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The Pollution Characteristics and Fate of Microplastics in Typical Wastewater Treatment Systems in Northern China

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Abstract: This study focuses on the occurrence status and removal efficiency of microplastics in wastewater treatment plant processes. Analysis of effluent and sludge samples from the Wulongkou and Shuangqiao wastewater treatment plants in Zhengzhou revealed an overall microplastic removal efficiency of 95.64% and 92.53%, respectively, indicating the effectiveness of wastewater treatment plants in reducing microplastic emissions. Microplastics primarily exist in forms such as fiber, fragment, floc, film, and grain. Fibers are predominant in the effluent of the Wulongkou plant, while fibers and films predominate in the effluent of the Shuangqiao plant. Moreover, microplastics are predominantly sized below 500 μm, with larger microplastics (2–5 mm) exhibiting higher removal efficiencies after secondary treatment. Analysis of microplastic types revealed that PE is the most common type in the effluent of the Wulongkou plant, while the Shuangqiao plant predominantly contains PE and PA66. The abundance of microplastics in sludge samples was found to be 6.4 ± 0.8 items/g and 11.3 ± 2.3 items/g, highlighting sludge as an important sink for microplastics. Surface analysis of microplastics revealed characteristics such as wrinkles and cracks, with energy-dispersive spectroscopy indicating significant adsorption of heavy metal elements such as Zn, Hg, and Pb onto microplastic surfaces in sludge. These findings underscore the importance of microplastic removal in wastewater treatment processes and provide scientific evidence for the control and management of microplastic pollution in the future.

Keywords: microplastics; wastewater treatment plants; heavy metals; remove

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1. Introduction

The new pollutants primarily encompass persistent organic pollutants, endocrine disruptors, antibiotics, and microplastics. Microplastic contamination within these new pollutants mainly arises from the extensive production and widespread use of plastics. Global plastic production has escalated from 250 million tons in 2009 to 367 million tons in 2020 [1], with China being the world's leading producer, contributing to 26% of the global production [2]. However, only 6–26% of plastics can be recycled globally [3], and a large number of plastics are placed in landfills or remain in the environment, broken and decomposed into microplastics, which accumulate in the environment and migrate to rivers, lakes, and seas through erosion, surface runoff, and other forms, resulting in microplastic pollution. Initially discovered by Carpenter et al. in the coastal areas of New England [4], microplastic pollution has since been observed by researchers like Colton and Neelavannan in various regions such as the Atlantic, the Himalayas, and the Arctic and Antarctic [5,6]. Microplastic contamination has also been detected in samples from animals, plants, and human blood, drawing significant attention to research on these new pollutants.

Wastewater treatment plants (WWTPs) contain a substantial amount of microplastics originating from personal care products, synthetic fiber clothing washing, tire abrasion, plastic product factories, etc. [7–9]. The concentration of microplastics varies among different sewage treatment plants, with varying removal efficiencies. Investigations by Murphy et al. revealed that a secondary sewage treatment plant reduced the microplastic abundance from an effluent concentration of 15.7 ± 5.23 items/L to a final effluent concentration of 0.25 ± 0.04 items/L, achieving a removal efficiency of 98.41% [7]. Talvitie et al. reported that the effluent microplastic concentration in a wastewater treatment plant was 180 items/L, with an average effluent concentration of 4.9 ± 1.4 items/L of fibers and 8.6 ± 2.5 items/L of particles after treatment [10]. Conventional pollutants (COD, NH3-N, and P) in sewage are oxidatively removed by activated sludge treatment, but microplastics cannot be oxidatively decomposed and are transferred spatially into residual sludge. Subsequently, the residual sludge may transfer a considerable amount of microplastics into the soil during subsequent treatment processes [8,9]. Furthermore, studies have shown that compared to pristine microplastics, microplastics in sludge exhibit significantly enhanced adsorption potential for heavy metal pollutants like Cd [11]. WWTPs not only serve as barriers but also serve as important pathways for microplastics to enter the environment. A large amount of microplastics is continuously transported to WWTPs through surface runoff, domestic wastewater, atmospheric deposition, and other means. During the wastewater treatment process, microplastics in the water are transferred back to the soil and atmosphere through precipitation and suspension, while the remaining microplastics in the wastewater are discharged into aquatic environments [12]. As the main sources and sinks of pollution, there is limited reporting on the full lifecycle of M-NPs in WWTPs. Therefore, investigating the presence and potential risks of microplastics in wastewater and sludge from treatment plants is of significant importance.

2. Materials and Methods

2.1. Sample Collection

The Zhengzhou Wulongkou Wastewater Treatment Plant is situated in northern China, in the western region of Zhengzhou city. The treatment process at Wulongkou utilizes an improved oxidation ditch technology, as the red dots illustrated in Figure 1a. Treated reclaimed water undergoes conventional treatment processes (coagulation, sedimentation, and filtration) and is repurposed for urban landscape irrigation. To study the removal efficiency of microplastics at various stages of a wastewater treatment plant, samples were collected at six sampling points: effluent from intake (EI), effluent from grid (EG), effluent from oxidation ditch (EOD), effluent from secondary sedimentation tank (ESST), and effluent from deep treatment (EDT). The sampling locations are illustrated in Figure 1a. Sludge samples from the Wulongkou Wastewater Treatment Plant were collected from the sludge dewatering workshop. After undergoing plate and frame filtration, the dewatered sludge was sealed in sampling bags and transferred to the laboratory for further analysis, followed by drying at 50 °C in an oven.

The Shuangqiao Wastewater Treatment Plant in northern China, in the western region of Zhengzhou city, employs an A_2O (Anaerobic-Anoxic-Oxic) process, as illustrated in Figure 1b. Similarly, to investigate the removal efficiency of microplastics at various stages of the wastewater treatment process, sampling was conducted at five sampling points: effluent from intake (EI), effluent from biological pool (EBP), effluent from secondary sedimentation tank (ESST), and effluent from deep treatment (EDT), as depicted in Figure 1b. Sludge samples from the Shuangqiao Wastewater Treatment Plant were collected from the sludge transportation vehicles, sealed in sampling bags, and transferred to the laboratory for further analysis, followed by drying at 50 °C.

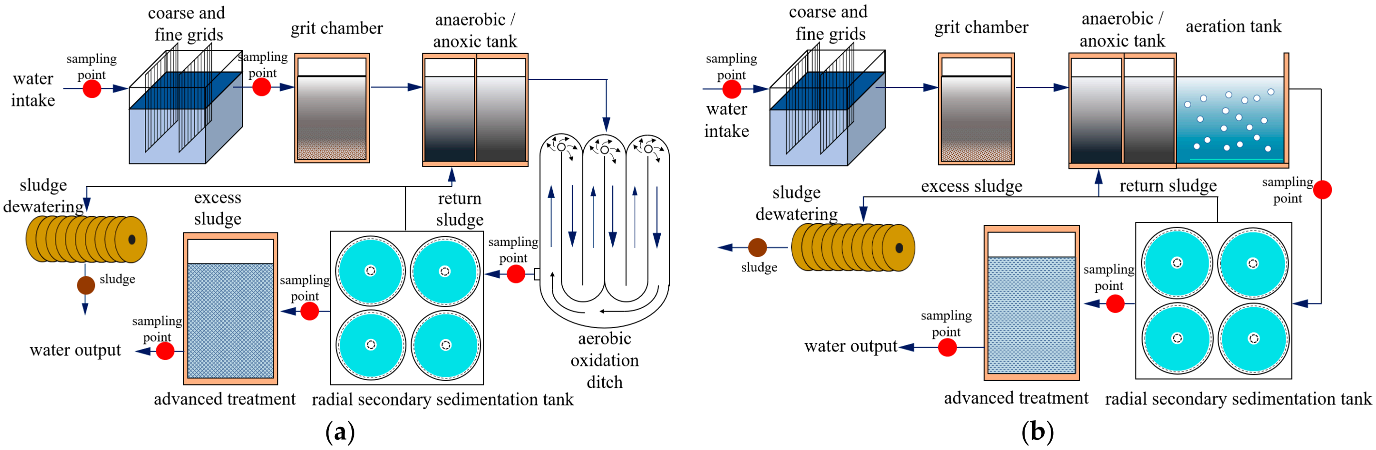


Figure 1. Process flow and sampling points of Wulongkou (**a**) and Shuangqiao (**b**) WWTP.

2.2. Separation and Extraction of Microplastics

2.2.1. Pretreatment of Sewage Samples

The pretreatment of sewage samples adopts Fenton advanced oxidation method, and the reagent preparation and reaction time list in Supplementary Information (Sampling method).

2.2.2. Pretreatment of Sludge Samples

Sludge samples were dried in a forced-air oven at 50 °C for 48 h. The dried sludge was ground into a powder using a mortar and pestle, followed by sieving through a 60-mesh (aperture size 0.25 mm) stainless steel sieve. The pretreatment of sludge involved the addition of 30% H_2O_2 to dissolve organic matter present in the sludge.

2.2.3. Density Separation and Extraction of Microplastics

Preparation of High-Density Solutions

Microplastics commonly found in the environment have densities ranging from 0.8 to 1.4 g/cm^3. Therefore, density separation methods are employed for isolation. Common high-density solutions include NaCl solution (ρ = 1.2 g/cm^3), $CaCl_2$ solution (ρ = 1.5 g/cm^3), $ZnCl_2$ solution (ρ = 1.5 g/cm^3), and NaI solution (ρ = 1.8 g/cm^3). In this experiment, NaI solution (1.7 ± 0.05 g/cm^3) was used for water samples, and $ZnCl_2$ solution (ρ = 1.5 ± 0.05 g/cm^3) was used for sludge samples, while low-density solutions consisted of anhydrous ethanol (0.8 ± 0.05 g/cm^3).

Extraction Steps for Water Samples

After Fenton advanced oxidation for 4 h, water samples were vacuum filtered through a 0.45 µm membrane filter. The precipitate was filtered onto filter paper, washed with NaI solution into a beaker, sonicated for 5 min, and stirred with a glass rod to disperse the precipitate and microplastics. After 2 h of settling with aluminum foil sealing, the supernatant was filtered through a 0.45 µm filter paper. The substance on the filter paper was flushed into a beaker using anhydrous ethanol and allowed to settle for 2 h. The precipitate was vacuum filtered through a 0.45 µm membrane filter, and the supernatant was collected using NaI solution. The extraction process with high-density solution was repeated three times, and the final filtered paper was placed in a clean Petri dish to air dry for more than 24 h for microplastic extraction.

Extraction Steps of Microplastics in Sludge Samples

A total of 5.00 g of dry sludge was weighed into a 50 mL conical flask, followed by the addition of 25 mL of 30% H_2O_2. The flask was sealed with aluminum foil and placed on a shaker at 100 rpm for 6 h. After digestion, the mixture was vacuum filtered through a

0.45 µm filter paper. The substances on the filter paper were washed with $ZnCl_2$ solution into a 40 mL glass bottle with a cap, shaken evenly, and then allowed to settle for 4 h. The solution was filtered through a 0.45 µm membrane filter, sealed, and allowed to settle for another 4 h. After repeating this process three times, the filter paper was placed in a Petri dish for drying.

2.3. Identification and Recognition of Microplastics

The separation method can be seen in Supplementary Information.

After separation and purification, microplastics in the environmental medium require further characterization to analyze their morphology, quantity, composition, and physicochemical properties. An optical microscope allows preliminary observation and identification of microplastics, enabling the determination of their shape, color, and quantity. The associated Scopelmage 9.0 software is used to photograph and measure the dimensions of microplastics. Fourier-transform infrared spectroscopy (FTIR) is widely used for the analysis and identification of microplastics. FTIR can identify microplastics above 20 µm. Microplastics larger than 2 mm extracted in the experiment were scanned using attenuated total reflectance FTIR (ATR-FTIR) to identify the types of microplastics. The scanning range was 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}, and 32 scans were performed. The OMNIC software was used to analyze the scanning results. For microplastics at the micron and nanometer scales, a scanning electron microscope (SEM) can be used for observation [13]. SEM provides clear images of the surface morphology of microplastics but cannot determine if the particles are plastic or identify the specific polymer composition. SEM-EDS (SEM with energy-dispersive X-ray spectroscopy) allows for the analysis of surface morphology and the assessment of heavy metal impurities adsorbed on the microplastic surfaces.

2.4. Statistical Analysis

Data analysis was performed using SPSS software. The homogeneity of variances was assessed using the F-test, followed by the *t*-test to determine differences. A significance level of $p \geq 0.05$ indicated no statistically significant difference.

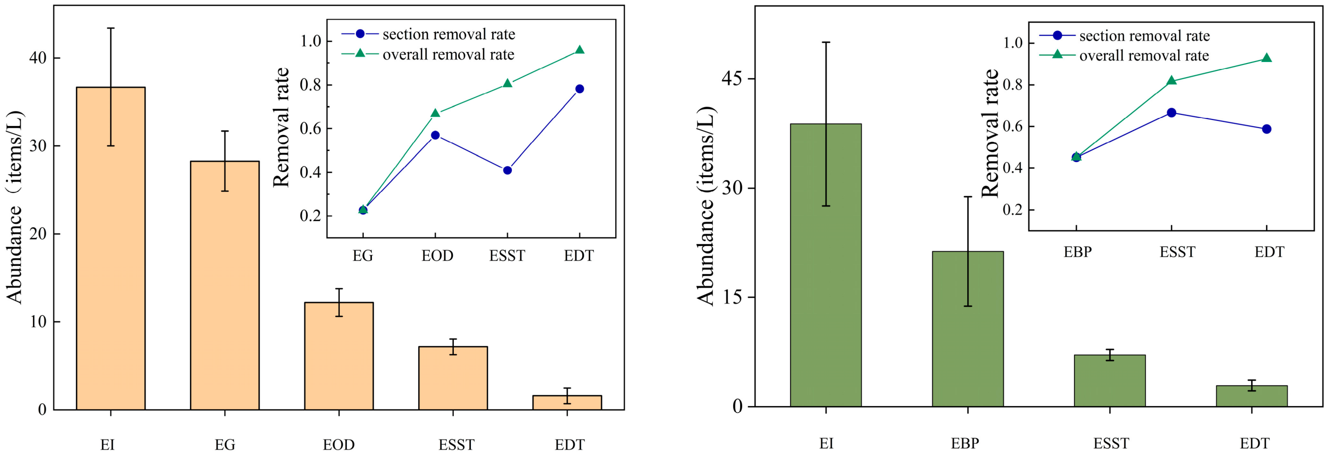
3. Discussion

3.1. Abundance of Microplastics in Each Section of a Sewage Treatment Plant

At the Wulongkou Wastewater Treatment Plant (Figure 2a), the effluent microplastic abundance was 36.7 ± 6.7 items/L. After grid, oxidation ditch, secondary sedimentation tank (with microplastic abundances of 28.3 ± 3.4 items/L, 12.2 ± 1.6 items/L, and 7.2 ± 0.9 items/L, respectively), and deep treatment, the effluent microplastic abundance decreased to 1.6 ± 0.9 items/L, resulting in an overall removal efficiency of 95.64%.

At the Shuangqiao Wastewater Treatment Plant (Figure 2b), the effluent microplastic abundance was 38.8 ± 11.3 items/L. The effluents from the biological pool, secondary sedimentation tank, and deep treatment, respectively, had microplastic abundances of 21.3 ± 7.5 items/L, 7.1 ± 0.8 items/L, and 2.9 ± 0.8 items/L, yielding an overall removal efficiency of 92.53%.

Overall, both wastewater treatment plants effectively removed microplastics from the effluent, with removal efficiencies exceeding 90%. However, the removal capacities varied among different treatment stages. In the Wulongkou Wastewater Treatment Plant, the deep treatment stage exhibited the strongest removal efficiency, whereas in the Shuangqiao Wastewater Treatment Plant, the secondary sedimentation tank demonstrated the highest removal efficiency. The efficacy of removal efficiency in different treatment stages is influenced by various factors, particularly the size, shape, and material composition of microplastics entering each stage. While removal efficiency reflects the proportion of microplastics removed from wastewater, the quantities removed are notably higher in the oxidation ditch and biological pool stages when considering the removal of microplastics.



(**a**) (**b**)

Figure 2. Microplastic abundance and removal rate of each section of Wulongkou (**a**) and Shuangqiao (**b**) WWTPs.

The microplastic abundance in activated sludge-based sewage treatment plants has been documented in various regions. In Wuhan, China, the microplastic abundance decreased from 79.9 items/L in effluent to 28.4 items/L in effluent, achieving a removal rate of 64.4% [14]. In Chaoyang District, Beijing, China, at a municipal level sewage treatment plant, the microplastic abundance decreased from 12.03 ± 1.29 items/L in effluent to 54.47 ± 14.73 items/L in effluent, with a removal rate of 95% [15]. In Nanjing, China, a wastewater treatment plant implemented an advanced process combining modified sequencing batch reactors, aerobic fluidized bed reactors, and other deep treatment technologies, resulting in a decrease in microplastic abundance from 44.07 items/L in effluent to 1.93 items/L in effluent, with a removal efficiency of 96% for microplastics in the effluent [16]. Comparative analysis with other regions in China and internationally reveals excellent removal efficiencies at the Wulongkou and Shuangqiao sewage treatment plants, reaching 95.64% and 92.53%, respectively.

In large secondary sewage treatment plants in the UK, the average microplastic concentration in effluent was 15.70 items/L, which decreased to 0.25 items/L after treatment with activated sludge, achieving a removal rate of 98.14% [7]. At the Aourir sewage treatment plant in Morocco, which primarily treats domestic wastewater, the average microplastic abundance decreased from 188 items/L in effluent to 50 items/L in effluent. Meanwhile, at the M'zar sewage treatment plant, which receives both domestic and industrial wastewater, the effluent microplastic abundance was higher at 519 items/L, with an effluent mean abundance of 86 items/L, resulting in a removal efficiency of 83.43% [17]. In South Korea, microplastic concentrations in effluents of wastewater treatment plants ranged from 102 to 266 particle/L (mean ± standard deviation, 164 ± 57 particle/L), while effluent concentrations ranged from 0.05 to 0.56 particle/L (mean ± S.D., 0.39 ± 0.16 particle/L) across four seasons, with removal rates exceeding 99% [18]. Discrepancies in removal efficiencies can be attributed to variations in the design and optimization of sewage treatment plants based on activated sludge methodology, differences in sampling locations, the varying composition and operational load of sewage sources, and the influence of seasonal weather conditions on treatment capacity and effectiveness [18]. Additionally, differences in microplastic sampling, processing, detection limitations, and the lack of standardized protocols can contribute to discrepancies.

3.2. The Shape and Color of Microplastics in Sewage Treatment Plants

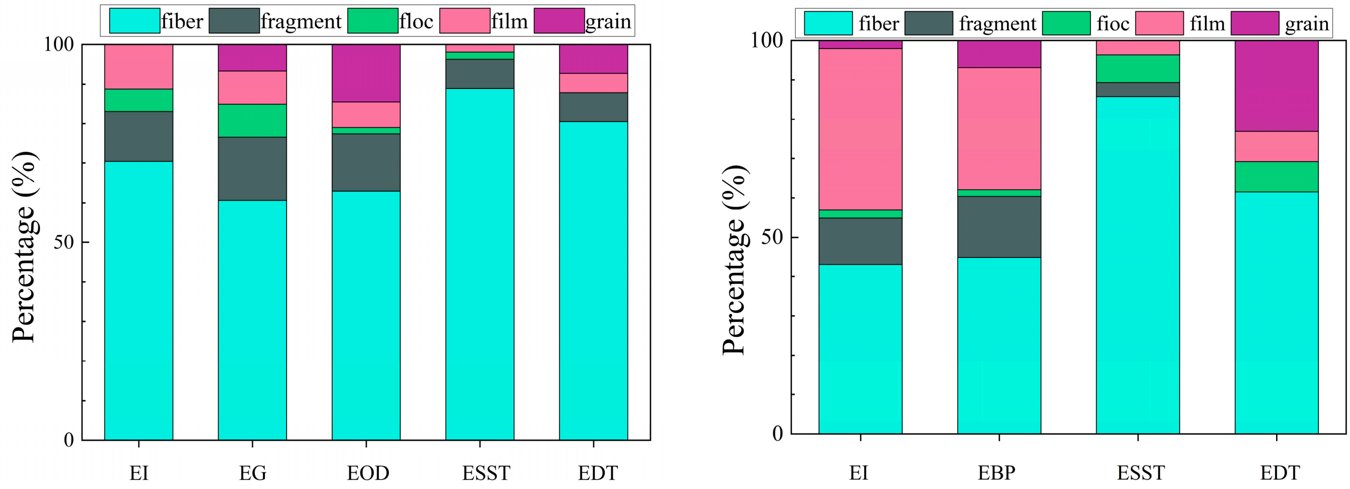
In wastewater treatment plants, extracted microplastics are classified into categories based on their shapes, including fibers, fragments, aggregates, films, and particles. Filmshaped microplastics are characterized as thin, yellowish membrane-like structures visible to the naked eye, as depicted in Figure S1.

Analysis of microplastic shapes and colors involves consolidating data from three parallel experiments. Fibrous microplastics dominate in wastewater treatment plants, which is attributed to the substantial release of fiber microplastics from household laundry wastewater. Microplastics exhibit a diverse range of colors, including red, green, blue, purple, brown, yellow, and colorless (with black, white, and gray categorized as colorless) [19]. For statistical purposes and to minimize errors arising from subjective assessments, colors of microplastics extracted from wastewater treatment plants are classified into two groups: colored and colorless. Colored microplastics encompass red, blue, green, orange, and purple, while colorless microplastics include black, gray, and transparent states. The highest proportion of microplastics in wastewater treatment plants is fiber-shaped, which is related to the significant release of fiber microplastics in domestic laundry wastewater [20–22]. When WWTPs are primarily tasked with treating domestic sewage, the composition of fibers in test samples is found to be predominant in detections [23]. This could be attributed to the fact that most microplastics in domestic sewage originate from synthetic fibers, with Browne et al. finding that polyester and acrylic fibers, common materials in clothing, constitute a significant portion of microplastics detected in water samples, as a large number of microplastic fibers from laundry wastewater enter domestic sewage [22]. The two WWTPs sampled in this study are located in the western and northern regions of Zhengzhou, with sewage primarily sourced from urban residents, densely populated areas, and processing capacities exceeding one hundred thousand tons per day. However, Margenat et al. found that less than 1% of microplastics in fibers were quantified in a sewage treatment plant in Spain, possibly due to differences in the location of sewage treatment plants, which mainly handle upstream municipal sewage and wastewater from three villages with lower daily processing capacities [24]. Moreover, the high degradation rate of natural fibers [25] or limitations in the fluorescence detection method used during experiments [26] may also contribute to these findings.

In the effluent of the Wulongkou Wastewater Treatment Plant, fibers exhibited the highest proportion, reaching 70.4% (Figure 3a). However, as subsequent treatment stages aimed at microplastic removal progressed, the proportion of fibrous microplastics in the effluent increased to 80.5%. This phenomenon may be attributed to the difficulty in removing fibrous microplastics in the secondary sedimentation tank and deep treatment processes, leading to a relative increase in the proportion of fibrous microplastics as the quantities of other shapes of microplastics decrease.

The proportion of fragmented microplastics remained relatively stable, while aggregates were generally less prevalent, with no detection of aggregated microplastics in the effluent of the deep treatment stage. Particle microplastics were not detected in the effluent of intake but accounted for 14.5% in the effluent of oxidation ditch. Particle microplastics are characterized by their small size, and in the oxidation ditch, they may adhere to activated sludge particles, leading to an increased proportion of particle microplastics in the effluent. However, the proportion of particle microplastics decreased again to 0 in the secondary sedimentation tank, indicating effective removal of particle microplastics through sedimentation in this stage.

In the effluent of the Shuangqiao wastewater treatment plant (Figure 3b), fibers similarly dominate, accounting for 43.1%, followed by film microplastics at 41.2%. Fibrous microplastics constitute 85.7% of effluent from the secondary sedimentation tank, while film microplastics decrease to 3.6%. Comparing with fibers, film microplastics remove easier in the wastewater from WWTP treatment. Fragment microplastics decrease in proportion as the treatment process progresses, with no detection of fragment microplastics in the effluent after deep treatment. Although the proportion of floc and grain increases, their quantities continue to decrease as the treatment process advances.



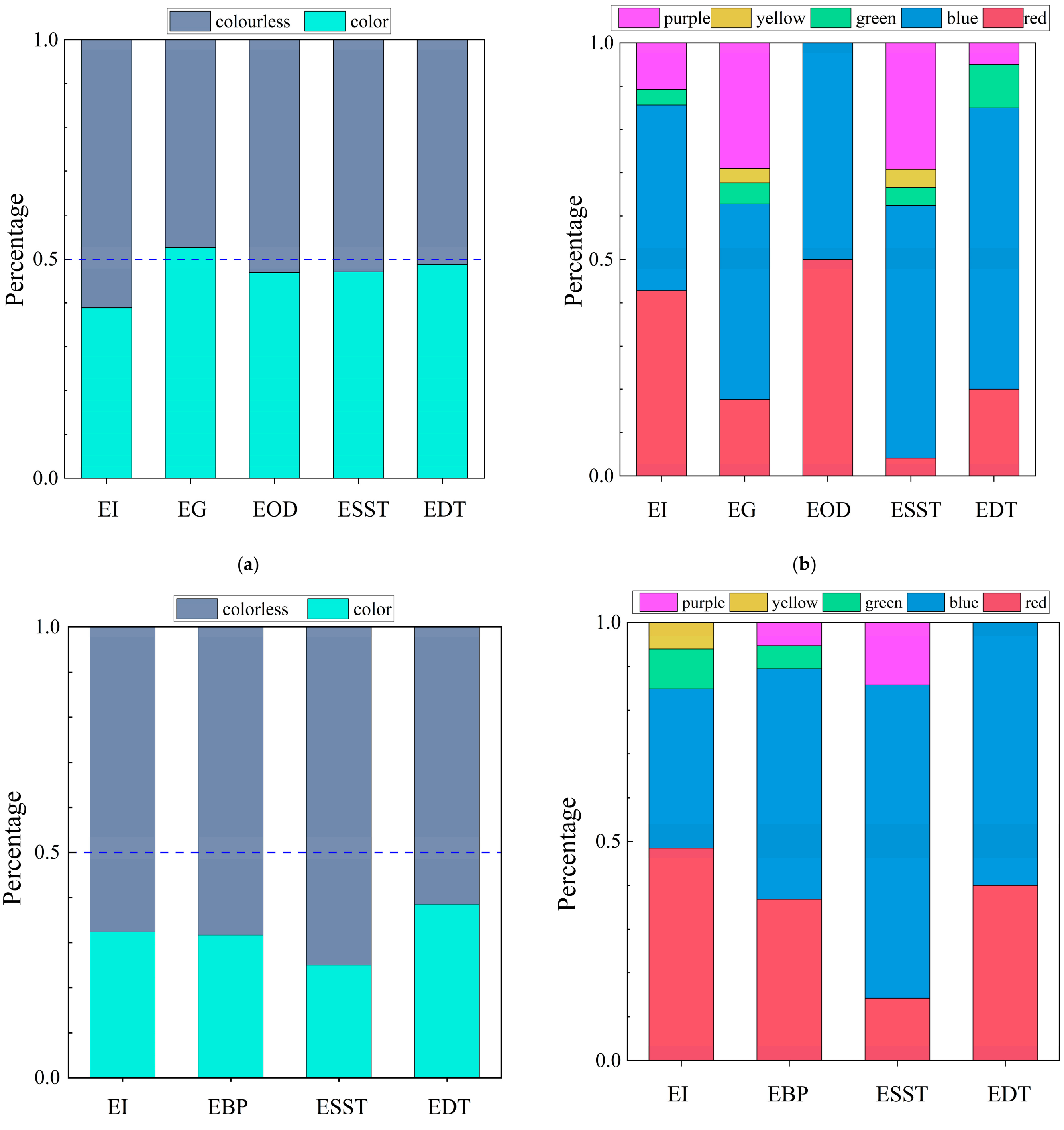
(**a**) (**b**)

Figure 3. Percentage of microplastic shapes in each section of Wulongkou (**a**) and Shuangqiao WWTP (**b**).

The significant disparity in the proportions of fiber and film microplastics in the effluents of two wastewater treatment plants may stem from variations in their respective catchment areas. The Wulongkou wastewater treatment plant, situated closer to residential areas, likely receives a higher proportion of domestic wastewater, whereas the Shuangqiao wastewater treatment plant, located farther from residential zones, may receive a greater influx of industrial wastewater. Consequently, the pronounced contrast in the proportions of fiber and film microplastics in their effluents arises. While fibers constitute the predominant form of microplastics in most wastewater treatment plants, there are instances where the proportion of film microplastics surpasses that of fibers [27]. Despite fibers being the most prevalent microplastic type in wastewater treatment plants, research suggests that natural fibers such as cotton and linen may account for over half of the fiber content in sewage [28]. Hence, effective differentiation between natural and synthetic fibers is crucial for accurately assessing microplastic pollution in wastewater. Film microplastics predominantly originate from everyday items like plastic bags and food packaging, whereas grain microplastics primarily arise from native microplastics added to personal care products.

From a holistic perspective, the Wulongkou WWTP exhibits a higher prevalence of colorless microplastics compared to colored microplastics in the effluent (Figure 4a), while in subsequent treatment stages, the distribution becomes nearly equal. Among colored microplastics, red and blue are the most prevalent (Figure 4b). This phenomenon can be attributed to the widespread use of red and blue plastics in daily life compared to other colors. Additionally, during microscopy observations, red and blue exhibit higher contrast, which makes it easier to be recognized and recorded.

The colorless microplastics in each section of the Shuangqiao were dominant parts of microplastics abundance (Figure 4c). Among colored microplastics, blue microplastic was the main proportion, followed by red. Only a small amount of green, orange, and purple were detected (Figure 4d). According to the proportion of colored and colorless microplastics in each section of these WWTPs, the color of microplastics does not affect the removal of microplastics from sewage.



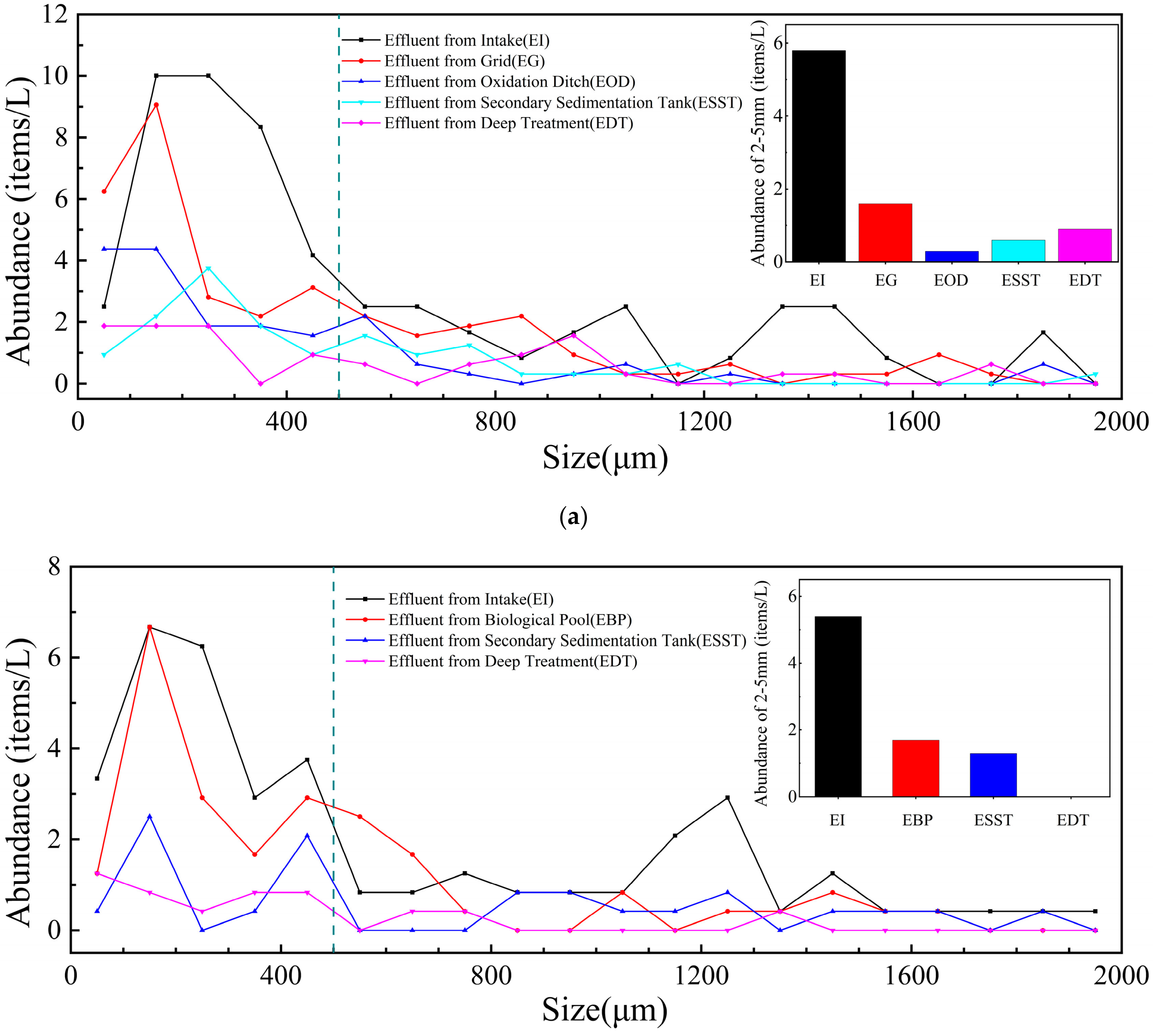
(**a**) (**b**)

(**c**) (**d**)

Figure 4. Percentage of microplastic color distribution in Wulongkou (**a**,**b**) and Shuangqiao (**c**,**d**) WWTPs.

3.3. *Size Distribution of Microplastics in Sewage Treatment Plants*

In both wastewater treatment plants, microplastic sizes across various treatment stages are predominantly concentrated within 500 μm (Figure 5a,b). Analysis of microplastic distribution within 2000 μm across treatment stages reveals a noticeable aggregation within 500 μm in all stages except for deep treatment, with distribution extending between 500 and 2000 μm as size increases. Microplastics ranging between 2 and 5 mm exhibit an abundance of 5.8 items/L in the effluent of the Wulongkou wastewater treatment plant, 1.6 items/L in the grid, and concentrations within the oxidation ditch, secondary sedimentation tank, and deep treatment effluent all remaining below 1 item/L. The effluent of the Shuangqiao wastewater treatment plant contains 5.4 items/L within this size range, with concentrations in the biological pool and secondary sedimentation tank at 1.7 items/L and 1.3 items/L, respectively. Notably, microplastics exceeding 2 mm are absent in the effluent of the deep treatment stage, indicating efficient removal of larger microplastics even within a secondary wastewater treatment system.



(**a**)

(**b**)

Figure 5. Distribution of microplastics in each section of Wulongkou (**a**) and Shuangqiao (**b**) WWTPs.

In the distribution of microplastics across various treatment stages (Figure 5a,b), an increase in the abundance of effluent microplastics between 1000 and 1500 μm is evident. Therefore, an analysis of the shape distribution of effluent microplastics in two wastewater treatment plants was conducted. In the Wulongkou wastewater treatment plant, there is an increase in the abundance of fiber microplastics between 1000 and 1500 μm (Figure S2a); whereas in the Shuangqiao wastewater treatment plant, there is an increase in the abundance of both fiber and film plastics within this size range (Figure S2b). Additionally, it should be noted that in the effluent of the Shuangqiao wastewater treatment plant, the abundance of film microplastics within the 1000–1500 µm range is the highest. This suggests that film microplastics have a larger average size compared to other shapes, and the proportion of film microplastics in the effluent of the secondary sedimentation tank decreases most significantly (Figure 3b). This may indicate that film microplastics, due to their larger size, are more prone to adhere to sludge in the secondary settling tank and are subsequently removed from the effluent as sludge is removed from the tank.

The size range of microplastics in wastewater treatment plants typically falls between 20 and 1000 µm. Studies have indicated that in the effluent of these plants, microplastics exceeding 500 µm sometimes comprise over 70%, whereas in the effluent, over 90% of microplastics are smaller than 500 µm, with approximately 60% of microplastics in some samples being smaller than 100 µm [29–33]. In the effluent of Wulongkou wastewater treatment plant, microplastics within 500 µm accounted for 57.3%, while in the effluent, microplastics smaller than 500 µm accounted for 51.2%; similarly, in the effluent of Shuangqiao wastewater treatment plant, microplastics within 500 µm accounted for 53.9%, while in the effluent, microplastics smaller than 500 µm accounted for 76.9%. The observed differences may be attributed to variations in sampling or microplastic extraction methods. Hence, in the future, efforts should be made to standardize the collection and detection methods for microplastics to facilitate better comparisons across different studies.

3.4. Types of Microplastics in Sewage

Existing studies have found that over 30 different types of microplastics have been detected in the effluent of WWTPs, including common types such as PET, PES, PAE, PE, PP, PVC, and PS [34,35]. Microplastics with sizes exceeding 2000 µm (excluding fibers) extracted from the effluent of wastewater treatment plants undergo Fourier-transform infrared spectroscopy analysis, and the scan results are compared and analyzed against the "Hummel Polymer and Additives library" spectral database to determine the types of microplastics present.

Samples from two sewage treatment plants were extracted and separated into microplastic fragments (except fiber shapes) with a particle size greater than 1 mm for Fourier infrared spectroscopy scanning and matched with the "Hummel Polymer and Additives library" atlas library, as shown in Figure 6. In the global production of non-fibrous plastics, PE production is the highest (36%), followed by PP (21%) and PVC (12%), while the main components of waste plastics in domestic waste in China are PE, PP, and PS [36], which is consistent with the results that polyethylene (PE) has the highest percentage of FTIR in the samples.

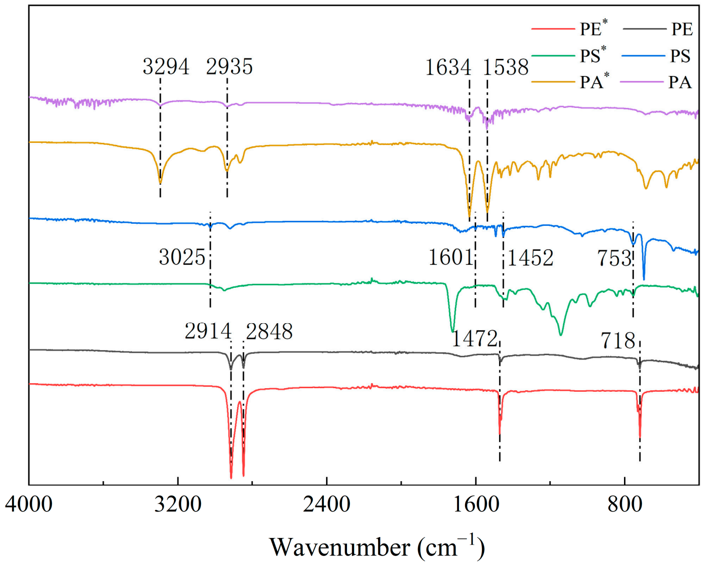


Figure 6. FTIR image of microplastics and primary plastics (*) extracted from samples.

Analyzing 14 film microplastics from the effluent of the Wulongkou wastewater treatment plant against the spectral library revealed that PE accounted for 11 particles (78.6%), with 1 identified as polyisocyanate and 2 as silk particles. Similarly, examining 21 film microplastics from the effluent of the Shuangqiao wastewater treatment plant against the spectral library indicated that PE and PA66 each accounted for 10 particles (47.6%), while PS accounted for 1.

The disparity in microplastic types between the two wastewater treatment plants may also stem from differences in their catchment areas. The catchment area of the Wulongkou wastewater treatment plant primarily encompasses residential zones, hence PE emerges as the predominant microplastic type, with some materials resembling silk potentially originating from textile washing processes infiltrating the sewage system. In contrast, the catchment area of the Shuangqiao wastewater treatment plant is more industrialized, leading to a higher proportion of nylon-like materials.

3.5. Microplastics in the Sludge

The sludge was dried in an oven at 105 °C for 24 h. The water content in the sludge was measured and the sludge water content is shown in Table 1.

Table 1. Sludge moisture content.

Water Treatment Plant	Water Content (%)
Wulongkou sewage treatment plant	85.07
Shuangqiao sewage treatment plant	76.63

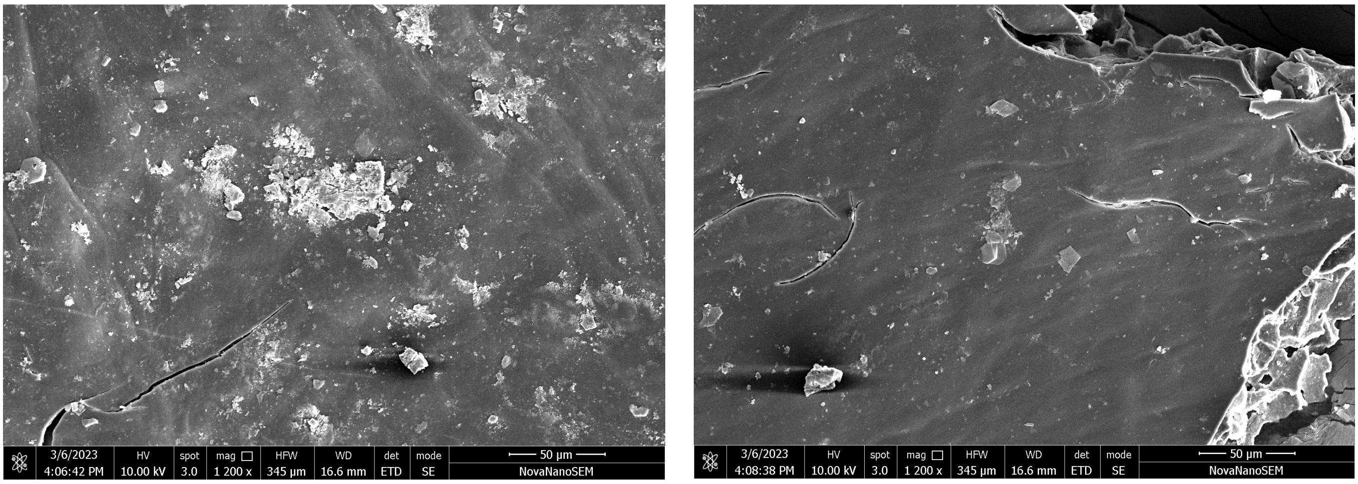
The size distribution of microplastics extracted from sludge primarily concentrates within the range of 500 μm and below (Figure S3). The proportions of microplastics within 500 μm in sludge from the Wulongkou and Shuangqiao wastewater treatment plants are 78.3% and 85.4%, respectively. Microplastics detected in sludge are predominantly found in smaller size ranges compared to those in wastewater, with sludge microplastics exhibiting smaller average sizes. This could be attributed to the compaction and hardening of sludge after drying, followed by grinding and sieving processes before microplastic extraction, which may lead to microplastic fragmentation. Hence, future research should consider direct microplastic extraction from wet sludge to mitigate potential microplastic fragmentation resulting from grinding dry sludge.

The microplastic abundances in dry sludge from the Wulongkou and Shuangqiao wastewater treatment plants are 6.4 ± 0.8 items/g and 11.3 ± 2.3 items/g, respectively. The abundance of microplastics in sludge is influenced by various factors, including population density, economic conditions, rainfall, and industrial wastewater ratios. Generally, compared to the A/O process, the oxidation ditch process has longer hydraulic retention time and sludge retention time, exerting a greater influence on microplastic abundance in sludge. Thus, sludge from oxidation ditch processes typically exhibits lower average microplastic abundances compared to A/O processes. Microplastic removal in wastewater treatment plants involves spatial transfer rather than degradation, as microplastics are transferred from wastewater to sludge. Studies by Li et al. on 28 wastewater treatment plant sludges in China revealed microplastic abundances ranging from 1.6 to 56.4 items/g (dry sludge), with an average abundance of 22.7 items/g [37]. Lassen et al. investigated wastewater treatment plant sludges in Germany, reporting microplastic abundances ranging from 1.0 to 24.0 items/g (dry sludge) [38]. Lusher et al. studied microplastic contents in sludges from eight wastewater treatment plants in Norway, with an average microplastic abundance of 6.077 items/g (dry sludge) [39].

Sludge contains a substantial amount of microplastics, and considering that China currently produces approximately 40 million tons of sludge annually with a moisture content of around 80%, an estimated 1.56 quadrillion microplastics are introduced into soil ecosystems annually due to improper sludge disposal or land use [37,40]. Hence, future efforts should focus on understanding the fate of microplastics in sludge to mitigate potential soil microplastic pollution resulting from improper sludge management practices.

3.6. Surface and Heavy Metal Adsorption of Microplastics

Observation of microplastic surfaces via scanning electron microscopy reveals that microplastics extracted from wastewater treatment plants exhibit relatively smooth surfaces with minimal wrinkles and only a small amount of attached impurities (Figure S4). In contrast, microplastics extracted from sludge exhibit cracked surfaces (Figure 7), with impurities adhering to the plastic surfaces.



(**a**) (**b**)

Figure 7. SEM images of microplastics in sludge from Wulongkou (**a**) and Shuangqiao (**b**) WWTPs.

The treatment processes for sludge may influence the microplastic content within it. Studies suggest that the abundance of microplastics in sludge may decrease after anaerobic digestion treatment [41]. Characterization of microplastics in sludge samples from seven wastewater treatment plants in Ireland by Mahon et al. indicated relatively lower microplastic abundances in anaerobically digested sludge, while lime-stabilized sludge exhibited increased microplastic abundances in the smaller size range [42]. Anaerobic digestion and composting processes for sludge can enhance the biodegradation of biodegradable plastics (PLA and PCL), making them more susceptible to biological degradation. Additionally, compared to fresh plastics, plastics in sludge surfaces exhibit abrasion and erosion, and are prone to fragmentation [43,44]. Changes in certain physicochemical properties of microplastics during sludge treatment processes may affect their adsorption properties towards heavy metals. Studies have shown that microplastics in sludge have an order of magnitude higher adsorption potential for Cd than fresh microplastics [7].

Considering the substantial presence of microplastics in sludge and the emerging challenge of rationalizing sludge disposal, future focus should be directed towards understanding the physicochemical properties of microplastics in sludge, particularly how sludge treatment processes influence them. This is crucial to mitigate potential environmental hazards resulting from the transportation and disposal of microplastics in sludge.

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) enables the analysis of heavy metal elements adsorbed on the surfaces of microplastics in sludge (Table 2). From previous studies, it is not difficult to find that many heavy metals such as Pb, Cu, Cd, Cr, and As can still be detected in sewage even after undergoing a series of treatments [45,46]. The predominant heavy metal element adsorbed on the surface of microplastics in sludge is zinc (Zn), while the adsorption amount of cadmium (Cd) is only 0.1% and 0.0%. This may be attributed to the low concentration of Cd in the effluent of the two wastewater treatment plants, resulting in insufficient adsorption of Cd onto microplastics in the sludge.

Table 2. Heavy metals adsorbed in sludge.

Element	Atomic Number Percentage (%)	
	Wulongkou Sewage Treatment Plant	**Shuangqiao Sewage Treatment Plant**
Zn	33.08	34.13
Hg	22.50	21.84
Cu	18.26	7.86
Pb	17.80	32.15
Sn	7.39	1.97
Cr	0.88	2.06
Cd	0.10	0.00

4. Conclusions

This study investigates the extraction and analysis of microplastics from different sections of effluent and sludge from two wastewater treatment plants, examining their abundance, size, shape, color, and surface adsorption of heavy metals. The results indicate the following:

(1) The overall removal efficiencies of microplastics in the Wulongkou and Shuangqiao wastewater treatment plants are 95.64% and 92.53%, respectively. The final microplastic abundances in the effluent are 1.6 ± 0.9 items/L and 2.9 ± 0.8 items/L, respectively. The abundances of microplastics in dry sludge from the two plants are 6.4 ± 0.8 items/g and 11.3 ± 2.3 items/g, respectively.

(2) Fibrous microplastics dominate the effluent of the Wulongkou wastewater treatment plant, accounting for 70.4%, with PE microplastics being the most prevalent at 78.6%. In contrast, fibers and film microplastics constitute 43.1% and 41.2% of the effluent in the Shuangqiao wastewater treatment plant, with PE and PA66 microplastics each accounting for 47.6%. These differences in shape and type may stem from variations in their respective catchment areas.

(3) Microplastics in wastewater exhibit numerous wrinkles on their surfaces, while microplastics in sludge display a higher occurrence of cracks. Energy-dispersive X-ray spectroscopy scanning of microplastics in sludge from both wastewater treatment plants reveals zinc (Zn) as the most adsorbed heavy metal element, followed by mercury (Hg) and lead (Pb).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations11060177/s1, Figure S1: Image of microplastics on filter paper after density separation; Figure S2: Abundance distribution of each shape in the effluent water of Wulongkou (a) and Shuangqiao (b) WWTP; Figure S3: Size distribution abundance and average abundance of microplastics in sludge; Figure S4: SEM images of microplastics in Wulongkou (a) and Shuangqiao (b) WWTPs.

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