

DEGRADATION OF POLYETHYLENE TEREPHTHALATE (PET) AS SECONDARY MICROPLASTICS UNDER THREE DIFFERENT ENVIRONMENTAL CONDITIONS

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ABSTRACT: Polyethylene terephthalate (PET) bottles have been widely used as biofilm media for residential-scale Wastewater Treatment Plants (WWTP) in Indonesia because of their advantages such as being inert. PET bottles can also be degraded as secondary microplastic contaminants during the operation of WWTPs. This study aimed to investigate the possibility of degradation of PET as secondary microplastics. The research was carried out in distilled water under three different environmental conditions (indoor laboratory scale, outdoor laboratory scale, and field-scale). The abundance, size, color, and shape of microplastics were observed through a light binocular microscope with a 100x magnification combined with Image Raster 3.0 software. Data of environmental properties (i.e., DO, temperature and pH) were collected. The solubility potential of PET as microplastics was identified after 7 months of indoor and outdoor laboratory experiments with concentrations of 18.67 ± 7.02 MP/L and 44.00 ± 12.77 MP/L, respectively. Experiments on UV irradiation showed faster degradation of PET and the presence of microplastics increased along with the exposure period with concentration at the first month, the second month, the third month, and the seventh month were 15.33 ± 7.09 MP/L, 51.67 ± 9.61 MP/L, 54.33 ± 8.39 MP/L, and 248.67 ± 29.09 MP/L, respectively. The major microplastics characteristics were fragments (92.37%), fiber (7.63%), transparent particle color (82.85%), and particle size of 10 μ m (61.04%).

Keywords: Degradation, Environmental conditions, Microplastics, Polyethylene terephthalate

1. INTRODUCTION

Polyethylene terephthalate (PET) plastic bottle waste has become a low-cost solution for biofilm media that had already been applied in residential scale wastewater treatment plants (RC-WWTPs) in Indonesia. This is based on its advantages, first, it is widely available, cheap, and easy to obtain as plastic waste. Indonesia is a country with the 4th highest consumption of PET bottles in the world [1]. Second, it has the desired properties as a supporting media, namely lightweight, inert (not easily biodegradable), high cavity volume fraction, large surface area, durable, not easy to rot, resistant, able of attaching microorganisms well in large numbers [1-4]. Third, “waste treat waste” [5,6] as well as a solution to reduce the plastic bottle waste in Indonesia.

Although studies on PET as a supporting media in attached growth systems are globally limited, in Indonesia this study raised attention since 2014, because of its advantages. PET as a low-cost media has been applied on a field scale at RC-WWTPs in Indonesia. PET is easy to form in various variations of shape and surface area. For this purpose, PET is cut, folded, and shaped in such away.

However, behind its advantages, the impact of using PET as a microplastics in the WWTP is still

unknown, thus raising concerns about the presence of microplastics in the WWTPs. Microplastics are novel contaminants, plastic particles smaller than 5 mm [7] are of global concern today because they are persistent in the environment for hundreds of years or even thousands of years due to their stability and durability [8] and its negative impact that allows it to enter the food chain and lead to humans as top predators in the food chain [9]. Microplastics in the environment in two forms, primary (plastics of microscopic size that are purposefully used) and secondary (fragmentation and degradation from larger plastic items).

PET is a thermoplastic polymer that has a slow rate of natural decomposition [10]. Physical processes (UV light, heat, photo-oxidation, reducing polymer size); chemical processes (use of chemical compounds to break polymer chains), and biological/degradation processes (bacteria and fungi activity) contribute to the fragmentation and degradation of plastics in the environment [11]. In addition, knowing the degradation process of PET plastics as secondary microplastics is critical for evaluating the status of PET bottles as supporting media in a WWTP. This study focuses to investigate the possibility of the degradation of PET as secondary microplastics under three different environmental conditions (indoor laboratory scale,

outdoor laboratory scale, and field-scale). Thus, data on different exposure times in three different environments was carried out.

2. MATERIAL AND METHODS

2.1 Experimental Set-up

The experiment was carried out in three different environmental conditions; indoor laboratory scale (Laboratory A; Lab-A), outdoor (Laboratory B; Lab-B, and field-scale (field), as shown in Figure 1. The laboratory scale was carried out at the Water Quality Laboratory of Environmental Engineering ITB and the field scale was carried out in exposed outdoor directly to the sunlight.

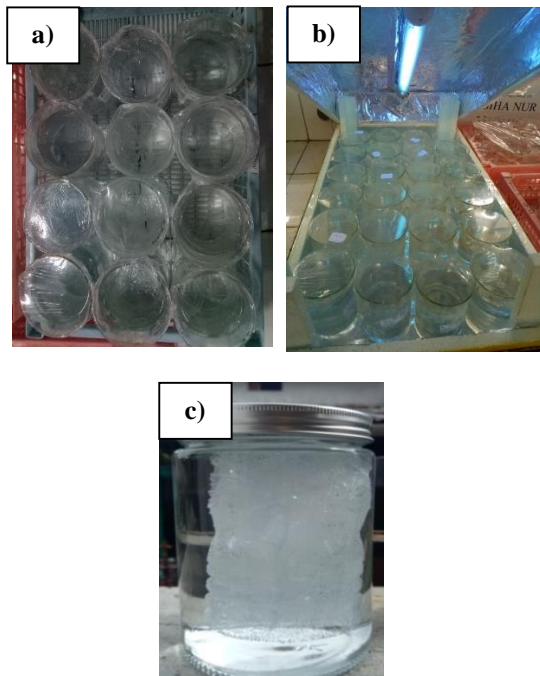


Fig.1 Experiment in three different environmental conditions; a) Lab-A, b) Lab-B, and c) Field

Lab-B used a UVA340 lamp, selected as a simulation of natural sunlight [12], and will then be compared with field conditions with direct exposure to sunlight. First, the 330 ml PET plastic bottles were cleaned, cut the top and bottom, filled with 2 other PET plastic bottles. The size of the bottle pieces was 6 cm in diameter and 8 cm in height. The samples were placed in a 250 ml glass beaker and submerged in distilled water. Second, each variation of samples Lab-A, Lab-B, and the field was equipped with a blank, which only used distilled water, without any PET. Each variation was made triple. Total of each 72 samples. Beaker glasses (sample Lab-B) were put into a handmade chamber (50 cm x 35 cm x 20 for length, width,

height, respectively) made of styrofoam coated with a zinc plate on the inside, equipped with a UV lamp, and tightly closed. Sample Field used a glass jar, exposed to UV irradiation all day. The experiment was conducted for seven months of observation. Each variation as long the observations were three repetitions, as shown in Table 1.

Table 1 The experiment matrix

Sample	Experiment	Observation (month)	Total sample
Lab-A	Laboratorium indoor		
	Blank (DW)	1,2,3,7	12
	PET dan DW	1,2,3,7	12
Lab-B	Laboratorium outdoor (UV lamp)		
	Blank (DW)	1,2,3,7	12
	PET dan DW	1,2,3,7	12
Field	Field (UV light)		
	Blank (DW)	1,2,3,7	12
	PET dan DW	1,2,3,7	12
Total			72

DW = distilled water

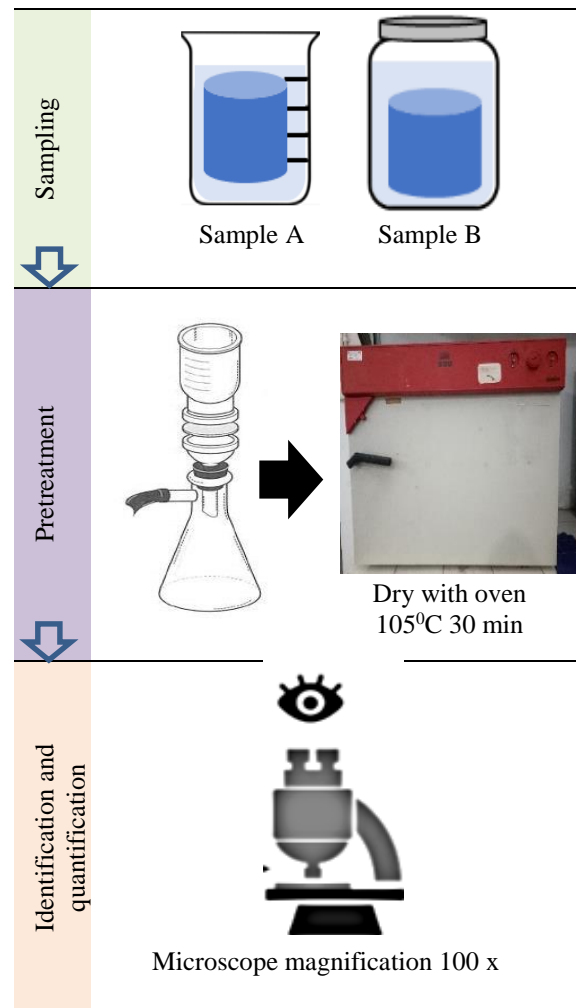


Fig.2 Illustrated of microplastics analysis

2.2 Data Analysis

Observations of Lab-A, Lab-B dan Field were carried out at months 1, 2, 3, and 7. The parameters of DO, pH, and temperature were measured at each observation. DO was measured using a DO-meter, pH, and temperature using a pH-meter.

All suspected microplastics particles were categorized by size, shape (fiber, fragments, microbeads, and others), and color [13]. All suspected microplastics were identified by three rules that distinguish plastic from non-plastic [14]: 1) the particle should not have an organic or cellular structure, 2) the color appears homogeneous as a whole; 3) fiber should be similarly thick all through the whole length, and 4) fiber particles do not break when pressed.

The quantification and identification of microplastics by filtering all the samples using a 0.45 μm cellulose acetate filter and 45 mm in diameter (Sartorius stedim) with a Buchner funnel and a vacuum pump. Then the filter paper was dried using an oven at 105 $^{\circ}\text{C}$ [15] for 30 minutes. Visual observation of filter paper using an Olympus CX-21 light microscope with a magnification of 100x coupled with Optilab Viewer 3.0 software and measurements of particle size using Image Raster 3.0 software (Fig. 2)

3. RESULTS AND DISCUSSION

There were no microplastics found in the blank samples until the 7th month. After 1 month of UV irradiation exposure, microplastics began to occur in field conditions although in small quantities, while in laboratory conditions they were only identified in the third month, although the addition was very small until the third month to the seventh month (shown in Fig. 3).

During the microplastics degradation test from the first month until the seventh month, it was found that the temperature factor from the sun's heat and UV irradiation greatly affected the degradation of PET as a secondary microplastics in distilled water. The temperature under field conditions was higher than the temperature under laboratory conditions. The average temperature measured under field conditions was 36.0 ± 0.19 $^{\circ}\text{C}$ in the blank and 35.9 ± 0.28 $^{\circ}\text{C}$ in the sample, with the highest temperature, measured 38.6 ± 0.26 $^{\circ}\text{C}$ and the lowest 34.4 ± 0.31 $^{\circ}\text{C}$. Field samples were exposed in the sunlight from 7 am until 5 pm, and measurements were taken around 11 AM to 1 PM at noon on a sunny day. Meanwhile, the average temperature in the blank indoor laboratory was 25.6 ± 0.11 $^{\circ}\text{C}$ and the sample was 25.4 ± 0.10 $^{\circ}\text{C}$ with a temperature range between 25.2 ± 0.06 $^{\circ}\text{C}$ until 25.5 ± 0.17 $^{\circ}\text{C}$ in the blank and 25.1 ± 0.06 $^{\circ}\text{C}$ until 25.7 ± 0.06 $^{\circ}\text{C}$ in the sample. The outdoor laboratory was

recorded at 25.8 ± 0.12 $^{\circ}\text{C}$ in the blank and 25.8 ± 0.20 $^{\circ}\text{C}$ in the sample with a temperature range between 25.8 ± 0.06 $^{\circ}\text{C}$ until 26.2 ± 0.25 $^{\circ}\text{C}$ in the blank and 25.5 ± 0.06 $^{\circ}\text{C}$ until 26.1 ± 0.26 $^{\circ}\text{C}$ in the sample. There were not many differences in the temperature of the outdoor and indoor environmental conditions on a laboratory scale. DO environmental conditions ranged from 8.33 ± 0.20 mg/L to 8.64 ± 0.07 mg/L under laboratory conditions and 6.06 ± 0.17 under field conditions and pH ranged from 5.57 ± 0.04 to 5.62 ± 0.02 did not have a significant effect on the solubility of PET in distilled water.

The temperature and duration of UV exposure affect the photo-oxidation process [12,16]. In laboratory conditions, the presence of microplastics began to be identified in the third month as much as 13.67 ± 5.69 MP/L at indoor and 24.33 ± 12.90 MP/L outdoor. In the 7th month, the identified microplastic particles in indoor and outdoor were 18.67 ± 7.02 MP/L and 44.00 ± 12.77 MP/L. Different from the case with field conditions that were directly exposed to UV light, the presence of microplastics in the first month was immediately identified as much as 15.33 ± 7.09 MP/L, then began to increase in the second, third, and seventh months by 51.67 ± 9.61 , 54.33 ± 8.39 and 248.67 ± 29.09 MP/L.

This study had a similar duration of exposure to UV light until microplastics were occurred [16], in that the first 2 months of exposure to UV light did not show the presence of microplastics. Another similar study by Cai [12] who observed three types of pellets exposed to UV light in 3 different environments on a laboratory scale on plastic pellets, showed that in the third month there was surface damage and fragmentation. The mechanism of plastic pellets in their research was photo-oxidation caused by a free radical chain reaction [16].

UV light has sufficient energy to generate initial free radicals as the main photochemical product and cause C-C (375 kJ/mol) and C-H (420 kJ/mol) bonds regardless of the main polymer or equivalent to 320 and 290 nm UV radiation [17,18]. It caused one or more chemical changes, resulting in the breakdown of the polymer surface, visible as cracks and fractures. UV oxidation results in damage to the polymer surface to a depth of more than 100 μm caused by cross-linking and chain reactions [19]. This brittle surface layer easily forms cracks and becomes clearer and thicker with increasing exposure time. Interestingly in the research of Song [16], brittle surfaces and cracks from photo-oxidation (or weathering) did not directly result in polymer fragmentation. Although many large and 290 nm UV radiation [17,18]. It caused one or more chemical changes, resulting in the breakdown of the polymer surface, visible as cracks and fractures.

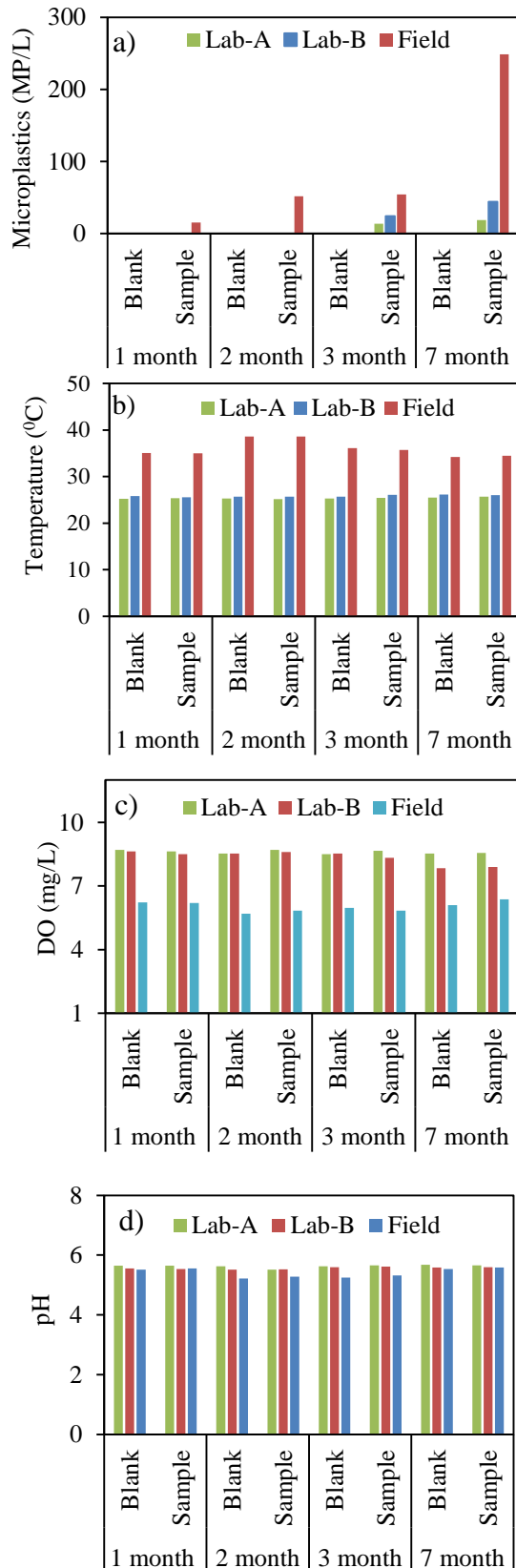


Fig.3 The conditions during the period of observation: a) the occurrence of microplastics, environmental conditions; b) temperature, c) DO, and d) pH

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However, in the absence of heat from the sunlight/ UV irradiation under indoor conditions in the laboratory, the presence of microplastics was also identified in the third month although a little. This means that microplastics were identified in distilled water under no UV exposure conditions. Physical processes such as UV, heat, photooxidative, and size reduction were affected for large plastics degrade to microplastics in the environment [20]. The solubility test of PET into microplastics during this research came from a physical process and no influence of chemical or biological factors. Other factors such as molecular weight, density, thickness, polymer morphology were other important factors in the degradation of a polymer into monomers [21].

PET biodegradation could be through hydrolysis [22]. PET hydrolysis using water produces terephthalic acid and ethylene glycol. Terephthalic acid is soluble in water at 0.0015 mg/100 mL at 20 $^{\circ}\text{C}$. The PET pieces under a microscope with 100x magnification (Fig. 4), show that the PET scrap has the potential to fragment into secondary microplastics. Many ends and pieces of PET plastic of various sizes are ready to be released into the water. Cracks and fractures as a form of fragmentation. The presence of UV light accelerates the process of dissolving PET into distilled water by breaking the main PET polymer chain.

The sample has no organic or cellular structure while observed under the microscope (Fig.5). This was because the particles identified in the PET biodegradability test as microplastic in distilled water were microplastics, and the sample was not contaminated by an external source throughout the experiment. All of the observed particles all had the microplastic characteristics described above.

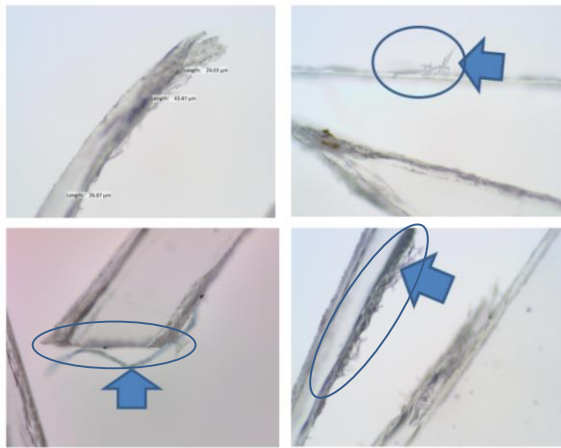


Fig.4 Observations of PET scrap under a microscope with a magnification 100 times

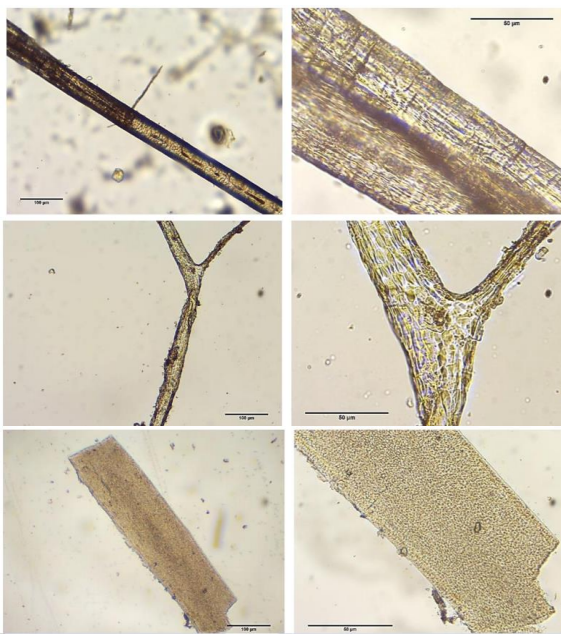


Fig.5 Organic or cellular structure [14]

Based on Fig.6, the presence of microplastic particles due to the solubility/fragmentation of PET in distilled water were dominated by size $< 50 \mu\text{m}$, the form of fragments with transparent color. The number of microplastics in the first, second, third to seventh month in the field samples were 15.33 ± 7.99 , 51.97 ± 9.62 , 54.33 ± 8.39 , and 248.67 ± 29.09 MP/L. Meanwhile, the indoor (Lab-A) and outdoor (Lab-B) samples in the third month were identified as 13.67 ± 5.69 MP/L and 24.33 ± 12.90 MP/L and in the seventh month as many as 13.67 ± 5.69 MP/L and 24.33 ± 12.90 MP/L. 18.67 ± 7.02 and 44.00 ± 12.77 MP/L. Only two forms of microplastics were identified in this study, namely fragments and fibers, where fragments predominated from fibers. Fragments ranged from 87.50-94.12% and fiber 5.88-12.5%. Similar results in the study of Song

[16] found the microplastics size as resulting fragmentation of larger plastic less than $100 \mu\text{m}$ was 73%.

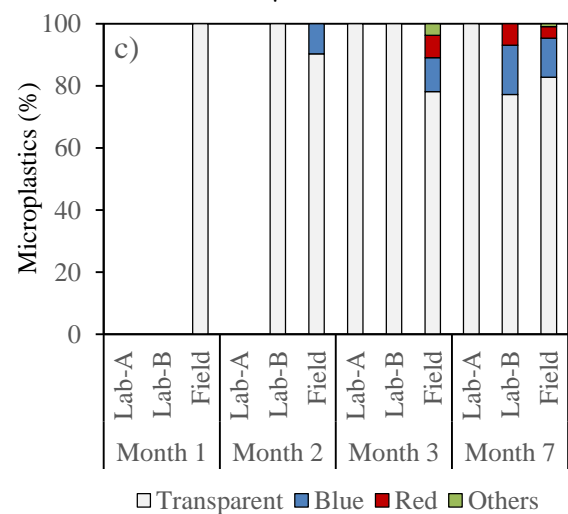
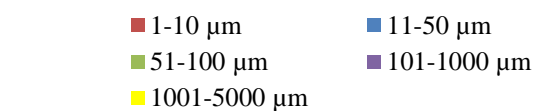
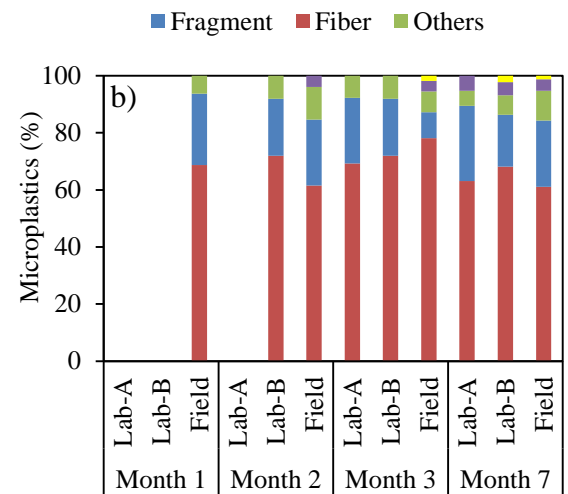
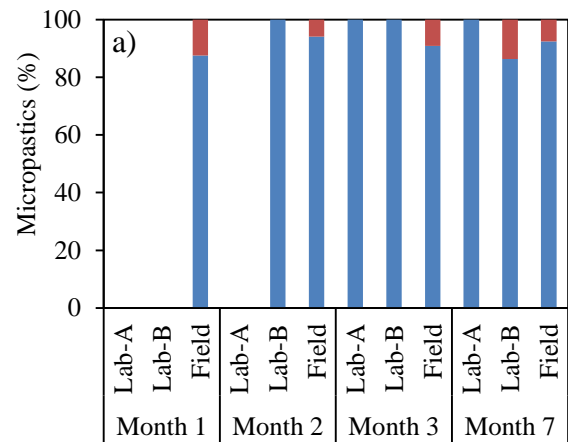


Fig. 6 Shape, size, and color of PET as secondary microplastics

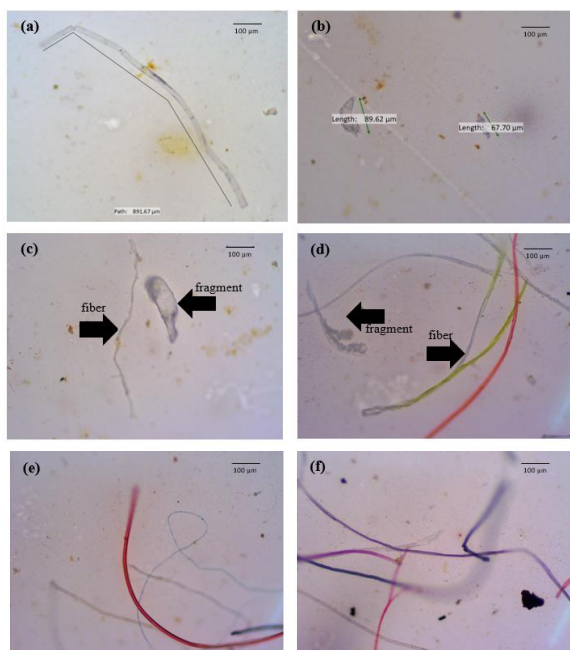


Fig. 7 Shape of secondary microplastics as the effect of PET degradation. (a-b) fragment, (c-d) fragment and fiber, and (e-f) fiber.

As shown in Fig.6c, transparent microplastics were dominant. Other colors were red and blue. In addition, the presence of red and blue colors as log as the observation was suspected from the various PET bottle brand used. All microplastic particles in this study were very thin, the thickness less than 7 µm. Even though they were more than 500 µm in length, but the limitation on picking up the particle from filter paper for further FTIR analysis. Fig. 7 shows the shape of secondary PET microplastics in the form of fragments and fibers under a microscope at 100x magnification.

4. CONCLUSIONS

Experiments under three environmental conditions for 7 months showed that physical and chemical factors were the main factors of PET degradation in aqueous solution. Physical factors as effect of PET scraps and chemical factors as effect of PET duration submerged in WWTPs. PET as secondary microplastics increased over time. Transparent fragments with 50 µm in size were the dominant shape found. Thus, more investigations on the degradation process of PET in WWTPs are still needed, this would help increase our understanding of predicting the fate of microplastics in the environment.

5. ACKNOWLEDGMENTS

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