

Molecular Dynamics Study of Microplastic-Pollutant Adsorption

Anamarija Pulitika,^a Panagiotis Karamanis,^b Hrvoje Kušić^a and Ana Lončarić Božić^a

pulitika@fkit.unizg.hr

^aUniversity of Zagreb Faculty of Chemical Engineering and Technology, Zagreb 10000, Croatia

^bE2S UPPA, CNRS, IPREM, Université de Pau et des Pays de l'Adour, Pau 64053, France

Microplastics (MPs), polymer particles smaller than 5 mm, are increasingly recognized as contaminants of emerging concern due to their persistence, accumulation and potential environmental risks. In aquatic systems, MPs can adsorb a wide range of organic and inorganic contaminants, while processes such as ageing, and surface modification significantly alter their behaviour and associated risk. Experimental studies of MP-pollutant interactions are often time-consuming and subject to considerable methodological variability, resulting in inconsistent findings across studies. To overcome this, our study combines molecular dynamics (MD) simulations with experimental analysis to investigate the adsorption of selected pesticides onto polyethylene terephthalate (PET) MPs. Two atomistic PET models were constructed: (i) a single, continuous 150-mer chain representing a pristine PET MPs, and (ii) an aggregate of thirty 5-mer chains representing a fragmented, aged-like structure with a higher density of terminal functional groups. The simulation results show that the fragmented PET model exhibits stronger interactions with all tested pesticides compared to the continuous chain model. This arises from an increase in both Coulombic and Lennard-Jones (LJ) interactions. The increase in Coulombic interactions is attributed to the presence of additional oxygen-containing functional groups. At the same time, the stronger LJ potential is attributed to increased structural flexibility and more pollutant-surface contacts. Experimental results further confirm a significant increase in adsorption capacity following the ageing of PET MPs. Surface characterization indicates that aged MPs exhibit rougher and more heterogeneous morphologies compared to pristine MPs, leading to a greater number of available adsorption sites. In agreement with these observations, MD simulations reveal that surface oxidation at the atomistic level enhances adsorption by increasing the density of reactive functional groups. Overall, this combined approach provides detailed molecular-level insight into MP-pollutant interactions, highlighting the critical role of surface chemistry. These findings also underscore the need for more advanced simulation frameworks incorporating surface heterogeneity, longer timescales, and environmental complexity to improve predictions of MPs behaviour in real-world systems.

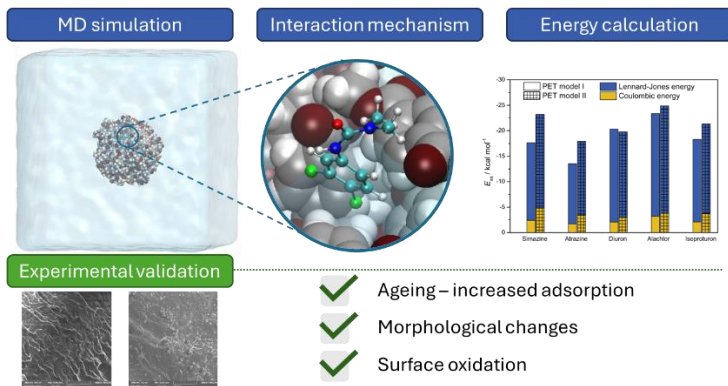


Figure 1. Molecular dynamics study of microplastic-pollutant adsorption