

ADSORPTION KINETICS OF 3-(4-METHYLBENZYLIDENE) CAMPHOR ON MICROPLASTICS IN WATER

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1 INTRODUCTION

- Microplastics (MPs)
 - plastic particles smaller than 5mm in size
 - ubiquitous in the environment, being found in marine sediments, marine and continental waters, terrestrial and agricultural environments
 - interact with polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and pharmaceuticals
- Ultraviolet (UV) filters
 - have unique photochemical properties
 - are the key ingredients in sunscreens, cosmetics and other personal care products in order to protect human skin from direct exposure to UV radiation
- 3-(4-methylbenzylidene) camphor (4-MBC)
 - one of the most commonly used organic UV filters
 - efficiently absorbs UV-B radiation
 - toxicological and adverse effects of 4-MBC; exhibit estrogenic, antiestrogenic, androgenic and antiandrogenic activities; it has been identified as an endocrine disruptor

2 MATERIAL AND METHODS

- Types of MPs: granulated polyethylene (PEg), polyethylene terephthalate (PET) and polypropylene (PP) and polylactic acid (PLA)
- Matrix: synthetic water
- Initial concentration of 4-MBC: 10 µg/L
- MPs mass: 40 mg
- Contact time: 1, 2, 3, 4, 5, 6, 24, 48, 72 and 96 h
- Mixing rate 150 rpm
- 4-MBC was analyzed by GC/MSD, after liquid-liquid extraction
- Kinetic models: The Lagergren pseudo-first order kinetic (PFO), pseudo second-order kinetic (PSO), Elovich and Weber-Morris models

4 CONCLUSION

- The adsorption kinetic of selected UV filter onto commercially available MPs mainly followed the PSO model indicating that monolayer adsorption which is controlled by chemical process.
- Multilayer adsorption occurs on the surface of selected biodegradable MPs.
- Weber-Morris model pointed out to multi-stage adsorption process, revealing that intraparticle diffusion is a limiting factor for the adsorption process.
- MPs can act as a carrier of 4-MBC if it get released into the environment.

3 RESULTS AND DISCUSSION

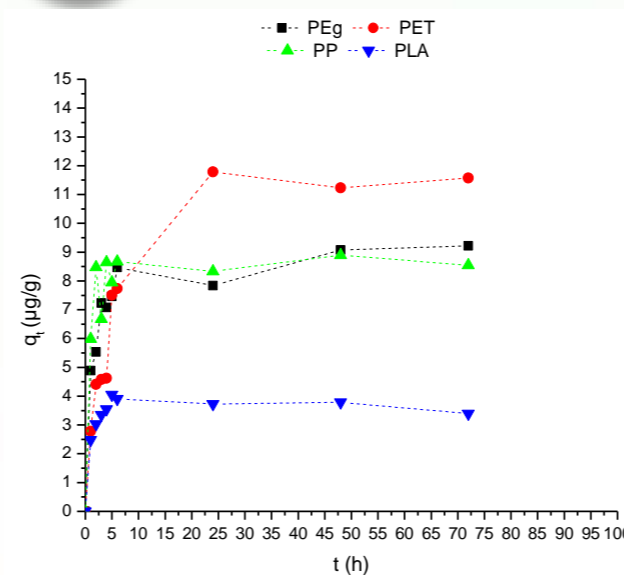


Figure 1. Experimental data (n =2, mean value ±SD) for adsorption kinetics of 4-MBC on PEG, PET, PP and PLA

- The adsorption equilibrium between 4-MBC and selected MPs was achieved after:
 - PEG, PP and PLA - 6 h
 - PET - 24 h.
- The 4-MBC has different adsorption affinities depending on type of MPs following this order: PET>PEG≈PP>PLA

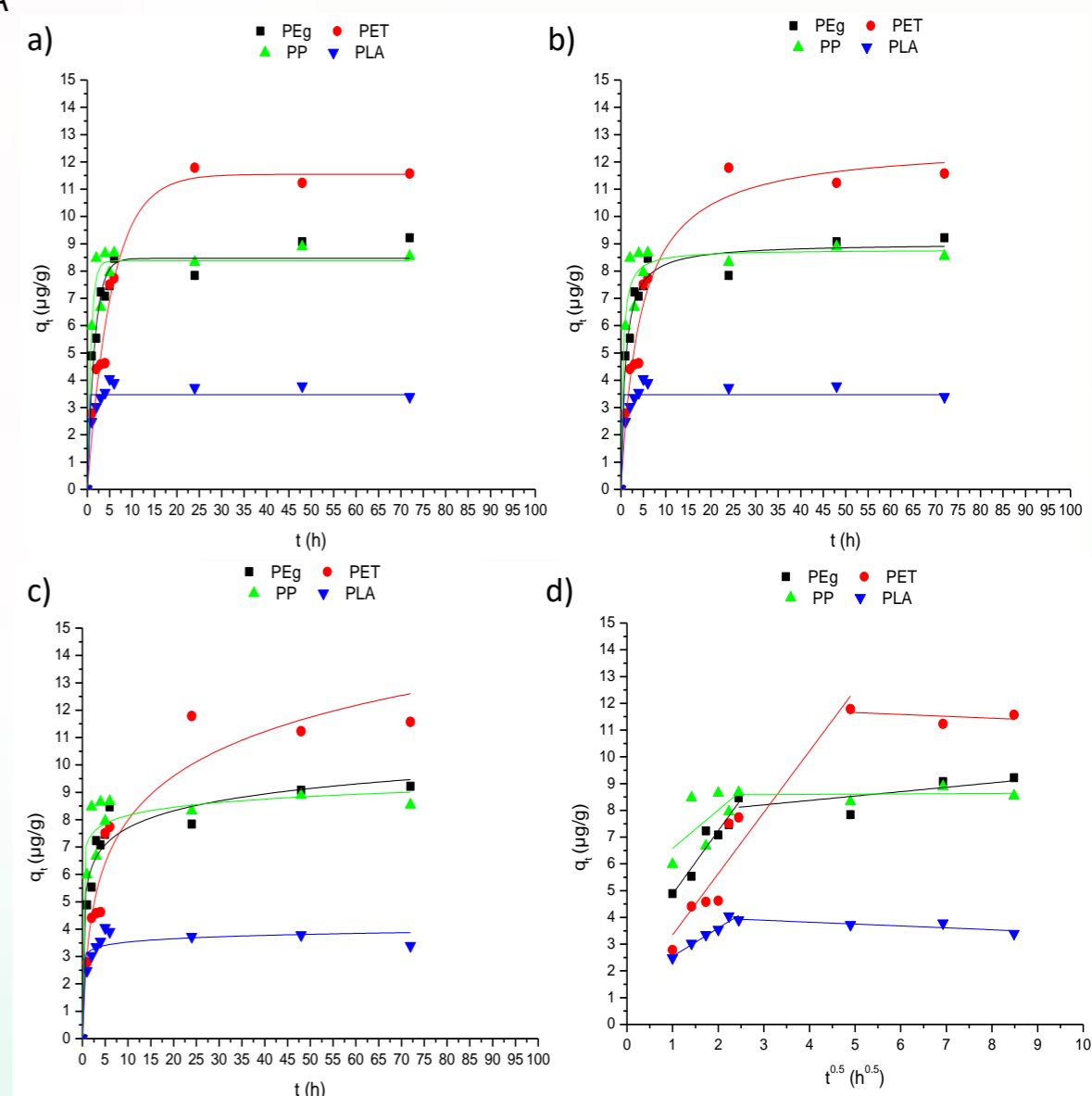


Figure 2. Plots for the adsorption kinetics, based on the (a) pseudo-first-order model, (b) pseudo-second order model, (c) Elovich and (d) Weber-Morris model, of 4-MBC on PEG, PET, PP and PLA particles in the synthetic water matrix

Table 1. Values calculated by kinetic models for adsorption of 4-MBC on MPs

| Sorbent | Pseudo-first order | | | Pseudo-second order | | | | Elovich | | | |
|---------|--------------------------|--------------|----------------|---------------------|--------------|----------------------------|-----------------------------|----------------|-----------------|--------------|----------------|
| | k_1 (h ⁻¹) | q_e (µg/g) | R ² | k_2 (g/µg h) | h (µg/g h) | q_e (theoretical) (µg/g) | q_e (experimental) (µg/g) | R ² | α µg/g h | β µg/g | R ² |
| PEg | 0.61 | 8.46 | 0.943 | 0.12 | 9.76 | 9.02 | 9.08 | 0.968 | 492.0 | 1.12 | 0.939 |
| PET | 0.18 | 11.5 | 0.960 | 0.02 | 3.20 | 12.7 | 11.7 | 0.962 | 6.602 | 0.42 | 0.932 |
| PP | 1.29 | 8.37 | 0.940 | 0.31 | 23.9 | 8.78 | 8.47 | 0.943 | 7.11E6 | 2.32 | 0.916 |
| PLA | 99.8 | 3.47 | 0.833 | 8.52E4 | 10.6E5 | 3.52 | 3.85 | 0.831 | 9.33E6 | 5.69 | 0.879 |

* k_1 - rate constant of first-order sorption; q_e - adsorption capacity; R² - correlation coefficient; k_2 - rate constant of second-order sorption; q_e - equilibrium adsorption capacity

- R² values attained by applying all selected kinetic models (Figure 2a-c, table 1) are high (R² = 0.831-0.968)
- Slightly higher R² values obtained with PSO model for adsorption of 4-MBC on PEG, PET and PP - chemisorption as possible adsorption mechanism
- Elovich model fitted data better for adsorption of 4-MBC on PLA.
- W-M model obtained results - first and fastest adsorption step occurred in the first few hours, after which the second, slower step occurs during the equilibrium stage