

Emerging Technologies for Waste Plastic Treatment

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ABSTRACT: The existence of waste plastics and microplastics has caused serious pollution to the ecological environment. Harsh reaction conditions or long reaction time are typically required for the current waste plastic treatment technologies, resulting in high energy consumption and capital cost. Recently, plasma, Fenton, and electrochemical technologies have emerged to upcycle waste plastics under mild conditions and remove microplastics efficiently. The fundamentals and applications of plasma, Fenton, and electrochemical technologies in waste plastic treatment are reviewed. The prospects of these emerging technologies are also discussed, aiming to provide the scientific background, application status, and technical challenges for these emerging technologies for waste plastic treatment.

KEYWORDS: *Plastic upcycling, Microplastic, Electrical plasma, Fenton process, Electrochemical*



INTRODUCTION

Plastics are macromolecules formed by polymerization or polycondensation of monomers. According to the type of monomer, plastics can be divided into polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and others.¹ Due to the advantages of being lightweight and highly durable, plastics have been widely used in industry, agriculture and many other fields.² So far, more than 8.3 billion tons of plastics are estimated to have been produced.³ The mass production of plastics and the short service life of many plastics have resulted in a large accumulation of waste plastics in the environment.⁴ Statistics show that 79% of waste plastics end up in landfills or the natural environment, while only 9% are recycled.³ Waste plastics in landfills can leach hazardous substances from polymers and additives, which may contaminate groundwater.⁵ Waste plastic in the ocean may entangle marine life, resulting in injury or even death.⁶ It can also be ingested by marine life and cause physical damage such as abrasion, obstruction, and inflammation of the gastrointestinal tract.⁷ The accumulation of waste plastic in the soil can affect the uptake of nutrients and water by crops, resulting in reduced crop yields. The continuous accumulation of waste plastics in the environment has threatened the ecosystem and caused severe environmental problems.

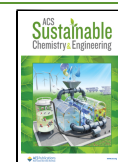
Recycling waste plastics can alleviate the above environmental and ecological problems. Currently, recycling of waste plastics mainly includes primary recycling, secondary recycling, tertiary recycling, and energy recycling.⁸ Both primary and secondary recycling is based on mechanical processes such as collection,

sorting, grinding, washing, remodeling, and extruding.^{8–10} Unlike primary recycling, which involves processing waste plastic into the same products they were originally recovered from, secondary recycling involves reprocessing waste plastic into products that are used for different purposes than the original material.^{8–10} Tertiary (chemical) recycling refers to the recovery of petrochemical components in waste plastics by chemical methods, mainly including pyrolysis, gasification, and hydrogenolysis.^{9–11} Energy recycling of waste plastic can be achieved by incineration, which recycles part of the energy of waste plastics into thermal energy for electricity or heat supply.⁹ Mechanical process-based recycling is typically used to treat almost pristine single-component waste plastic from known sources.^{11,12} Due to the high temperature and mechanical forces present in the processing process, the recycled plastics' optical, thermal, or mechanical properties are often degraded, limiting their further application.⁸ Incineration emits toxic air pollutants and large amounts of greenhouse gases into the atmosphere and produces far less energy than other recycling processes save.^{11,13} Compared with other recycling methods, chemical recycling is an upcycling strategy.¹⁰ Chemical recycling can treat contaminated plastics or complex mixtures of plastics and convert them into high value/quality monomers or oligomers that can be used

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as feedstocks to produce other chemicals.^{9,11} However, current chemical recycling is usually not implemented on an industrial scale because of the harsh reaction conditions (high temperature or even high pressure) that require a large amount of energy input.⁹ The development of new methods to directly convert waste plastics into monomers or polymers under mild conditions is a feasible scheme to accelerate chemical recycling on an industrial scale.

While chemical recycling can deal with most of the waste plastics in the environment, it is difficult to deal with nonrecoverable microplastics (MPs). MPs are a subclass of plastics with an effective diameter of less than 5 mm that exist in a variety of forms, including spheres, fragments, and fibers, and can be divided into primary and secondary MPs.^{14,15} Primary MPs include specially manufactured microbeads for personal care products and industrial abrasives for delicate surfaces.^{8,14,15} Secondary MPs come from the decomposition of larger plastic waste in the environment.⁸ MPs exist widely in soil, air, sediments, aquatic systems and biological systems and have become an emerging microcontaminant.^{16–22} When ingested by animals, MPs can cause physical damage to organs and even lead to death.^{23,24} MPs can damage algal species by inhibiting the photosynthesis of algae through external adsorption or affecting the root growth of duckweed by mechanical blocking.^{25,26} The persistent organic pollutants (POPs) absorbed by MPs can change physiological and metabolic processes.²¹ When MPs are transported in the food chain, they may lead to the accumulation of POPs in animals and further threaten human health.²¹

Physical methods such as rapid sand filtration, disc filtration, dissolved air flotation membrane filtration, and magnetic extraction have been applied to remove MPs from the environment.²⁷ Despite the high removal efficiency, the above technologies only separate MPs and require additional efforts to process the separated MPs. Degradation technology can degrade MPs into environmentally benign or degradable intermediates, or even completely mineralize them to carbon dioxide and water, which is an effective solution to the above problem.⁸ Biodegradation and photodegradation are the main degradation technologies currently. Biodegradation is a process in which microorganisms (such as bacteria and fungi) form biofilms on the surface of the plastic and catabolize to produce specific enzymes that destroy the main skeleton structure of plastic and depolymerize side chains to produce oligomers, dimers, and monomers.²⁸ Photodegradation is a process in which the separated electron–hole pairs generated after the absorption of photon energy in the semiconductor react with OH^- , O_2 or H_2O adsorbed on the semiconductor surface to produce reactive oxygen species such as hydroxyl and superoxide radicals, resulting in the chain breaking, branching, cross-linking of microplastics, and mineralization into H_2O and CO_2 .^{4,29} Due to their ecological friendliness and environmental affordability, biodegradation and photodegradation are considered promising methods for degrading MPs and have attracted many researchers to carry out relevant studies. For details, readers can refer to excellent specialized reviews.^{4,28,30,31} However, photodegradation usually takes hours or even days to degrade MPs, while biodegradation takes a longer time, usually days or even months.^{4,28,30,31} The low efficiency has hindered their further development.

Recently, three technologies have emerged to upcycle waste plastics at mild conditions, typically below 100 °C and atmospheric pressure, as well as to remove microplastics efficiently, achieving 50–90% removal rates in a matter of

hours, as shown in Figure 1. To enable readers to understand the state-of-the-art technologies in the field of waste plastic

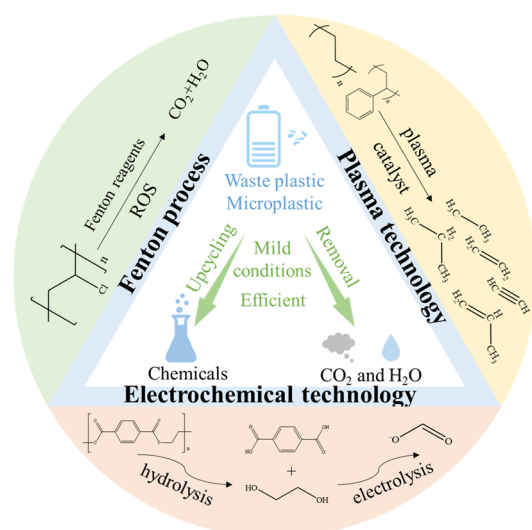


Figure 1. Three emerging technologies for waste plastic treatment.

treatment, herein we summarize an up-to-date review of these emerging technologies. This review aims to provide the scientific background and technical challenges for these emerging research fields to address the ecological problems posed by waste plastic. The following aspects are summarized in this paper: (1) the scientific background of plasma technology, Fenton process, and electrochemical technology; (2) the application of the above technologies in waste plastic treatment; (3) the mechanism of the above technologies in waste plastic treatment; and (4) the technical challenges and the need for future research of the above technologies.

■ PLASMA TECHNOLOGY

Plasma is a partially ionized gas composed of electrons, ions, radicals, excited species, and neutral molecules.³² It is regarded as the fourth state of matter beyond solid, liquid, and gas. Plasma in a laboratory is usually produced by gas discharge and can be divided into thermal plasma and nonthermal plasma according to the relative temperatures of electrons, ions, and neutral particles.³³ The thermal plasma approaches thermodynamic equilibrium, that is, the temperatures of the ion and neutral particles approach the temperature of the electron.³³ Thermal plasma technology has been widely used in metallurgical processing, materials synthesis, waste treatment, and other research fields.³⁴ Plastic pyrolysis/gasification with thermal plasma has been frequently reported by previous researchers.^{35–43} Although plasma pyrolysis/gasification technology has been widely used in the chemical recycling of plastics, it often requires high-temperature or even high-pressure conditions due to limitations in the thermodynamics and kinetics of the reaction. Recently, Peng and co-workers have realized waste plastic upcycling under mild conditions using nonthermal plasma technology.^{44,45} The nonthermal plasma is far from thermodynamic equilibrium because electrons have higher temperatures, while ions and neutral particles have temperatures much lower than electrons, sometimes even close to the ambient temperature.³² Nonthermal plasma can be generated by dielectric barrier discharge (DBD), which is a nonequilibrium gas discharge with a dielectric inserted into the discharge space.

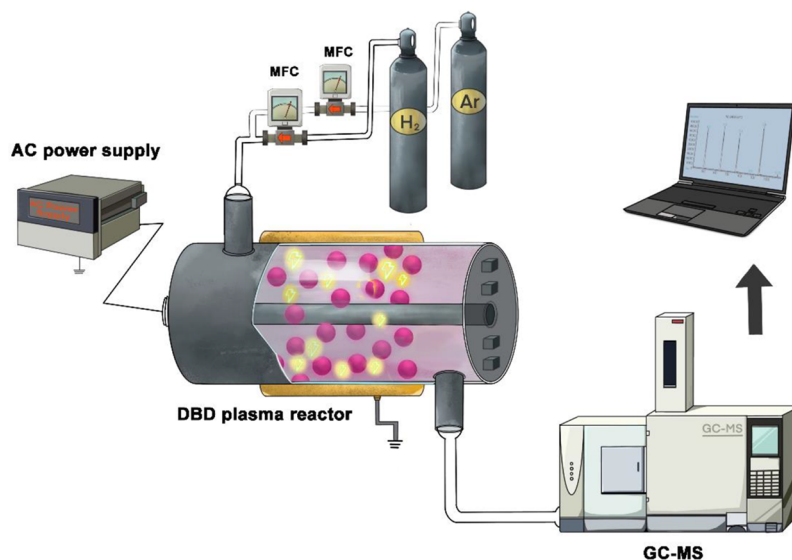


Figure 2. Diagram of nonthermal DBD plasma reactor and reaction test system. Reprinted with permission from ref 45. Copyright 2022 Springer Nature.

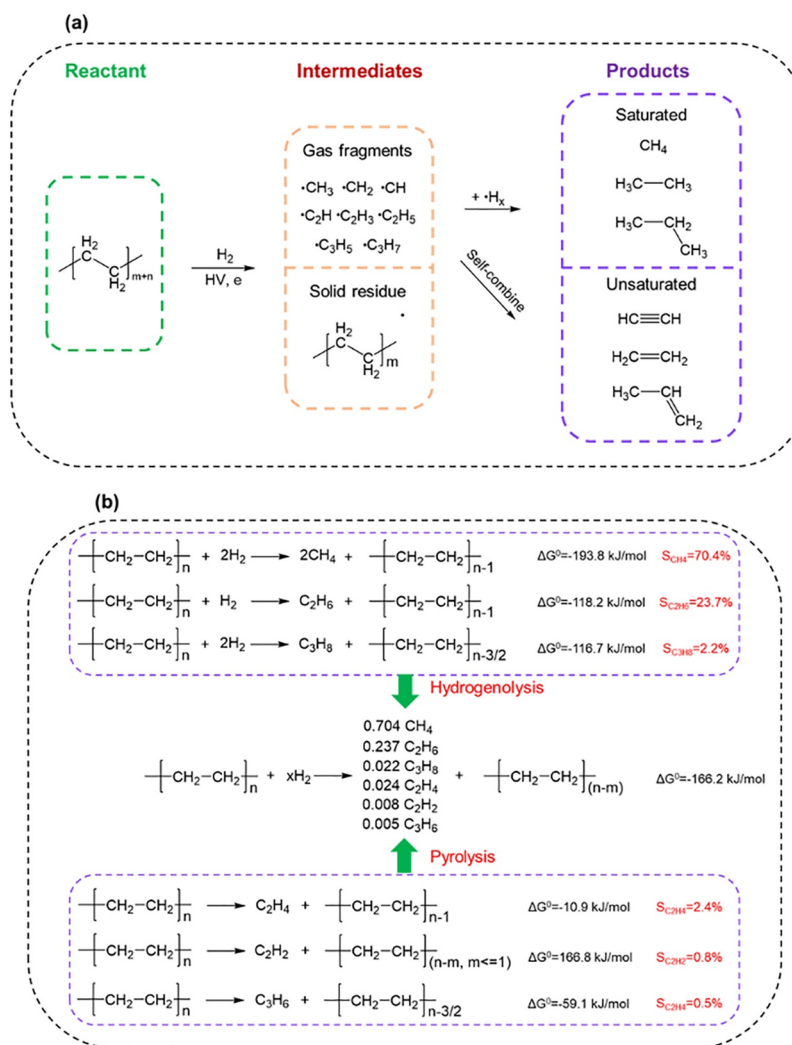


Figure 3. (a) Reaction path of HDPE in hydrogen plasma. (b) Reaction formula and Gibbs free energies (ΔG°) of plasma-assisted hydrogenolysis. Reprinted with permission from ref 44. Copyright 2021 Elsevier.

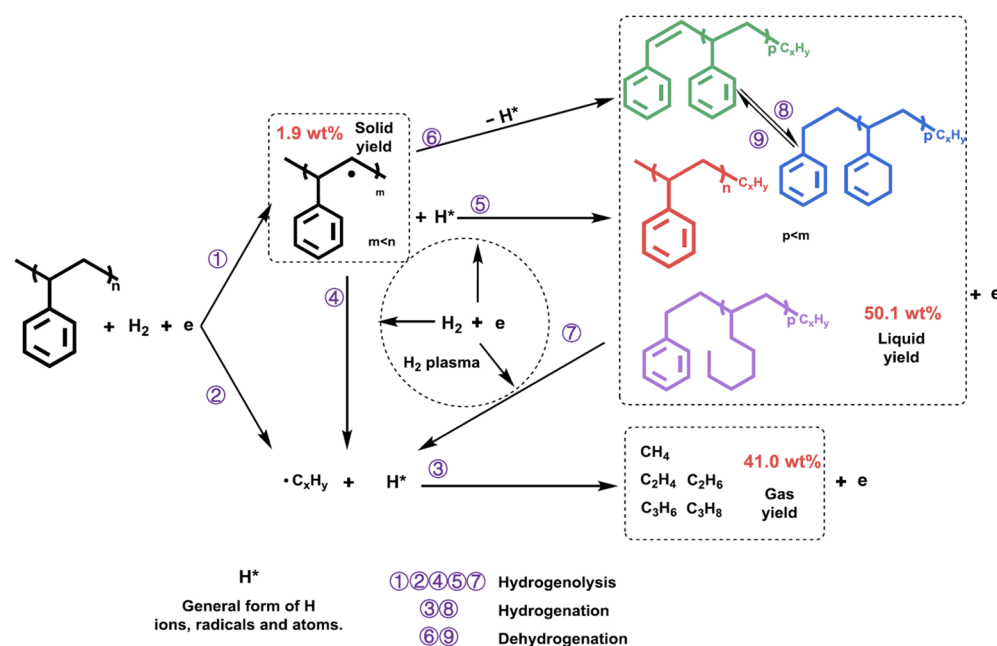


Figure 4. Illustrated reaction pathways for plasma-assisted PS hydrogenolysis. Reprinted with permission from ref 45. Copyright 2022 Springer Nature.

Peng and co-workers first achieved hydrogenolysis of high-density polyethylene (HDPE) to C1–C3 hydrocarbons at ambient condition using nonthermal plasma with a selectivity greater than 95%.⁴⁴ Without the assistance of plasma, hydrogenolysis of HDPE usually needs to be carried out at a temperature above 200 °C with thermal catalysis. The experiment of HDPE hydrogenolysis assisted by nonthermal plasma was carried out in the reaction system as shown in Figure 2. Nonthermal hydrogen plasma is generated by DBD in a quartz tube reactor in the presence of an AC plasma generator. Although the reactor is at ambient temperature and there is no external heating source to heat it, a lot of heat is generated when the hydrogen gas is ionized in the DBD area of the reactor to produce hydrogen plasma. HDPE pellets uniformly mixed with catalysts (Pt/C or SAPO-34 zeolite) were placed in the center of the plasma generation zone. HDPE was then destroyed under the dual action of heat and active hydrogen plasma and converted to gaseous hydrocarbons (methane, acetylene, ethylene, ethane, propene, and propane) under ambient conditions. Hydrogen plasma can overcome the activation barrier of the reaction under ambient conditions and drive the exothermic HDPE hydrogenolysis. Hydrogen plasma also plays a leading role in controlling the overall hydrogenolysis kinetics. Although the presence of catalysts (Pt/C or SAPO-34 zeolite) also helped to improve the hydrogenolysis kinetics, the improvement was limited as the total gas yield increased by less than 10%. However, the presence of catalysts can significantly change product selectivity and improve the energy efficiency by up to 9 times in the lower plasma power range. A plausible reaction pathway of HDPE hydrogenolysis is shown in Figure 3a. Bombardment by high-energy H₂ plasma ($\cdot H_x$) destroys the HDPE structure (primarily the C–H and C–C bonds in HDPE based on the results of IR), producing intermediates that include small gaseous fragments ($\cdot C_xH_y$, not limited to the presented ones) and solid residues. Hydrogenation reactions between $\cdot C_xH_y$ and $\cdot H_x$ or recombination reactions between $\cdot C_xH_y$ intermediates produce gaseous products. In the abundant hydrogen plasma, the hydrogenation

reaction to form alkanes mainly occurs because the hydrogenation kinetics is faster than the recombination process. The Gibbs free energy (ΔG^0) of various reactions is shown in Figure 3b. The hydrogenolysis of HDPE to alkanes is highly spontaneous; however, the formation of olefin products is limited by thermodynamics, leading to low selectivity toward their formations. The ΔG^0 of the overall reaction is -166.2 kJ/mol, indicating that plasma-assisted HDPE hydrogenolysis has a favorable reaction thermodynamics.

Since the nonthermal hydrogen plasma showed the ability to induce highly spontaneous thermodynamic features and fast reaction kinetics, Peng and co-workers further investigated the plasma-assisted hydrogenolysis of polystyrene (PS) at ambient temperature and atmospheric pressure conditions using the same reaction system (Figure 2).⁴⁵ The results indicate that the reactive hydrogen species in the form of ions and free radicals in the nonthermal hydrogen plasma can effectively break the C–C bond in PS and drive efficient hydrogenolysis of PS under ambient conditions. More than 95% of PS was converted to high yield (>40 wt %) of C1–C3 gaseous hydrocarbons and 50–56 wt % liquid products within only 12 min. The selectivity of high-value ethylene in the gases was greater than 70%. ¹H NMR spectroscopy, ¹³C NMR spectroscopy, and gel permeation chromatography (GPC) were used to characterize the significant extent of depolymerization in the liquid components. Matrix-assisted laser desorption/ionization (MALDI-MS) and electrospray ionization (ESI-MS) techniques were used to obtain the detailed structure and composition information on the liquid products. D₂ isotope labeling experiment was carried out by substituting D₂ for H₂, and the gas products were analyzed by an online gas chromatograph to further understand the reaction mechanism. Based on the above analysis of the gas and liquid products, the plausible reaction pathway was proposed as shown in Figure 4. In H₂ plasma, the C–H and C–C bonds in PS are effectively broken, resulting in hydrocarbon fragments consisting of smaller units of PS (step 1) and $\cdot C_xH_y$ species (step 2). $\cdot C_xH_y$ species are hydrogenated to form gas products (step 3). The smaller units of PS can be

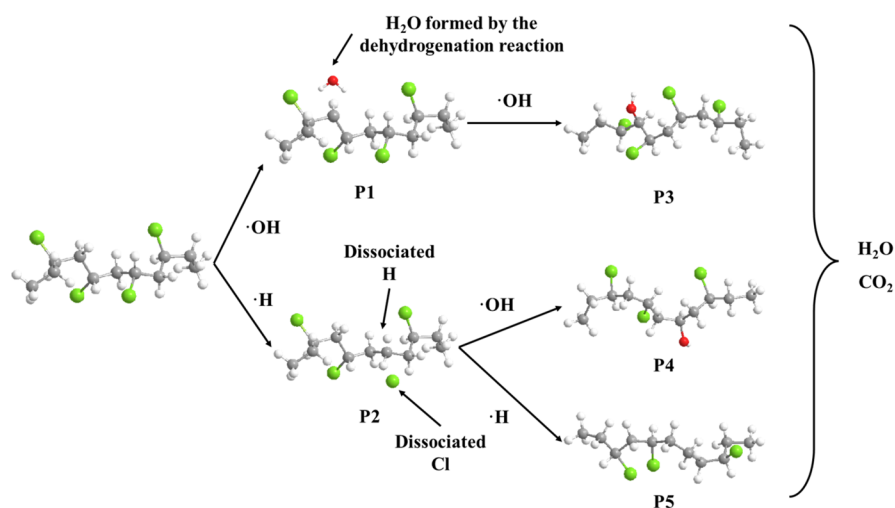


Figure 5. Possible degradation pathway of PVC in DBD plasma. Adapted with permission from ref 46. Copyright 2022 Elsevier.

Table 1. Applications of Plasma Technology in the Field of Waste Plastic Upcycling and Microplastic Removal

Field	Plastics	Conditions	Reaction time	Conversion/removal rate	Main products	DBD structure	Plasma	Ref
Waste plastic upcycling	HDPE	Ambient condition	/	/	CH_4 , C_2H_6 and C_3H_8 with >95% selectivity	Tubular electrode structure	Hydrogen plasma	44
Waste plastic upcycling	PS	Ambient condition	2–12 min	More than 95%	>40 wt % of C1–C3 gaseous hydrocarbons and 50–56 wt % liquid products	Tubular electrode structure	Hydrogen plasma	45
Waste plastic upcycling	Postconsumer PS	Ambient condition	4–12 min	85.25%	40.99 wt % of gaseous hydrocarbons and 38.99 wt % liquid products.	Tubular electrode structure	Hydrogen plasma	45
Waste plastic upcycling	PP	Ambient condition	10 min	More than 70%	>65 wt % of C1–C3 gaseous hydrocarbons	Tubular electrode structure	Hydrogen plasma	45
Waste plastic upcycling	Mixture of PE, PP, and PS	Ambient condition	10 min	80%	~50 wt % of C1–C3 gaseous hydrocarbons and ~25 wt % liquid products	Tubular electrode structure	Hydrogen plasma	45
Microplastic removal	PVC	Ambient condition	100 min	85.9%	CO_2 and H_2O	Plate electrode structure	Air plasma	46

further converted by three pathways: (a) further fragmentation by H_2 plasma to produce more $\cdot\text{C}_x\text{H}_y$ radicals (step 4); (b) hydrogenolysis to form liquid products (hydrogenated polystyrene) (step 5); (c) dehydrogenation to form liquid products (dehydrogenated polystyrene) (step 6). Interconversion between liquid products may also occur (steps 8 and 9). To evaluate the application of this technology, the plasma-assisted hydrogenolysis of postconsumer PS and a mixture of polyethylene (PE), polypropylene (PP), and PS was further investigated. The results showed that postconsumer PS and plastic mixtures had lower conversion rate and liquid yield. The results suggest that material thickness, surface properties, contaminants and impurities have a certain influence on the effect of the plasma-assisted hydrogenolysis. However, even in the presence of impurities, the conversion rate of postconsumer PS was still over 85%, and the total liquid and gas yield was close to 80%, indicating the potential of plasma technology in the upcycling of real-world waste plastics under mild conditions.

Plasma technology has also been used to efficiently remove microplastics. Ren and co-workers first used DBD plasma to achieve the efficient removal of PVC microplastics, with a removal efficiency of 85.9% in 100 min under optimal reaction conditions (discharge voltage 16.8 kV, ratio of water to PVC 4:10, discharge frequency 7 kHz, mass of PVC 0.1 g).⁴⁶ The DBD reactor used in this experiment is a plate electrode structure, with PVC uniformly dispersed on the dielectric attached to the ground electrode. Based on the effects on PVC removal of NO_3^- , isopropanol, tetrachloromethane, and *p*-benzoquinone, as scavengers to e_{aq}^- , $\cdot\text{OH}$, $\cdot\text{H}$, and O_2^- ,

respectively, Ren and co-workers revealed that DBD produced e_{aq}^- , $\cdot\text{OH}$, $\cdot\text{H}$, and O_2^- , which are oxidizing species and reducing species. The results indicated that e_{aq}^- produced by the impact between energetic electrons and water has strong reducibility and was the most effective substance for PVC removal, while $\cdot\text{OH}$, $\cdot\text{H}$, and O_2^- weakened PVC removal because they could capture e_{aq}^- . Density functional theory (DFT) calculation and Fourier transform infrared (FTIR) results indicated that $\cdot\text{H}$ offered electrons to C ions of $-\text{CH}$ on PVC, and then electrons were transferred to $-\text{H}$ and $-\text{Cl}$ groups, causing the dissociation of $-\text{H}$ and $-\text{Cl}$ groups on PVC, thus achieving the dehydrogenation and dechlorination of PVC. The chlorine dissociated from PVC ends up in the aqueous phase. In addition, the results of structural relaxation indicated that $\cdot\text{OH}$ also promoted the dehydrogenation of PVC by electron transfer. Therefore, both oxidizing species and reducing species produced by DBD can react with PVC. When degradation products that are not easily oxidized are formed, the reducing species can continue to degrade these products. Based on the above results, the possible degradation pathways of PVC are proposed as shown in Figure 5. PVC is dehydrogenated and dechlorinated at the $-\text{CH}$ site by $\cdot\text{OH}$ and $\cdot\text{H}$, resulting in P1 and P2. P1 further reacts with $\cdot\text{OH}$ to form P3 at the $-\text{CH}$ site. P2 is attacked by $\cdot\text{OH}$ and $\cdot\text{H}$, forming P4 and P5 at the $-\text{CH}$, respectively. Then, the length of the carbon chain of PVC is sequentially reduced to produce CO_2 and H_2O . This study confirmed that DBD plasma has an excellent ability to remove microplastics.

Currently, plasmas used to treat waste plastics are generated by dielectric barrier discharge. The application of nonthermal plasmas generated by corona discharge and glow discharge in waste plastic treatment remains to be explored, which may achieve high waste plastic treatment efficiency with lower energy consumption. Air plasma is used to remove microplastics, while hydrogen plasma is used to upcycle waste plastics. Given the high price of hydrogen and the potential lack of activity that air plasmas face, the application of other cheap and highly active gas plasmas in waste plastic treatment remains to be explored to achieve low-cost upcycling of waste plastics and efficient removal of microplastics. The plasma reactor used for waste plastic upcycling is a tubular electrode structure, and that for microplastic removal is a plate electrode structure.

Applications of plasma technology in the field of waste plastic upcycling and microplastic removal are summarized in Table 1. Although only a few studies have been published, plasma technology has shown great potential to upcycle waste plastics under ambient conditions and efficiently remove microplastics, as shown in Table 1. In addition, the plasma technology requires simple equipment, only a plasma generator to ionize the gas to form the plasma. Current plasma technology is expensive because hydrogen is used in waste plastic upcycling.^{47,48} For microplastic removal, however, much of the operating cost comes from the electricity needed to ionize the gas. Energy efficiency is an important challenge for the large-scale application of plasma technology. The mismatch between power input and product output will limit its further application.⁴⁹ Although the current energy efficiency of the nonthermal plasma-assisted PS hydrogenation reaction in terms of gas generation alone is as high as 12.2 g/kWh, which is comparable to the energy efficiency of the plasma-assisted CO₂ conversion and VOC removal reactions, and higher than that of the nitrogen fixation reaction, it can be even higher considering the unaccounted liquid products.^{44,45,50,51} However, the energy efficiency of plasma technology will gradually decrease with the extension of reaction time. To further improve energy efficiency and enhance the sustainability of the plasma technology, the design of the plasma reactor can be improved to reduce power loss and energy loss in the nonplasma region. Second, the introduction of catalysts can improve gas yield and energy efficiency, so it is feasible to improve energy efficiency by screening suitable catalysts.⁴⁴ Third, since the energy efficiency will gradually decrease with the extension of reaction time, the use of pulsed or segmented plasma instead of continuous plasma can effectively improve the energy efficiency.

■ FENTON PROCESS

In 1894, Fenton found that tartaric acid can be effectively oxidized when Fe²⁺ and H₂O₂ exist simultaneously in an acidic solution (pH 2–5).⁵² In his honor, ferrous salts and H₂O₂ are called Fenton reagents, and the reaction of Fe²⁺ and H₂O₂ is the classic Fenton process. In the Fenton process, Fe²⁺ activates H₂O₂ to produce various reactive oxygen species (ROS), including ·OH, superoxide anion radical (·O²⁻), and singlet oxygen (¹O₂), among which ·OH is the main functional ROS and has the second highest oxidation potential of 2.8 eV in nature.^{53,54} The Fenton process is widely used to degrade biorefractory organic contaminants such as phenols, pesticides, pharmaceuticals, and organic solvents into harmless inorganic matter, such as carbon dioxide and water due to the production of ROS with strong oxidation potential.⁵⁵ Recently, some

researchers have realized the removal of microplastics by using the Fenton process.

■ CLASSIC FENTON PROCESS

Qiu's group achieved the removal of nylon 6 (PA6) and PS MPs using classic Fenton reagents.⁵⁶ The Fenton reaction system consists of 0.5 g MPs, 19.3 mL ultrapure H₂O, 0.3 mL 30% H₂O₂ and 0.3 mL 0.2 M Fe²⁺. The pH of the reaction system was adjusted to 3 to avoid the formation of ferric hydroxide, which inhibited the catalytic activity of Fe²⁺. The reaction system was stirred at a rotation speed of 150 rpm. The whole reaction was carried out at ambient temperature and atmospheric pressure. To study the degradation mechanisms of nylon 6 (PA6) and polystyrene (PS) MPs, scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were employed to confirm the MP oxidation and polymer chain scissions, while surface-enhanced Raman scattering (SERS) and gas chromatography–mass spectrometry (GC-MS) were employed to analyze the degradation products. The comprehensive application of these characterization techniques shows how the Fenton process acts on the oxidation degradation of microplastics and clarifies the products formed after the degradation of microplastics. The results showed that the organic carbon content (low-molecular-weight alkanes, alcohols, aldehydes, and carboxylic acids derived from the derivatization of alcohols) in the degradation products accounted for only 37.7% of the total degradation mass loss. The majority of MP degradation products were mineralized to inorganic carbon.

Although the work of Qiu's group confirmed that the classic Fenton process could remove microplastics, it was less efficient. To improve the removal efficiency of microplastics, modified Fenton processes including sulfate radical-based Fenton-like process, electro-Fenton-like process, microbially driven Fenton process, and Fenton process combined with other unit processes have been applied to degrade microplastics, and they show higher removal efficiency. These modified Fenton processes produce more reactive oxygen species to efficiently remove microplastics by changing one or more of the oxidants, catalysts, and generation modes of reactive oxygen species in the classic Fenton process.

■ SULFATE RADICAL-BASED FENTON-LIKE PROCESS

Compared with classic Fenton processes, Fenton-like processes utilize a variety of homogeneous and heterogeneous catalysts (alkaline, metal oxide, phosphorus materials, carbon materials, etc.) and different oxidants (H₂O₂ and persulfate).^{57–59} Persulfate mainly includes peroxymonosulfate (PMS) and peroxydisulfate, and the active components are HSO₅⁻ and S₂O₈²⁻, respectively. Persulfate can be activated by thermal, alkaline, ultraviolet light, activated carbon, transition metal (such as Fe⁰, Fe²⁺, Cu²⁺, Co²⁺, Ag⁺), ultrasound, and hydrogen peroxide to form sulfate radical (SO₄^{·-}).⁶⁰ Compared with ·OH, SO₄^{·-} has higher redox potential and longer half-life.^{57,61} Therefore, the sulfate radical-based Fenton-like process can better ensure the effective and sustainable removal of microplastics.

Qiu et al. compared the effects of Fe²⁺-activated PMS and Fenton reagents on the removal of nylon 6 (PA6) and PS MPs and confirmed that the Fe²⁺-activated PMS reaction system has a stronger oxidation capacity than Fenton reagents.⁵⁶ However,

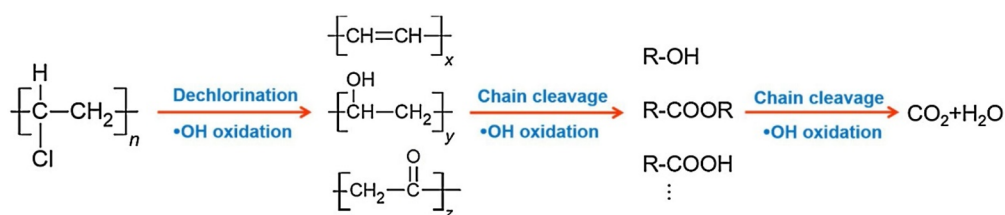


Figure 6. Proposed degradation process of PVC MPs in the electro-Fenton-like process. Reprinted with permission from ref 64. Copyright 2020 Elsevier.



Figure 7. Chemical degradation process of UPRs in the hydrolysis-Fenton oxidation. Reprinted with permission from ref 68. Copyright 2021 Elsevier.

the removal of microplastic by Fe^{2+} -activated PMS is still limited, and the results showed that after 4 cycles of treatment, the mass losses of PA6 and PS MPs were only 25.6% and 22.1%, respectively.

To improve the removal of microplastics by activated PMS, Duan and co-workers first designed the magnetic spring-like carbon nanotubes ($\text{Mn}@\text{NCNTs}$) for the activation of PMS to generate highly oxidizing radicals for the removal of cosmetic polyethylene-based MPs under hydrothermal conditions.⁶² The magnetic N-doped nanocarbon springs exhibited outstanding MP removal performance (54 wt % of MP removal) by catalytic activation of PMS to generate reactive radicals. The responsible ROS in the $\text{Mn}@\text{NCNTs}$ /PMS system were identified by electron paramagnetic resonance (EPR) and radical quenching experiments. The intermediates in the removal process of MPs were evaluated by HPLC, GC-MS, and total organic carbon (TOC). According to the degradation intermediates and their evolution, the possible degradation pathways of MPs in the $\text{Mn}@\text{NCNTs}$ /PMS system were proposed. Under hydrothermal conditions, the backbone chain of polyethylene is cleaved to trigger the production of hydrocarbon radicals. Metastable hydrocarbon species are oxidized by ROS, resulting in further chain cleavage into smaller fragments with a lower molecular weight such as alcohols, aldehydes/ketones, and carboxylic acids. These organic intermediates are eventually mineralized into CO_2 and H_2O under the action of ROS, thus achieving a high TOC removal efficiency.

■ ELECTRO-FENTON-LIKE PROCESS

When hydrogen peroxide in a Fenton-like process is electrochemically produced in situ through the cathodic reduction of dissolved oxygen, the process is called electro-Fenton like.^{53,63}

The electro-Fenton-like (EF-like) process is a combination of electrooxidation (EO) and the Fenton process. With the assistance of effective heterogeneous catalysts, the EF-like process can achieve the efficient removal of microplastics.

Gao et al. achieved efficient removal of PVC by an electro-Fenton-like process based on TiO_2 /graphite (TiO_2/C) cathode.⁶⁴ Through cathodic reduction dechlorination and

hydroxyl radical oxidation simultaneously, the dechlorination and removal efficiency of PVC reached 75% and 56%, respectively, within 6 h. Removal experiments of PVC microplastics were carried out in a three-electrode system in an O_2 saturated environment. Dissolved oxygen generates the intermediate hydrogen peroxide through oxygen reduction reaction on the TiO_2 /graphite (TiO_2/C) cathode, and the adsorbed hydrogen peroxide is reduced in situ to hydroxyl radical, which is used for oxidative degradation of PVC MPs. Combined with the analysis results of FTIR, GPC, XPS, TOC, HPLC, and GC-MS, a possible degradation process of PVC MPs is proposed in Figure 6. The reduction dechlorination of PVC microplastics occurred when electrons were obtained from the TiO_2/C cathode under heating conditions. At the same time, PVC is oxidized by $\cdot\text{OH}$ to generate oxygen-containing organic compounds containing $\text{C}=\text{O}$, $\text{O}-\text{H}$, and other oxygen groups, which fall off into the solution. Among these intermediates, the exfoliative hydrocarbon species are further oxidized by $\cdot\text{OH}$ to form smaller fragments such as alcohols, carboxylic acids, and esters. Eventually, some of these substances are mineralized into CO_2 and H_2O . The chlorine that dissociates from PVC may eventually exist in the aqueous phase as chloride ions.

■ MICROBIALLY DRIVEN FENTON PROCESS

Microorganisms can attach and colonize the surface of plastics or MPs to form biofilms, which then cause the plastic to age or degrade through metabolic activity.⁶⁵ However, the efficiency with which plastics are degraded directly by microorganisms is still very low.^{28,30} Chen et al. found that a large number of thermophilic iron-reducing bacteria in thermophilic composting can promote the redox process of iron, resulting in the production of $\cdot\text{OH}$ in composting.⁶⁶ Therefore, they developed a microbially driven Fenton process to accelerate the degradation and removal of MPs in the composting system by adding iron oxides to the compost to generate $\cdot\text{OH}$ spontaneously.⁶⁷ Their results showed that the process was able to remove 35.93% of polyethylene microplastics within 36 days of treatment. Although the removal efficiency is still low compared to other methods, the removal efficiency of this

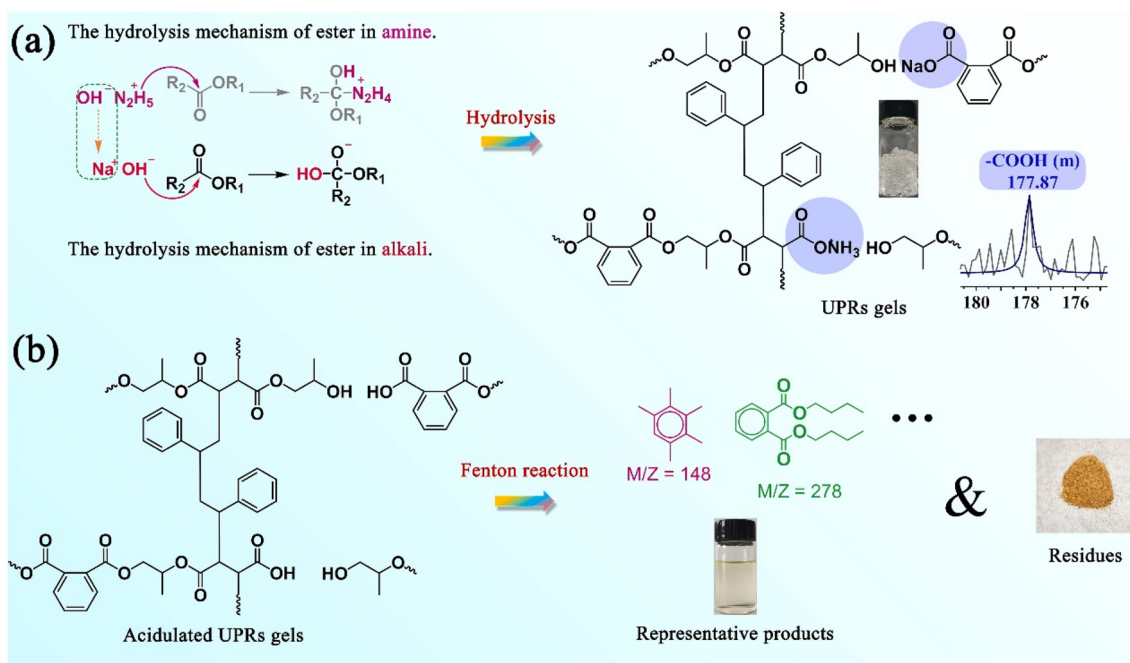


Figure 8. (a) Hydrolysis mechanism and (b) Fenton oxidation of UPRs. Reprinted with permission from ref 68. Copyright 2021 Elsevier.

process is 5.53 times higher than that of ordinary thermophilic composting.

FENTON PROCESS COMBINED WITH OTHER UNIT PROCESSES

Recently, Hu et al. developed a synergistic catalytic process combining the Fenton process with hydrolysis to achieve efficient treatment of thermosetting plastics.⁶⁸ They achieved a 98.28% treatment rate of unsaturated polyester resins (UPRs) and successfully recovered carbon fibers (CFs) from UPRs at 100 °C below. The chemical removal process of UPRs is shown in Figure 7. The ester bond in UPRs was cleaved by hydrolysis of 80% hydrazine hydrate and NaOH. The UPR gel is then completely degraded by the cleavage of the carbon–carbon bond via the Fenton reaction. The characteristic absorption of C=O in amides and alcohols was detected by FTIR spectra. The results of GC-MS showed that there were more than 10 kinds of short chain organic compounds in the degradation liquid. In addition, SEM images indicated the surface breakup of the resin in the Fenton process. The results of FTIR, GC-MS, and scanning electron microscopy (SEM) indicated an efficient removal of gelatinous UPRs by using the Fenton reaction. Most copolymers of the gel are oxidized by ·OH radical to produce CO₂, naphthalene derivatives, benzene derivatives, esters, and amides. The formation of residues is due to the binding of a small number of functional groups on the resin surface to Fe(III), which blocks the reaction between the resin and hydroxyl radicals. The degradation mechanism of UPRs by the hydrolysis-Fenton oxidation is shown in Figure 8. This work provides a promising way for efficient removal of thermosetting composites containing ester bonds and carbon–carbon bonds.

In the Fenton process, it is important to activate oxidants such as hydrogen peroxide and persulfate to produce reactive oxygen species. At present, the addition of catalysts, including ferrous ions, Mn@NCNTs, TiO₂/graphite, etc., is the main activation method. Further development of efficient catalysts will help to generate more reactive oxygen species and improve the removal

efficiency for microplastics. Additionally, activation of oxidants by heat and ultraviolet light is also a feasible method to generate reactive oxygen species, which remains to be explored. Microplastics degraded by the Fenton process are sometimes converted into toxic byproducts rather than being directly mineralized into nontoxic carbon dioxide and water. To avoid the potential risks to human health and the ecological environment caused by these hazardous byproducts, it is important to evaluate their toxicity before being released into the environment.

Applications of Fenton processes in the field of microplastic removal are summarized in Table 2. Although only a few studies

Table 2. Applications of Fenton Processes in the Field of Microplastic Removal

Subclassification	Plastic	Reaction time	Removal rate	Ref
Classic Fenton process	PA6 and PS	80 h	25.6% for PA6 and 22.1% for PS	56
Sulfate radical-based Fenton-like process	PE	8 h	54%	62
Electro-Fenton-like process	PVC	6 h	75% dechlorination efficiency and 56% removal efficiency	64
Microbially driven Fenton process	PE	36 days	35.93%	67
Fenton process combined with hydrolysis	UPRs	/	98.28%	68

have been published, Fenton processes have shown potential to efficiently remove microplastics. Although the classic Fenton process has a limited effect on microplastics removal, modified Fenton processes such as the sulfate radical-based Fenton-like process and electro-Fenton-like process can achieve a high removal rate of microplastics in a short reaction time. The Fenton process has strong coupling and can be easily coupled

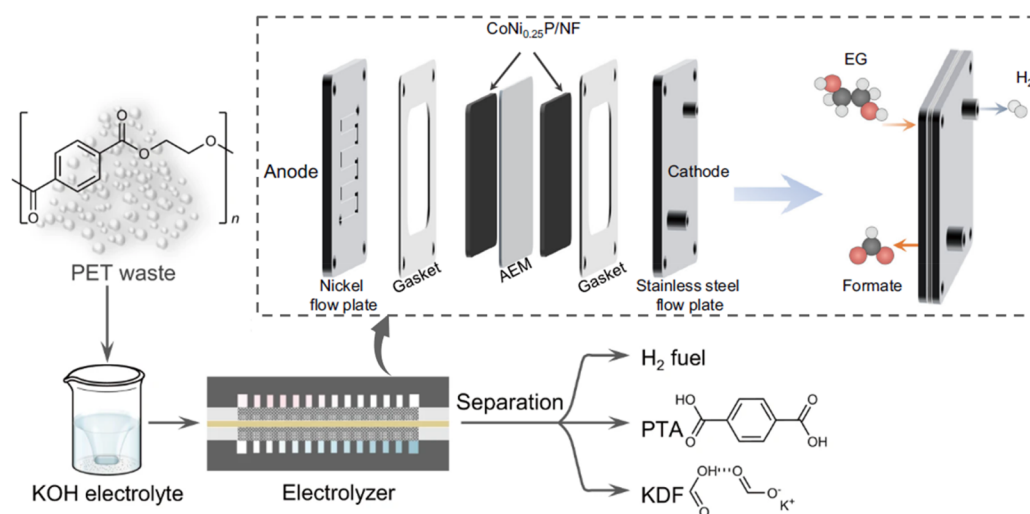


Figure 9. Electrochemical upcycling of PET in the MEA reactor. Adapted with permission from ref 48. Copyright 2021 Springer Nature.

with other processes such as hydrolysis to achieve a high removal rate of microplastics. However, despite the simplicity and low cost of the Fenton process, the large number of chemicals added to the process may lead to subsequent recycling difficulties.

The energy efficiency of the Fenton process varies greatly depending on the specific conditions and parameters used. In general, however, the Fenton process is considered to be an energy-intensive process. Compared with other advanced oxidation processes (AOPs) such as photocatalysis, the Fenton process typically requires more energy.^{69–71} One of the main reasons for the high energy consumption of the Fenton process is the need to produce high levels of free radicals, which requires the use of strong oxidants such as hydrogen peroxide, production of which is energy-intensive. Despite its relatively high energy consumption, the Fenton process has the advantage of being able to effectively remove a wide range of recalcitrant compounds that are difficult to remove by other methods, as demonstrated by its ability to remove microplastics. There are several strategies that can be used to improve the energy efficiency of Fenton processes, including (a) using alternative oxidants such as ozone or peroxyxynitrite, the production of which is less energy-extensive than hydrogen peroxide; (b) combining with other technologies to reduce the amount of oxidant required and reduce the overall energy consumption of the process; (c) screening suitable catalysts to improve the reaction kinetics of microplastic removal; and (d) using renewable energy sources such as solar or wind power to generate the required electricity.

■ ELECTROCHEMICAL TECHNOLOGY

Due to its environmental compatibility, high efficiency, and potential cost effectiveness, electrochemical technologies including electrooxidation, electrodisinfection, electrocoagulation, electrodialysis, and electroremediation have been widely applied to remediate environmental problems ranging from the treatment of contaminated soil to the removal of hazardous species from wastewater.^{72,73} Recently, some researchers have realized the upcycling of waste plastic under mild conditions and the efficient removal of microplastics through electrochemical technology, especially electrooxidation, to reduce the pollution of waste plastics to the environment.

■ ELECTROCHEMICAL UPCYCLING OF WASTE PLASTICS

Electrochemical upcycling of waste plastics is based on electrochemical cells, which can be divided into galvanic cells and electrolytic cells. Fuel cells, a type of galvanic cell, have been used to recycle waste plastics. Hibino and his co-workers reported the use of proton exchange membrane fuel cells and solid oxide fuel cells to recycle waste plastics for electricity.^{74–76} However, the researchers prefer to use electrolytic cells for the upcycling of waste plastics compared to galvanic cell-based electrochemical recycling, which directly recycles waste plastics into electricity and usually requires high temperatures (solid oxide fuel cells operate at 800 °C). The electrolytic processes include the cathodic deposition of metals and oxidation of organic compounds, the latter of which may occur directly on the anode surface or be mediated by oxidants produced at the anode or cathode surface.⁷³

In an electrolytic cell, Duan et al. achieved highly selective (>80% selectivity) electrooxidation of PET hydrolysates into formates with a designed nickel-modified cobalt phosphate ($\text{CoNi}_{0.25}\text{P}$) electrocatalyst under mild conditions, along with the formation of hydrogen.⁴⁸ The experimental process and membrane electrode assembly (MEA) reactor are shown in Figure 9. PET is first digested in an alkaline solution at 60 °C to obtain its monomers including terephthalic acid (PTA) and ethylene glycol (EG), and then the C–C of EG is selectively broken to form formate on the anodic $\text{CoNi}_{0.25}\text{P}$ catalyst, while hydrogen is generated on the cathode. Subsequently, formate is used as an acidifier in PET electrolytes for precipitation and regeneration of PTA, and the filtered liquid, which includes formic acid and potassium formate, is converted to KDF through concentration and crystallization. Based on the dynamic conversion of EG tracked by HPLC and the electrochemical and kinetic evaluation of EG and its intermediates, the conversion path of EG was proposed as follows. EG is initially oxidized to glycolic aldehyde, most of which is cleaved to formate by rapidly oxidized C–C and a small amount to glycolic acid, followed by slow C–C cleavage to formate. Detailed characterization of the electrocatalyst reveals that the advantageous performance of EG oxidation can be attributed to the in situ evolution of the $\text{CoNi}_{0.25}\text{P}$ catalyst to a low-crystalline CoNi oxyhydroxide as the active state. Preliminary techno-economic

analysis (TEA) demonstrates that the technology is economically viable for upcycling waste PET into commodity chemicals and hydrogen under mild conditions.

To further improve the high activity and selectivity of electrochemical upcycling of waste PET in the electrolytic cell and effectively drive the hydrogen evolution reaction (HER) process, researchers have explored different types of electrocatalysts. Zheng and co-workers designed $\text{Ni}_3\text{N}/\text{W}_5\text{N}_4$ electrocatalysts with barrier-free heterogeneous interfaces by a transition metal nitride-inducing growth strategy.⁷⁷ Due to the interfacial synergistic effect, superhydrophilic surface and multilevel Janus nanostructure, $\text{Ni}_3\text{N}/\text{W}_5\text{N}_4$ has Pt-like HER performance and excellent stability (~ 300 h), showing high activity and selectivity in the electrochemical upcycling of waste PET. A value-added HCOOH product with high Faradaic efficiency of about 85% was produced. In a solar-driven electrolytic cell, $\text{Ni}_3\text{N}/\text{W}_5\text{N}_4$ also demonstrated the ability to efficiently recycle PET from seawater into H_2 and HCOOH. Wang et al. prepared CuO nanowire catalysts by in situ self-growth by simply immersing a copper sheet into an alkaline solution containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and then annealing it in an air atmosphere.⁷⁸ In the electrochemical upcycling of PET waste in the electrolytic cell, the electrocatalyst can achieve high selectivity (selectivity up to 86.5%) of PET hydrolysate to formate product, and the total Faradaic efficiency is 88%, indicating that the electrocatalyst has high selectivity and energy efficiency. Chen et al. synthesized a Pd-modified nickel foam (Pd/NF) catalyst by a simple displacement reaction of Ni foam in H_2PdCl_4 aqueous solution.⁷⁹ The Pd/NF electrocatalyst exhibited excellent electrocatalytic activity (400 mA cm^{-2} at 0.7 V vs RHE) and high product selectivity in electrolytic cell-based electrochemical upcycling of waste PET. The selectivity and Faradaic efficiency of carbonate products were 95% and 93%, respectively, while the yield of terephthalate was 99%.

In addition to waste PET, other waste plastics can also be recycled by electrochemical technology based on electrolytic cells. Vernoux and co-workers first achieved the upcycling of waste poly(methyl methacrylate) (PMMA) into hydrogen by electrooxidation in an electrolytic cell under mild conditions (atmospheric pressure, 70°C).⁸⁰ Since PMMA is a solid material insoluble in water and soft acid/alkaline electrolytic solution, to overcome the mass transfer limitation, the isopropanol (IPA)/ H_2O binary solvent/electrolyte solution (1 M H_2SO_4 in 80% v/v IPA/ H_2O) was used to dissolve PMMA by stirring and heating at 50°C for 30 min. The binary solvent composition of 80% v/v IPA/ H_2O dissolves PMMA by forming hydrogen bonds between water molecules and polymer ester groups to make polymer chains hydrophilic and expose hydrophobic side chains to IPA molecules. This results in isolated PMMA chains in solution avoiding cluster formation. The electrooxidation of dissolved real PMMA particles in IPA/ H_2O binary solvent was carried out on commercial and homemade Pt/C-based anodic electrocatalyst in an acidic medium at 70°C , and the upcycling of waste PMMA to H_2 in an electrolytic cell was successfully achieved.

Using diluted nitric acid as a solvent to depolymerize waste plastics, Reisner and co-workers even achieved electrochemical upcycling of chemically inert PE into gaseous hydrocarbons.⁸¹ PE was first oxidized and decomposed into dicarboxylic acids by 6 wt % HNO_3 at a low temperature of 180°C for 4 h, with a carbon yield of about 40%. The results of HPLC showed that the decomposition products mainly included succinic acid (44%) and glutaric acid (22%). Other products are acetic acid (21%),

adipic acid (9%), and propionic acid (4%). Then, in a two-electrode electrolytic cell, with carbon paper as the working electrode and platinum foil as the counter electrode, the decomposition products (carboxylic acid intermediates) are electrochemically converted to alkenes (ethylene and propylene) in a solvent mixture of water and methanol with sodium hydroxide adjusted to pH 10, accompanied by the formation of hydrogen and carbon dioxide as byproducts. Although the current total yield from PE to hydrocarbons (ethylene and propylene) is low at 7.6%, the technology is relatively mild (180°C) and significantly reduces the thermal energy input compared to other upcycling technologies such as pyrolysis, gasification, and hydrogenolysis. In addition, the resulting gaseous hydrocarbons are easily separated and can be used to synthesize new plastics or other valuable chemicals, which provides an entry point for closed-loop chemical recycling of waste PE. With the process improvement and the development of highly efficient catalysts, it is believed that there is a lot of scope to improve the yield and selectivity.

■ ELECTROCHEMICAL REMOVAL OF MICROPLASTICS

The electrochemical technology based on the electrolytic cell can also be used for the efficient removal of microplastics. In an electrolytic cell, Xing et al. achieved efficient removal of epoxy resins in carbon fiber reinforced plastic (CFRP), a polymer blend, to recover carbon fibers (CFs).⁸² In NaCl electrolyte containing KOH catalyst, CFRP was immersed as an anode and stainless-steel strip as the cathode. In the process of electrochemical removal, the C–N bond of the amide bond in CFRP formed by the cyano group of the cross-linker dicyandiamide and the hydroxyl group of the bisphenol A epoxy resin was first broken, and then the ether, benzyl, secondary and tertiary amine groups were broken, resulting in the gradual degradation of the epoxy resin matrix. The results showed that up to 99.9% of the epoxy resins in CFRP were degraded after 36 h at 75°C . Compared to the temperature required for thermal decomposition of epoxy resins (approximately $300\text{--}600^\circ\text{C}$ under nitrogen or air atmospheres), the electrochemical technology can achieve efficient removal at low temperatures.

Through electrooxidation (EO) technology, Drogui and his co-workers even achieved efficient removal of polystyrene in the electrolytic cell.^{83,84} Electrooxidation is an electrochemical technology that generates hydroxyl ($\cdot\text{OH}$) and other oxidizing radicals in situ through direct and indirect electrochemical methods to break the polymeric bonds of microplastics and thus degrade microplastics into nontoxic molecules such as water and carbon dioxide. Drogui and co-workers first reported the electrochemical removal of polystyrene microbeads of $26 \mu\text{m}$ size and obtained a degradation rate of $58 \pm 21\%$ within 1 h.⁸³ The experiments were carried out in an electrolytic cell placed in a box with ice cubes at room temperature. The anode and cathode of the electrolytic cell with a spacing of 1 cm are fixed vertically and connected to the positive and negative outputs of the DC power supply, respectively. Boron-doped diamond (BDD), mixed metal oxide, and iridium oxide electrodes were used as anodes and titanium electrodes were used as cathodes. Na_2SO_4 , NaNO_3 , and NaCl were added as electrolytes to improve the conductivity. No MPs of smaller size were detected in DLS and SEM analysis, no characteristic peak of $\text{C}=\text{O}$ was detected in the FTIR spectra, and TOC analysis showed that no liquid byproducts were formed by the electrooxidation of MP. The above results indicated that MP was directly converted into

gaseous products such as CO₂ rather than smaller particles. Based on the above analysis results, they proposed a preliminary mechanism for the degradation of polystyrene MPs by anodic oxidation with the BDD electrode. First, the water on the anode surface produces hydroxyl radicals that can break the C—H of polystyrene, leading to the formation of the C—O. Subsequently, the C—C or C—Ph (where Ph denotes the phenolic group) of the polystyrene break, and the MPs are eventually fully oxidized to produce carbon dioxide and water. It is worth noting that in addition to direct anodic oxidation on the anode surface, indirect electrochemical oxidation through hypochlorite ions and persulfate ions (S₂O₈²⁻) in an aqueous solution can also lead to the removal of MPs when NaCl and Na₂SO₄ are used as supporting electrolytes.

To further investigate the effect of reactive oxygen species (ROS) on the electrochemical removal of plastics, Drogui and co-workers further performed electrooxidation (EO) and electro-peroxidation (EO-H₂O₂) experiments on PS nanospheres with a diameter of 100 ± 4 nm, which are more toxic compared to microplastics because they can absorb higher concentrations of contaminants.⁸⁴ The BDD electrode was chosen as the anode on which hydroxyl radicals were generated. Ti and carbon felt (CF) were selected as cathodes for electrooxidation (EO) and electro-peroxidation (EO-H₂O₂), respectively. The H₂O₂ in electro-peroxidation is generated by the two-electron reduction of O₂ on the CF cathode. Sodium sulfate (Na₂SO₄) was used as the supporting electrolyte to generate persulfate ions (S₂O₈²⁻) on the BDD anode. Due to the formation of strong oxidants such as hydroxyl radical, persulfate and hydrogen peroxide, the removal rate of the nanoplastics reached 86.8% ± 1.8% in 40 min. The removal of nanoplastics was evaluated by high-resolution mass spectrometry, TOC, UV-vis spectrophotometry, and 3D excitation and emission matrix (3D EEM) fluorescence analyses.

Although a study by Drogui et al. demonstrated that EO technology can efficiently degrade MPs in water to innocuous substances, further investigations are needed to determine whether the EO technology can remove MPs in real wastewater to ensure practical application of the technology. Real wastewater from washing machines is one of the main sources of mixed microplastics in surface water. Ganiyu et al. investigated the removal of mixed microplastics in washing machine effluent by electrooxidation technology.⁸⁵ The experiment was performed in a prepilot plant-scale electrochemical flow reactor with Ti/Pt or BDD as the anode, Ti as the cathode, and Na₂SO₄ as the supporting electrolyte. The experimental results reveal that the active species generated in the process of electrooxidation, such as hydroxyl radicals, sulfate radicals (SO₄²⁻), persulfate (S₂O₈²⁻) and active chlorine species (chlorite, chlorine dioxide, chlorite and chlorate), can efficiently degrade microplastics in washing machine wastewater and realize the mineralization of more than 90% of microplastics after 360 min. Therefore, electrooxidation technology is an efficient and effective technology to remove microplastics in real wastewater, which has practical application prospects.

The first step in waste plastics upcycling by electrochemical technology is usually to dissolve/predecompose the plastic solid in a solvent, such as the hydrolysis of PET by potassium hydroxide and the dissolution of PMMA by a binary solvent, followed by subsequent electrochemical upcycling. The type and yield of the intermediate products formed in the first step may determine the selectivity and yield of the final products. In addition, the solvent type also affects the Faradaic efficiency of

the electrolytic cell. Therefore, the discovery of suitable solvents that can dissolve/decompose different waste plastics is critical for electrochemical upcycling of waste plastics. Efficient electrocatalysts contribute to the generation of free radicals in the electrochemical removal, which is beneficial to improve the removal efficiency of microplastics. Additionally, the electrocatalyst is helpful to improve the selectivity and yield of target products in the electrochemical upcycling of waste plastics and achieve high Faradaic efficiency. A series of excellent electrocatalysts such as ConI_{0.25}P, Ni₃N/W₅N₄, and Pd/NF have been developed. However, the development of simple, cheap, and efficient electrocatalysts is still the focus of current research. Machine learning algorithms have been shown to accelerate the discovery and optimization of functional materials. For example, Ryan et al. developed a deep neural network (DNN) model based on known crystal structures to predict the possible composition and structure of unknown intermetallics.⁸⁶ Therefore, machine learning can be used to screen potential electrocatalysts with suitable band edge positions that meet the thermodynamic potentials of (micro)plastic removal/upcycling. The comprehensive application of conventional characterization techniques such as SEM, SERS, FTIR spectroscopy, Raman spectroscopy, XPS and in situ characterization techniques such as in situ transmission electron microscopy (TEM), in situ X-ray absorption spectroscopy, and in situ X-ray diffraction can help to clarify the structure–activity relationship of electrocatalysts, thus guiding the design and development of catalysts. At present, the electrolytic cell used for waste plastic treatment is mainly alkaline electrolytic cell and polymer electrolyte membrane (PEM) electrolytic cell. To overcome the energy loss caused by ohmic resistance at high current density and improve the energy efficiency of the electrolytic cell, more efforts are recommended to focus on the design of the electrolytic cell, for example, the use of membrane-electrode assembly. In addition to developing new types of electrolytic cells, further improvement of electrode structure, electrode spacing, electrode material, and power supply type is also needed for existing electrolytic cells.

Applications of electrochemical technology in the field of waste plastic upcycling and microplastic removal are summarized in Table 3 and Table 4. Although only a few studies have been published, electrochemical technology has shown potential to upcycle waste plastics under mild conditions and efficiently remove microplastics. However, the types of waste plastics in electrochemical upcycling are limited, and the current focus is on polyester plastics. Whether the highly selective upcycling of

Table 3. Applications of Electrochemical Technology in Waste Plastic Upcycling

Plastics	Conditions	Products	Faradaic efficiency	Ref
PET	Atmospheric pressure, 60 °C	Formates, >80% selectivity	/	48
PET	Atmospheric pressure, 80 °C	HCOOH	85%	77
PET	Atmospheric pressure, 180 °C	Formate, selectivity up to 86.5%	88%	78
PET	Atmospheric pressure, 60 °C	99% carbonate yield, 95% selectivity	93%	79
PMMA	Atmospheric pressure, 70 °C	H ₂	/	80
PE	Atmospheric pressure, 180 °C	Ethylene and propylene	/	81

Table 4. Applications of Electrochemical Technology in Microplastic Removal

Plastics	Conditions	Removal rate	Reaction time	Ref
CFRP (polymer blends)	Atmospheric pressure, 75 °C	99.9%	36 h	82
PS	Ambient condition	58 ± 21%	1 h	83
PS	Ambient condition	86.8% ± 1.8%	40 min	84
Mixed MPs in washing machine effluent	Ambient condition	More than 90%	360 min	85

other plastics, especially polyolefin plastics, can be achieved under mild conditions needs further exploration. At present, for polyester plastics, electrochemical technology can achieve upcycling with high selectivity and high yield. When electrochemical technology is applied to microplastic removal, a high removal rate can be achieved in a short time through electrooxidation. However, electrooxidation, similar to the electro-Fenton process, requires the consumption of electrolytes to produce active species, resulting in other operating costs besides electricity. The Faradaic efficiency of waste plastics upcycling through electrochemical technology can be higher than 90%, which has a competitive energy efficiency compared with other waste plastic treatment methods such as pyrolysis, gasification, and hydrotreatment.^{79,87–91} However, the upcycling of waste plastics through electrochemical technology requires a few hours of pretreatment of the plastic, during which the high concentration of potassium hydroxide solution and heat provided will reduce the energy efficiency of the entire upcycling process. In view of this, the energy efficiency of the entire process remains to be investigated to further evaluate the sustainability of electrochemical technology.

CONCLUSION: REMARKS AND PERSPECTIVES

The previous studies mentioned above indicate that plasma technology, Fenton process, and electrochemical technology have great potential in waste plastic treatment due to their mild conditions and high efficiency. Among the three technologies, plasma technology and electrochemical technology can be used for not only the removal of microplastics but also the upcycling of waste plastics, while the Fenton process is only used for the former. Plasma technology achieves the highest removal efficiency, followed by electrochemical technology, and finally the Fenton process. For the upcycling of waste plastics, plasma technology can realize the upcycling of more kinds of plastics under the mildest conditions, which can be achieved under ambient conditions, and the process is simple, highly efficient, and low cost, while electrochemical technology is conducive to the highly selective upcycling of waste plastics. In general, plasma technology is the most promising emerging technology for waste plastics upcycling and microplastics removal.

However, these emerging technologies have a low level of technological readiness. To expedite the development of these technologies, it is suggested to conduct more in-depth studies in the fields of efficient catalyst development, reaction mechanism understanding, etc. Further understanding of the reaction mechanism will help to adjust the type of active substance in the reaction, to achieve high selectivity of target products and high conversion or removal rates of waste plastics. The application of advanced analytical techniques, such as

MALDI-MS, ESI-MS, 3D EEM fluorescence, HPLC, GC-MS, NMR spectroscopy, UV–vis spectrophotometry, and isotope tracer technique, is helpful to clarify the type of active substances in the reaction, the effects of different active substances on waste plastic conversion/removal, and the conversion/removal pathways of waste plastic. Computational chemistry, such as DFT calculations, is also beneficial to further understanding the reaction mechanism. As previous studies have investigated only a few plastic types, further research is suggested to verify whether these emerging technologies can efficiently remove or upcycle other types of waste plastics, especially mixed plastic waste in the real world, under mild conditions. In addition, the scattered studies of these emerging technologies on composites are limited to CFRP. The results indicate that they have positive effects on the removal of plastics in composites and the recovery of carbon fiber. Further exploration of the application of these emerging technologies to composite materials can expand their practical applications. Pilot-scale studies are also needed to facilitate the commercial application of these emerging technologies. Moreover, techno-economic analysis and life cycle analysis are essential for the scale-up of these emerging technologies.

By using renewable energy sources such as solar and wind to power these processes, these emerging technologies can become more sustainable and cost-effective compared to traditional methods that rely on fossil fuels. Renewable energy sources are becoming increasingly competitive with fossil fuels in terms of cost, and over time, they are likely to become even more affordable. This means that powering the upcycling of waste plastics with renewable energy could potentially lead to lower operational costs and increase its economic viability. Additionally, the reduced overall carbon footprint makes it more environmentally sustainable. Overall, by using renewable energy sources to drive the upcycling of waste plastics, it can help to reduce plastic waste, create valuable products, and promote sustainable and cost-effective practices.

In addition, microplastics are widely distributed in the environment and need to be identified, quantified, and separated before they can be treated with these emerging technologies. Currently, microscope-combined software, Raman spectroscopy and FTIR spectroscopy have been used to measure and identify the shape and type of microplastics in the environment. Sequential pyrolysis gas chromatography–mass spectrometry (PY-GC-MS) and thermal extraction desorption gas chromatography–mass spectrometry (TED-GC-MS) have also been used to determine microplastic content in the environment in addition to identifying microplastic types. The separation and collection of microplastics can be carried out by filtration, flotation and other methods.²¹ For the most efficient removal of microplastics in the environment, emerging technologies such as plasma technology need to be combined effectively with these approaches, and there needs to be further development of advanced methods for the identification, quantification and separation of microplastics in the environment. In addition, for the removal of PVC microplastics, understanding the behavior and ultimate fate of chlorine, the main component in PVC, is of great significance for assessing its environmental impact. In current studies on the removal of PVC microplastics by the mentioned emerging technologies, the investigation into the behavior of chlorine in PVC only focuses on how chlorine is dissociated from PVC. Combined with other literature, it can be inferred that the chlorine may be released in the form of hydrogen chloride and further react with inorganic matter to

form metal chloride.⁹² However, in-depth investigations are still required to understand the behavior and ultimate fate of chlorine in the PVC removal process.

Overall, these three emerging technologies hold great promise in waste plastics treatment, despite their low level of technological readiness. It is anticipated that with efficient catalyst development, reaction mechanism understanding, etc., these emerging technologies will eventually lead to commercial applications to address the potential ecological and human health threats posed by the increasing amount of waste plastics and microplastics in the environment.

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Jing Su: Methodology, investigation, writing—original draft. Tan Li: Methodology, investigation. Wen Xie, Cong Wang, Linjia Yin and Tianrun Yan: Investigation. Kaige Wang: Conceptualization, writing—review and editing, funding acquisition.

Notes

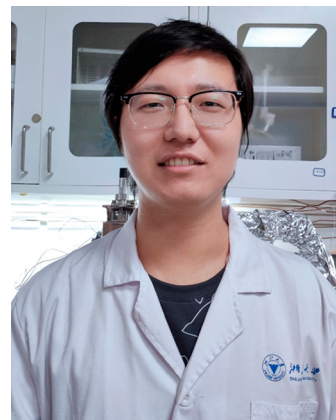
The authors declare no competing financial interest.

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Wen Xie is a Master's student in the Department of Energy Engineering at Zhejiang University. Her current research mainly focuses on the oxidative pyrolysis of plastic waste. She hopes to explore the impact of incorporation of oxygen on the kinetics and product of plastic waste pyrolysis.



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Kaige Wang is a professor in the College of Energy Engineering at Zhejiang University. His research mainly focus on thermochemical conversion of organic wastes for the production of fuels, chemicals and other value-added products. Dr. Wang has published over 70 refereed papers and book chapters. He edited *Fast Pyrolysis of Biomass Advances in Science and Technology*, published in 2017 by The Royal Society of Chemistry. Dr. Wang obtained his Ph.D. in Mechanical Engineering and Biorenewable Resources and Technology (co-major) from Iowa State University at 2014 under the supervision of Dr. Robert Brown. He

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ABBREVIATIONS AND NOMENCLATURE

PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PET	Polyethylene terephthalate
MPs	Microplastics
POPs	Persistent organic pollutants
HDPE	High-density polyethylene
DBD	Dielectric barrier discharge
AC	Alternating current
DC	Direct current
NMR	Nuclear magnetic resonance
GPC	Gel permeation chromatography
MALDI	Matrix-assisted laser desorption/ionization
ESI	Electrospray ionization
GC-MS	Gas chromatography–mass spectrometry
ROS	Reactive oxygen species
SEM	Scanning electron microscopy
FTIR	Fourier-transform infrared
XPS	X-ray photoelectron spectroscopy
SERS	Surface-enhanced Raman scattering
PMS	Peroxymonosulfate
EPR	Electron paramagnetic resonance
HPLC	High-performance liquid chromatography
TOC	Total organic carbon
UPRs	Unsaturated polyester resins
CFs	Carbon fibers
PTA	Terephthalic acid
EG	Ethylene glycol
TEA	Techno-economic analysis
MEA	Membrane electrode assembly
HER	Hydrogen evolution reaction
PMMA	Poly(methyl methacrylate)
IPA	Isopropanol
CFRP	Carbon fiber reinforced plastic
EO	Electrooxidation
BDD	Boron-doped diamond
DLS	Dynamic light scattering
CF	Carbon felt
3D EEM	3D excitation and emission matrix
UV–vis	Ultraviolet–visible

REFERENCES

- (1) Xu, S.; Ma, J.; Ji, R.; Pan, K.; Miao, A.-J. Microplastics in aquatic environments: occurrence, accumulation, and biological effects. *Sci. Total Environ.* **2020**, *703*, 134699.

- (2) Lehner, R.; Weder, C.; Petri-Fink, A.; Rothen-Rutishauser, B. Emergence of nanoplastic in the environment and possible impact on human health. *Environmental science technology* **2019**, *53* (4), 1748–1765.
- (3) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, use, and fate of all plastics ever made. *Science Advances* **2017** *3* (7), e1700782. (accessed 2022/06/27).
- (4) Ouyang, Z.; Yang, Y.; Zhang, C.; Zhu, S.; Qin, L.; Wang, W.; He, D.; Zhou, Y.; Luo, H.; Qin, F. Recent advances in photocatalytic degradation of plastics and plastic-derived chemicals. *Journal of Materials Chemistry A* **2021**, *9* (23), 13402–13441.
- (5) He, P.; Chen, L.; Shao, L.; Zhang, H.; Lü, F. Municipal solid waste (MSW) landfill: A source of microplastics? -Evidence of microplastics in landfill leachate. *Water Res.* **2019**, *159*, 38–45.
- (6) Wilcox, C.; Heathcote, G.; Goldberg, J.; Gunn, R.; Peel, D.; Hardesty, B. D. Understanding the sources and effects of abandoned, lost, and discarded fishing gear on marine turtles in northern Australia. *Conservation Biology* **2015**, *29* (1), 198–206 (accessed 2022/06/27).
- (7) Fossi, M. C.; Pedà, C.; Compa, M.; Tsangaris, C.; Alomar, C.; Claro, F.; Ioakeimidis, C.; Galgani, F.; Hema, T.; Deudero, S.; et al. Bioindicators for monitoring marine litter ingestion and its impacts on Mediterranean biodiversity. *Environ. Pollut.* **2018**, *237*, 1023–1040.
- (8) Hou, Q.; Zhen, M.; Qian, H.; Nie, Y.; Bai, X.; Xia, T.; Laiq Ur Rehman, M.; Li, Q.; Ju, M. Upcycling and catalytic degradation of plastic wastes. *Cell Reports Physical Science* **2021**, *2* (8), 100514.
- (9) Rahimi, A.; García, J. M. Chemical recycling of waste plastics for new materials production. *Nature Reviews Chemistry* **2017**, *1* (6), 0046.
- (10) Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and chemical recycling of solid plastic waste. *Waste Manage.* **2017**, *69*, 24–58.
- (11) Chen, X.; Wang, Y.; Zhang, L. Recent Progress in the Chemical Upcycling of Plastic Wastes. *ChemSusChem* **2021**, *14* (19), 4137–4151 (accessed 2022/07/03).
- (12) Coates, G. W.; Getzler, Y. D. Y. L. Chemical recycling to monomer for an ideal, circular polymer economy. *Nature Reviews Materials* **2020**, *5* (7), 501–516.
- (13) Morris, J. Recycling versus incineration: an energy conservation analysis. *Journal of Hazardous Materials* **1996**, *47* (1), 277–293.
- (14) Zitko, V.; Hanlon, M. Another source of pollution by plastics: Skin cleaners with plastic scrubbers. *Mar. Pollut. Bull.* **1991**, *22* (1), 41–42.
- (15) Hale, R. C.; Seeley, M. E.; La Guardia, M. J.; Mai, L.; Zeng, E. Y. A Global Perspective on Microplastics. *Journal of Geophysical Research: Oceans* **2020**, *125* (1), No. e2018JC014719, (accessed 2022/06/28).
- (16) Nizzetto, L.; Bussi, G.; Futter, M. N.; Butterfield, D.; Whitehead, P. G. A theoretical assessment of microplastic transport in river catchments and their retention by soils and river sediments. *Environmental Science: Processes & Impacts* **2016**, *18* (8), 1050–1059.
- (17) Enyoh, C. E.; Verla, A. W.; Verla, E. N.; Ibe, F. C.; Amaobi, C. E. Airborne microplastics: a review study on method for analysis, occurrence, movement and risks. *Environmental Monitoring and Assessment* **2019**, *191* (11), 668.
- (18) Munari, C.; Infantini, V.; Scoponi, M.; Rastelli, E.; Corinaldesi, C.; Mistri, M. Microplastics in the sediments of Terra Nova Bay (Ross Sea, Antarctica). *Mar. Pollut. Bull.* **2017**, *122* (1), 161–165.
- (19) Rodrigues, M. O.; Abrantes, N.; Gonçalves, F. J. M.; Nogueira, H.; Marques, J. C.; Gonçalves, A. M. M. Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). *Science of The Total Environment* **2018**, *633*, 1549–1559.
- (20) Cole, M.; Lindeque, P.; Fileman, E.; Halsband, C.; Goodhead, R.; Moger, J.; Galloway, T. S. Microplastic Ingestion by Zooplankton. *Environ. Sci. Technol.* **2013**, *47* (12), 6646–6655.
- (21) Zhang, S.; Wang, J.; Liu, X.; Qu, F.; Wang, X.; Wang, X.; Li, Y.; Sun, Y. Microplastics in the environment: A review of analytical methods, distribution, and biological effects. *TrAC Trends in Analytical Chemistry* **2019**, *111*, 62–72.
- (22) Hidalgo-Ruz, V.; Gutow, L.; Thompson, R. C.; Thiel, M. Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification. *Environ. Sci. Technol.* **2012**, *46* (6), 3060–3075.
- (23) Ng, E.-L.; Huerta Lwanga, E.; Eldridge, S. M.; Johnston, P.; Hu, H.-W.; Geissen, V.; Chen, D. An overview of microplastic and nanoplastic pollution in agroecosystems. *Science of The Total Environment* **2018**, *627*, 1377–1388.
- (24) Boerger, C. M.; Lattin, G. L.; Moore, S. L.; Moore, C. J. Plastic ingestion by planktivorous fishes in the North Pacific Central Gyre. *Mar. Pollut. Bull.* **2010**, *60* (12), 2275–2278.
- (25) Bhattacharya, P.; Lin, S.; Turner, J. P.; Ke, P. C. Physical Adsorption of Charged Plastic Nanoparticles Affects Algal Photosynthesis. *J. Phys. Chem. C* **2010**, *114* (39), 16556–16561.
- (26) Kalčíková, G.; Žgajnar Gotvajn, A.; Kladnik, A.; Jemec, A. Impact of polyethylene microbeads on the floating freshwater plant duckweed *Lemma minor*. *Environ. Pollut.* **2017**, *230*, 1108–1115.
- (27) Tang, K. H. D.; Hadibarata, T. Microplastics removal through water treatment plants: Its feasibility, efficiency, future prospects and enhancement by proper waste management. *Environmental Challenges* **2021**, *5*, 100264.
- (28) Ganesh Kumar, A. G.; Anjana, K.; Hinduja, M.; Sujitha, K.; Dharani, G. Review on plastic wastes in marine environment – Biodegradation and biotechnological solutions. *Mar. Pollut. Bull.* **2020**, *150*, 110733.
- (29) Liu, L.; Xu, M.; Ye, Y.; Zhang, B. On the degradation of (micro)plastics: Degradation methods, influencing factors, environmental impacts. *Science of The Total Environment* **2022**, *806*, 151312.
- (30) Agarwal, S. Biodegradable Polymers: Present Opportunities and Challenges in Providing a Microplastic-Free Environment. *Macromol. Chem. Phys.* **2020**, *221* (6), 2000017.
- (31) Nabi, I.; Bacha, A.; Ahmad, F.; Zhang, L. Application of titanium dioxide for the photocatalytic degradation of macro- and micro-plastics: A review. *Journal of Environmental Chemical Engineering* **2021**, *9* (5), 105964.
- (32) Dimitrakellis, P.; Delikonstantis, E.; Stefanidis, G. D.; Vlachos, D. G. Plasma technology for lignocellulosic biomass conversion toward an electrified biorefinery. *Green Chem.* **2022**, *24* (7), 2680–2721.
- (33) Topolovec, B.; Škoro, N.; Puač, N.; Petrovic, M. Pathways of organic micropollutants degradation in atmospheric pressure plasma processing – A review. *Chemosphere* **2022**, *294*, 133606.
- (34) Tang, L.; Huang, H.; Hao, H.; Zhao, K. Development of plasma pyrolysis/gasification systems for energy efficient and environmentally sound waste disposal. *J. Electrostat.* **2013**, *71* (5), 839–847.
- (35) Guddeti, R. R.; Knight, R.; Grossmann, E. D. Depolymerization of Polyethylene Using Induction-Coupled Plasma Technology. *Plasma Chemistry and Plasma Processing* **2000**, *20* (1), 37–64.
- (36) Guddeti, R. R.; Knight, R.; Grossmann, E. D. Depolymerization of Polypropylene in an Induction-Coupled Plasma (ICP) Reactor. *Ind. Eng. Chem. Res.* **2000**, *39* (5), 1171–1176.
- (37) Guo, X.-F.; Kim, G.-J. Ultrafine carbon black produced by pyrolysis of polyethylene using a novel DC-thermal plasma process. *J. Phys. Chem. Solids* **2008**, *69* (5), 1224–1227.
- (38) Park, H. S.; Kim, C. G.; Kim, S. J. Characteristics of PE Gasification by Steam Plasma. *Journal of Industrial and Engineering Chemistry* **2006**, *12* (2), 216–223.
- (39) Punčochář, M.; Ruj, B.; Chatterj, P. K. Development of Process for Disposal of Plastic Waste Using Plasma Pyrolysis Technology and Option for Energy Recovery. *Procedia Engineering* **2012**, *42*, 420–430.
- (40) Sekiguchi, H.; Orimo, T. Gasification of polyethylene using steam plasma generated by microwave discharge. *Thin Solid Films* **2004**, *457* (1), 44–47.
- (41) Tang, L.; Huang, H. Decomposition of polyethylene in radio-frequency nitrogen and water steam plasmas under reduced pressures. *Fuel Process. Technol.* **2007**, *88* (6), 549–556.
- (42) Tang, L.; Huang, H.; Zhao, Z.; Wu, C. Z.; Chen, Y. Pyrolysis of Polypropylene in a Nitrogen Plasma Reactor. *Ind. Eng. Chem. Res.* **2003**, *42* (6), 1145–1150.
- (43) Huang, H.; Tang, L. Treatment of organic waste using thermal plasma pyrolysis technology. *Energy Conversion and Management* **2007**, *48* (4), 1331–1337.

- (44) Yao, L.; King, J.; Wu, D.; Chuang, S. S. C.; Peng, Z. Non-thermal plasma-assisted hydrogenolysis of polyethylene to light hydrocarbons. *Catal. Commun.* **2021**, *150*, 106274.
- (45) Yao, L.; King, J.; Wu, D.; Ma, J.; Li, J.; Xie, R.; Chuang, S. S. C.; Miyoshi, T.; Peng, Z. Non-thermal plasma-assisted rapid hydrogenolysis of polystyrene to high yield ethylene. *Nat. Commun.* **2022**, *13* (1), 885.
- (46) Ren, J.; Li, J.; Zhen, Y.; Wang, J.; Niu, Z. Removal of polyvinyl chloride microplastic by dielectric barrier discharge plasma. *Sep. Purif. Technol.* **2022**, *290*, 120832.
- (47) Proost, J. State-of-the art CAPEX data for water electrolyzers, and their impact on renewable hydrogen price settings. *Int. J. Hydrogen Energy* **2019**, *44* (9), 4406–4413.
- (48) Zhou, H.; Ren, Y.; Li, Z.; Xu, M.; Wang, Y.; Ge, R.; Kong, X.; Zheng, L.; Duan, H. Electrocatalytic upcycling of polyethylene terephthalate to commodity chemicals and H₂ fuel. *Nat. Commun.* **2021**, *12* (1), 4679.
- (49) Bogaerts, A.; Neyts, E. C. Plasma Technology: An Emerging Technology for Energy Storage. *ACS Energy Letters* **2018**, *3* (4), 1013–1027.
- (50) Winter, L. R.; Chen, J. G. N₂ Fixation by Plasma-Activated Processes. *Joule* **2021**, *5* (2), 300–315.
- (51) Wu, Z.; Zhu, D.; Chen, Z.; Yao, S.; Li, J.; Gao, E.; Wang, W. Enhanced energy efficiency and reduced nanoparticle emission on plasma catalytic oxidation of toluene using Au/ γ -Al₂O₃ nanocatalyst. *Chem. Eng. J.* **2022**, *427*, 130983.
- (52) Fenton, H. J. H. LXXIII.—Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society, Transactions* **1894**, *65*, 899–910.
- (53) Babuponnusami, A.; Muthukumar, K. A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering* **2014**, *2* (1), 557–572.
- (54) Liang, D.; Li, N.; An, J.; Ma, J.; Wu, Y.; Liu, H. Fenton-based technologies as efficient advanced oxidation processes for microcystin-LR degradation. *Science of The Total Environment* **2021**, *753*, 141809.
- (55) Walling, S. A.; Um, W.; Corkhill, C. L.; Hyatt, N. C. Fenton and Fenton-like wet oxidation for degradation and destruction of organic radioactive wastes. *npj Materials Degradation* **2021**, *5* (1), 50.
- (56) Liu, B.; Jiang, Q.; Qiu, Z.; Liu, L.; Wei, R.; Zhang, X.; Xu, H. Process analysis of microplastic degradation using activated PMS and Fenton reagents. *Chemosphere* **2022**, *298*, 134220.
- (57) Pan, X.; Gu, Z.; Chen, W.; Li, Q. Preparation of biochar and biochar composites and their application in a Fenton-like process for wastewater decontamination: A review. *Science of The Total Environment* **2021**, *754*, 142104.
- (58) Ahmed, N.; Vione, D.; Rivoira, L.; Carena, L.; Castiglioni, M.; Bruzzoniti, M. C. A Review on the Degradation of Pollutants by Fenton-Like Systems Based on Zero-Valent Iron and Persulfate: Effects of Reduction Potentials, pH, and Anions Occurring in Waste Waters. *Molecules* **2021**, *26* (15), 4584.
- (59) Xiang, Y.; Liu, H.; Zhu, E.; Yang, K.; Yuan, D.; Jiao, T.; Zhang, Q.; Tang, S. Application of inorganic materials as heterogeneous cocatalyst in Fenton/Fenton-like processes for wastewater treatment. *Sep. Purif. Technol.* **2022**, *295*, 121293.
- (60) Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* **2018**, *334*, 1502–1517.
- (61) Zhao, X.; Jiang, J.; Pang, S.; Guan, C.; Li, J.; Wang, Z.; Ma, J.; Luo, C. Degradation of iopamidol by three UV-based oxidation processes: Kinetics, pathways, and formation of iodinated disinfection byproducts. *Chemosphere* **2019**, *221*, 270–277.
- (62) Kang, J.; Zhou, L.; Duan, X.; Sun, H.; Ao, Z.; Wang, S. Degradation of Cosmetic Microplastics via Functionalized Carbon Nanosprings. *Matter* **2019**, *1* (3), 745–758.
- (63) Ziembowicz, S.; Kida, M. Limitations and future directions of application of the Fenton-like process in micropollutants degradation in water and wastewater treatment: A critical review. *Chemosphere* **2022**, *296*, 134041.
- (64) Miao, F.; Liu, Y.; Gao, M.; Yu, X.; Xiao, P.; Wang, M.; Wang, S.; Wang, X. Degradation of polyvinyl chloride microplastics via an electro-Fenton-like system with a TiO₂/graphite cathode. *Journal of Hazardous Materials* **2020**, *399*, 123023.
- (65) Rummel, C. D.; Jahnke, A.; Gorokhova, E.; Kühnel, D.; Schmitt-Jansen, M. Impacts of Biofilm Formation on the Fate and Potential Effects of Microplastic in the Aquatic Environment. *Environmental Science & Technology Letters* **2017**, *4* (7), 258–267.
- (66) Xing, R.; Chen, Z.; Sun, H.; Liao, H.; Qin, S.; Liu, W.; Zhang, Y.; Chen, Z.; Zhou, S. Free radicals accelerate in situ ageing of microplastics during sludge composting. *Journal of Hazardous Materials* **2022**, *429*, 128405.
- (67) Xing, R.; Sun, H.; Du, X.; Lin, H.; Qin, S.; Chen, Z.; Zhou, S. Enhanced degradation of microplastics during sludge composting via microbially-driven Fenton reaction. *Journal of Hazardous Materials* **2023**, *449*, 131031.
- (68) Wang, B.; Wang, X.; Xu, N.; Shen, Y.; Lu, F.; Liu, Y.; Huang, Y.; Hu, Z. Recycling of carbon fibers from unsaturated polyester composites via a hydrolysis-oxidation synergistic catalytic strategy. *Compos. Sci. Technol.* **2021**, *203*, 108589.
- (69) Gusain, R.; Gupta, K.; Joshi, P.; Khatri, O. P. Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Adv. Colloid Interface Sci.* **2019**, *272*, 102009.
- (70) Babuponnusami, A.; Muthukumar, K. Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes. *Chem. Eng. J.* **2012**, *183*, 1–9.
- (71) Deng, Y.; Zhao, R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Current Pollution Reports* **2015**, *1* (3), 167–176.
- (72) Zheng, T.; Wang, J.; Wang, Q.; Meng, H.; Wang, L. Research trends in electrochemical technology for water and wastewater treatment. *Applied Water Science* **2017**, *7* (1), 13–30.
- (73) Lacasa, E.; Cotillas, S.; Saez, C.; Lobato, J.; Cañizares, P.; Rodrigo, M. A. Environmental applications of electrochemical technology. What is needed to enable full-scale applications? *Current Opinion in Electrochemistry* **2019**, *16*, 149–156.
- (74) Hori, T.; Kobayashi, K.; Teranishi, S.; Nagao, M.; Hibino, T. Fuel cell and electrolyzer using plastic waste directly as fuel. *Waste Manage.* **2020**, *102*, 30–39.
- (75) Hibino, T.; Kobayashi, K.; Hitomi, T. Solid Oxide Fuel Cell Using Plastic Waste Directly as Fuel. *Chem. Lett.* **2021**, *50* (10), 1729–1732.
- (76) Hibino, T.; Kobayashi, K.; Teranishi, S.; Hitomi, T. Solid Oxide Fuel Cell Using Municipal Solid Waste Directly as Fuel: Biomass, Resin, Plastic, and Food Waste. *ACS Sustainable Chem. Eng.* **2021**, *9* (8), 3124–3136.
- (77) Ma, F.; Wang, S.; Gong, X.; Liu, X.; Wang, Z.; Wang, P.; Liu, Y.; Cheng, H.; Dai, Y.; Zheng, Z.; et al. Highly efficient electrocatalytic hydrogen evolution coupled with upcycling of microplastics in seawater enabled via Ni₃N/WSN₄ janus nanostructures. *Applied Catalysis B: Environmental* **2022**, *307*, 121198.
- (78) Wang, J.; Li, X.; Zhang, T.; Chen, Y.; Wang, T.; Zhao, Y. Electro-Reforming Polyethylene Terephthalate Plastic to Co-Produce Valued Chemicals and Green Hydrogen. *J. Phys. Chem. Lett.* **2022**, *13* (2), 622–627.
- (79) Shi, R.; Liu, K.-S.; Liu, F.; Yang, X.; Hou, C.-C.; Chen, Y. Electrocatalytic reforming of waste plastics into high value-added chemicals and hydrogen fuel. *Chem. Commun.* **2021**, *57* (94), 12595–12598.
- (80) Grimaldos-Osorio, N.; Sordello, F.; Passananti, M.; González-Cobos, J.; Bonhommé, A.; Vernoux, P.; Caravaca, A. From plastic-waste to H₂: A first approach to the electrochemical reforming of dissolved Poly(methyl methacrylate) particles. *Int. J. Hydrogen Energy* **2023**, *48*, 11899.
- (81) Pichler, C. M.; Bhattacharjee, S.; Rahaman, M.; Uekert, T.; Reisner, E. Conversion of Polyethylene Waste into Gaseous Hydrocarbons via Integrated Tandem Chemical–Photo/Electrocatalytic Processes. *ACS Catal.* **2021**, *11* (15), 9159–9167.

(82) Zhu, J.-H.; Chen, P.-y.; Su, M.-n.; Pei, C.; Xing, F. Recycling of carbon fibre reinforced plastics by electrically driven heterogeneous catalytic degradation of epoxy resin. *Green Chem.* **2019**, *21* (7), 1635–1647.

(83) Kiendrebeogo, M.; Karimi Estahbanati, M. R.; Khosravanipour Mostafazadeh, A.; Drogui, P.; Tyagi, R. D. Treatment of microplastics in water by anodic oxidation: A case study for polystyrene. *Environ. Pollut.* **2021**, *269*, 116168.

(84) Kiendrebeogo, M.; Karimi Estahbanati, M. R.; Ouarda, Y.; Drogui, P.; Tyagi, R. D. Electrochemical degradation of nanoplastics in water: Analysis of the role of reactive oxygen species. *Science of The Total Environment* **2022**, *808*, 151897.

(85) Durán, F. E.; de Araújo, D. M.; do Nascimento Brito, C.; Santos, E. V.; Ganiyu, S. O.; Martínez-Huitle, C. A. Electrochemical technology for the treatment of real washing machine effluent at pre-pilot plant scale by using active and non-active anodes. *J. Electroanal. Chem.* **2018**, *818*, 216–222.

(86) Ryan, K.; Lengyel, J.; Shatruk, M. Crystal Structure Prediction via Deep Learning. *J. Am. Chem. Soc.* **2018**, *140* (32), 10158–10168.

(87) Zhou, N.; Dai, L.; Lv, Y.; Li, H.; Deng, W.; Guo, F.; Chen, P.; Lei, H.; Ruan, R. Catalytic pyrolysis of plastic wastes in a continuous microwave assisted pyrolysis system for fuel production. *Chem. Eng. J.* **2021**, *418*, 129412.

(88) Zhang, Y.; Ji, G.; Ma, D.; Chen, C.; Wang, Y.; Wang, W.; Li, A. Exergy and energy analysis of pyrolysis of plastic wastes in rotary kiln with heat carrier. *Process Safety and Environmental Protection* **2020**, *142*, 203–211.

(89) Midilli, A.; Kucuk, H.; Haciosmanoglu, M.; Akbulut, U.; Dincer, I. A review on converting plastic wastes into clean hydrogen via gasification for better sustainability. *International Journal of Energy Research* **2022**, *46* (4), 4001–4032 (accessed 2023/03/01).

(90) Dogu, O.; Pelucchi, M.; Van de Vijver, R.; Van Steenberghe, P. H. M.; D'Hooge, D. R.; Cuoci, A.; Mehl, M.; Frassoldati, A.; Faravelli, T.; Van Geem, K. M. The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Prog. Energy Combust. Sci.* **2021**, *84*, 100901.

(91) Wang, J.; Jiang, J.; Dong, X.; Zhang, Y.; Yuan, X.; Meng, X.; Zhan, G.; Wang, L.; Wang, Y.; Ragauskas, A. J. Catalytic cascade vapor-phase hydrotreatment of plastic waste into fuels and its sustainability assessment. *Green Chem.* **2022**, *24* (21), 8562–8571.

(92) Keane, M. A. Catalytic conversion of waste plastics: focus on waste PVC. *J. Chem. Technol. Biotechnol.* **2007**, *82* (9), 787–795 (accessed 2023/02/25).