MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Impact of photodegradation on the adsorptive properties of common plastics for environmental contaminant

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Abstract

The production, use, and disposal of a wide variety of plastics have become significant environmental issues, especially when not managed correctly. Plastics can undergo environmental weathering, breaking down into smaller particles known as microplastics. These microplastics can exhibit adsorptive characteristics, binding with other environmental contaminants such as chlorpyrifos, an organophosphate pesticide. Commonly used plastics, including polyethylene (PE), polystyrene (PS), and polyethylene terephthalate (PET), are known to interact with such contaminants. In this study, Scanning Electron Microscopy (SEM) and X-ray Diffractometry (XRD) were used to characterize both photodegraded and non-photodegraded microplastics, and their adsorption capacities were also tested. XRD showed the crystalline (PE), semi-crystalline (PET), and amorphous (PS) nature of the materials studied. The SEM showed the appearance of cavities and pores in PE and PET, which are important structures in adsorption studies. Such morphological changes were not identified for PS. The adsorption tests showed that materials exhibiting cavities after photodegradation had enhanced adsorption capacities, underscoring the influence of material morphology on the adsorption process.

Keywords: Adsorption; Microplastics; Photoaging; Characterization; Chlorpyrifos.

Introduction

Large-scale production of plastics began in the mid-1940s due to their unique properties. These characteristics have made plastic useful to produce various industrial and research applications. However, the durability of plastic alsomakes it a problem in waste management. It isestimated that more than 260 million tons of plastic are used globally every year [1].

Thermoplastics are a subdivision of plastics characterized by their flexibility and thermal resistance, enabling them to be recycled. Examples of these materials are polystyrene (PS), polyethylene (PE), and polyethylene terephthalate (PET) [2]. Polystyrene (PS) was the industry's first amorphous thermoplastic to be successfully marketed. Developed by Ostro Mislensky and Staudinger in Germany in 1930, and from the 1940sonwards, it began to be produced on a commercial scale in the United States, thanks to its properties such as high durability, low cost, and lightness [3]. Polyethylene (PE) is used in food packaging and fluid containment. PE is essentially a semi-crystalline polymer, inert to common chemicals. A wide range of ethylene homopolymers and copolymers is possible, especially in low and high density [4]. Finally, polyethylene terephthalate (PET) is a semi-crystalline polymer whose properties depend on this degree of crystallinity, ranging from injection-blow packagingto bioriented films and application in the textile industry [5]. These characteristics have made these plastic materials widely used in society.

Improper disposal of plastic products leads to the release of microplastics into the environment. This can occur at unregulated disposal sites, where dumping is not monitored and can spread through the soil, water and air. When in the environment and exposed to the weather, they undergo chemical, physical, and biological degradation, in addition to abiotic factors contributing to the process, such as

ultraviolet (UV) radiation, resulting in the degradation of the material into small particles called Microplastics (MPs), which have a range of 0.01 < 5mm [6]. Studies show that MPs can adsorb environmental contaminants like the organophosphate pesticide Chlorpyrifos (CP). The extensive use of chlorpyrifosin agriculture and its persistence in the environmenthave raised concerns about its pollution and toxicity[7].

Analyses of the degradation of these materials and their interaction with existing contaminants in the environment are used to assess the natural toxicologicaleffect of these PMs on the environment due to the complexity and variation of environmental conditions. These processes can be accelerated on alaboratory scale, and the photoaging process standsout, with ultraviolet (UV) lamps as the main sourceof light energy [8].

Based on the above, this study aimed to comparatively evaluate the effect of accelerated photoaging on PS, PET, and PE microplastics and their relationship to chemical and morphological properties, as well as their behavior towards the organic environmental contaminant chlorpyrifos and the influence of these effects on the material's adsorption capacity.

Materials and Methods

The PE microspheres were obtained in particle sizes between 100 and 200µm from a cosmetics store (Fortaleza - CE). The PET microspheres, on the other hand, were obtained with a particle size of between 1 and 100µm from the company MICROPET (Ribeirão Pires, SP). The crystal PS was obtained from Dow (São Paulo, Brazil). The PS was ground to a particle size range of 150 to 250 µm using a pan mill.

All the microplastics were irradiated in an accelerated aging chamber with 8 UV-B 40W lamps, in which 10g of microplastics were placed inPetri dishes at a distance of approximately 30 cm from the sample to the lamp during exposure timesof 8h.

Scanning electron microscopy (SEM) was used to obtain micrographs of the surface structure of the material before and after the photoaging process at various magnifications. X-ray diffractometry (XRD) analysis was carried out to verify the crystallinity peaks that refer to the nature of the materials studied.

The adsorption tests were carried out in batches with 0.01g of MPs in 50 mL of Clorpirofós solution in water at a concentration of 1 mg. L^{-1}. The flasks were shaken on an Incubator Shaker Table, rotating at 170 rpm, at a temperature of 30ºC.

Results

The samples before and after photoaging were sent for scanning electron microscopy to observepossible morphological changes in the materials. The micrographs are shown in Figure 1.

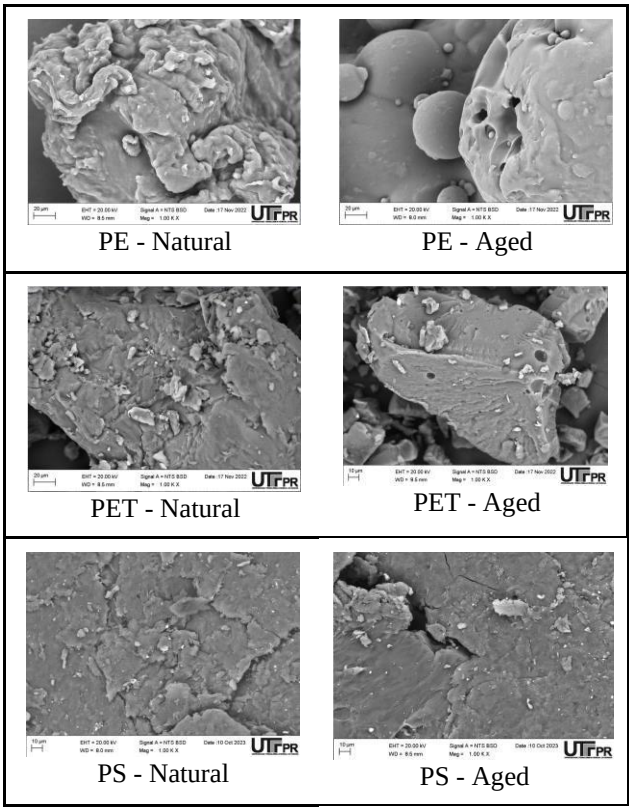

Fig. 1. SEM images of PE, PET and PS. natural and aged.

According to the micrographs, both PE and PET had a rough surface before aging, with agglomerated and irregular particles, which is expected due to the semi-crystalline nature of the materials [9]. After photodegradation, both materials showed the appearance of cavities and pores. This indicates the degradation of the material's surface by the action of UV light. However, when PS was exposed to photodegradation, there were no significant changes to the surface of the material, due to the unorganized (amorphous) nature of its structure.

The crystal structures of the natural and aged materials were analyzed using X-ray diffractometry. The diffractograms obtained are shown in Figure 2.

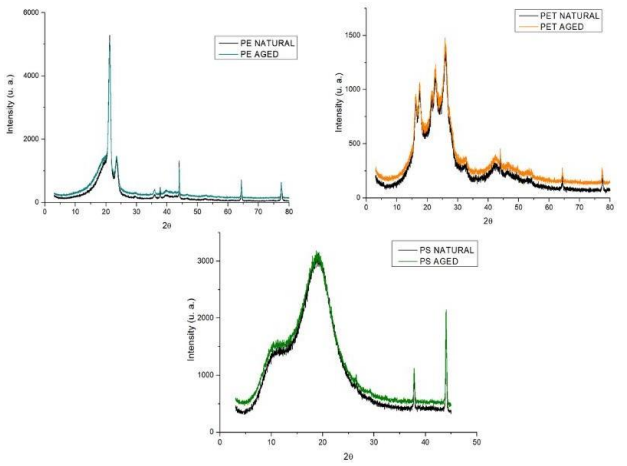

Fig. 2. Diffractograms of photodegraded and non-photodegraded PE, PET and PS.

The diffractograms made it possible to see the classifications of the materials since PE has more defined peaks than PET and PS, which have a more expressive amorphous area, confirming that they are crystalline, semi-crystalline, and amorphous materials, respectively.

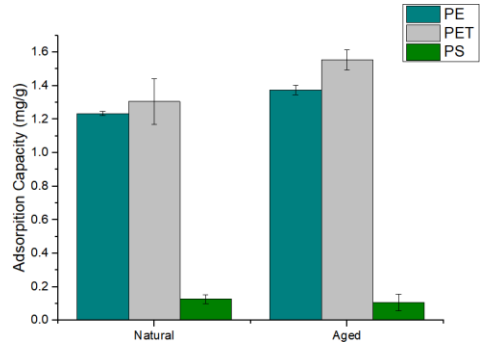

Fig. 3. Adsorption capacity for natural and photoaged microplastics

The adsorption capacities with CP were increased in PE and PET microplastics. Natural PE had a capacity of (1.23 ±0.013) mg/g and after aging (1.37 ±0.029) mg/g. Natural PET had a higher capacity of (1.30 ±0.14) mg/g, and when degraded, (1.55 ±0.059) mg/g. This increase in adsorption capacity may have occurred due to the appearance of the surface cavities observed in the SEMs; these cavities increase the contact area of the adsorbent, which consequently favors the adsorption process [10]. Unlike the others, PS showed a reduction in adsorption capacity, although not as distinct: PS Natural (0.13 ±0.03) mg/g to PS Aged (0.10 ±0.05) mg/g, which was expected, given that when comparing the size of PS to other MPs, it hasa larger grain size, which reduces its specific surface area, thus reducing the number of active adsorption sites [11].

Conclusion

XRD analysis shows that the materials have a crystalline (PE), semi-crystalline (PET), and amorphous (PS) structure. According to SEM results, PE and PET showed the appearance of pores and cavities, demonstrating the effectivephotodegradation process on their surfaces, unlike PS, which showed no morphological changes over the proposed exposure time. These changes contribute tounderstanding the adsorption test, where it can be seen that both PE and PET have an increase in adsorption capacity due to the increase in contact area caused by the photodegradation process. At the same time, PS shows no change in its adsorption capacity due to its smaller contact area and no significant morphological changes.

Acknowledgments

The authors thank CNPq for the scientific initiation grant, the Federal Technological University of Paraná for the Multiuser Center for Materials Characterization, and the Multiuser Laboratory for Environmental Equipment and Analysis.

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