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Abstract: Microplastics are generated from plastic waste in landfills due to physical, chemical, and biological effects, and eventually enter into the leachate. Leachate is a potential source of environmental microplastics which has not been emphasized. Here, we summarized the investigation of microplastics in leachate in 9 countries from 28 papers, provided a comprehensive review of the sampling, detection, and separation of microplastics in leachate, and elaborated on the quality control in each process. There are more than forty types of microplastics in leachate, with diverse shapes, wide size distribution, and concentrations of 0–25 items/L. Commonly used techniques are FTIR, Raman, SEM, and py-GC–MS for characterizing microplastics, while standardization of micro- or nanoplastics for leachate with a complex composition should be further studied. We also discussed in depth the degradation mechanism of microplastics in advanced oxidation processes (AOPs). Microplastics can be decomposed into small molecules such as aldehydes and ketones, and some can even eventually be degraded into CO₂ and H₂O in AOPs, which may be further implemented in leachate treatment plants. This review provides the scientific fundamentals for understanding the microplastics in landfill leachate and proposes removal strategies for future research.

Keywords: microplastics; landfill leachate; occurrence; detection; advanced oxidation treatment

1. Introduction

The annual global production of plastic has exceeded 300 million tons with the increased use of plastic products [1]. In particular, approximately 89 million medical masks and 76 million test gloves are needed every month globally to cope with COVID-19, based on data from the World Health Organization [2,3]. Globally, 21–42% of plastic waste is landfilled, leading to microplastic pollution [4]. A total of 75.4% of plastics waste was landfilled in 2017 in the U.S. [5], and China generated 14.21 million tons of plastic waste, of which 39.6% was landfilled from 1950 to 2020 [6]. Approximately 12,000 Mt of plastic waste will be deposited in landfills and the natural environment by 2050 if current production and treatment trends continue [7]. Plastic waste undergoes numerous treatment stages during landfill stabilization, and microplastics are generated by multiple physical, biological, and chemical effects throughout the entire landfill bodies and further into landfill leachate. Landfill leachate is an essential source of microplastics, which needs more attention.

Microplastics were first mentioned by Thompson in 2004 [8] and defined as plastic particles ≤5 mm in size [9]. Microplastic pollution has recently become a global challenge with increased plastics [9]. These small particles are particularly concerning compared to
large plastic particles, as they do not only easily absorb contaminants in leachate but can also be translocated in the bodies of organisms due to the leakage of the leachate [10]. Many studies have shown that microplastics can seriously damage the growth and reproduction of organisms and even threaten human health [11]. Previous studies mainly focused on the identification, accumulation, pollution, and ingestion of microplastics in the environment (Figure 1b). The occurrence and effects of microplastics were mainly investigated in the aquatic environment, including the ocean, freshwater, and wastewater [1,12]. Microplastics in leachate were first studied in 2018 [13], with only a few studies to date in several countries, such as China, the United States, Australia, Italy, and India, (Figure 1c), at concentrations ranging from 0 to 25 items/L [13–18]. The different concentrations of microplastics in leachate may be region specific or due the lack of uniform identification criteria to a certain extent. Microscopes are commonly used to identify microplastics’ size, quantity, and shape [1,3]. The surface morphology of microplastics can be characterized by SEM [19]. Information on microplastic types, structures, and surface additives can be detected using FTIR [20–22], Raman [23], and py-GC–MS [24].

There are physicochemical and biological methods for the removal of microplastics. The physical treatment process includes coarse sieves, fine sieves, and sedimentation based on the different densities to separate the microplastics [25]. However, gravity-induced density separation is less effective in the treatment of microplastics. In wastewater treatment, membrane filtration is a crucial treatment technology, and 85% of microplastics are trapped after ultrafiltration and thus removed from wastewater [26]. This technology requires proper wastewater pretreatment, and membrane contamination is a serious problem [27]. Existing methods are based on microplastics in wastewater or seawater, and research on
removing microplastics in leachate is very limited. Advanced oxidation technology based on various reactive oxygen species (ROS) has excellent degradability of persistent organic pollutants, which can effectively degrade microplastics into small molecules, efficiently removing microplastics [28]. For wastewater, especially leachate, with many pollutants and complex compositions, advanced oxidation is expected to become an effective technology for eliminating microplastics in leachate.

This study conducted a focused literature search of the keywords ‘microplastics AND leachate’, ‘micro-plastic AND leachate’, ‘micro AND plastic AND leachate,’ and ‘nano AND plastic AND leachate’ in scientific databases (particularly WOS, ACS publications, and Google Scholar) to find papers on microplastics in leachates. A total of 28 were thought to have been selected after reading abstracts and scanning the papers. Based on the existing 28 papers, the sampling, separation, detection, and characteristics of microplastics in leachate were reviewed. The degradation of microplastics was also reviewed according to the degradation methods of existing microplastics by selecting advanced oxidation treatment technologies with optimal potential. In addition, the degradation mechanism of some microplastics in advanced oxidation treatment is also elaborated, which provides a theoretical basis for future microplastic degradation in leachate.

2. The Detection of Microplastics in Leachate

The detection of microplastics in leachate usually includes leachate sampling, separation, characterization, and quality control (Figure 2). The methods used in each step have not been standardized yet, leading to the indeterminacy of results. Therefore, quality control is commonly implied in many studies to reduce the possible error caused by microplastic loss. Here, the effectiveness and limitations of these methods are reviewed.

![Figure 2. Leachate sampling, separation, and characterization of microplastics in leachate.](image-url)
2.1. Microplastic Sampling

Different microplastic sampling methods are developed in the aquatic environment, mainly including container collection [29], trawl methods [30–32], and a surface microlayer method [12]. The containers used in leachate sampling should be carefully selected to avoid the release of contaminants, and the leachate is generally stored in steel buckets or glass containers [14]. The containers are thoroughly cleaned before sampling, and leachate samples are collected as directly as possible to reduce interference from the surrounding environment, such as wind erosion [30,31].

The microplastics in leachate mainly focus on two sampling sites, including in situ at the landfill and leachate treatment plants. The representativeness of the leachate sampling should be given priority to avoid potential error due to the low concentration and heterogeneity of microplastics. For in situ leachate at the landfills, many factors, such as sampling location, time, and season, will significantly affect the representativeness of the leachate taken [33]. Therefore, the sampling points need to be set reasonably to reflect the actual landfill situation. Plastics can degrade into microplastics over time in landfill and further flow into leachate, so landfill age should be considered, especially for landfills built in phases [33]. In addition, the composition of leachate at different landfill depths will also be different, and the same sampling point should be sampled according to the various depths and mixed into a sample. For leachate treatment plants, increasing the sampling volume and taking long-time sampling are commonly used to make the leachate representative [14]. The sample volume is as needed and can also be adequately filtered to remove large particles of garbage or other substances. Samples must be packed in sealed containers and stored in a freezer if not immediately used for follow-up studies [34]. A more comprehensive sampling guide is worthy of further development, which can offer an informed sampling method based on specific sampling modes to improve the data quality and comparability.

2.2. Separation of Microplastics from Leachate

The microplastics must be separated from leachate before determination and characterization. Filtration and purification are the two main steps in leachate separation.

2.2.1. Sieving and Filtration

Sieving and filtration are commonly used to separate microplastics from leachate, and the microplastics detected would be determined by the mesh size. Stainless steel screens initially separate samples with pore sizes of 47 µm [13] and 411 µm (<50 µm and <50 µm). Then, they pass through the nylon membrane with a pore size of 20 µm [33]. So far, the mesh sizes applied have been unified, ranging from 0.047 to 5 mm [13], and this mesh-based separation can be a little less accurate. The small mesh size is less applicable for leachate, which contains a high organic matter content and causes mesh clogging. The large mesh size may cause the loss of some smaller microplastics, which makes the microplastics underestimated. In addition, some particles with irregular shapes would not be captured by the mesh; for example, the fibers would pass longitudinally through the small mesh. Therefore, it is important to standardize the mesh size to allow comparison between different works.

2.2.2. Purification

Double-density separation is an effective method for separating microplastics from leachate. NaCl is among the most used salts for density separation due to its being highly available, cheap, and environmentally friendly [35]. However, it was found that sodium chloride (NaCl, \(\rho = 1.2 \text{ g/cm}^3\)) had low recovery rates (<90%) and larger error bars to separate heavier polymers, while 99% of recovery rates could be achieved using sodium iodide (NaI, \(\rho = 1.7 \text{ g/cm}^3\)) [33,36]. In addition, NaI can be recycled up to 10 times, and the cost is similar to NaCl, which is recommended for microplastic separation in leachate. Using density to separate microplastic from other contaminants is among the easiest and
most economical methods. The double-density separate operation involves rinsing the
particles on the membrane with NaI solution and then rinsing the residue with ethanol
\((\rho = 0.79 \text{ g/cm}^3)\). The rinse solution was left to stand for two hours, the sediment was taken,
and the resulting substance was soaked and dried at ambient temperature [14]. Density
separation is unsuitable for cellulose-rich water quality because it clumps with microplastic
polymers [37]. To avoid the influence of organic matter in the sample, the sample can be
digested with acids, alkalis, and oxidants before treatment.

2.3. Identification and Characterization

The microplastic items, size, and morphology in leachate are usually identified by vi-

sual observation. Microscopes can identify some of the physical properties of microplastics.
The light microscope is an excellent technique for selecting the suspicious microplastic and
then continuing magnification for analysis [38]. Stereo microscopes can also characterize
the abundance of microplastics [39]. For example, the Suny SZN71 stereo microscope was
used to describe the MPS in number, size, and morphology [34,38]. Other methods used to
identify microplastic particles include Coulter Counters, nanoparticle tracking analysis [40],
stains such as Nile Red dye, and visual sorting [41]. The above methods rely on visual
sorting to determine microplastics and are prone to deviations in practice. More than
5000 types of polymers are widely used, and it becomes more challenging to distinguish
the micro/nanoparticle sizes through visual judgment [42] (Table S1). We must look for
more precise analytic tools to get more accurate information about microplastics(Table 1).

Spectroscopic approaches are more reliable tools for identifying microplastic frag-

ments, which can provide more accurate information. Techniques mainly include sequential
pyrolysis-gas chromatography coupled to mass spectrometry (py-GC/MS) [24], Scanning
electron microscope (SEM) [19,24,43], and Fourier-transform infrared (FT-IR) [44–46]. By
the signal analytical technique, it is difficult to identify microplastics’ type, size, and shape
from the complex leachate. Therefore, combinatorial techniques are particularly important
in the microplastic inspection.

2.3.1. SEM

SEM is a technique generally used to visualize the surface characteristics of parti-
cles and confirm the microplastics’ presence in leachate samples. Based on the impact
signal of the incident electron, an image of the particle surface can be drawn [47]. Those
high-resolution images can provide information about ionic chemistry and morphological
characterization [43], such as fractures, cracks, and pits [19,22]. Meanwhile, it can also
provide information about the structure of microplastic surfaces [19]. However, SEM is
not suitable for handling large batches of samples [22], and the results are affected by
the surrounding environment, noise, vibration, and electromagnetics [34]. The combina-
tion of SEM with other technologies can effectively solve those defects for microplastic
characterization. The spectroscopies and thermal filed emission scanning electron mi-
croscopy (FE-SEM) combination simplifies the sample handling process while obtaining
high-quality sample images at low voltages [19]. Combining SEM and energy dispersive
X-ray spectroscopy (EDS) enables obtaining the microplastic element composition and
surface additive information. The EDS detectors can not only perform qualitative and
quantitative analysis of plastics [24,48] but also help distinguish between plastic and non-
plastic products [9]. However, SEM-EDS is usually considered an expensive technique
that requires much time to prepare samples. Future research can innovatively combine
SEM with other technologies to make sample detection faster and to obtain high-quality,
high-magnification, and high-resolution images of microplastics.

2.3.2. FT-IR

FT-IR has been an ideal technology for identifying microplastics in recent years due
to its low cost, reliability, and efficiency [42]. It can determine the type of plastics by
different spectra of plastic chemical bonds [20–22], which has been successfully used to
identify microplastics from the aquatic environment. FT-IR measures the transition between molecular vibration energy levels based on the interaction of radiation with molecular vibrations [45]. Additionally, there are many limiting factors; for example, the detection of sample molecules needs to be in a wide spectral range. Samples must be carefully dried before testing [45], and macroscopic particles require manual operation [44]. Digestion as a decomposition process can lead to a degree of spectral deviation [23]. The crystal’s contact with the sample surface makes both susceptible to contamination and damages the crystal [44].

The recent development of FT-IR could be more effective in evaluating microplastics of different sizes. Microplastics with larger particles (>500 nm) are analyzed using ATR-FTIR [15], which allows the direct study of large-sized and irregularly shaped microplastics without preparation [22, 46]. Micro-FTIR is used for small particle-size microplastics by combining FT-IR with an optical microscope [19]. Focal plane array spectroscopy (FPA-FTIR) is much faster than FTIR because it allows unbiased high-throughput microplastics analysis. Additionally, it is superior to micro-FTIR in obtaining spectra of irregularly shaped microplastics [45]. However, the FPA-micro-FTIR technique still has its limitation. Small microplastics exhibit a higher abundance than large microplastics [49], and it is hard to distinguish small MPs (<100 µm) from other fragments, even though a high-power lens [15]. Therefore, it is urgent to develop a feasible, effective, and convenient method to identify microplastics of various sizes in wastewater and freshwater.

Table 1. Techniques for chemical characterization of microplastics.

<table>
<thead>
<tr>
<th>Identification Method</th>
<th>Findings</th>
<th>Microplastic Size</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Observe the surface morphology and texture characteristics of plastic particles</td>
<td>1 µm~1 mm</td>
<td>[19,23,43]</td>
</tr>
<tr>
<td>EDS</td>
<td>Qualitative and quantitative analysis of different elements in plastic products</td>
<td>&lt;1 mm</td>
<td>[24,48,50]</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Reduced sample handling processing allows high-quality microplastic images to be obtained at low voltages</td>
<td>&lt;100 nm</td>
<td>[19,51]</td>
</tr>
<tr>
<td>FTIR</td>
<td>Used to identify microplastic types isolated from the water to characterize it. Suitable for the analysis of large microplastic products</td>
<td>Smaller particles down to 20 µm</td>
<td>[19,45]</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Suitable for small particle size microplastics</td>
<td>Microplastics less than 50 µm</td>
<td>[19,52]</td>
</tr>
<tr>
<td>Micro-FTIR</td>
<td>Microplastic information can be obtained quickly in a short period, making it suitable for detecting smaller particles</td>
<td>Microplastics less than 10 µm</td>
<td>[19]</td>
</tr>
<tr>
<td>FPA-FTIR</td>
<td>Provides structural information about polymers.</td>
<td>This method can detect microplastics with a size down to 1 µm</td>
<td>[23,45]</td>
</tr>
<tr>
<td>Raman</td>
<td>Identify the chemical properties of microplastics</td>
<td>The shape, size, and color of the microplastics do not affect this method</td>
<td>[45]</td>
</tr>
</tbody>
</table>

2.3.3. Raman

Raman spectroscopy is another widely used technique based on the interaction between radiation and materials [19]. It provides information about the vibration of the molecules of the system by generating vibrational spectroscopy through the inelastic scattering of light [39]. This technique, which can provide structural information about polymers, is the preferred method for identifying small microplastics (<20 µm) [23]. Compared with FT-IR, the Raman technique is not interfered with by sample thickness and moisture, and it has higher reliability, a more comprehensive spectral range, and narrower spectral bands. However, surface additives and adherent chemicals would cause interference, leading to lower fluorescence. There are special requirements for the fluorescence of inorganic and organic materials during the inspection process [45]. The combination of
Raman and FT-IR technologies would be a focus in future development to obtain faster and more accurate MPs detection.

2.3.4. Pyrolysis-GC–MS

The thermo-analytic method can identify the chemical properties of microplastics depending on their thermal stability [45]. Pyrolysis-gas chromatography-mass spectrometry (Pyrolysis-GC–MS) is a destructive technique that analyzes sample structure by identifying fragments from lysis. No pretreatment is required during the identification of microplastic samples [19]. As a cheaper and simpler technique, it can identify and quantify complex microplastic samples and obtain degraded product information [19]. The related organic plastic additives can also be determined simultaneously [24]. The major disadvantage is that large particles of microplastics can interfere with detection due to the higher mass and surface rations [44]. In addition, samples must be manually pleased into the analysis tube, and a long-running time is required for individual samples [45]. Hence, the analysis of a large-scale sample requires careful selection. Moreover, it cannot provide information on microplastics’ quantity, type, and morphology and can only be chemically characterized [15,33].

2.4. Quality Control

When testing leachate microplastic, strict quality control throughout the process is essential. Quality assurance and quality control are important to ensure reliable results. Choosing the right sampling tools, implementing a well-designed sampling protocol, and setting up blank labs during the experiment can all help improve the reliability of experimental data.

2.4.1. Contamination Control during Sampling

It is essential to avoid contamination during leachate sampling [31]. Any process, from sampling to detection, can contaminate the sample, such as samplers, sampling processes, and sample holding containers. Fibers in the clothing the samplers wore were even detected in the samples [53]. Therefore, the operator should wear 100% cotton clothes and use nitrile gloves to reduce the risk of contamination of the sample [31]. A steel or glass bottle should be used to save the samplings to avoid releasing plastic from the container into the sample and deviation of the results [54]. All containers must be acidified with nitric acid before use and then rinsed with pure water [55]. After sampling, the container is sealed and back to the laboratory [14]. A clean and preferably closed environment is necessary during laboratory operations, such as a fume hood [54]. All open jars and beakers are covered with foil [55]. Avoid contact with plastic equipment during operation [56], and reduce exposure time in the air [31]. If these cannot be avoided in the experiments, blank experiments are needed to verify whether more plastic particles will be generated during preparation [31]. Three filed blanks were prepared for each sampling point. The microplastics in the field blanks were counted and characterized by the same method and then subtracted from the corresponding categories for the samples [57]. To detect the effect of airborne particles on the experiment, Petri dishes containing white filter paper can be placed nearby (<1 m). Or set up several blank experiments [58] for correction of subsequent experimental results.

2.4.2. Quality Control in the Separation of Microplastic

During sample separation, the loss of microplastics should be minimized. Dual-density separation removes some inorganic and organic matter from the leachate and separates the microplastics [14]. Although the use of density separation can obtain microplastics from leachate, the solution and the number of extractions greatly influence the extraction efficiency of microplastics. Chemical digestion can remove some impurities, but it can also adversely affect the microplastics, such as shape and size [59]. Compared with sodium chloride, sodium iodide has the advantages of high density, safety, and high repeatability [60]. The repeated extraction process is an efficient method to recover microplastics from the
sample matrix [22]. The extraction process is generally repeated three times to ensure that the microplastics are extracted efficiently [59]. Using sodium chloride extraction, particle recovery increase from 60% to 90% as the number of extractions increases [61]. However, higher recoveries were obtained using sodium iodide solution (98–100%) [62] and zinc chloride solution (96–100%) [63]. The recovery of microplastic is still low, which is an urgent problem to be solved. Due to the plastic’s weak thermal resistance, the sample’s temperature should not exceed 60 °C when it is dried after separation [64].

3. Microplastic Characteristics in Leachate

There is no significant attention to the microplastic pollution in landfill leachate compared to the aquatic systems. The level of microplastic pollution is likely to be higher in undeveloped areas [65]. The size, shape, concentration, and chemical composition of microplastics in leachate are various [12]. Since there is still no uniform standard for microplastics in leachates, it is difficult to compare them with microplastics in other systems. The results of some existing leachate samples from different regions, although very limited in research, reflect some characteristics of microplastics in leachate (Figure 3).

3.1. Microplastics Type

The type of microplastics refers to the chemical structure and properties of microplastics [17]. Different microplastics have different chemical compositions, which may affect their removal, and polymers with low density often float on the surface of the water, while polymers with higher density are more likely to sink to the bottom [68]. At the same time, the performance of the plastics products themselves will also affect their distribution in the environment. PE easily breaks down into small particles and is more likely to be

![Figure 3](image)

*Figure 3. (a) Type and percentage of Microplastics in leachate, Urban, China. A: Shanghai B: Wuxi C: Suzhou D: Changzhou [14,66]; (b) concentrations of microplastics in leachate in different cities in different countries [20,38]; (c) microplastic shapes in leachate in different cities in different countries [38,67]; (d) the percentage of microplastic size in leachate in different cities [14,67].*
3.1. Microplastics Type

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The type of microplastics in leachate directly reflects the consumption of plastic products. For example, PP strongly correlates with the automotive industry, medical applications, and consumer products [73]. Future microplastic in leachate can also be predicted from plastics used daily. The extensive use of Personal Protective Equipment (PPE) will increase the amount of PET in the environment [74]. There are also regional differences in the types of microplastics in leachate. The current research on microplastics in leachate mainly involved four countries, including China, Finland, Iceland, and Indonesia (Figure 3a). The most detected microplastics in leachate were PE, PP, PVC, PET, and PS. The microplastics found in leachate from different cities in China were mainly PE and PP [14,18], and PE was the primary type of microplastics in leachate in Norway and Iceland. However, the microplastics detected in leachate samples collected in Finland were mainly PE, PS, and PET [13].

3.2. Microplastics Concentration

The global production of plastic waste has increased sharply yearly, accounting for 2.95–21.76% of solid waste in landfills [17]. Therefore, the concentration of microplastics in the leachate is affected [12]. In existing studies, the concentrations of microplastics detected from the leachate ranged from 0 to 25 items/L. The leachate samples used for testing were taken from several countries in Asia and Europe (Figure 3b). For China, the concentration of microplastics in the leachate samples in Shanghai and Guangzhou was relatively high, while that in Wuxi was low [14,15,18]. The concentration of microplastics detected in leachate in some European countries was very low or even zero [13,14,20]. This gap in concentration may be related to sampling techniques, analytical methods, or leachate treatment [17]. Existing test methods were mainly used for microplastics in seawater or laboratory water [12,15,32], and many other variables also affected the concentration of microplastics in the leachate, including human activities, the physical and chemical properties of plastics, the meteorological conditions of landfills, and the topography of landfills [75]. For leachate liquids, many contaminants may also interfere with detecting microplastics. This puts forward future requirements for optimizing microplastic detection methods in leachate.

3.3. Microplastics Shape

The plastic particles in the leachate can have wired flakes, strips, fragments, foamy, spherical, tablet-like, irregular shapes, and ovate and round [67,75]. Fragments are particles with jagged edges. Granules refer to spherical. Foam is plastic particles with a spongy texture [76]. Plastic entering the environment breaks into various shapes with different decomposition processes and residence times [65,76,77]. Slender microplastics are easily separated by filtration, while spherical microplastics are more likely to remain in the leachate [68,78]. According to the study evaluated (Figure 3c), the shape of microplastics
in the leachate differed from region to region [67]. Among the 12 leachate samples in Indonesia, the three forms of fibers, fragments, and foam dominated [66]. The type of microplastic in leachate samples from different cities in China varies greatly. However, the fragments are the main components of it [14,66]. The shape affects the interaction of microplastics with other contaminants in the leachate [29]. Various pollutants in the leachate can be enriched on the surface of microplastics, making it more difficult to remove. MPs’ shape can also influence the act of transferring. For example, spherical microplastics can move faster than others [78].

Fibers and fragments are easier to filter out of the garbage and become the most abundant form of leachate. The same trend has been found in wastewater [79]. The fibers come from the wear of the fiber cloth during cleaning, contaminating the fibers in the sewage [80]. On the other hand, fibrous is dominant mainly because of its small size and easier of entering the leachate through the garbage. The shape can indicate the source of the microplastic. Plastic bags and other plastic packaging usually produce flakes. Most pellets and spheres are derived from cleaning products and plastic containers [72,81]. Plastics in scrubs and cleansers are made into microbeads [82]. Film and foam are mainly corrosion of plastic bags and packing [79].

3.4. Microplastics Size

Microplastic size refers to the maximum length of microplastics, and the size is an essential property in the study of microplastics [17]. The size of microplastics is related to their properties. Lighter plastics are more likely to break in the environment, while denser plastics are more difficult to break and prone to collisions with other environmental substances [83]. The size of microplastics detected from leachate in the studies reviewed varied widely. The particle sizes of microplastics in leachate ranged from <80 µm to >5000 µm. These studies have shown that the size of microplastics in leachate ranges from a few microns to several thousand microns. As shown in Figure 3d, the microplastics found in the leachate from Shanghai, Wuxi, and Guangzhou in China were large (100–5000 µm), of which 100–1000 µm dominated [14,66]. However, the microplastics found in 12 leachate samples from Indonesia were concentrated in 80–1000 µm [66]. This difference may be because different countries have different standards for landfills, resulting in differences in the degradation of plastics. This difference can also be caused by the fact that the plastic material affects the final shape of its degradation in the environment.

Since leachate is a liquid filtered out of garbage, it can be inferred that smaller microplastic particles tend to accumulate in the leachate while the larger ones remain in landfill garbage [84]. Small particles stay suspended in the fluid, more likely to precipitate the larger ones. As the size of microplastics decreases, their specific surface area will increase. Small microplastics are more likely to bind to contaminants such as heavy metals in the leachate [85].

4. Removal of Microplastics by Advanced Oxidation Techniques

A series of processes have been applied in the existing leachate treatment plants, which are not explicitly designed to remove microplastics. Most of the microplastics have not been effectively removed and still re-entered the aquatic environment from the leachate in the existing leachate treatment technology, so effective treatment technologies must be developed. Microplastics are inherently stubborn to biological processes due to the polymer molecular structure’s complexity. Advanced oxidation processes (AOPs) show excellent performances in treating persistent and refractory contaminants in water, which make themselves good choices for degrading microplastics [86]. Hydroxyl radical (•OH), superoxide radical (•O2−), and sulfate radical (SO4−•) are the prominent free radicals in AOPs that can erode microplastics and cause their long chains to break and gradually degrade [28]. Here, we reviewed and summarized recent studies on treating microplastics with AOPs, such as photodegradation, Fenton, ozone oxidation, and activated persulfates.
In particular, the physical and chemical variation of microplastics and the mechanism of the degradation pathway were illustrated.

Figure 4. (a) Degradation pathways of microplastics during photodegradation; (1) PS and PE under ultraviolet light exposure (R is a benzene ring, H) \([87]\); (2) the degradation pathway of PET under ultraviolet light exposure \([88,89]\); (3) the degradation pathway of PVC under ultraviolet light exposure \([90]\). (b) Degradation pathways for microplastics during the Fenton/Fenton-like process; (4) degradation pathway of PVC under Fenton conditions \([91]\); (5) degradation pathway of PS under Fenton conditions \((R\) is benzene ring) \([92]\). (c) Degradation pathways of microplastics during ozonation; (6) ozonation degradation pathway of PP \([93]\); (7) polystyrene (PS) ozonation degradation pathway \([94]\); (8) PE ozonation degradation pathway \([95]\). (d) Activation of the mechanism of action of persulfates.

4.1. Photodegradation

Photolysis is mainly studied to degrade microplastics present in the environment because the most common contributing source is sunlight inducing the formation of free radicals. Additionally, there have not been many investigations on microplastic degradation applied in leachate treatment plants. Currently, the laboratory’s studies on microplastics’ degradation by ultraviolet mainly include photochemical oxidation and photocatalytic oxidation.

4.1.1. Photochemical Oxidation

Photochemical oxidation degrades microplastics by directly inducing ultraviolet radiation to produce free radicals, such as \(\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·\h_{2}O_{2}, OH, and O_{2}−\cdot [96]. It can not only change the chemical properties of microplastics but also affect the hydrophobicity of their surfaces. Some studies have revealed the aging mechanism of microplastics under ultraviolet radiation (Figure 4a) \([97–99]\). The degradation mechanisms were different for different microplastics under ultraviolet radiation. Under accelerated photodegradation conditions in the laboratory, oxygen-containing functional groups and cracks formed on the surface of microplastics \([100]\). The pristine PS microplastics are smooth and spherical, leaving broken fragments as the reaction proceeds \([101]\). Then, their surface became much rougher, and finally, microplastics could be broken down into smaller ones. The UV radiation degradation products from PE, PP, and PS polymers are generally olefins, aldehydes, and ketones \([102]\). PS polymers had a significantly shorter aging time under ultraviolet radiation \([97]\). When
exposed to ultraviolet light, PE polymers, whether in air, water, or soil, release their surface additive, PAE [99]. The release of surface additives may accelerate the degradation of microplastics [103]. The high chroma of leachate would seriously affect the action of UV light, thereby affecting the removal efficiency of microplastics [28].

### 4.1.2. Photocatalytic Oxidation

Most microplastics are partially degraded under ultraviolet radiation, and catalytic oxidation is often combined with photochemical to form photocatalytic oxidation technology [86]. Photocatalysis is a relatively mature green technology, mainly based on semiconductor materials (TiO$_2$, ZnO, etc.) [104]. Photocatalysis is a good technique for removing contaminants from water by generating electron arc pairs from ultraviolet light onto semiconductor materials [105]. Semiconductor catalytic photocatalysis can accelerate the degradation of microplastics by producing more free radicals. Zinc oxide materials have excellent catalytic activity and high redox potential, often used as catalysts for photocatalytic oxidation [106]. The catalytic photodegradation of zinc oxide nanorods significantly changed the surface and increased the brittleness [107], and the degree of oxidation of microplastics was proportional to the surface area of the catalyst [108]. Photocatalyst TiO$_2$ can also efficiently produce oxidants to promote microplastic degradation. When mesoporous N-TiO$_2$ coatings are used for photocatalytic degradation of HDPE and LDPE, the size of microplastics is reduced [109]. Using Ag-doped modified TiO$_2$ greatly improved the degradation capacity of TiO$_2$ to microplastics [110]. Other contaminants in the leachate may be preferentially oxidized, resulting in poor removal efficiency of microplastics when treated with photocatalysis [66]. The recovery of catalysts is a critical point in photocatalytic oxidation, and if not handled properly, it may cause secondary pollution.

### 4.2. Fenton/Fenton-like Systems

Fenton is an advanced oxidation process developed and improved for over 100 years. During the Fenton reaction, H$_2$O$_2$ is activated by Fe$^{2+}$ and produces a large number of hydroxyl radicals (•OH) [111]. The Fenton reaction is also widely used in the degradation of microplastics. It degraded microplastics into small-molecule substances and further degraded into simple inorganic CO$_2$ and H$_2$O, significantly promoting microplastics’ degradation [112]. Polystyrene and high-density polyethylene had a notch-like shape on the surface, with cracks and rough textures appearing as Fenton reaction times lengthen [113]. The Fenton reaction also caused nylon 6 (PA6) and PS chains to break and expose aromatic groups [114]. Meanwhile, the size of microplastics decreased, the surface carbonyl structure increased, the hydrophilicity increased, and the aging of microplastics accelerated [113]. Ozone had an efficiency of 89.9% for removing microplastics when used as a disinfection technology in sewage treatment [115]. Due to the high number of contaminants in the leachate, the efficiency of the treatment may be reduced.

Fenton is commonly combined with other techniques, such as the combination with ultraviolet–visible radiation called the light-Fenton process. The specific surface area of LDPE and polycarbonate (PC) increased significantly after the light-Fenton treatment, mainly due to the fracture formed on its surfaces [116]. It also accelerated the aging of PS and changed the adsorption capacity of microplastic surfaces through electrostatic interaction and hydrogen bonding [117]. The stretching vibrations of O-H, C=O, and C-O groups were observed on the PS surface by ATR-FTIR under the microbial-driven Fenton reactions (Figure 4b) [92].

### 4.3. Ozonation

Ozonation is another efficient technique for the degradation of microplastics [105]. There are two main degradation mechanisms by ozone. Ozone can react directly with contaminants, but the process is relatively slow and selective [118]. Ozone can also be decomposed into strong oxidation •OH and interact indirectly with pollutants. The indirect process is very fast and not selective [119]. At the same time, indirect reactions may also
trigger chain reactions, causing subsequent reactions to continue. The strong oxidation capacity of reactive oxygen species degrades plastic polymers in the aqueous environment [4]. The degradation pathway of microplastics in ozonation is shown in Figure 4c.

The surfaces of PE produced a variety of new functional groups, such as R-CHO, R-CO-OR’, and RC(=O) R’, when treating microplastics in the aqueous phase with ozone [120]. As a standard technology in sewage treatment plants, the removal rate of microplastics in sewage is as high as 98% [115]. Ozone mainly acts on C=C bonds, aromatic rings, and the main chain of hydrocarbon chains of microplastics, after which the microplastics are decomposed into small molecules [121]. PE, PP, and PET had significant changes in hydrophilicity after ozone oxidation, which significantly affected the subsequent fate of microplastics [122]. The changes in microplastics during ozonation are shown in Figure 4. Some studies combine ozone with ultraviolet light to form a UV/O₃ system to degrade microplastics. Studies have found that as the ozone treatment time increases, new functional groups such as C-C=O, C-OH, C=O, and C-OH are detected on the surface of microplastics [123]. Microplastics in leachate are also degraded under attack from free radicals and oxidants [124]. Due to the ozonation process *OH is not selective and does not produce a specific removal effect for microplastics in the leachate.

4.4. Activates Persulfates

Persulfates advanced oxidation is an advanced oxidation technique based on the activation of persulfates to produce sulfate free radicals (SO₄⁻•). The sulfate radicals produced have a high redox potential. Therefore, on the one hand, it can promote the oxidation and degradation of microplastic surfaces, and on the other hand, it can oxidize or even mineralize the organic additives released by microplastics. Due to its stability, efficiency, environmental friendliness, and safety, it has been widely used in the environmental field in recent years [125,126]. Although PMS and PDS have low direct oxidation efficiency to contaminations [127], the active species generated via PS activation can quickly oxidize various organic compounds [128]. Common activation methods are heat, MW, UV, and catalyst. The degradation of contaminants by the PS oxidation system mainly includes free radical (O₂⁻•, SO₄⁻•,*OH) [129] and non-free radical (¹O₂, electron transfer) [130] pathways.

Persulfate oxidation can not only effectively degrade the surface additives released by microplastics but also simultaneously change the surface functional groups of microplastics. The treated microplastics had higher oxidation properties compared to ozonation [131]. After PVC oxidation, the crystallinity increased, and the size decreased while producing short-chain organics such as alcohols and carboxylic acids [132]. At the same time, the structure and C-Cl bonds of PVC are destroyed, which is easier to decompose small particles [98]. In PS and HDPE that have been oxidized by persulfate, the number of surface carbonyl groups and active sites is significantly reduced [113]. After the treatment of microplastics in wastewater, the proportion of particles (>150 µm) dropped from 66.6% to 8.3% [132]. The treated microplastics had a hard surface and a high glass transition temperature [66]. The study showed that the oxidation of -CH₃ and -CH₂ bonds occurs on the surfaces of treated microplastics and is more oxidized after persulfate treatment than ozone and Fenton systems. However, there is no definitive study of changes in microplastics in leachate. This is a point that can be deepened in future research.

5. Conclusions and Future Perspectives

This article reviewed the sampling, detection, and separation of microplastics in leachate and the degradation mechanism of microplastics by advanced oxidation techniques. To date, many techniques have been used to detect microplastics, but the complexity of leachate makes it necessary to consider when choosing a detection technology carefully. Commonly used techniques are FTIR, Raman, SEM, and py-GC–MS, which may be the best choice for characterizing microplastics in leachate because they provide comprehensive information about the particles tested, including quantity, size, chemical composition, and surface structure. There are more than 40 types of microplastics in leachate, with
diverse shapes, wide size distribution, and concentrations of 0–25 items/L. The distribution characteristics of microplastics in leachate are related to economic development because the economy determines the type and amount of plastic. Advanced oxidation has a good effect on the degradation of microplastics, and microplastics can be decomposed into small molecules such as aldehydes and ketones, and some can even eventually be degraded into CO₂ and H₂O.

Leachate, as a source and sink of microplastics in the environment, will impact the environment, which has been of concern in recent years. However, current research on microplastics in leachate is limited to characterization, and there are no definitive methods and techniques for how microplastics are removed in leachate. Therefore, some future research prospects are proposed.

1. Microplastics in landfill leachate were only detected in several countries; more studies worldwide should be investigated. The relationship between microplastics in leachate and plastics waste can be built based on more data, which can predict the microplastic emission from landfill leachate.

2. Standardization of leachate sampling, quality control, and characterization of microplastics in leachate, especially for smaller micro- or nanoplastics. The methods in other environmental media may not be suitable for leachate with a complex composition.

3. Due to the small particle size and pores of microplastics, they inevitably become carriers of other pollutants in the leachate, which increases the difficulty of removing other contaminants. The adsorption of microplastics to other pollutants in the leachate has not been well studied, which is critical for the subsequent degradation of microplastics in leachate.

4. At present, membrane technology is widely used in leachate treatment. However, its microplastics will only be intercepted and cannot be degraded. At the same time, the microplastics in it will also cause membrane blockage. How to effectively remove it from the leachate is still an important issue.

5. Advanced oxidation technology is a promising method for treating microplastics in leachate in the future, but there is limited relevant research on the degradation process of microplastics in leachate.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15020252/s1, Table S1: Common microplastic properties.

Author Contributions: Conceptualization, Table 1, Q.H. and C.Y.; methodology, Table S1, C.N.; software, Q.Z.; validation, T.W.; investigation, C.Y.; writing—review and editing, Figures 1–4, L.W. (Lan Wang); visualization, H.W.; supervision, L.W. (Luochun Wang); project administration, Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China for Youth (No. 5210100109), Natural Science Foundation of Chongqing, China (cstc2021jcyj-msxmX0893) and China Postdoctoral Science Foundation (No. 2021M702121). We also appreciated the Shanghai Engineering Research Center of Solid Waste Treatment and Resource Recovery.

Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflict of interest.

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