Investigating the sorption of selected pharmaceuticals, personal care products and endocrine-disrupting compounds to different types of microplastics

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ABSTRACT
The present study investigates the sorption behaviour of different emerging micropollutants to two of the most commonly identified microplastics in the aquatic environment, polystyrene (PS) and polyethylene (PE). Experiments were conducted with eight (8) synthetic chemical which belong to three different categories, pharmaceutical compounds (PhCs), personal care products (PPCPs) and endocrine-disrupting compounds (EDCs). Among target compounds, important removal due to sorption to microplastics was noticed for the antihypertensive drugs Valsartan (VAL) and Losartan (LOS), when PS was used as sorbent material. Their sorption was a slow and gradual process. After 216 h, 31% of VAL and 66% of LOS had been sorbed. Experiments that conducted under different pH values show that the existence of acidic conditions enhance the sorption of these micropollutants to PS. At pH 4, their sorption reached 63% and 73%, respectively. When different concentrations of NaCl were used in sorption experiments, it was observed that differences in ionic strength did not affect the sorption of VAL to PS. On the other hand, the highest sorption of LOS was observed at concentration of NaCl equal to 0.1 M.

KEYWORDS
microplastics; pharmaceuticals, sorption; pH; ionic strength

INTRODUCTION
Plastic pollution is a major issue of global concern and has received ever-increasing attention over the last decade. Microplastics (plastic fragments < 5 mm) are intentionally manufactured or formed by larger plastics debris breakdown in the environment [1]. Their existence has been reported worldwide and the deleterious effects from their physical accumulation on different organisms have been highlighted [2, 3]. Given their tension to sorb and transport toxic chemicals, their durability in nature, and their capacity to be transferred within food chain, render adverse effects more intense [1]. During the last five years, microplastics have been detected in drinking water, raw and treated wastewater, as well as in sewage sludge, worldwide [4, 5].
Among different microplastics, polystyrene (PS) and polyethylene (PE) are two important categories that are widely used in numerous applications. PS is often used in products that require clarity, such as food packaging and laboratory ware. When combined with various colorants, additives or other plastics, PS is used to make appliances, electronics, automobile parts, toys and gardening pots. PE is used in several packaging applications such as crates, trays, bottles for milk and fruit juices, in household/consumer goods as well as in fibers and textiles. Previous studies have shown the common detection of PS and PE in water and wastewater samples as well as their tension to sorb organic micropollutants belonging to different groups such as polycyclic aromatic hydrocarbons [6] and polybrominated diphenyl ethers [7]. On the other hand, limited information is, so far, available for the sorption of pharmaceuticals (PhCs), personal care products (PPCPs), and endocrine disrupting compounds (EDCs) to microplastics.
Among different PPCPs, parabens is an important category. These compounds are esterified molecules of hydroxybenzoic acid at the C-4 position and they are used as food, pharmaceutical, and cosmetic preservatives due to their antimicrobial properties. Among them, methyl-, ethyl-, propyl-, butyl-, and benzyl-paraben are the most commonly used compounds. Their environmental concentrations range from ng/L to μg/L in the surface waters and the wastewater, respectively. Recent studies have raised concerns about the use of parabens, with special focus on propyl-paraben as possibly having estrogenic potential [8].
Concerning pharmaceuticals, valsartan (VAL) and losartan (LOS) are commonly used antihypertensive drugs. After their consumption, they are partially metabolized in the human body and as a result an important amount of the parent compound is excreted unchanged through the urine. They have been detected in the aquatic environment at concentrations ranging between few ng/L (seawater) to more than 2700 ng/L (wastewater) [9].
Based to the above, the main objectives of this study was to examine the sorption potential of various micropollutants that belong to different categories such as PhCs (valsartan, VAL, losartan, LOS, sulfamethoxazole, SMX), PPCPs (methyl paraben, methyl-P, ethyl paraben, ethyl-P, propyl paraben, propyl-P, butyl paraben, butyl-

P) and EDCs (bisphenol A, BPA) to two types of microplastics (polystyrene, PS and polyethylene, PE). The role of of pH and ion strength on their sorption potential was also assessed. Through these experiments, our understanding on the environmental behaviour of organic micropollutants, affected by microplastics, is anticipated to be broadened.

MATERIALS AND METHODS

Chemicals and Reagents

Losartan (LOS), valsartan (VAL), sulfamethoxazole (SMX), bisphenol A (BPA), parabens (methyl-P, ethyl-P, propyl-P, butyl-P), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), sodium chloride (NaCl), calcium chloride ($CaCl_2$), methanol CH_3OH) and acetonitrile (ACN) were supplied by Sigma-Aldrich. The two types of microplastics (polysterene, PS and polyethylene, PE) were purchased from Sigma-Aldrich. Samples were filtrated with 0.45 μm polypropylene filters.

Sorption Experiments

Batch experiments were initially performed to check the tension of target micropollutants to sorb onto the studied microplastics. For this reason, specific amounts of PS or PE were added to serum bottles containing 100 mL of bottled drinking water and 1 mM NaN_3 was added to prevent microbial degradation. The target micropollutants (VAL, LOS, SMX, BPA, methyl-P, ethyl-P, propyl-P, and butyl-P) were spiked at an initial concentration of 500 $\mu g\, L^{-1}$. The serum bottles were capped and wrapped with aluminium foil to prevent any potential photochemical reactions during mixing and were agitated horizontally at 150 rpm and 25 °C for 216 h. Samples were collected using glass syringes at specific time intervals (0, 24, 36, 48, 72, 96, 120, 144, 168 and 216 h) and filtered to remove microplastics. The filtered aqueous samples were stored in the dark at 4 °C until analysis. Control experiments (with no addition of microplastics) were also prepared under the same testing conditions to determine possible abiotic degradation or sorption of studied micropollutants to the serum bottles.

The solution's pH effect and the influence of two divalent cations (Ca^{2+}, Na^{+}) on the sorption potential of the examined pollutants were also evaluated for the compounds that presented important removal (>20%) during preliminary sorption experiments. For examining the role of pH, experiments were conducted at pH values of 4, 7.5 and 10 and samples were taken at different time intervals (0, 22, 96 and 216 h). The role of ionic strength was evaluated in experiments with NaCl and $CaCl_2$. Three different salt concentrations were tested: 0.1, 0.01 and 0.001M and samples were taken at 0, 22, 96, and 216 h. All experiments were conducted in triplicates.

Chemical Analysis

For the determination of target compounds in aqueous samples, a High Performance Liquid Chromatography (HPLC, Waters Alliance 2695) system was used, interfaced by a Photodiode Array Detector (PDA, Waters 2996), and equipped with a C18 reverse phase column (Kinetex XB-C18, 2.1 mm; 2.6 mm internal diameter × 50 mm length) (Milford, MA, USA). An isocratic elution program with 0.1% H_3PO_4 and ACN was also used. Samples were injected on the column with a full-loop injection of 100 μL, and PDA was set at 220, 230, 254, and 270 nm, for LOS, VAL, parabens and SMX, respectively. BPA was measured using a fluorescence detector.

RESULTS AND DISCUSSION

The sorption affinity of the eight (8) target organic micropollutants was initially examined in experiments containing PS, PE or no microplastics (Control experiment). Based to the results of the Control experiments, it seems that none of the compounds are hydrolysed or sorbed to the serum bottles. Concerning their sorption to microplastics, important sorption was noticed for VAL and LOS, when PS was used as sorbent material (Figure 1).

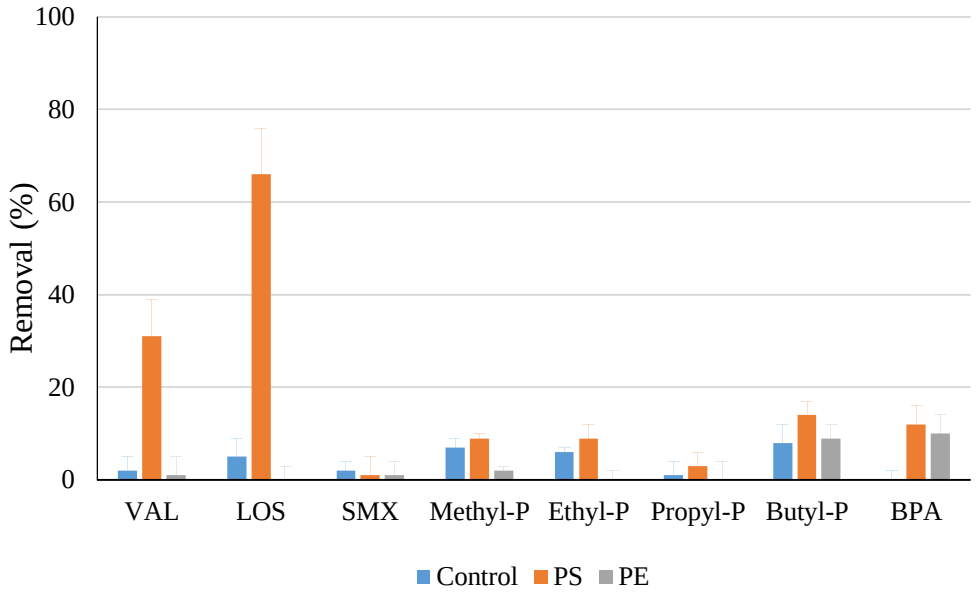

Figure 1. Sorption of target organic micropollutants to polystyrene (PS) and polyethylene (PE) microplastics. The duration of the experiments was 216 h. In Control experiments, no microplastics had been added.

The sorption of these compounds to PS seems to be a slow process. During the first 72 h, only 5% of VAL and 19% of LOS had been sorbed, while their sorption was gradually increased reaching 31% and 66% up to the end of the experiment (216 h). On the other hand, their sorption to PE was negligible, indicating that different behaviour of these compounds is expected in the natural and engineered environment depending to the type of available microplastics. Concerning the other micropollutants (parabens, SMX and BPA), no important removal was noticed in any of the sorption experiments (Figure 1). For this reason, the following experiments for the role of pH and ionic strength were conducted with VAL and LOS using PS as studied microplastic.

The experiments that were conducted at different pH values showed that water pH affects significantly the sorption of target pharmaceuticals to PS. The highest sorption was observed at pH 4 and it was equal to 63% and 73% for VAL and LOS, respectively (Figure 2). On the other hand, under alkaline conditions (pH 10), the sorption of these compounds to PS was negligible (Figure 2).

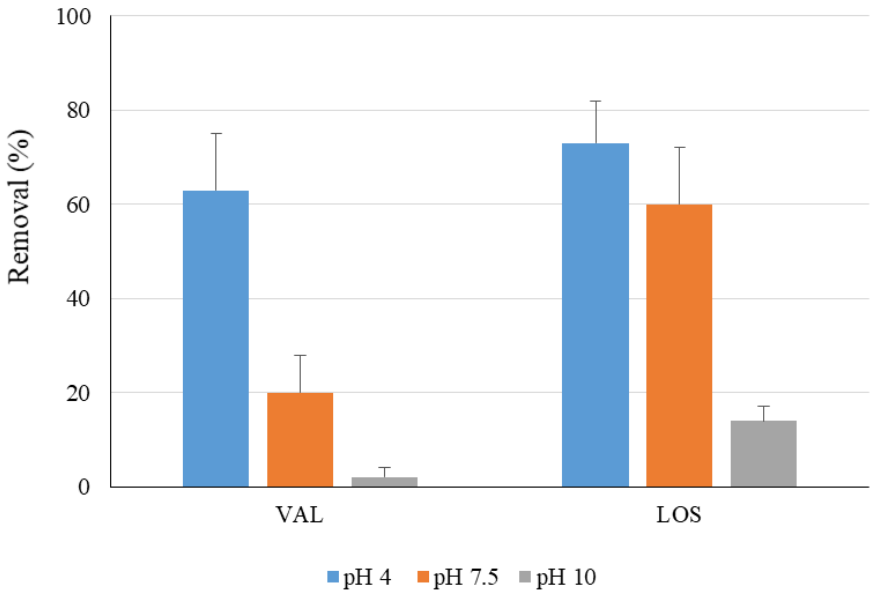

Figure 2. Effect of pH on the sorption of valsartan (VAL) and losartan (LOS) to polystyrene (PS) microplastics. The duration of the experiments was 216 h.

Concerning the role of ionic strength, when different concentrations of NaCl were added, no differences of VAL sorption were noticed. On the other hand, the increase of the ionic strength enhanced LOS sorption to PS. The highest removal (58%) was observed when 0.1 M of NaCl was added (Figure 3).

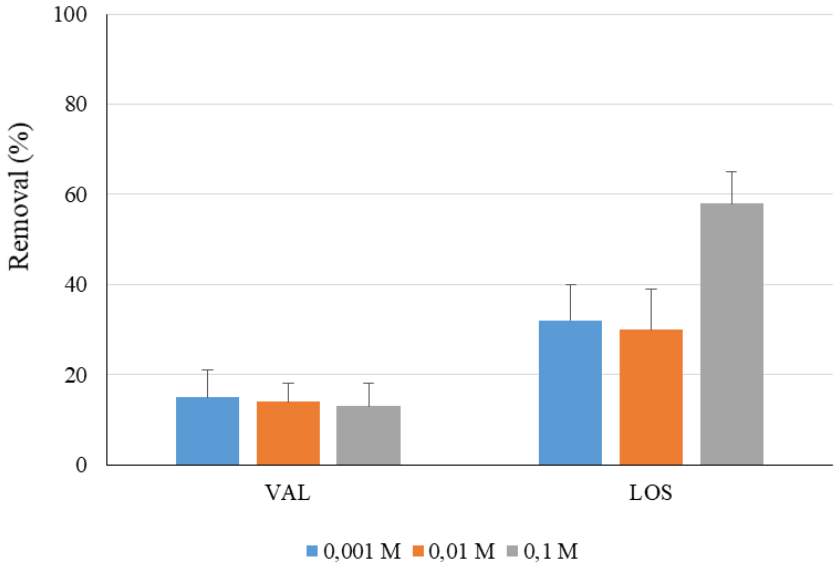

Figure 3. Effect of ionic strength on the sorption of valsartan (VAL) and losartan (LOS) to polystyrene (PS) microplastics. The duration of the experiments was 216 h, NaCl was used at different concentrations (0.001 M, 0.01 M, and 0.1 M).

REFERENCES

[1] Gatidou, G., Arvaniti, O. S., Stasinakis, A. S. 2019. Review on the occurrence and fate of microplastics in Sewage Treatment Plants. Journal of hazardous materials 367, 504-512.

[2] Chae, Y., An, Y. J. 2017. Effects of micro-and nanoplastics on aquatic ecosystems: Current research trends and perspectives. Marine pollution bulletin 124(2), 624-632.

[3] Paul-Pont, I., Tallec, K., Gonzalez-Fernandez, C., Lambert, C., Vincent, D., Mazurais, D., Zambonino-Infante, J. L., Brotons, G., Lagarde, F., Fabioux, C., Soudant, P., Huvet, A. 2018. Constraints and priorities for conducting experimental exposures of marine organisms to microplastics. Frontiers in Marine Science 5, 252.

[4] Murphy, F., Ewins, C., Carbonnier, F., Quinn, B. 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. Environmental science & technology 50, 5800-5808

[5] Ben-David, E. A., Habibi, M., Haddad, E., Hasanin, M., Angel, D. L., Booth, A. M., Sabbah, I. 2020. Microplastic distributions in a domestic wastewater treatment plant: Removal efficiency, seasonal variation and influence of sampling technique. Science of the Total Environment 752, 141880.

[6] Yu, H., Yang, B., Waigi, M.G., Li, Z., Hu, X. (2020) The effects of functional groups on the sorption of naphthalene on microplastics. Chemosphere 261,127592.

[7] Singla, M., Díaz, J., Broto-Puig, F., Borrós, S. (2020) Sorption and release process of polybrominated diphenyl ethers (PBDEs) from different composition microplastics in aqueous medium: Solubility parameter approach. Environmental Pollution 262, 114377.

[8] Wei, F., Mortimer, M., Cheng, H., Sang, N., Guo, L.-H. (2021) Parabens as chemicals of emerging concern in the environment and humans: A review. Science of the Total Environment 778, 146150.

[8] Kaur, B., Dulova, N. (2020) UV-assisted chemical oxidation of antihypertensive losartan in water. Journal of Environmental Management 261, 110170.

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