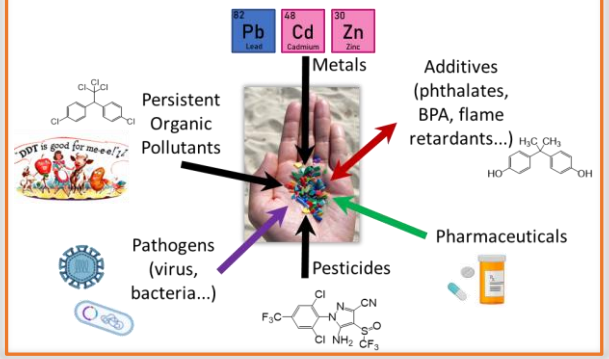
Combining experimental and theoretical approaches to investigate the sorption behavior of contaminants onto polyamide microplastics

Emerging pollutants in aquatic ecosystems

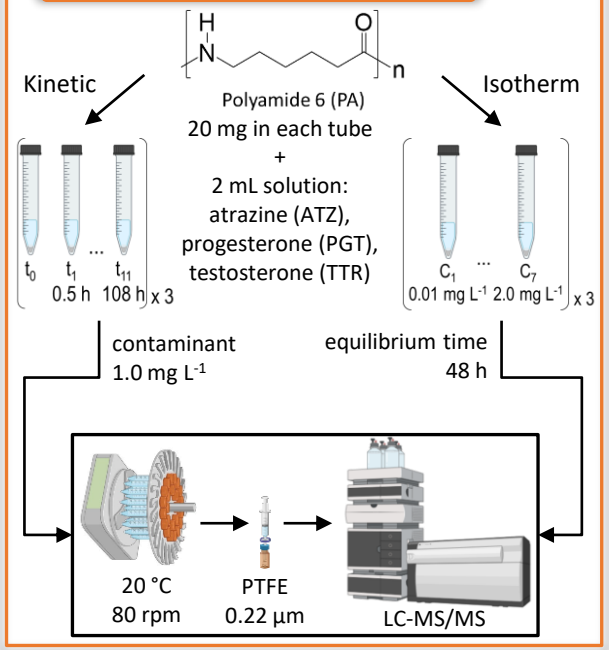
UNESCO-IWRA ONLINE CONFERENCE 17-19 JANUARY 2023 3rd IN THE IWRA ONLINE CONFERENCE SERIES

INTRODUCTION

MICROPLASTICS AS A VECTOR FOR CONTAMINANTS



EXPERIMENTAL METHODS



COMPUTATIONAL METHODS

OPLS-AA Force Field
- contaminant + microplastic (4 PA monomers)
- cubic box: 30.50 Å
- NVE (energy minimization)
- NVT: 30 ns, 300 K, 30000 configurations
- time step: 0.1 fs

Gaussian 16
- 32 configurations
- solvation and sorption average energies
- DFT M06-2X-D3/cc-pVDZ

RESULTS

Kinetic

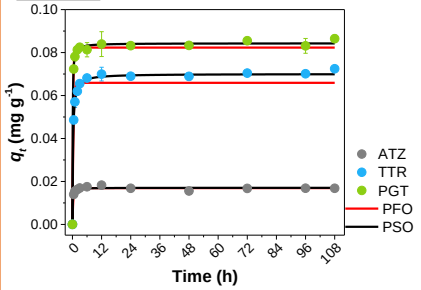


Fig. 1 Pseudo first order (PFO) and pseudo second order (PSO) kinetic models.

Isotherm

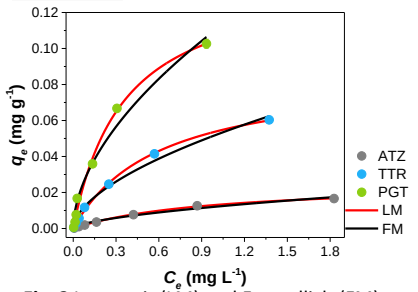


Fig. 2 Langmuir (LM) and Freundlich (FM) isotherm models.

Kinetic
- Equilibrium time: 48 h for both contaminants
- PSO presented a better fit ($R^2 > 0.98$)
- Experimental q_e (mg g^{-1}): ATZ (0.0156) < TTR (0.0689) < PGT (0.0833)
- k_2 (g mg^{-1} h^{-1}): TTR (61) < PGT (145) < ATZ (583)

Isotherm
- LM presented a better fit ($R^2 > 0.99$)
- K_L (L mg^{-1}): ATZ (1.054) < TTR (1.646) < PGT (2.790)

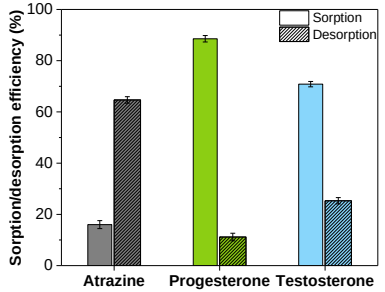


Fig. 3 Sorption/desorption efficiencies of PA microplastics in ultrapure water.

RESULTS

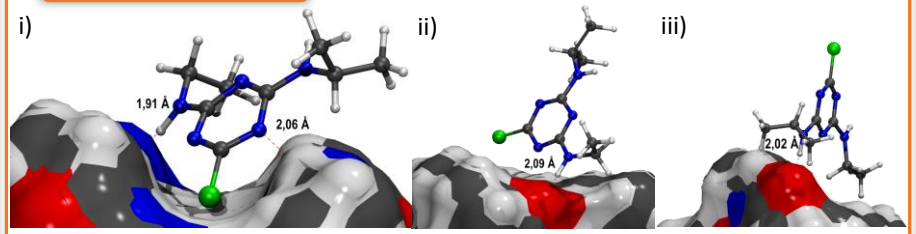


Fig. 4 ATZ both as N-H···N hydrogen bond donor and acceptor (i) and ATZ as N-H···O hydrogen bond donor (ii, iii).

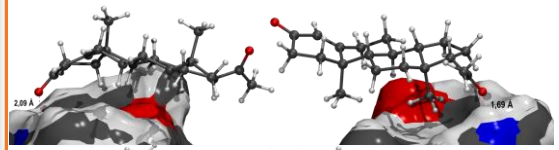


Fig. 5 PGT as N-H···O hydrogen bond aceptor.

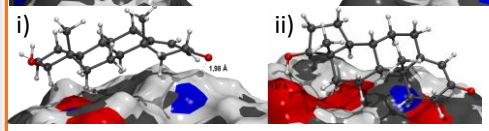


Fig. 6 TTR as N-H···O hydrogen bond aceptor (i) and TTR as O-H···O hydrogen bond donnor (ii).

Hydrogen bond count
- ATZ (6127) < TTR (16,238) < PGT (16,686)

Sorption energies* (kcal mol^{-1})
- ATZ (21.73) < TTR (15.67) < PGT (15.05)

*transfer energy of the contaminant from the solvent network to the microplastic surface → the lower the energy, the more easily the contaminant sorbs into the microplastic

REFERENCES

- Ateia M. et al. (2020) *Sci. Total Environ.* 720, 137634.
- Cortés-Arriagada D. (2021) *Environ. Pollut.* 270, 116192.
- Lara L.Z. et al. (2021) *Sci. Total Environ.* 796, 148983.

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