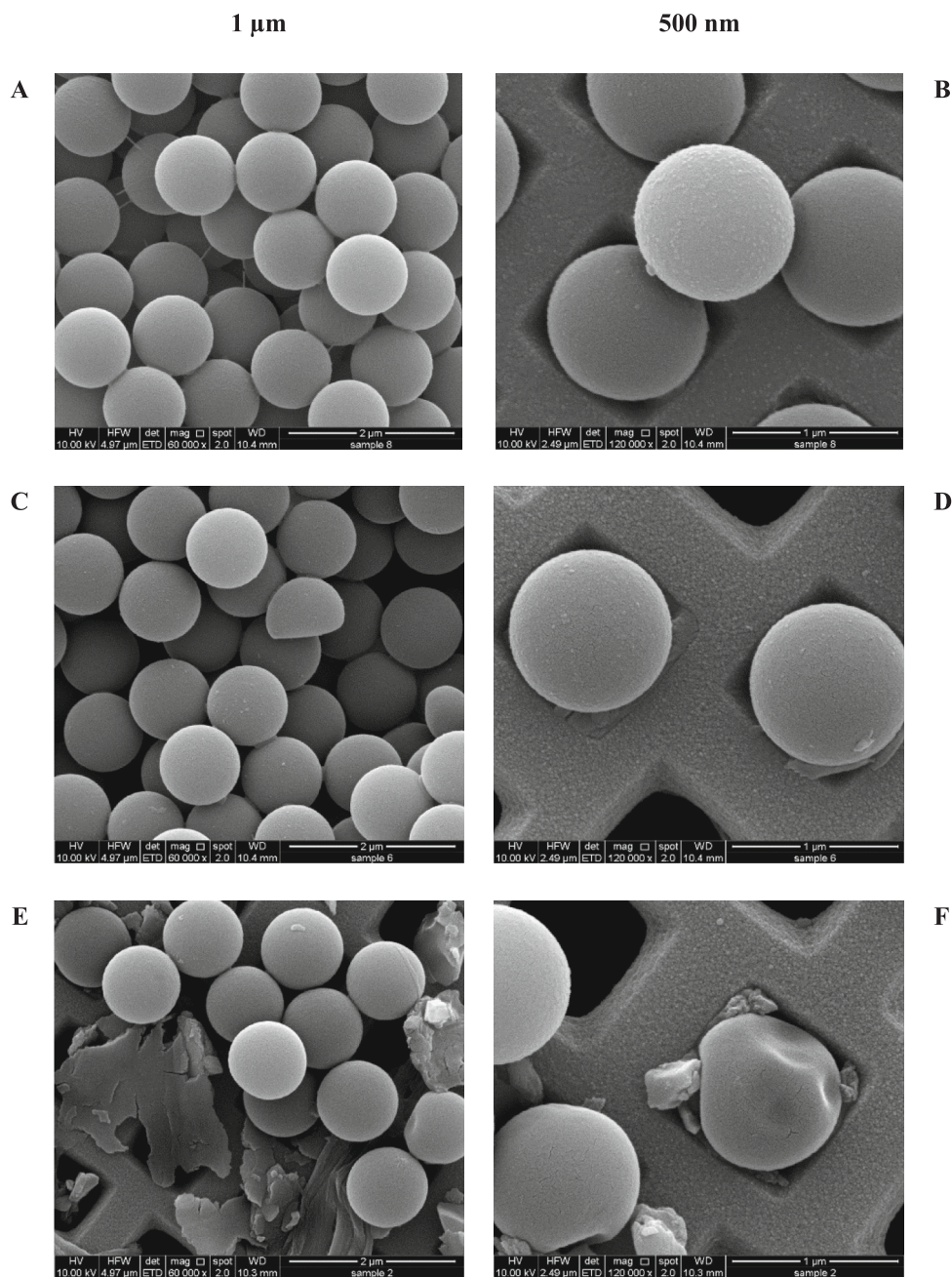


Fig. 5. SEM micrographs of PS MPs before EO (A and B); PS MPs after 300 min of EO with Na_2SO_4 0.04 M and a J of 20 A m^{-2} (C and D); PS MPs after 300 min of EO with Na_2SO_4 0.02 M and a J of 60 A m^{-2} (E and F); PS MPs after 300 min of EO with Na_2SO_4 0.04 M and a J of 100 A m^{-2} (E and F); Baseline PS concentration = 25 mg L^{-1} .

PS MPs (Fig. S2). These outcomes may imply that the degradation rate of the PS MPs, responsible for the PS morphological changes, was more affected by the current density applied to the system rather than to the type of salt used during the EO process.

The results were in contrast with those provided by Kienrebeogo et al. [52], who stated that the applied EO process had no clear effects on the spherical shape of the treated MPs. Conversely, Lu and co-workers [53] confirmed that the changes in surface morphology of PS MPs increased with the increase of current density in EO process. The differing opinions presented in the literature have bolstered the significance of the current investigation, which aimed to enhance the understanding of the EO process on MPs.

3.6. Spectroscopic analysis

In order to examine the changes in chemical properties of PS MPs after EO treatments, FTIR analyses of recovered PS MPs on silicon filters were performed. Samples of MPs before EO treatments (Fig. 6A) present a FTIR spectrum typical of PS, in which characteristics absorption bands were detectable such as those at 3082 , 3060 , and 3026 cm^{-1} corresponding to C–H stretching vibrations of aromatic ring, 2923 and 2848 cm^{-1} due to the stretching of aliphatic chain, and $-\text{CH}_2$ asymmetric stretching vibrations, 1601 , 1583 , and 1493 cm^{-1} corresponding to benzene ring stretching vibrations, 1452 cm^{-1} due to $-\text{CH}_2$ deformation vibrations, 1069 and 1028 cm^{-1} corresponding to deformation and skeletal vibrations of C–H, 697 and 757 cm^{-1} corresponding to C–H out-of-phase bending vibration of benzene ring [84–86].

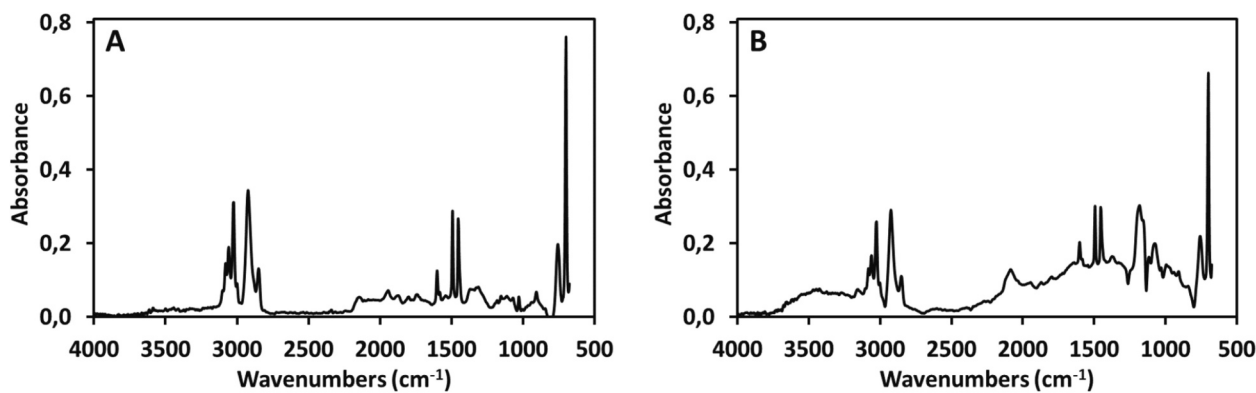


Fig. 6. FTIR spectra of (A) pristine PS before EO and (B) PS after 5 h of treatment in the presence of Na_2SO_4 0.04 M and an applied current density of 100 A m^{-2} .

However, the FTIR spectrum of the sample collected after the EO treatment (Fig. 6B) showed three additional bands beyond the main bands of the pristine PS. Specifically, a broad band in the range of $3200\text{--}3700 \text{ cm}^{-1}$, associated with stretching the O—H bond, and a band at 2088 cm^{-1} , likely arising from the C=C=O stretching related to ketone formation, were observed. Additionally, absorption in the range of $900\text{--}1200 \text{ cm}^{-1}$ was identified, probably attributable to the movements of C=C bonds present in alkenes or vinyl groups [75,87]. These functional groups were similar to those reported in previous studies focused on applying AOPs to degrade MPs in water [54,88–91].

In line with the results reported by Lu et al. [53], the above findings suggested that the degradation of PS MPs occurred mainly via indirect EO due to strongly oxidizing active radical formation.

3.7. Preliminary operative cost evaluation: energy consumption and electrical cost

Energy consumption is widely recognized as a crucial factor that directly influences the overall costs associated with any EO treatment [92,93]. The specific energy consumption (SEC) has been widely used to evaluate the cost-effectiveness of the process [62,94–96]. Table S2 reports the SEC and ETC calculated by Eqs. (2) and (3) for each experimental condition investigated.

The findings pointed out that similar SECs of 7.11, 10.45, and $16.40 \text{ kWh g}_{\text{TOCremoved}}^{-1}$ were required to operate with 0.06 M of Na_2SO_4 , NaCl, and NaNO_3 , resulting in ETC of 1.45, 2.12, and $3.33 \text{ € g}_{\text{TOCremoved}}^{-1}$, respectively. However, a higher PS degradation efficiency (%) of 59.5 was achieved with Na_2SO_4 , highlighting the better performance of the latter with respect to the other electrolytes.

Overall, the highest SEC and ETC values of $61.77 \text{ kWh g}_{\text{TOCremoved}}^{-1}$ and $12.54 \text{ € g}_{\text{TOCremoved}}^{-1}$ were obtained operating 100 A m^{-2} , Na_2SO_4 0.06 M, and initial PS concentration of 13.0 mg L^{-1} , achieving the lowest PS degradation of 26.9 %. The highest PS degradation efficiency of 65.5 % was achieved operating at 60 A m^{-2} , Na_2SO_4 0.02 M, and an initial PS concentration of 60.0 mg L^{-1} . Under these conditions, SEC and ETC values of $2.81 \text{ kWh g}_{\text{TOCremoved}}^{-1}$ and $0.57 \text{ € g}_{\text{TOCremoved}}^{-1}$ were obtained, pointing out that lower Na_2SO_4 concentrations and not very high applied current densities allow for carrying out efficient and feasible EO processes. Elkathib et al. [97] applied an electrocoagulation treatment (with aluminum electrodes) to remove commercial Red Pearl Brilliant (909 RB) polyester glitter powder with 56.2 % of the particles in the range of 25–65 μm from synthetic water. They achieved a MP removal of 98.5 % operating with an initial MP concentration of 25 mg L^{-1} , a current density of 8.07 mA cm^{-2} , a pH equal to 4, and a treatment time of 90 min. Under these operative conditions, ETC was estimated to be $5.6 \text{ € g}_{\text{TOCremoved}}^{-1}$ (given an energy unit cost of $0.2031 \text{ € kWh}^{-1}$, and assuming that the MP content in the sample equated the TOC content). While the treatment successfully removed MPs from water, the sludge generation during the process constituted a drawback, leading to

additional operational costs associated with waste disposal.

4. Conclusions

MPs are emerging contaminants, accumulating in diverse environments and posing threats to ecosystems. Among various methods to mitigate this environmental problem, electrochemical oxidation has shown promise as a viable technology for treating water contaminated with MPs. However, further efforts and investigations are necessary to address the current lack of comprehensive information provided by the literature [98]. In this context, the current study examined the electrochemical oxidation of PS MPs by analyzing the impact of several process parameters on system performance, such as electrolyte composition and concentration, initial PS concentration, and applied current density.

The experimental results revealed that the highest efficiency in degrading PS microparticles with an average diameter of $1.0 \mu\text{m}$ was achieved by employing Na_2SO_4 (0.02 M) as a supporting electrolyte, an initial PS concentration of 60 mg L^{-1} , and an applied current density of 60 A m^{-2} for a treatment duration of 5 h. However, increasing the Na_2SO_4 concentration led to a decline in system performance due to self-combination reactions among the electrogenerated $\text{SO}_4^{\cdot-}$, which are the primary reactive species involved in the oxidation of PS. Overall, the degradation mechanism of PS microparticles can be attributed to indirect electro-oxidation via the formation of highly oxidizing active radicals rather than direct electro-oxidation between the anode surface and PS molecules. SEM analyses indicated that applying high current densities to the system could result in morphological changes and deformations of PS microparticles. Moreover, FTIR analyses of treated samples confirmed the formation of additional functional groups on the surface, validating the oxidation of PS microparticles.

In conclusion, this study demonstrates that EO is a promising approach that should be optimized to improve the degradation of MPs from contaminated water and lays the groundwork. Future efforts should focus on operating EO treatments in continuous reactors rather than batch processes. This shift would improve mass and charge transfer and reduce energy consumption.

Ethics declarations

This study did not involve any human samples and was approved by all authors.

CRediT authorship contribution statement

Giovanni Falco: Writing – review & editing, Investigation, Formal analysis. **Angelo Fenti:** Writing – original draft, Software, Investigation, Formal analysis, Data curation. **Simona Galoppo:** Writing – review & editing, Investigation, Formal analysis. **Simeone Chianese:** Writing – original draft, Validation, Software, Methodology, Conceptualization.

Dino Musmarra: Writing – review & editing, Validation, Supervision, Resources. **Mariacristina Cocca:** Writing – review & editing, Formal analysis. **Salvatore Mallardo:** Writing – review & editing, Formal analysis. **Pasquale Iovino:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2024.106418>.

Data availability

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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