Thermodynamics and kinetics of enzymatic degradation of nanoplastic particles analysed by isothermal microcalorimetry

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Plastics are used worldwide for a variety of purposes. As a result of inadequate recycling or reuse, improperly disposed plastic waste accumulates to a significant extent in terrestrial and aquatic ecosystems. Large plastic waste items become fragmented to small particles through mechanical and (photo)chemical processes. Particles ranging in size from millimeter (microplastics, <5 mm) to nanometer (nanoplastics, NP, <100 nm) are apparently persistent and have negative impacts on ecosystems and human health. Current research is therefore focused on whether and to what extent microorganisms or enzymes can degrade these NP. Instead of tracking the degradation progress indirectly, e.g., by chemical analysis, weight loss or microscopic methods, we addressed the question of what information isothermal titration calorimetry, which tracks the heat of reaction of the chain scission of a polyester, can provide about the kinetics and completeness of the degradation process. Most of the heat represents the cleavage energy of ester bonds in polymer backbones and provides real-time kinetic information. Calorimetry works even in complex matrices. Using the cutinase-catalyzed degradation of polyethylene terephthalate (PET) nanoparticles as an example, we have found that calorimetry (isothermal titration calorimetry-ITC) in combination with thermokinetic models is perfectly suited for an in-depth analysis of NP degradation processes. For instance, we can separately quantify i) the enthalpy of surface adsorption $\Delta_{\mathrm{Ads}}H = 129 \pm 2\ \mathrm{kJ\ mol^{-1}}$, ii) the enthalpy of the cleavage of the ester bonds $\Delta_{\mathrm{EB}}H = -58.0 \pm 1.9\ \mathrm{kJ\ mol^{-1}}$ and the apparent equilibrium constant of the enzyme substrate complex K=0.046±0.015 g L^{-1}. It was quantified that the heat production of PET NP degradation depends to 95% on the reaction heat and only to 5% on the adsorption heat. Of particular practical importance is the fact that the fraction of cleaved ester bonds (η=12.9±2.4%) can be quantified by the new method. The new method promises a quantification of enzymatic and microbial adsorption to NP and their degradation under mimicked real aquatic conditions.