A Review of the Current Microplastics Pollution and Degradation Methods

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Abstract:

Plastic pollution has been one of the most prominent problems humanity faces. In this paper, we will focus on Polypropylene (PP). The damage brought by microplastics and how the recent Covid-19 pandemic has worsened the situation will be described. The approaches by our team and others to process the waste PP into harmless or even value-added products will be discussed as well.

1. Microplastics and Covid-19

1.1 Detriments of Microplastics and the Severity of Microplastic Pollution

Microplastics can bring damage to the environment and potentially harm the human body. The microplastic pollution is getting more severe, and the ubiquity of microplastics can pose an immense threat to the world.

Microplastics have been proven to be harmful to certain aquatic life and might heavily damage the ecosystem and food chain in the long run. The negative impact of microplastics derived from surgical masks on *Tigriopus japonicus* has been investigated. *Tigriopus japonicus* is a kind of marine copepod that helps complete the food chain by linking the primary producer with other aquatic consumers (Raisuddin et al., 2007). At the concentration of 100 pieces of microplastics per mL, the maturation time and the birth spacing of *T. japonicus* become significantly longer (Sun et al., 2021). The fecundity also decreases when the microplastic concentration increases (Sun et al., 2021). Given the role of *T. japonicus* in the food chain, the impact can reduce the available food resources for other marine lives and disturb the balance of the marine ecosystem (Sun et al., 2021). Microplastics have also been found to be toxic to bivalves. The uptake of microplastics will cause lysosomal perturbations and oxidative stress (Canesi et al., 2012). Apart from that, studies have found that the consumption of microplastics can cause various degrees of harm to fish, molluscs, crustaceans, marine mammals and microbiota, affecting a wide range of aquatic lives (Ajith et al., 2020).

The impact of microplastics on human health is still under investigation. However, different studies show that the debris can pose various potential health risks. Microplastics can induce oxidative stress in human cells and give rise to cytotoxicity (Rahman et al., 2021). Evidence also shows that microplastics might influence cell metabolism and disrupt body immune function (Rahman et al., 2021).

Microplastic pollution is becoming more severe, and microplastic debris is ubiquitous. In 2005, on average, around 2 billion pieces of microplastics entered the California Coast every 24 hours (Moore et al., 2005). Denmark was also emitting around 21,500 tons of microplastics per year (Auta et al., 2017). Microplastics were found to be present in different Oceans with various concentrations. They are present in the East Asian Seas and the Mediterranean Sea at a high concentration. Even remote regions in the Arctic and Antarctica are contaminated with microplastics (Auta et al., 2017). The ubiquity of microplastics is now posing an acute threat to humanity, as a study has found that 77% of its participants contain microplastics in their blood (Leslie et al., 2022).

Microplastic pollution is progressing at an alarming rate. Worse still, the Covid-19 pandemic is further fuelling it.

1.2 Covid-19 and microplastic pollution

In light of the Covid-19 pandemic, the general public wears disposable face masks to protect themselves from infections. Because of that, there is a massive surge in the usage and disposal of face masks. In Asia, it was estimated that more than 2.2 billion masks were used daily (Sangkham, 2020). The global monthly usage of masks was also roughly estimated to be 129 billion (Prata et al., 2020).

The use of face masks inevitably exacerbates microplastic pollution. The face masks are mainly made of polypropylene (PP) (Selvaranjan et al., 2021), and they could be eroded or fragmented by ocean waves and currents to give microplastics (Thompson, 2015) when they are present in the oceans or lakes. Unfortunately, 1.56 billion masks were estimated to be released into the oceans in 2020 (Teale Phelps Bondaroff, 2020) due to inappropriate disposal. A study has found that a typical surgical mask could generate 254 pieces of microplastics per day in oceans, and upon complete decomposition, 0.88 million pieces of microplastics could be generated (Sun et al., 2021). When factoring in the 1.56 billion masks in the oceans, this implies that there are 396 billion pieces of microplastics being generated in the ocean every day (1.56 billion × 254 pieces) and up to 1370 trillion pieces (1.56 billion × 0.88 million pieces) of microplastics could be released potentially (Sun et al., 2021). The study also suggests that the release rate of microplastics increases with the amount of damage done to the masks, meaning that the masks will release microplastics faster when they have been in the oceans for a longer time (Sun et al., 2021).

The massive disposal of face masks poses an immense threat to the environment by generating microplastics, particularly PP microplastics. Different approaches to degrade and remove the microplastics were proposed to tackle the threat.

2. Degradation and Upcycling of Microplastics using Electrochemical Methods

2.1 Current Available Approaches

One of the approaches to degrade microplastics is using electrochemical methods.

Electrooxidation (EO) was found to be effective in degrading polystyrene microplastics. When using Boron-doped diamond (BDD) as anode and 0.03M Na_2SO_4 as electrolyte, the degradation efficiency of polystyrene microplastics was found to be 89%±8% under a current of 9A in a 6-hour session (Kiendrebeogo et al., 2021). All the degraded microplastics were transformed into gaseous products like CO_2.

Another approach is to couple the degradation with an electrochemical hydrogen evolution reaction (HER). As the HER progresses while using Ni_3N/W_5N_4 electrodes, PET microplastics can be selectively degraded into methanoic acid with a high Faradic efficiency of around 85% (Ma et al., 2022). Although the degradation percentage remains unknown, the application can open up the possibility of combining microplastics processing with other electrochemical reactions and make the degradation be economically more efficient, especially when given the high product selectivity.

Simultaneously, an electro-Fento-like system was proven to be effective in degrading PVC microplastics. While passing a current through a TiO_2/graphite cathode, hydroxyl radicals were generated to dechlorinate and degrade the PVC microplastics. The dechlorination efficiency was found to be 75%, and 56 wt% of the PVC microplastics were removed after a potentiostatic electrolysis (Miao et al., 2020). (At 100°C, -0.7V, 6-hour long, against Ag/AgCl electrode) Various water-soluble organic products like formic acid, acetic acid, and oxalic acid were given.

2.2 Our Approach

As mentioned in Session 1, the usage of face masks will inevitably generate an immense amount of PP microplastics. In light of that, we would like to prioritise PP microplastics and attempt to degrade and upcycle them using electrochemical methods.

The ability to produce upcycled products during the degradation is crucial as it enhances the economic efficiency of the process. It also minimizes the amount of CO_2 produced and can lower the greenhouse gas emission. Aside from that, yielding useful products from the microplastics might help enable the achievement of a cradle-to-cradle life cycle of plastics.

After factoring in the structural similarity of PVC and PP, the simplicity and high effectiveness of the set-up as well as the possibility of generating upcycled products from the microplastics, we have decided to follow the direction marked by Miao and Liu's group and try to replicate the experiment on PP microplastics.

We propose a 3-electrode system for degrading PP. The system consists of a TiO_2/graphite cathode prepared by the "sol-gel method" (Miao et al., 2020), a graphite anode, and a silver reference electrode serving as the baseline for measuring the voltage applied (Miao et al., 2020).

The solution is a mixture of PP microplastic, water and hydrogen peroxide. Hydroxyl radicals are produced from hydrogen peroxide by electrocatalysis via the TiO_2 catalyst, which attacks and degrades the microplastics, and water is the medium to propagate the radicals.

When a moderate current is applied to the electrode with TiO_2, it can effectively generate highly reactive hydroxyl radicals. Despite its high reactivity, it is non-toxic and environmentally friendly (Miao et al., 2020). This reactive species can react with the PP molecules through direct bombardment. The process will break the carbon chain and fragmentate the microplastics into useful carbon compounds.

From the reaction, smaller organic molecules such as acetic acid and oxalic acid can be collected, with a higher value than the PP waste (Miao et al., 2020). They can be used as fuel or feedstock for other chemical syntheses. Acetic acid is widely used in drug synthesis and rubber manufacturing, while oxalic acid is used in producing cleaning products (Miao et al., 2020).

The final mixture in the chamber will not contain toxic chemicals as the PP microplastics are decomposed into harmless molecules, such as water and upcycled products.

3. Other Approaches for PP upcycling

While our team proposed an electrochemical strategy to decompose PP into harmless products, the ideal solution would be to upcycle the waste plastic into useful products instead of carbon dioxide. Here we reviewed two other approaches attempted by scientists to upcycling PP.

3.1. Hydrogenolysis

Hydrogenolysis is a chemical method to cleave C-C bonds or C-heteroatom bonds in feedstocks using hydrogen gas. Catalysts for hydrogenolysis are being designed for the effective and selective generation of oligomeric or monomeric compounds from plastic wastes (Chen et al., 2021).

Back in 1988, V. Dufaud and J.-M. Basset has already attempted to degrade PP into olefinic oligomers or monomers by the microscopic reverse of Ziegler-Natta Polymerisation (Dufaud & Basset, 1998). Using silica-supported Zirconium hydride catalyst, which is highly electrophilic, PP (MW ~250,000 Da) was degraded into saturated oligomers after five hours or lower alkanes after 10 hours at 190 °C, 1 bar H_2.

More recently, in 2021, Tomishige and Nakagawa's group published their attempt at utilising Ru/CeO_2 catalyst for depolymerisation of PP (Dufaud & Basset, 1998). Hydrogenolysis under mild conditions, at 200−250 °C, 20−50 bar H_2 for 16 hours, is performed to produce liquid and gaseous n-alkanes. The yield of C5−C32 iso-alkane is above 68% in the absence of solvent.

3.2. Photocatalysis

3.2.1. Photo-reforming of plastic wastes to generate H_2

In photo-reforming, the plastic is oxidised to small organic compounds or carbonate ions under the presence of light and photocatalyst, while water reacts to give hydrogen gas. Reisner's group developed a $CN_x|Ni_2P$ catalyst. Different plastics are selected as substrates, and photo-reforming is performed under atmospheric N_2 with exposure to simulated sunlight at room temperature in alkaline aqueous solution (Uekert et al., 2019). PP is amongst the plastics they have studied and provided a relatively poor yield of hydrogen per gram of substrate. Nevertheless, the experiment indicated the viability of this approach for upcycling PP.

3.2.2. Generating C2 fuel from plastic wastes

Besides H_2, photocatalysis of plastics into C2 Fuels is also being studied. In 20202, Sun and Xie's group published their work on a photoinduced sequential C−C cleavage and coupling pathway for photocatalysis of waste plastics into CH_3COOH without using sacrificial agents (Jiao et al., 2020).

PP was first completely decomposed into CO_2 intermediate using the single-unit-cell thick Nb_2O_5 layers under simulated natural environment conditions after a reaction time of 60 h. Then, the formed CO_2 was further photo-reduced to produce CH_3COOH with prolonged reaction time. The average CH_3COOH formation rates were 40.6 μg per gram of catalyst per hour. While this work is proof of concept, the low acetic acid yield means further improvements are required.

4. Conclusion

Microplastic pollution is a severe problem harming aquatic lives and humanity. Here we proposed an electrochemical method to degrade PP into harmless products and reviewed other approaches for upcycling PP. While further research and development are necessary before it can be commercially employed, chemical upcycling is a powerful and promising strategy to handle plastic wastes and tackle plastic pollution.

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