Persistence of the pesticide atrazine in aqueous media: Influence of microplastics

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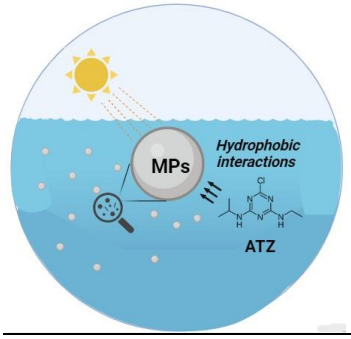
A. O. S. Dantas[1], *G. D. Braga*[1], *R. Antonelli*[1], *G. C. Assis*[1], *G. J. M. Fechine*[2,3], *A. C. S. C. Teixeira*[1] *(1) Research Group in Advanced Oxidation Processes, Department of Chemical Engineering, University of Sao Paulo, Sao Paulo, Brazil, adila.dantas@usp.br. (2) 2 School of Engineering, Mackenzie Presbyterian University, Rua da Consolação, 930, CEP 01302-907, Sao Paulo, Brazil. (3) Mackenzie Institute of Research in Graphene and Nanotechnologies, Mackenzie, Sao Paulo, Brazil.*



Cross-contamination between organic pollutants and microplastics (MPs) can cause bioaccumulation through adsorption, in which MPs act as a vehicle for these contaminants. This study evaluates the persistence of atrazine (ATZ) in aqueous media by adsorption onto polystyrene (PS) and polymethylmethacrylate (PMMA) microplastics (MPs). The MPs were aged in a UV-A chamber and adsorption was conducted at concentrations of 0.5 and 1.0 g L^{-1} for neat and aged MPs. The SEM images showed that neat MPs have structures with greater roughness, which corroborates the decrease in adsorption capacity in the following order: PS > PMMA > aged PS > aged PMMA. Mathematical modeling of predicts adsorption is governed by external diffusion, highlighting the importance of hydrophobic interactions.

Introduction

Atrazine (ATZ) is a triazine pesticide that is moderately toxic to several fish species and aquatic invertebrates [1]. ATZ has a water solubility of 33 mg L^{-1} at 25 °C and a log k_{ow} of 2.61; these properties facilitate the occurrence of ATZ in surface and groundwater [2]. The environmental persistence of ATZ in aqueous matrices depends on photochemical and biological degradation mechanisms [3] and adsorption processes in suspended solids.

Microplastics (MPs) are particulate polymeric materials less than 5 mm in size [4], commonly found in rivers, sea, groundwater, and wastewater. Some MPs have a hydrophobic nature and may act as adsorbents for organic pollutants, which means that MP particles can act as vectors for the transport, release, and bioaccumulation of chemical pollutants, often exerting more harmful effects than the contaminants or the plastic particles separately [5]. Therefore, this study aims to evaluate the impact of PS and PMMA MPs on the persistence of ATZ.

Material and Methods

Reagents

ATZ (≥ 98%) was purchased from Sigma-Aldrich. PS and PMMA MPs with a size of < 500 µm were obtained by grinding.

Analytical Method

ATZ was analyzed using an HPLC system (Shimadzu - LC20 model) and a C18 column. In isocratic elution, the mobile phase was 30% aqueous acetic acid 1% (v/v) and 70% acetonitrile. The wavelength, temperature, injected volume, and mobile phase flow rate were 225 nm, 40 °C, 100 µL, and 1 mL min^{-1}, respectively.

Preparation of aged MPs

The PS and PMMA MPs were aged in a UV-A chamber with four lamps (Sylvania 15W 350 BL T8) for 96 h, mixing every 24 h to ensure uniform aging. The surface morphology of the MPs was analyzed by scanning electron microscopy (SEM) (Inspect F50) with a horizontal field width of 11.1 µm and coverage with conductive carbon film.

Adsorption experiments

The adsorption experiments were carried out by adding 20 mL of ATZ solution (5 mg L^{-1}) to test tubes with neat and aged PS or PMMA concentrations (1.0 and 0.5 g L^{-1}). The test tubes were sealed and placed in a flask rotation shaker (Heidolph Reax 20) at ten revolutions min^{-1}. The adsorption kinetics were adjusted according to the pseudo-first-order and pseudo-second-order models.

Results and Discussion

Fig. 1 shows the SEM images of the MPs.

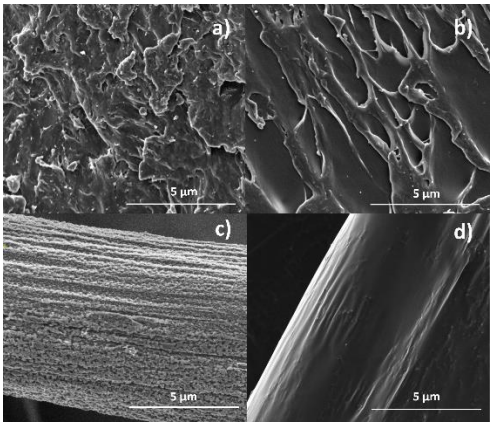


Figure 1. SEM images: (a) neat PS, (b) aged PS, (c) neat PMMA, and (d) aged PMMA.

Regarding morphology, the neat MPs samples had rough surfaces with disordered rugosity. In contrast, the aged ones had flat, smooth surfaces with ordered microcracks, suggesting that aging under UV-A caused changes to the surface of both MPs. These results agree with [6]; the literature has also reported low surface areas for neat and aged MPs [7]. From the micrographs presented here, it is possible to infer that the tendency towards a smooth, flat surface of the aged MPs may contribute to a decrease in surface area and, consequently, a reduction in the molecular adsorption of contaminants.

The kinetics of ATZ adsorption on neat and aged PS and PMMA are shown in Fig. 2, and the respective model fits. According to Fig. 2, it was possible to observe that neat MP particles had a higher adsorption capacity when compared to aged MP. This behavior occurred for both concentrations of MPs used (0.5 and 1.0 g L^{-1}). Thus, the adsorption capacity decreases in the following order: neat PS > neat PMMA > aged PS > aged PMMA. The decrease in adsorption capacity for aged MP was also reported by [5], who found a lower adsorption capacity for diclofenac on polystyrene oxidized in a Fenton-type oxidative process. MPs' aging/oxidation process can decrease their hydrophobicity, affecting hydrophobic interactions between the material and a pollutant. It is worth noting that ATZ has hydrophobic characteristics [8], suggesting that this type of interaction is an essential mechanism for the adsorption of this compound on PS and PMMA.

The ATZ adsorption results suggest that the process is characterized by fast adsorption kinetics, from 0-10 h, reaching equilibrium in 24 h. In addition, the pseudo-first-order model is more representative, with a better R^2 (values not shown) in most cases. Therefore, the adsorption process is expected to be controlled mainly by external diffusion, indicating a lower dependence on ATZ concentration, highlighting the importance of hydrophobic interactions [9].

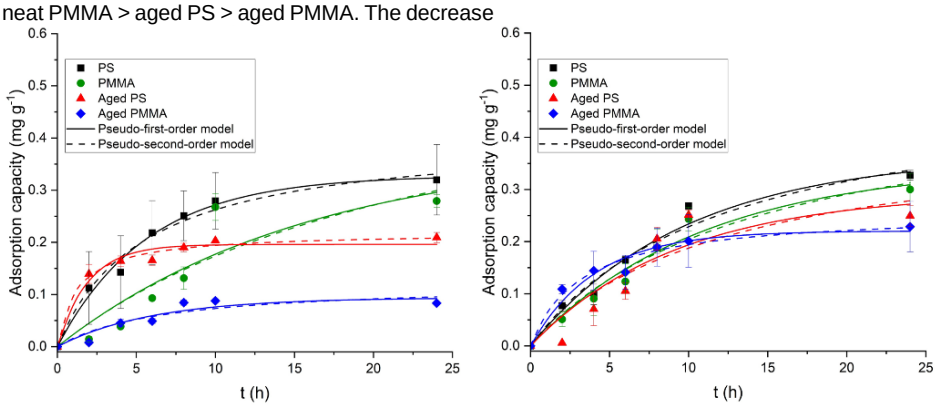


Figure 2. ATZ adsorption kinetic data on neat and aged PS and PMMA and their respective pseudo-first order and pseudo-second order model fits: (a) $[MP]_0$ = 1.0 g L^{-1} and (b) $[MP]_0$ = 0.5 g L^{-1}.

Conclusions

SEM images show a greater disuniformity in neat MPs compared to aged ones, which justifies the increased adsorption capacity for the neat PS and PMMA. According to the mathematical modeling, external mass transfer is expected to exhibit a strong influence, suggesting that hydrophobic interactions between ATZ and MPs may be the primary mechanism driving this phenomenon. However, it is essential to note that different contaminants can present various mechanisms due to their affinity with the surface of microplastic particles.

Acknowledgments

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