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Significance of Chlorinated Phenols Adsorption on Plastics and Bioplastics during Water Treatment

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Abstract: Microplastics and chlorinated phenols (CPs) are pollutants found ubiquitously in freshwater systems. Meanwhile, bioplastics are attracting much attention as alternatives to conventional plastics, but there is little data about their effect on the behaviour of pollutants. This work therefore investigates the sorption of four CPs (4-chlorophenol—4-CP, 2,4-dichlorophenol—2,4-DCP, 2,4,6-trichlorophenol—2,4,6-TCP and pentachlorophenol—PCP) on three different plastics (polyethylene (PEg), polypropylene (PP) and polylactic acid (PLA)) using kinetics and isotherm studies. All experiments were carried out in a synthetic water matrix and in spiked Danube river water. In all cases, adsorption kinetics fitted well with the pseudo-second order rate model. Adsorption proceeded through two linear phases, corresponding to transport from the bulk solution to the external surfaces and then into the interior pores of the sorbents. Maximum adsorption capacities calculated with the Langmuir isotherm indicated that whereas adsorption of 4-CP was not significantly affected by the type of plastic present, the adsorption of 2,4-DCP, 2,4,6-TCP and PCP varied greatly, with polypropylene showing the greatest affinity for CPs adsorption. The differences observed between the adsorption behaviour of CPs in the synthetic and natural water matrices suggest further investigation is required into how the different fractions of natural organic matter impact interactions between CPs and plastics.

Keywords: microplastic; bioplastic; chlorinated phenols; sorption; kinetics; matrix effect

1. Introduction

It is well established that water environments have been contaminated by various pollutants, including chlorinated phenols and plastics [1–4].

Chlorophenols are ubiquitous contaminants in the environment originating from various anthropogenic activities such as chemical, textile and pharmaceutical activities [1,5]. Chlorophenols include widely applied pesticides and their degradation products. Thus, pentachlorophenol is a herbicide and insecticide used in various industries [5] and 2,4-dichlorophenol and 2,4,6-trichlorophenol are transformation products of the pesticide Triclosan [2]. Chlorophenols can also be present in drinking water due to the reaction between organic matter left in treated water and chlorine during the process of disinfection [2,5]. Furthermore, it has been confirmed that chlorophenols can be formed during disinfection, which raises particular concerns [2,6]. The European Union (EU) and United States Environmental Protection Agency (USEPA) [7–9] have therefore defined certain chlorinated phenols as priority contaminants, including 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP).

It has been determined that rivers are the most at risk of all water bodies, where chlorophenols have been detected at concentrations in the range of 2–2000 µg/L [5]. Additionally, since rivers are highly connected to groundwaters, especially by bank filtration, the presence of chlorinated phenols can pose a significant issue for drinking water treatment, not only in surface drinking water sources, but also in shallow groundwaters.

In addition to broad data indicating the adverse effects of organic pollutants to water environments and human health, in recent years plastic contamination has also attracted a lot of attention in the scientific community [3,4,10,11]. The presence of microplastics in freshwater systems is, in most cases, the consequence of inadequate communal and industrial waste management, as well as the discharge of both treated and untreated wastewater. This is becoming a major issue not only because of their direct influence on water biota, but also because many surface waters are actually drinking water sources. Polyethylene (PE) and polypropylene (PP) have been reported to represent more than 90% of the microplastics detected in drinking water sources and surface waters [4]. Recent studies have highlighted that these plastics are also frequently used as construction materials in drinking water treatment facilities, which can contribute further to the presence of these microplastics in drinking water [12]. Matsuzawa et al. (2010) [13] reported that some types of biodegradable polymers can adsorb certain hydrophobic organic compounds, including chlorinated phenols. Bioplastics have attracted much attention as alternatives of conventional plastics. Nowadays, following new EU legislation banning plastics for single use consumption, it is of special interest to investigate whether biodegradable plastics as well as petrochemical plastics can adsorb organic pollutants.

Data relating to the influence of microplastics (MP) on the marine environment and their toxicological effects on marine organisms have been thoroughly assessed. On the other hand, data on the influence of microplastics on inland water bodies and especially on drinking water sources are still very limited [4,12]. Consequently, the interactions of MPs with other pollutants that can be found in water sources, such as chlorinated phenols, are not yet fully understood. Novotna et al. (2019) [4] even suggest that some drinking water treatment plants will have to deal with microplastics as a “new” polluting agent.

The goal of this research is therefore to increase understanding of the challenges priority substances and MPs pose to groundwater treatment, by evaluating how chlorinated phenols are adsorbed both on PE and PP, the most abundant microplastics in drinking waters, and to compare these plastics with bioplastics.

2. Materials and Methods

2.1. Materials

In this study, granulated materials were used as sorbents. Two kinds of microplastic (MP) particles, polyethylene standard (PEg) and polypropylene (PP), and one bioplastic (polylactic acid, PLA), all manufactured by Sigma-Aldrich, were used. The basic physico-chemical properties of PEg of the investigated MPs and bioplastic PLA are given in Table 1.

Table 1. Physico-chemical properties of the investigated polymers.

Compound	Particle size (mm)	Density (g/cm ³)	Crystallinity (%)	Melting Temp. (°C)	Glass Transition Temp. (°C)	Reference
PEg	3.0 *	0.918 *	44.0	114	−120	[14]
PP	3.0 *	0.9 *	38.0	165	−18	[15,16]
PLA	3.0 *	1.24 *	20.9	173–178	60–65	[17,18]

Polyethylene (PEg), polypropylene (PP), polylactic acid (PLA)*Provided by the supplier.

Four chlorinated phenols (purchased from Pestanal® Sigma-Aldrich), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) were investigated in this work. The physico-chemical properties of the CPs are presented in Table 2.

Table 2. Physico-chemical properties of the investigated chlorophenols.

Compound	MW	$\log K_{ow}^a$	V_i^a	S_w^a	pK_a^a
4-CP	129	2.40	1.02	27,100	9.41
2,4-DCP	163	3.06	1.14	4500	7.90
2,4,6-TCP	197	3.69	1.26	800	6.40
PCP	266	5.12	1.39	14	4.80

Pentachlorophenol (PCP). MW, molecular weight (g/mol); K_{ow} , octanol-water partition coefficient; V_i , McGowan volume in units of (cm³/mol)/100; S_w , water solubility (mg/L); pK_a dissociation constant. ^a Kragulj et al. (2013).

These CPs differ in hydrophobicity (octanol–water partition coefficient, $\log K_{ow}$), water solubility (S_w) and acid dissociation constants (pK_a).

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 (CaCl₂), sodium hydrogen carbonate (NaHCO₃), and magnesium sulphate heptahydrate (MgSO₄·7H₂O), were also purchased from Sigma-Aldrich.

Sorption experiments were run using a batch equilibrium method. Adsorption kinetics and isotherms were investigated in two matrices. One matrix was synthetic water containing three salts (CaCl₂, NaHCO₃ and MgSO₄·7H₂O), and the other was Danube river water, since it is polluted with plastics [19] and connected to groundwater drinking water sources obtained by riverbank filtration. The pH of the synthetic matrix was 7.23 ± 0.06 and thus did not require further adjustment to be comparable with the Danube river water ($pH\ 7.45 \pm 0.07$). The characteristics of the investigated matrices are given in Table 3.

Table 3. Characteristics of the synthetic water and Danube river water.

Parameter	Synthetic Water	Danube River Water
pH	7.23 ± 0.06	7.45 ± 0.07
Electro conductivity 25 °C (μS/cm)	226 ± 23	333 ± 7.0
Dissolved organic carbon (mg/L)	<0.5	2.84 ± 0.12
Chloride concentration (mg/L)	52.1 ± 3.59	44.0 ± 1.52
Sulphate concentration (mg/L)	21.2 ± 4.89	25.5 ± 3.18
Hydrogen carbonate concentration (mg/L)	134 ± 6	218 ± 43

2.2. Sorption Experiments

All kinetics experiments were conducted in 30 mL glass vials at room temperature (25 °C) using 20 mg of investigated adsorbents, which were added to the synthetic matrix or freshwater. Stock solutions of all investigated CPs (1000 μg/mL) were prepared in MeOH (J.T. Baker, for organic residue analysis). The initial concentration of CPs in the experiments was 100 μg/L. The vials were sealed and placed on a digital shaker at a speed of 150 rpm (IKA® Orbital shaker KS 501 Digital). All experiments were performed in triplicate. Samples were collected at specified time intervals (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 carried out at CP concentrations in the range of 0–100 μg/L (1, 25, 50, 75, 100 μg/L). All experiments were carried out at the pH of Danube river water ($pH\ 7.45 \pm 0.07$). 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 (see Li et al. (2018) for the formulae applied) were used to fit the adsorption isotherm data [20].

2.3. Analytical Procedure, Quality Assurance and Quality Control

Determination of the selected chlorinated phenols in water was performed using gas chromatography with mass spectrometry (Agilent Technologies, 7890A GC System/5975C VL MSD) after derivatization and liquid–liquid extraction with hexane. Blank and control experiments were performed with the sorption experiments. Blank tests, containing the same amounts of water matrix and solid particles as the samples, but without the addition of chlorinated phenols, were carried out using conditions similar to those described previously, and no target compounds were found. Control tests were carried out in 20 mL of water matrix containing the same gradient of CP concentrations as the samples, but without solid particles, in order to evaluate the loss of CP resulting from additional removal processes, such as volatilization and/or sorption to the walls of the glass bottles. The method detection limits (MDLs) of the applied analytical methods ranged from 0.11 to 0.53 µg/L. The correlation coefficient for the chlorinated phenols calibration curve was higher than 0.99. All the reported concentrations of CP were corrected with the recovery efficiency and internal standards.

3. Results

3.1. Sorption Kinetics

The results of the sorption kinetics of chlorinated phenols on the PEG, PP and PLA particles in the synthetic matrix (PEG-S, PP-S, PLA-S) and Danube river water (PEG-D, PP-D, PLA-D) are shown in Figure 1. The adsorption of CPs onto plastics reached equilibrium after 48 h for all the sorbate–sorbent combinations investigated. PP exhibited the highest uptake for the compounds (2,4-DCP, 2,4,6-TCP and PCP) with higher hydrophobicity ($pK_{ow} > 2.50$), and pK_a values near or lower than pH of the water matrices.

The uptake of chlorinated phenols by the two kinds of microplastics and bioplastic PLA increases with time until sorption equilibrium is achieved after 48 h (Figure 1). These results are in the range of the usually reported periods for gaining sorption equilibrium of the organic compounds on various types of MPs [10,21]. PP adsorbs the highest amount of 2,4-DCP, 2,4,6-TCP and PCP (from 126–144 µg/g), while 4-CP is best adsorbed on PLA (85–101 µg/g). Matrix effects are evident in the behaviour of all the MPs, and are the most pronounced for PEG, which adsorbed the lowest amounts of all the CPs in the synthetic matrix (up to 65.9 µg/g for 4-CP, 104 µg/g for 2,4-DCP, 99.5 µg/g for 2,4,6-TCP and 53.7 µg/g for PCP), while the amounts adsorbed in the Danube river water were much higher (up to 77.7 µg/g for 4-CP, 134 µg/g for 2,4-DCP, 116 µg/g for 2,4,6-TCP and 88.0 µg/g for PCP). The same trend, but with much lower differences between the amounts of CPs adsorbed from the synthetic and Danube river water matrices, can be observed for PLA. The lowest matrix effect was observed for PP.

The kinetics data were fit to the pseudo-first order and pseudo-second order kinetic models. Correlation coefficients (R^2) for the first-order kinetics models were in the range of 0.10 for sorption of PCP on PLA to 0.95 for sorption of 2,4,6-TCP on PP_D, and in general were very low, suggesting that the pseudo-first-order model is not a good fit for the experimental data. In contrast, R^2 values for the pseudo-second order model were very high (see Figure 2). The R^2 values were greater than 0.99 for the sorption of 2,4-DCP, 2,4,6-TCP and PCP on all three materials. Slightly lower R^2 values were obtained for 4-CP, but the values are still high, ranging from 0.9460 to 0.9890. The calculated q_e , k_2 , and R^2 values for the pseudo-second order model are listed in Table 4. The q_e values obtained agree well with the experimentally measured q_e values. Based on these results, the pseudo-second order equation can successfully be used to describe the sorption process of the four investigated chlorinated phenols onto PEG, PP and PLA particles, from the beginning of the sorption process to the equilibrium stage. This means that chlorinated phenols can be adsorbed to different binding sites on the investigated MPs and PLA [11].

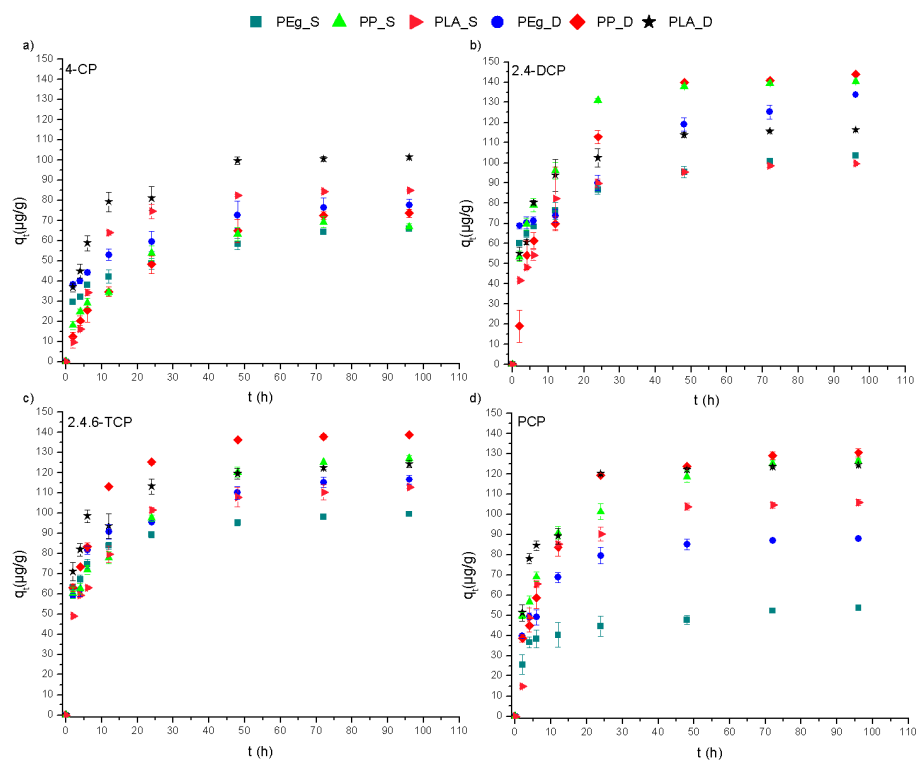


Figure 1. Experimental data ($n = 3$, mean value \pm SD) of (a) 4-CP; (b) 2,4-DCP; (c) 2,4,6-TCP and (d) PCP on PEG, PP and PLA particles in the synthetic matrix (PEG_S, PP_S and PLA_S) and Danube river water (PEG_D, PP_D and PLA_D).

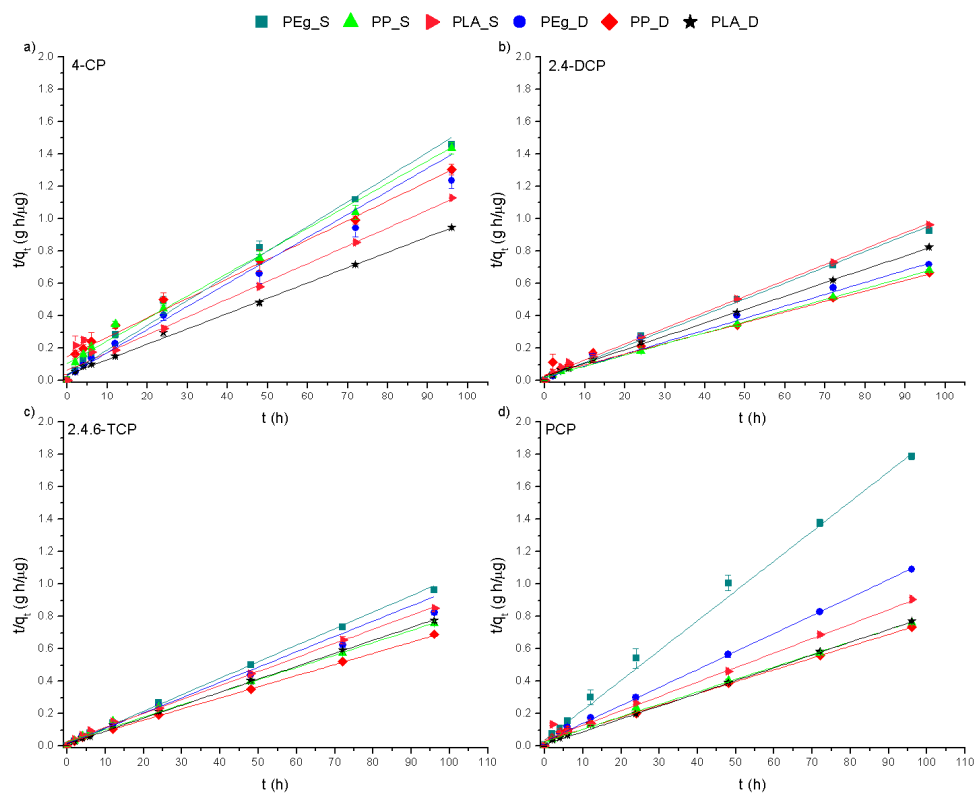


Figure 2. Plots for the sorption kinetics, based on the pseudo-second order model, of (a) 4-CP; (b) 2,4-DCP; (c) 2,4,6-TCP and (d) PCP on PEG, PP and PLA particles in the synthetic matrix (PEG_S, PP_S and PLA_S) and Danube river water (PEG_D, PP_D and PLA_D) ($n = 3$, mean value \pm SD).

Table 4. Parameters calculated with pseudo-second order kinetic models for the sorption of chlorinated phenols onto PEg, PP and PLA particles in synthetic and Danube river water.

Compounds	Solid Phase	k_2 (h ⁻¹)	R ²	q _e (Theoretical)	q _e (Experimental)
4-CP	PEg_S	0.0063	0.9890	65.85	65.49
	PEg_D	0.0065	0.9460	77.69	70.22
	PP_S	0.0018	0.9749	66.85	71.84
	PP_D	0.0010	0.9815	73.62	83.13
	PLA_S	0.0019	0.9939	85.02	90.83
	PLA_D	0.0025	0.9981	101.4	105.6
2,4-DCP	PEg_S	0.0059	0.9912	103.7	102.2
	PEg_D	0.0032	0.9925	133.8	135.3
	PP_S	0.0022	0.9978	140.4	145.8
	PP_D	0.0012	0.9915	143.8	153.8
	PLA_S	0.0031	0.9977	99.62	101.8
	PLA_D	0.0026	0.9993	116.4	120.6
2,4,6-TCP	PEg_S	0.0085	0.9973	99.56	98.14
	PEg_D	0.0056	0.9930	116.5	105.8
	PP_S	0.0022	0.9974	126.9	130.7
	PP_D	0.0020	0.9991	138.9	145.6
	PLA_S	0.0026	0.9937	112.9	115.6
	PLA_D	0.0046	0.9992	124.1	125.2
PCP	PEg_S	0.0087	0.9990	53.68	54.38
	PEg_D	0.0041	0.9985	88.05	90.09
	PP_S	0.0021	0.9952	126.3	129.9
	PP_D	0.0017	0.9935	130.5	136.8
	PLA_S	0.0020	0.9789	105.9	112.1
	PLA_D	0.0060	0.9988	124.5	126.7

Differences were observed between the most hydrophilic 4-CP and the most hydrophobic PCP on PEg, PP and PLA, with adsorptions ranging from 65.9 to 101 µg/g to 53.7 to 126 µg/g, respectively.

The plots obtained using the Weber–Morris intraparticle diffusion model (shown in Figure 3) imply that the sorption of all four chlorophenols on PEg, PP and PLA proceeds through two linear phases, corresponding to the transport of the sorbate from the bulk solution to the external surfaces and then into the interior pores of the sorbent [10,22]. For most combinations of CPs and MPs/bioplastics, adsorption at the beginning is fast for the first five hours. After that period, a slower adsorption process is observed. The slowest adsorption rate was observed for all four CPs on PEg in both water matrices. The linear plots obtained by the Weber–Morris model do not pass through the origin for the sorption of all four chlorinated phenols on all three materials, which indicates that surface sorption could be the rate-controlling step [11].

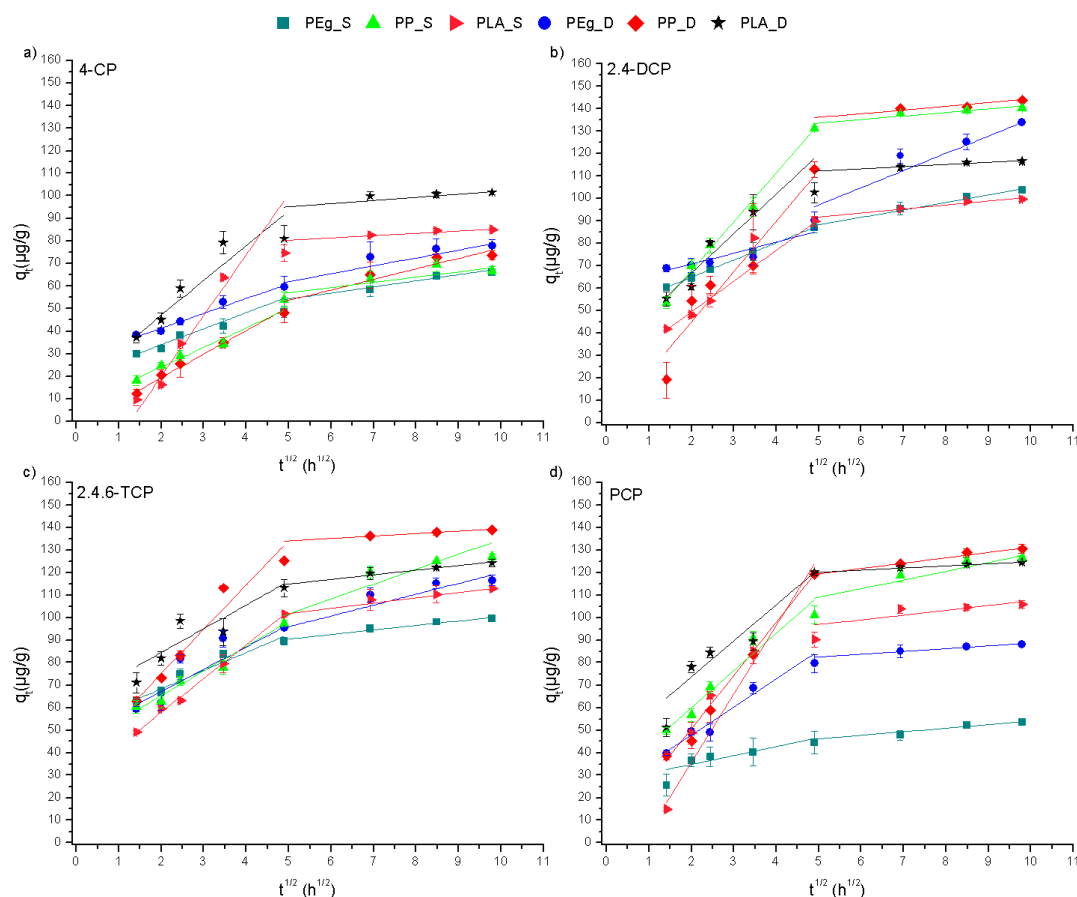


Figure 3. Plots for the sorption kinetics, based on the Weber–Morris model, of (a) 4-CP; (b) 2,4-DCP; (c) 2,4,6-TCP and (d) PCP on PEG, PP and PLA particles in the synthetic matrix (PEG_S, PP_S and PLA_S) and Danube river water (PEG_D, PP_D and PLA_D) ($n = 3$, mean value \pm SD).

3.2. Adsorption Isotherms

In order to investigate the sorption mechanism of the chlorinated phenols on microplastics and bioplastics in the two matrices investigated, the Freundlich and Langmuir models were applied. These are the two most commonly applied models for describing the mechanism of interactions between sorbents and sorbates. The Freundlich model is applicable to both monolayer and multilayer sorption and assumes that the sorption process takes place on the heterogeneous surface of a sorbent [10,23]. The application of the Langmuir model can show whether the sorbate makes a monolayer coverage on homogenous sorbent surfaces [1,10]. Figure 4 presents the adsorption isotherms of chlorinated phenols on PEG, PP and PLA in the synthetic and Danube river water matrices. The values of the Freundlich and Langmuir model parameters are listed in Table 5.

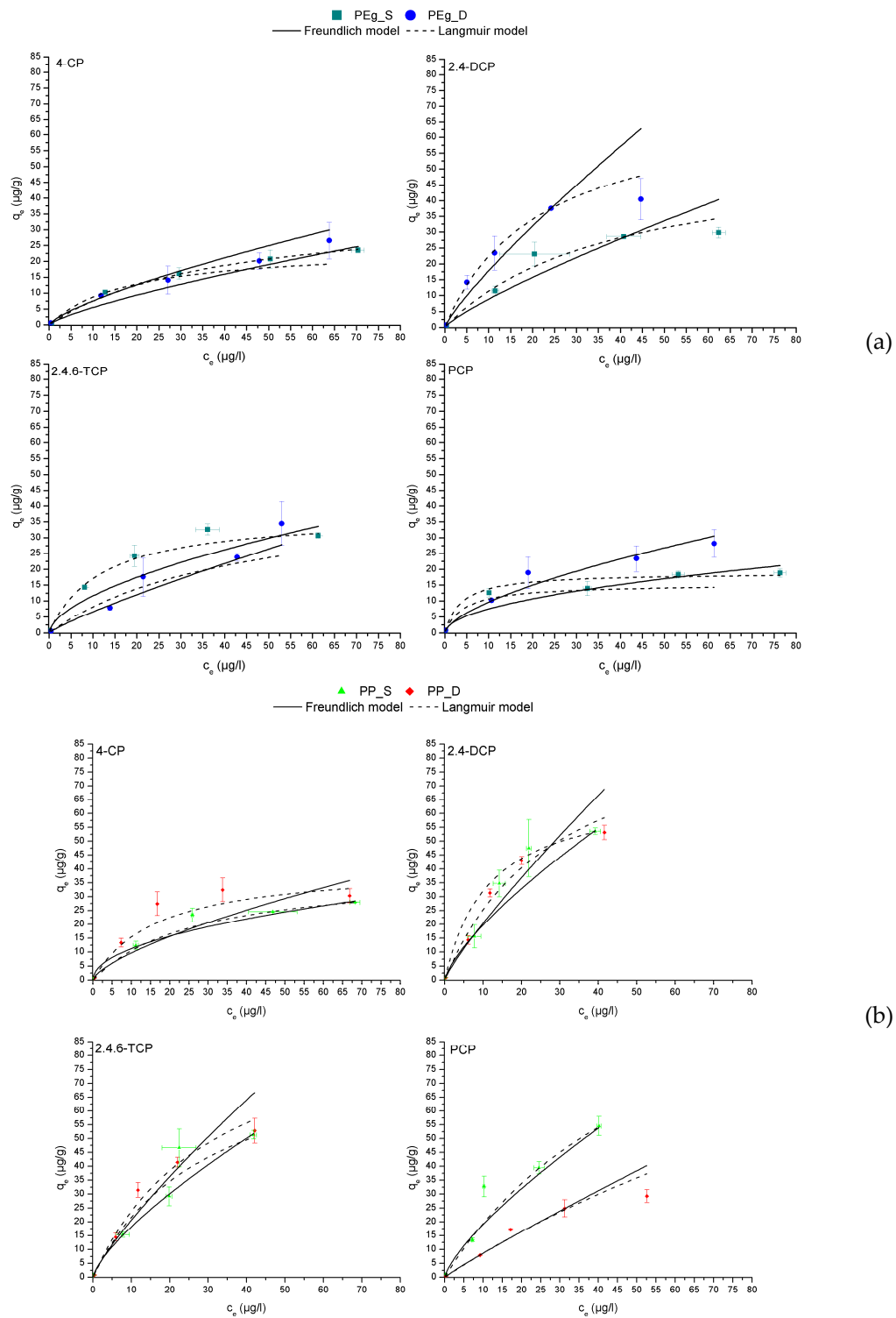


Figure 4. Cont.

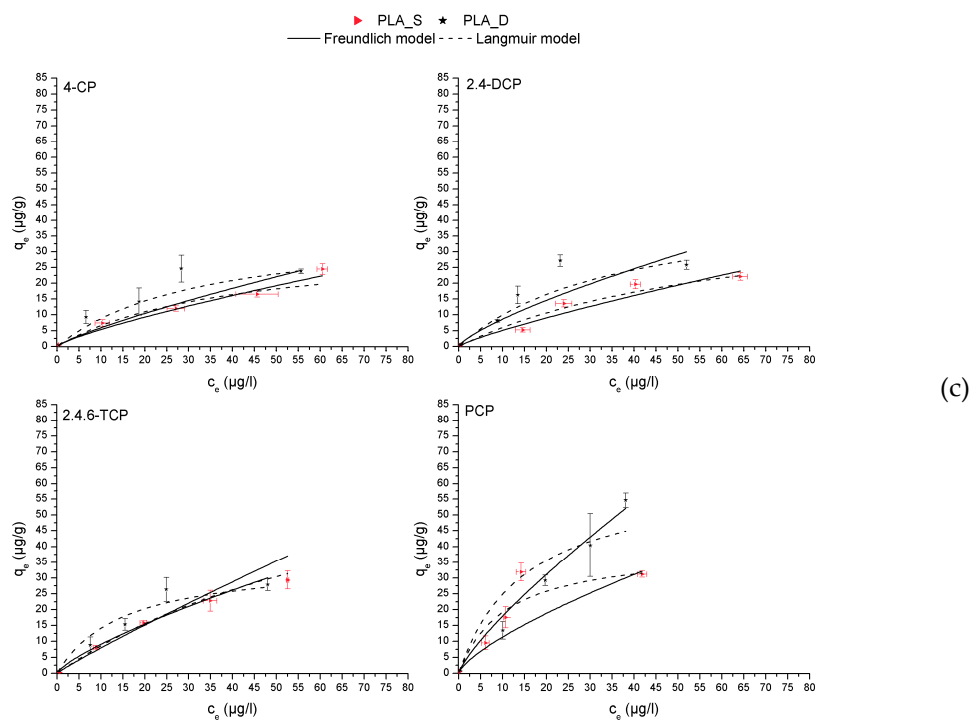


Figure 4. Sorption isotherms of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on (a) PEG, (b) PP and (c) PLA particles obtained for the synthetic matrix (PEg_S, PP_S and PLA_S) and Danube river water (PEg_D, PP_D and PLA_D) ($n = 3$, mean value \pm SD).

Table 5. Values of the Freundlich and Langmuir model parameters for the sorption of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on PEG, PP and PLA.

Compounds	Adsorbents	Freundlich model			Langmuir model		
		R ²	<i>n</i>	K _F (µg/g)/(µg/L) ⁿ	R ²	q _{max} (µg/g)	K _L (l/µg)
4-CP	PEg_S	0.9478	0.77	0.92	0.9892	37.03	0.0255
	PEg_D	0.9816	0.74	1.36	0.9825	24.55	0.0551
	PP_S	0.9974	0.48	3.69	0.9984	39.17	0.0365
	PP_D	0.8292	0.69	1.98	0.9687	41.15	0.0599
	PLA_S	0.9869	0.80	0.85	0.9762	32.74	0.0252
	PLA_D	0.9835	0.82	0.91	0.9938	38.40	0.0298
2,4-DCP	PEg_S	0.9949	0.83	1.33	0.9989	55.60	0.0258
	PEg_D	0.9998	0.84	2.58	0.9998	71.36	0.0457
	PP_S	0.9970	0.74	3.63	0.9945	68.98	0.0869
	PP_D	0.9347	0.85	2.86	0.9884	100.2	0.0338
	PLA_S	0.9585	0.83	0.74	0.9423	45.48	0.0152
	PLA_D	0.9268	0.76	1.52	0.9392	46.35	0.0275
2,4,6-TCP	PEg_S	0.9397	0.59	3.02	0.9390	37.47	0.0839
	PEg_D	0.9897	0.86	0.90	0.9919	44.95	0.0222
	PP_S	0.9960	0.73	3.37	0.9631	87.13	0.0330
	PP_D	0.9599	0.82	3.14	0.9911	100.1	0.0313
	PLA_S	0.9703	0.93	0.95	0.9881	82.23	0.0118
	PLA_D	0.9668	0.76	1.59	0.9796	35.59	0.0662
PCP	PEg_S	0.9521	0.51	2.32	0.9913	18.93	0.2681
	PEg_D	0.9958	0.63	2.24	0.9349	15.32	0.2261
	PP_S	0.9708	0.75	3.39	0.9438	135.2	0.0167
	PP_D	0.9884	0.93	1.02	0.9898	168.2	0.0054
	PLA_S	0.9531	0.73	2.15	0.9817	62.74	0.0940
	PLA_D	0.9925	0.80	2.88	0.9246	39.54	0.0658

The correlation coefficients for the Freundlich and Langmuir models are, respectively, $R^2 = 0.8292$ – 0.9998 and $R^2 = 0.9246$ – 0.9998 for all four CPs on all of the polymers. Significant differences between these two models were not observed.

In the Freundlich isotherm, the parameter n is an indicator of sorption linearity, with larger deviations from $n = 1$ indicating greater nonlinearity. All the isotherms obtained are nonlinear (n values ranging from 0.48 to 0.93), suggesting heterogenic binding sites on the surface of the sorbents (Table 5). In general, greater nonlinearity was observed in the synthetic matrix than in the Danube river water, demonstrating the influence of this matrix on the sorption process.

In the case of the Langmuir model, it is assumed that sorption of the sorbate molecule occurs at a specific site on the sorbent, with no further sorption occurring at the same site [10,23]. The q_{\max} are in the ranges 24.55–41.15 $\mu\text{g/g}$, 46.35–100.2 $\mu\text{g/g}$, 35.59–100.1 $\mu\text{g/g}$ and 15.3–168.2 $\mu\text{g/g}$ for 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on PEg, PP and PLA, respectively. These differences confirm that the structure of the compound has a significant impact on its interactions with the plastic surfaces. PP showed a considerably higher sorption affinity for CPs than PLA and PEg, which confirms that sorption is dependent on the sorbent properties. The difference between the three sorbents investigated is most pronounced regarding PCP sorption. The highest amounts of PCP ($q_{\max} = 135.2$ – 168.2 $\mu\text{g/g}$) are adsorbed on PP, following 2,4,6-TCP, 2,4-DCP and 4-CP. The lowest q_{\max} values were obtained for the sorption of PCP on PEg ($q_{\max} = 15.32$ – 18.93 $\mu\text{g/g}$). In general, all the CPs had lower sorption affinities for PEg than either of the other two plastics investigated. Matrix influences on q_{\max} can also be observed, with higher values generally observed for PEg and PP in Danube river water compared to the synthetic matrix. The adsorption capacity of PLA towards CPs in Danube river water had similar values (35.52–46.35 $\mu\text{g/g}$), and these are similar or lower than in the synthetic matrix.

4. Discussion

Plastic debris is now found throughout the environment, and may serve as a carrier for organic pollutants, influencing not just their transport through various environments, but potentially also influencing how they express their toxicity towards aquatic organisms and humans [3]. Bioplastics are also becoming more broadly applied in everyday life, increasing their discharge to the environment. Understanding the interactions between various plastics and organic pollutants is therefore extremely important [10,11,21,24].

The adsorption kinetics and isotherm data presented above demonstrate significant variations in the degree to which microplastics interact with chlorinated phenols in neutral pH aqueous environments. The different polarities of the phenols studied, as demonstrated by their various pK_a values, mean that under the conditions investigated some of these compounds are partially present in disassociated forms, rather than as neutral species [11,13]. The different plastics have differing monomeric compositions, with the linear aliphatic PE, and the slightly branched aliphatic PP and PLA which is an aliphatic polyester. They are therefore likely to undergo different interactions with non-hydrophobic compounds such as phenols, as suggested by other authors [10,25]. The obtained results indicate that the structure of microplastic is significant for sorption processes when the available surfaces of the polymers are similar, which is in accordance with the finding of other authors [24,25]. PP showed the highest sorption capacity towards all four CPs, followed by PLA and PEg, suggesting that nonlinear polymers exhibit a higher potential to adsorb and transport ionisable compounds through the environment. One can assume that the hydrophobic character of these compounds is responsible for the majority of interactions between CPs and PP, because with increases in compound hydrophobicity, in both water matrices increases in the adsorption capacity were observed. The poor sorption of ionised PCP and 2,4,6-TCP observed on PEg are probably explained by electrostatic repulsion (Table 5). The best sorption on this plastic was observed for 2,4-DCP, which is hydrophobic and non-ionised under the prevailing pH conditions of the experiment. The adsorption capacity of PE towards 4-CP is similar to 2,4,6-TCP, indicating that the slightly hydrophilic nature of this compound and its non-ionised structure

both influence the sorption. In the synthetic matrix, the capacity of PLA to adsorb the hydrophobic ionised molecules of 2,4,6-TCP and PCP is two times higher than for the non-ionised 4-CP and 2,4-DCP.

The presence of other water constituents in the Danube river water, especially the natural organic matter (NOM), was expected to potentially interfere with the adsorption of the CPs by competing for adsorption sites on the surface of the plastics. However, the reverse trend was observed, whereby the q_{\max} of CPs in the presence of PEG, PP and PLA was generally greater or similar in the experiments carried out with Danube river water, in comparison to the synthetic matrix. This could indicate that additional interactions with the NOM were present. The adsorption of 2,4,6-TCP and PCP on PLA were the only cases where the q_{\max} values were significantly lower in the presence of NOM. NOM itself is a complex mixture of organic substances with various properties and functional groups. Earlier characterisation of the Danube river NOM [26] revealed that the majority of NOM present is mainly of hydrophilic character, while the hydrophobic fraction is relatively insignificant. This topic will certainly be of interest for future research, as also indicated by Xu et al. [21,25].

5. Conclusions

The results obtained in this work demonstrate that the presence of microplastics and bioplastics in aquatic environments may have a significant impact on the fate and transport of certain chlorinated phenols.

The adsorption of 4-CP was not significantly affected by the type of plastic present or the water matrix. In contrast, the type of plastic had a great impact on adsorption of 2,4-DCP, 2,4,6-TCP and PCP, with PCP demonstrating the most pronounced variation. In general, polypropylene showed the greatest affinity for the adsorption of CPs, whereas adsorption onto polyethylene and polylactic acid was more dependent on the structure of the compounds.

The differences observed between the adsorption behaviour of CPs in the investigated synthetic and natural water matrices demonstrate the need for further investigation, particularly in terms of how the role of different fractions of natural organic matter impact these interactions.

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