Modelling of the adsorption of chlorinated phenols on polyethylene and polyethylene terephthalate microplastic

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Abstract: The role of microplastics (MPs) on the fate and transport of various pollutants in water matrices is of major concern, but it is still relatively under investigated. In order to consider the conditions in real aquatic environments, the changes to polyethylene (PE) structure during the fabrication of micro-plastic particles for specific uses should not be neglected. Thus, this work considers isolated PE from two types of personal care products, which are possible sources of microplastic contamination in aquatic environments. The adsorption affinity of these PE microplastics towards ionisable compounds was compared with those of standards of PE and polyethylene terephthalate (PET), using chlorinated phenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) as adsorbates. The pseudo-second order kinetic model described well the sorption process for all chlorinated phenols on all four types of MPs (R^2 range: 0.900–0.998). The kinetic study showed that sorption rates are mainly controlled by hydrophobic interactions and molecule size. Adsorption isotherms were best described by the Freundlich model for all MPs. The obtained results indicate that MPs could serve for the transport of chlorinated phenols through ambient waters.

Keywords: Microplastics; ionisable organic pollutants; PE; PET.

INTRODUCTION

Plastic debris in water environments have become persistent pollutants of increasing concern due to their extensive discharge over the years.[1] The increasing amounts of plastic debris in water are a consequence of the release of primary and secondary microplastics into the environment, such as *via* industrial accidental spillages or microbeads used in cosmetics.[2,3] Furthermore, under the

influence of different chemical, physical and biological processes, large plastic particles could breakdown over time into small particles, resulting in an increase in the concentration of secondary microplastics.[4,5]

Microplastics have been detected in surface waters, water columns and bottom sediments.[3,6,7] Although freshwaters are recognized as the source and transport pathway of plastics to the oceans, there is still a comparative lack of knowledge about these environmental compartments. It is highly likely that microplastics will accumulate within continental environments, especially in areas of high anthropogenic influence.[8] According to previous studies, the most frequently detected types of microplastics in water matrices are polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polyamide (PA), poly-propylene (PP) and poly(vinyl chloride) (PVC).[9,10]

Like other pollutants, microplastics are widespread in global aquatic environments.[11,12] Depending on their physicochemical properties, organic chemicals have a tendency to adsorb on microplastic debris.[13,14] The sorption capacities of microplastics towards various contaminants from the groups of perfluoroalkyl acids, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, pharmaceuticals, personal care products and metals have been estimated.[15–18] The results indicate that microplastics could act as a sink for hazardous organic pollutants in aquatic ecosystems. Some authors found that the adsorption of organic pollutants onto microplastics could have a broad spectrum of negative effects on aquatic organisms.[14,19,20] However, a recent study showed that microplastic do not increase the toxic effects of hydrophobic organic pollutants on some marine species (*e.g.*, Beiras and Tato, 2019).[21] Despite these contradictory conclusions regarding the effect of microplastics on organic pollution toxicity, there is still a need to understand the behaviour of various organic pollutants in the presence of microplastics in water, as they can play an important role in the fate and transport of such pollutants.

Recently, several authors suggested that further studies on the sorption behaviour of wider range of pollutants, including ionisable organic pollutants, on various types of microplastics need to be undertaken.[22,23] Following this, it was found that there is little information about the sorption behaviour of ionisable compounds on microplastics, such are the chlorinated phenols (CPs). These are broadly applied industrial chemicals in terms of pesticides, disinfectants, herbicides, biocides and more.[24] CPs have been detected in groundwater, surface water, wastewater, air and soils because of their uncontrolled disposal, leaching from landfills and waste incineration. Due to their low biodegradability, high toxicity and environmental persistence, CPs have been identified as priority pollutants by the U.S. Environmental Protection Agency under the Clean Water Act.[25,26] Pentachlorophenol (PCP) is believed to be the most toxic chlorinated phenol. Besides PCP, many CPs, such as 2,4,6-trichlorophenol, 2,4-dichloro-

phenol and 4-chlorophenol, are listed as pollutants of environmental concern, due to their resistance to degradation and high toxicity.[24] This group of pollutants have also been added to the International Agency for Research on Cancer list as possible carcinogens.[27,28] Despite the control measures that have been taken, the emission of CPs is high and they are readily detected in aqueous environments.[26]

Ziajahromi *et al.*[29] showed that PET fibres and PE particles are the most frequently detected MPs in wastewater, which are source of contamination to the aquatic environment. A literature review showed that most studies on microplastic interactions with organic pollutants in water are still conducted with clean standard MPs. However, clean standards of PE and other plastic substances most likely differ in structure from the PE microplastic particles that can be found in products used in everyday life, such are personal care products (PCPs), due to mixing with other components during production. Napper *et al.*[30] pointed out the importance of studies related to the sorption of organic pollutants on microplastic isolated from personal care products. To the best of our knowledge, microbeads originating from actual personal care products and PET have not been the subject of any previous studies relating to chlorinated phenols.[30] The aim of this study was, therefore. to evaluate the adsorption mechanisms of chlorinated phenols, as ionisable compounds, on PE microplastics isolated from personal care products and PET, as a source of water contamination. For this purpose, four chlorinated phenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) with different physicochemical properties were selected. Their adsorption affinity toward PE isolated from two different types of personal care product was investigated. In addition, the adsorption mechanisms of chlorinated phenols on pure standard plastic PE microbeads and PET were compared.

EXPERIMENTAL

Adsorbents and adsorbats

Four types of microplastics were investigated: PE microparticles isolated from two personal care products (PE_PCPs_1 and PE_PCPs_2), low-density polyethylene standard substance (PE; Thermo Fisher Scientific) and polyethylene terephthalate standard substance (PET; manufactured by Sigma–Aldrich). The type of microplastics isolated from commercially available personal care products (facial scrubs) were first identified after isolation using FT-IR ATR analysis (Thermo-Nicolet Nexus 670). Their particle size distributions are discussed in detail further in the text.

Four Pestanal® chlorophenols (purchased from Sigma–Aldrich), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) were used in this study. The physico-chemical properties of the CPs are presented in Table S-1 of the Supplementary material to this paper. These CPs differ in hydrophobicity (octanol–water partition coefficient, log K_{ow}), water solubility (S_w) and acid dissociation constant (pK_a). Analytical procedure, quality assurance and quality control of chlorinated phenol analysis are given in the supplementary material. Hexane and methanol were purchased from J. T. Baker (for organic residue analysis), acetic anhydride and hydrogen peroxide from

Sigma–Aldrich. Analytical grade reagents, anhydrous calcium chloride, sodium hydrogen carbonate, and magnesium sulphate heptahydrate were also purchased from Sigma–Aldrich.

Isolation and characterisation of the investigated microplastics

The isolation of polyethylene from personal care products was realised following the modified method described by Napper *et al.*[30] The first step in the isolation of polyethylene from personal care products was mixing each product with water at 100 °C. After shaking at 180 rpm, the solution was transferred to a separation funnel and NaCl was added in order to separate the microplastic particles. Isolated microbeads were treated with 30 % H_2O_2 at room temperature in the dark for 24 h. Subsequently, the samples were diluted with distilled water and filtered through a membrane filter (0.45 μm), placed in a clean Petri dish and dried at room temperature. The thus obtained samples were labelled PE_PCPs_1 and PE_PCPs_2.

The following techniques were used to analyse the structural properties and particle size of all the investigated MPs: FTIR ATR analysis (Thermo-Nicolet Nexus 670, single reflection on Ge crystal, in the range of 4000–600 cm⁻¹, at a resolution of 4 cm⁻¹) and light microscopy with an image analysis system (image analyzing system Motic 2000).

Adsorption experiments

All kinetics experiments were conducted in 30 mL glass vials at room temperature (25 °C) as follows: 10–20 mg of investigated adsorbents were added to each vial that contained 20 mL of background solution (deionised water with $CaCl_2$, $NaHCO_3$, $MgSO_4 \cdot 7H_2O$). Stock solutions of all investigated CPs (1000 μg mL⁻¹) were prepared in MeOH (J.T. Baker, for organic residue analysis). The initial concentration of CPs in the experiments was 100 μg L⁻¹. Experiments were conducted using mixture of CPs. The vials were sealed and placed on a digital shaker at a speed of 200 rpm (IKA® orbital shaker KS 501 Digital). All experiments were performed in triplicate, and in the figures, the mean value ± *SD* are presented. Samples were collected at specified time intervals (0, 2, 4, 6, 12, 24, 48, 72 and 96 h) and filtered through a 0.45 μm membrane filter. Filtered samples were prepared for gas chromatographic analysis. The obtained experimental data were fitted with three kinetic models: the pseudo-first-order, pseudo-second-order and Weber–Morris models. Adsorption isotherm experiments were performed at CP concentrations in the range of 0–100 μg L⁻¹. All experiments were performed at pH 6.80±0.5. The influence of extreme basic and acidic conditions was not addressed in this work, because the main focus of the study was related to more realistic conditions in aquatic environments. After being continuously agitated for 48 h (equilibrium time), samples were collected to quantify the equilibrium concentrations of CPs in the aqueous phase. The Freundlich and Langmuir adsorption models were used to fit the adsorption isotherms (see Li *et al.* for the applied formulae).[1]

RESULTS AND DISCUSSION

The FTIR results of all the investigated MPs are shown in Fig. 1. The bands at 2900 and 1470 cm⁻¹ are characteristic of C–H stretching, and indicate the presence of polyethylene particles in the isolated personal care products (Fig. 1b and c). The presence of polyethylene was also confirmed based on the similarity match >80 % with the Hummel Polymer Sample Library, which is the criterion used by other researchers.[31]

Characteristic bands originating from polyethylene terephthalate (PET, Fig. 1d) were detected at 2956 (C–H stretch from –CH_2 and –CH_3 groups), 1713

(C=O stretching of the keto group), 1409 (C–O stretching and O–H group deformation), 1238 (terephthalate group –OOCC$_6$H$_4$–COO), 1091 (vibrations of the ester C–O bond from poly(ethylene terephthalate)) and 1016 cm^{-1} assigned for in-plane vibration of benzene.[32,33]
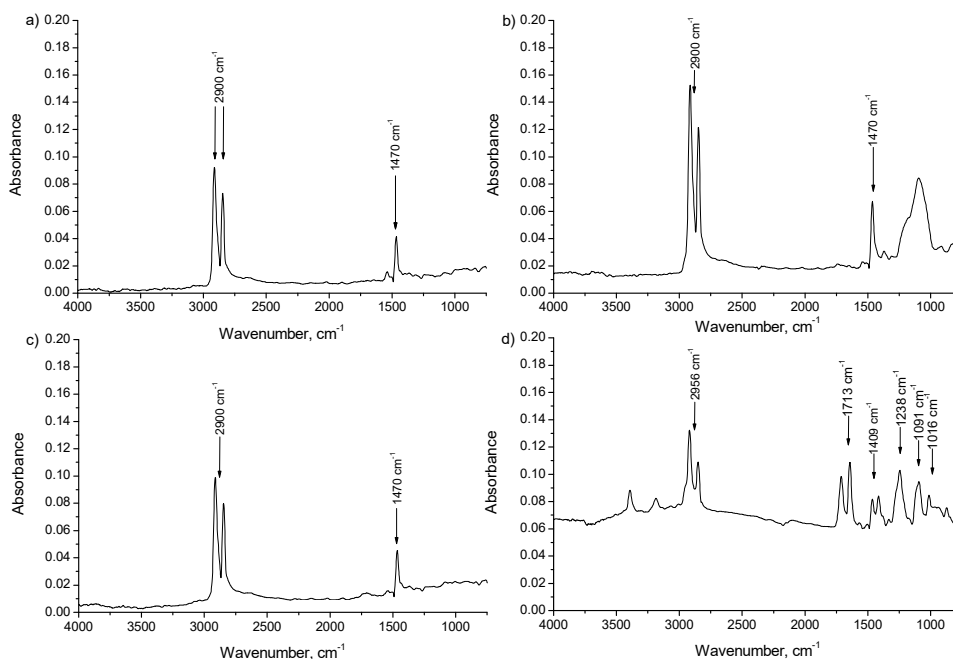

Fig. 1. FTIR ATR spectra of the microplastics used in the experiments: a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET.

In addition to the FTIR characterisation, the microplastic PE particles were characterised by stereomicroscopy (Fig. S-1a–c of the Supplementary material). A photograph of PET is not presented in Fig. S-1, since the particle size of this polymer did not allow for microscope imaging. As can be seen in Fig. S-1, the investigated microplastic particles have various shape forms, such as granules, ellipses, and threads, with different size ranges depending on the type. The same forms of PE isolated from personal care products were obtained by other authors.[2] The difference in the particles shape of the isolated MPs could be the result of chemical and mechanical treatment of the MPs during the production of the personal care products, as suggested by Goedecka *et al.*[34] The particle size of the isolated PE ranged from 165 to 436 μm, while standard PE microbeads ranged from 64 to 217 μm (Fig. S-1). This is in accordance with the typical size range of MPs particles found by other authors.[35] The particles of the clean PET standard were 3 mm (according to the manufacturer).

Kinetics experiments

The adsorption kinetics of the selected phenols on the different types of microplastics are shown in Fig. S-2 of the Supplementary material. The values obtained represent the concentrations of phenol (c_t) in the water after time t divided by the initial concentration in water (c_0). The results in Fig. S-2 show that the adsorption equilibrium was achieved after 48 h for all CPs (4-CP, 2,4--DCP, 2,4,6-TCP and PCP) on all the investigated MPs.

The obtained results also indicated that the CPs showed different adsorption affinities towards particles of PE and PET, in the following order: 2,4-DCP > > 4-CP > 2,4,6-TCP > PCP. The adsorption of 2,4-DCP on all investigated MPs was the highest (around 70 % of the initial concentration). In contrast, the adsorption of PCP on all samples of MPs was the lowest and ranged from 10–30 %. The different behaviour of the investigated CPs on MPs could be due to the different physicochemical properties of the investigated CPs and adsorbents. In order to describe the adsorption kinetics of CPs on MPs, three models were applied: the pseudo-first-order, pseudo-second-order and Weber–Morris models (Figs. S-3 and S-4 and Table S-II of the Supplementary material). The obtained R^2 values for the pseudo-first order model were lower than 0.7500 and for the pseudo-second order model were in the range 0.900–0.998. Furthermore, the theoretical q_e values calculated by the pseudo-second order model were similar to the experimental q_e values, with significantly lower standard deviations than those of the pseudo-first order model. Based on the R^2 values and the comparison between the experimental and theoretical q_e values, the pseudo-second-order model better described the experimental adsorption data. This indicates that chemical interactions between the CPs and surface of the MPs could be successfully used to describe the adsorption process. Similar results were obtained by Wang and Wang[14] and Li *et al.*,[1] who investigated the adsorption of hydrophobic organic compounds on PE.

In order to investigate the contribution of intraparticle diffusion to the overall adsorption process of CPs on MPs, the intraparticle diffusion model was applied (Fig. S-4). Intraparticle diffusion may be the rate-limiting factor controlling an adsorption process.[14] The plots of the intraparticle diffusion model show a first and fastest adsorption step in the first few hours. The second, slower step occurs during the equilibrium stage with a much lower slope compared to the initial adsorption step. Generally, if the regression of q_t *vs.* $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the only rate-limiting step. The plots shown in Fig. S-4 do not pass through the origin indicating that intraparticle diffusion is not the only rate controlling adsorption process. Based on these results, two-step processes are proposed for the adsorption of the investigated phenols on MPs, which is in accordance with the results obtained by Cheung *et al.*[36] However, since intraparticle diffusion depends on many factors,

such as temperature, particle size of the selected pollutant and others, the time required for it to occur is difficult to control or predict.[37]

Adsorption experiments

In order to investigate the adsorption mechanisms of CPs on MPs, the Freundlich and the Langmuir adsorption models were applied. The parameters of the Freundlich and Langmuir models (Fig. 2) are presented in Table S-III. The average values of three measurements with corresponding error bars for each point are shown in Fig. 2. The correlation coefficients for the Langmuir and Freudlich models were in 0.9208–0.9990 and 0.914–0.992 ranges, respectively, for all the investigated CPs on all MPs. There was no significant difference between the correlation coefficients of the Langmuir and Freudlich model. The values of maximum sorption capacity (q_{max}) for all investigated CPs were in the range 7.7–336 µg g^{-1}. For all CPs, the highest q_{max} values were obtained for PET, ranging between 104 and 336 µg g^{-1}. On the other hand, most of the q_{max} values for all types of PE were significantly lower and ranged between 7.7 and
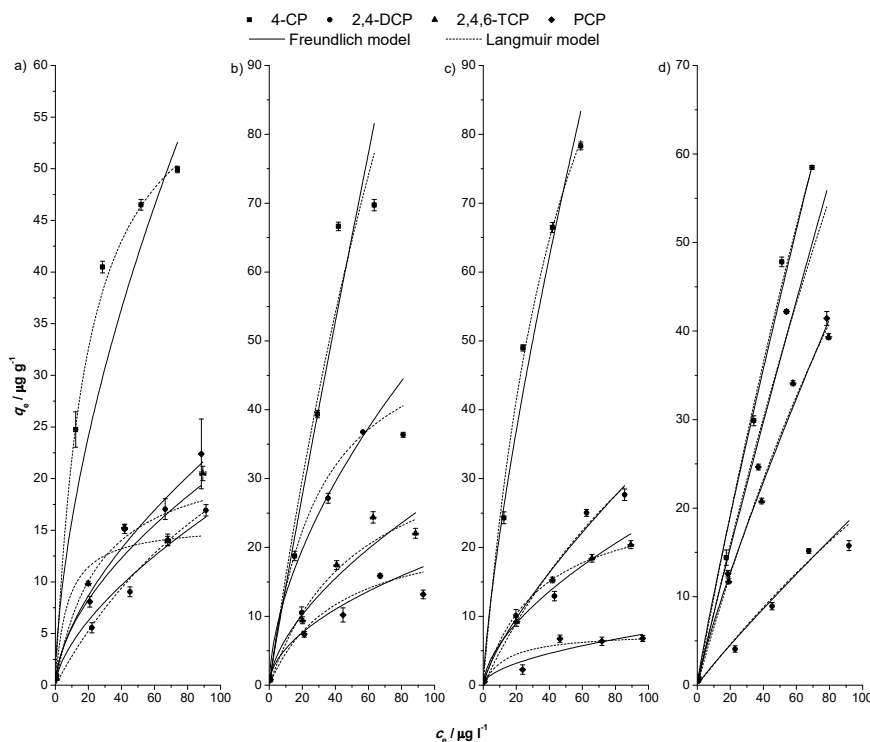

Fig. 2. Plot of the Freundlich and Langmuir adsorption isotherms for 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on: a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET (during 48 h, pH 6.8±0.5, initial concentration 0–100 µg L^{-1}).

86.9 µg g^{-1}. The values of the separation factor (R_L) for all adsorption isotherms were in the range from 0–1, which indicates that the adsorption process is favourable (Table S-III).

As shown in Table S-III, the values of the Freundlich exponent n for all four selected microplastics was nonlinear and in the range of 0.53–0.94, resulting in a decrease in adsorption affinity as the CP concentrations increase. Previous studies have shown that the sorption isotherms of different organic pollutants onto different microplastics were highly nonlinear.[18,37] However, it should be noted that the linearity of adsorption isotherms depends on the properties of the pollutants and the types of plastic.[38] The higher K_F (L g^{-1}) values for PE standard and PE isolated from personal care products implies it has a higher sorption capacity than PET. Direct comparison of the adsorption coefficients could not be made due to their different units because of the nonlinearity. Therefore, the distribution coefficients (K_d) were calculated at selected equilibrium concentrations (c_e of 0.01, 0.05 and 0.5S_w) using the Freundlich parameters (Table S-III).

The adsorption affinities (log K_d at c_e of 0.01, 0.05 and 0.5 S_w) of all CPs ranged from 0.63 to 2.84. The obtained log K_d values were much lower compared to those that can be found in the literature, for some other compounds, such as PAH, PCB or DDT.[39] This implies that chlorinated phenols will be adsorbed to a lower extent compared to these organic pollutants, despite the fact that their log K_{ow} values are comparable. In general, higher K_d values were obtained for PET than for the three investigated PE samples for all CPs. This is another difference, since usually organic compounds are better adsorbed to PE than to PET.[39] Adsorption affinities increased in the following order: 4-CP < 2,4-DCP < 2,4,6--TCP < PCP. It is interesting to note that slightly higher adsorption affinities were obtained only for 2,4-DCP on both MPs isolated from personal care products, compared to pure PE. As discussed earlier, this may be due to changes to the surface of the isolated MPs during the production processes of the personal care products. The importance of electrostatic interactions in the overall adsorption mechanisms of ionisable organic compounds such as CPs on carbon-rich materials was previously demonstrated by Kragulj *et al.*,[40] which is in accordance with results given in this paper. The higher K_d values obtained for PET compared to the K_d values for PE indicate the role of other mechanisms controlling adsorption onto this material.

Effects of hydrophobicity and molecule size on CPs adsorption

In order to investigate the influence of hydrophobicity and the molecular size of the CPs on adsorption onto MPs, the relationships between the distribution coefficients (log K_d at 0.5 S_w) and physico-chemical properties of CPs, such as molecular weight (MW), molecular size expressed as McGowan volume (V_i) and

octanol–water partitioning coefficient (log K_{ow}), were correlated. The obtained results are presented in Figs. 3 and 4.
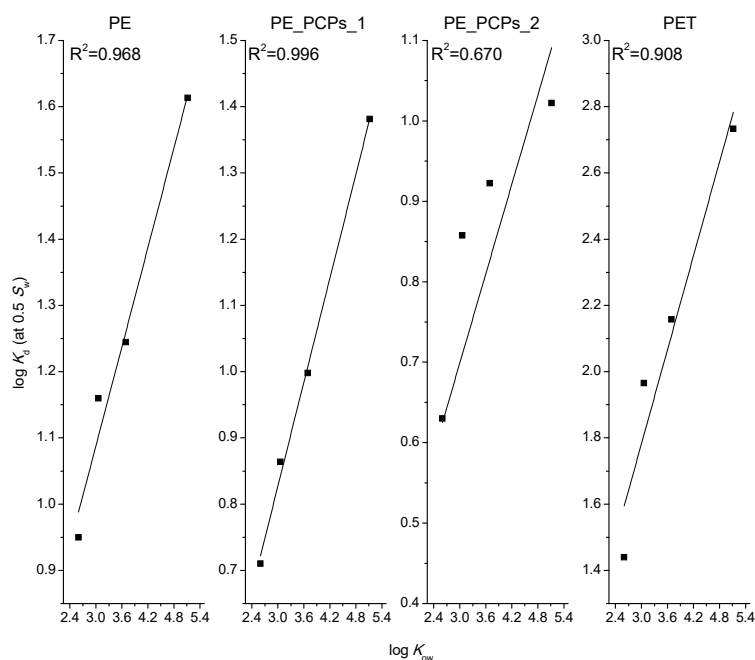

Fig. 3. Relationships between log K_d of chlorinated phenols on all the investigated MPs and their log K_{ow}.

A positive correlation between the hydrophobicity of the CPs with their adsorption on MPs was obtained, with a correlation coefficient in the range 0.670–0.995 at 95 % confidence. For all the investigated adsorbents, the lowest log K_d values were obtained for 4-CP, which also has the lowest log K_{ow} value of 2.60, while the highest log K_d were obtained for PCP (log K_{ow} = 5.12). These results indicate that mainly hydrophobic interactions control the adsorption of CPs on these materials. Positive correlations (R^2 in 0.66–0.94 range) between K_d and K_{ow} were recently obtained for the adsorption of various organic pollutants on MPs.[39,41,42]

Further evidence for surface interactions between the MPs and the investigated adsorbents is found in the correlation between the K_d values and the molecular size of the CPs (Fig 4a). Correlation coefficients were between 0.883 and 0.959, indicating that larger molecules show a higher adsorption affinity, probably because of better contact areas with the adsorbents. These results are in line with the fact that intraparticle diffusion is not the only rate controlling adsorption process and that surface interactions mainly control the adsorption of CPs on MPs. In addition, the effects of molecular size on the overall adsorption mech-

anism was proven through significant correlations between K_d and molecular weight values, R^2 in 0.767–0.992 range, for all CPs (Fig. 4b).
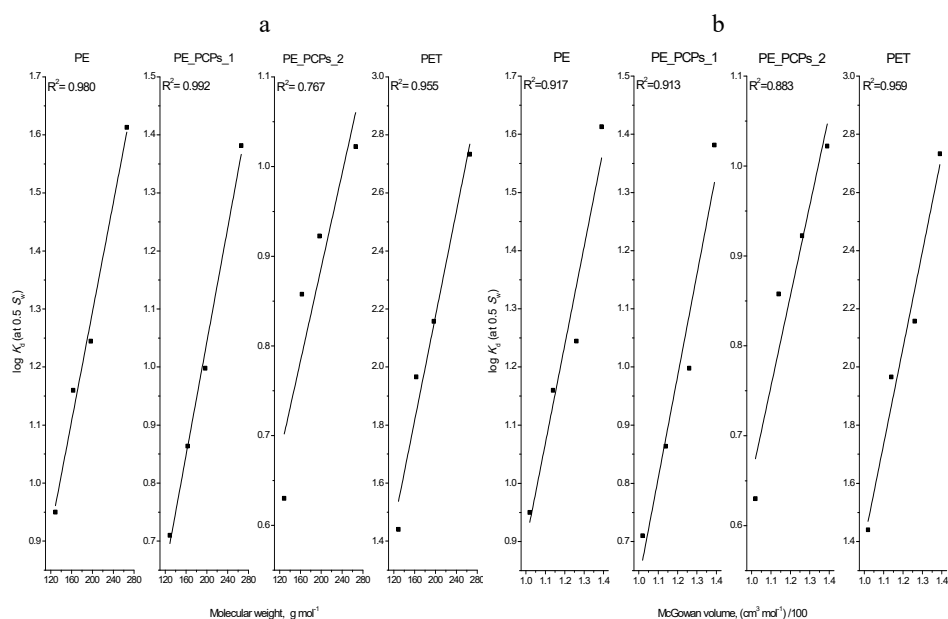

Fig. 4. Relationship between the K_d of chlorinated phenols on selected MPs and:
a) molar volume and b) McGowan volume of the molecules.

CONCLUSIONS

In this study, the adsorption behaviour of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on PE particles isolated from personal care products and standard PE and PET particles were investigated using batch experiments. Based on the results of the kinetic study, it could be concluded that the adsorption of selected chlorinated phenols onto microplastics is mainly maintained by chemical interactions and intraparticle diffusion. The PE standard and the PE isolated from both personal care products showed lower adsorption capacities towards the chlorinated phenols than PET. The results indicate that both adsorbent (*e.g.* monomeric composition or glass/rubber-like character of the polymer) and the adsorbate properties (*e.g.*, hydrophobicity and molecule size) are essential in determining the extent of adsorption.

SUPPLEMENTARY METERIAL

Additional data are available at http://www.shd.org.rs/JSCS/, or from corresponding author on request.

И З В О Д

МОДЕЛОВАЊЕ АДСОРПЦИОНОГ ПОНАШАЊА ХЛОРОВАНИХ ФЕНОЛА НА ПОЛИЕТИЛЕНУ И ПОЛИЕТИЛЕН-ТЕРЕФТАЛАТУ КАО МОДЕЛИМА МИКРОПЛАСТИКЕ

МАЈА ЛОНЧАРСКИ, АЛЕКСАНДРА ТУБИЋ, МАРИЈАНА КРАГУЉ ИСАКОВСКИ, БРАНИСЛАВ ЈОВИЋ, ТАМАРА АПОСТОЛОВИЋ, ЈАСМИНА НИКИЋ и ЈАСМИНА АГБАБА

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Улога микропластике (MP) у судбини и транспорту полутаната у воденим систе-мима је од велике важности, али је још увек недовољно испитана. Велики акценат се ставља на испитивање понашања микропластичних честица присутних у средствима за личну хигијену услед њихове промене у структури до које долази током технолошког процеса производње. Стога је у овом раду вршено испитивање на полиетилену (PE) изо-лованом из два типа препарата за личну хигијену, као могућим изворима микроплас-тике у воденим срединама. Са друге стране, формирање интеракција између органских једињења и микропластике један је од главних процеса који утичу на расподелу орган-ских једињења како у седименту тако и у воденом медијуму. Афинитет адсорпције мик-ропластике изоловане из козметичких препарата према јонизујућим једињењима упоре-ђен је са афинитетом стандарда PE и полиетилен-терефталата (PET), користећи хлори-сане феноле (4-хлорофенол, 2,4-дихлорофенол, 2,4,6-трихлорофенол и пентахлорофе-нол) као адсорбати. Кинетички модел псеудо-другог реда добро је описао процес сорп-ције за све хлорисане феноле на све четири врсте MP (R^2 у опсегу 0,900–0,998). На основу добијених резултата кинетичких експеримената утврђено је да су стопе сорпције углавном контролисане хидрофобним интеракцијама и величином молекула. Адсорп-ционе изотерме најбоље описује Freundlich модел за све одабране врсте MP. Добијени резултати указују да MP може служити за транспорт хлорованих фенола кроз амбијен-талне воде.

(Примљено 12. јула, ревидирано 14. новембра, прихваћено 15. новембра 2019)

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