Modeling of chlorinated phenols adsorption on polyethylene and polyethylene terephtalate microplastic

LONČARSKI MAJA[1], TUBIĆ ALEKSANDRA[*,1], KRAGULJ ISAKOVSKI MARIJANA[1], JOVIĆ BRANISLAV[1], APOSTOLOVIĆ TAMARA[1], NIKIĆ JASMINA[1], AGBABA JASMINA[1]

Supplementary material

Table S1. Physico-chemical properties of the investigated chlorophenols

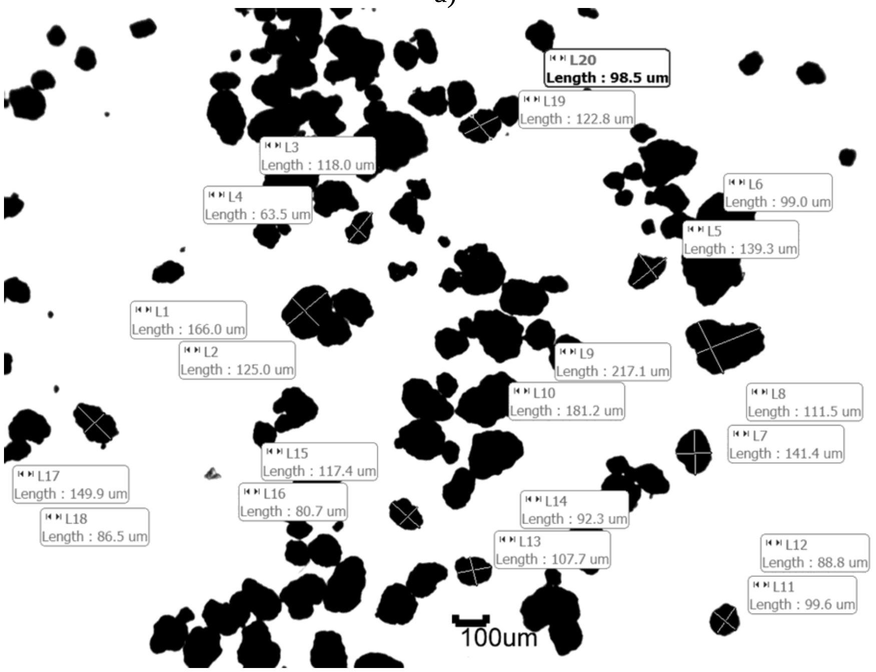
Compounds	**MW,** g mol^{-1}	**log K_{ow}^{a}**	**V_i^{a} /** cm^3 mol^{-1} 10^{-2}	**S_w^{a} /** mg l^{-1}	**pK_a^{a}**
4-CP	129	2.40	1.02	27100	8.85
2,4-DCP	163	3.06	1.14	4500	7.90
2,4,6-TCP	197	3.69	1.26	800	6.40
PCP	266	5.12	1.39	14	4.80

MW - molecular weight; K_{ow}, octanol-water partition coefficient; V_i - McGowan volume. [a]Kragulj *et al*.

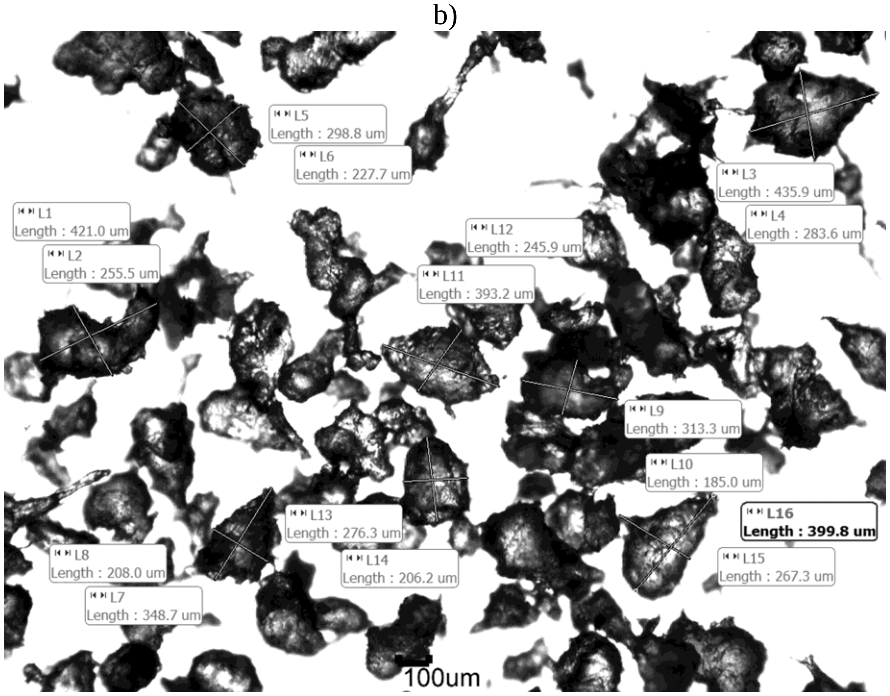
Analytical procedure, quality assurance and quality control

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 in parallel to the sorption experiments. Blank tests, containing same amounts of background solution 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 compound was found. Control tests were carried out in 20 mL of background solution containing a same gradient of CP concentrations as the samples, but without solid particles, in order to evaluate the loss of CP resulting from some additional removal processes, such as volatilization and/or sorption to the wall of glass bottles. Recovery of selected CP after derivatization with acetanhydride and liquid-liquid extraction with hexane ranged from 80-116 with the relative standard deviations (RSD) being below 10 % for all CPs. The method detection limits (MDLs) of the applied analytical methods ranged between 0.11-0.53 μg L^{-1}. The correlation coefcient 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 standard.

a)


L20
Length : 98.5 um
L19
Length : 122.8 um
L3
Length : 118.0 um
L6
Length : 99.0 um
L4
Length : 63.5 um
L5
Length : 139.3 um
L1
Length : 166.0 um
L2
Length : 125.0 um
L9
Length : 217.1 um
L10
Length : 181.2 um
L8
Length : 111.5 um
L7
Length : 141.4 um
L15
Length : 117.4 um
L17
Length : 149.9 um
L16
Length : 80.7 um
L14
Length : 92.3 um
L18
Length : 86.5 um
L13
Length : 107.7 um
L12
Length : 88.8 um
L11
Length : 99.6 um
100um

b)


L5
Length : 298.8 um
L6
Length : 227.7 um
L3
Length : 435.9 um
L1
Length : 421.0 um
L4
Length : 283.6 um
L12
Length : 245.9 um
L2
Length : 255.5 um
L11
Length : 393.2 um
L9
Length : 313.3 um
L10
Length : 185.0 um
L16
Length : 399.8 um
L13
Length : 276.3 um
L8
Length : 208.0 um
L14
Length : 206.2 um
L15
Length : 267.3 um
L7
Length : 348.7 um
100um

c)

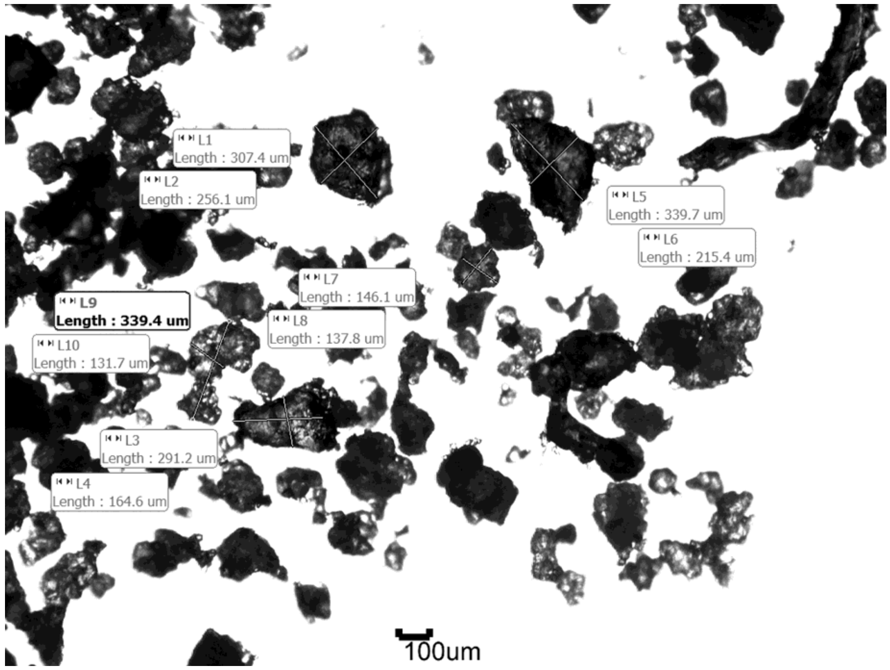


Fig.S1 Images of the microplastic particles used in experiments: a) PE, b) PE_PCPs_1 and c) PE_PCPs_2

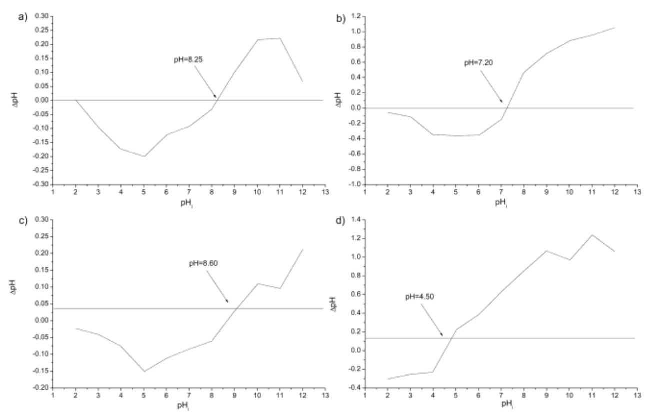


Fig. S2. The points of zero charge of the microplastics investigated: a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET

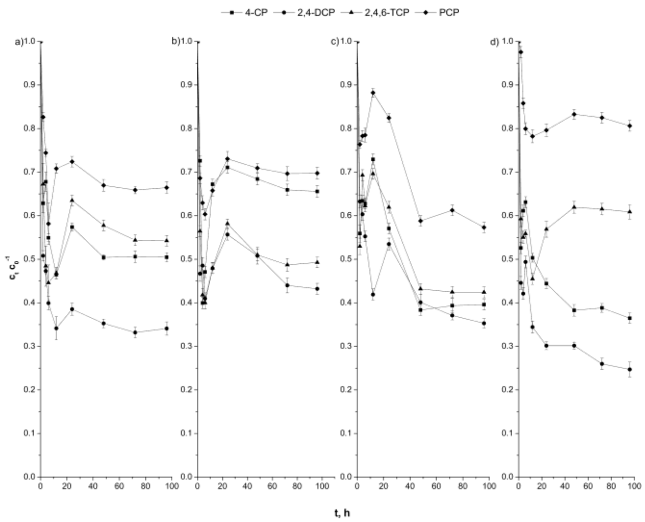


Fig.S3 Kinetic study results of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET during 96 h

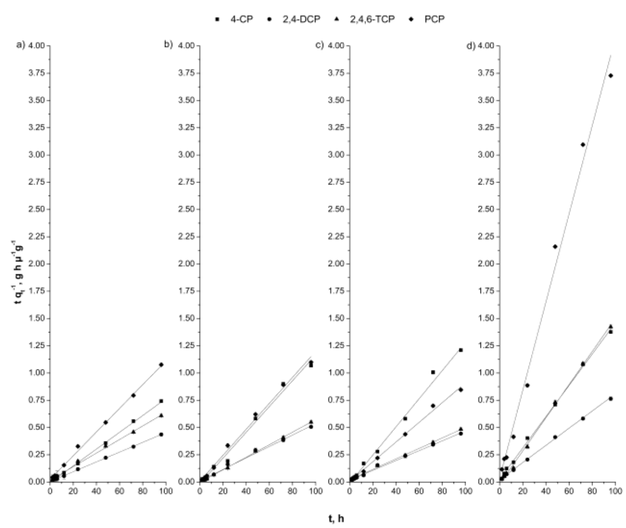


Fig. S4. Linear plots of sorption pseudo-second-order kinetic model for 2,4-DCP, 2,4,6-TCP and PCP onto a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET

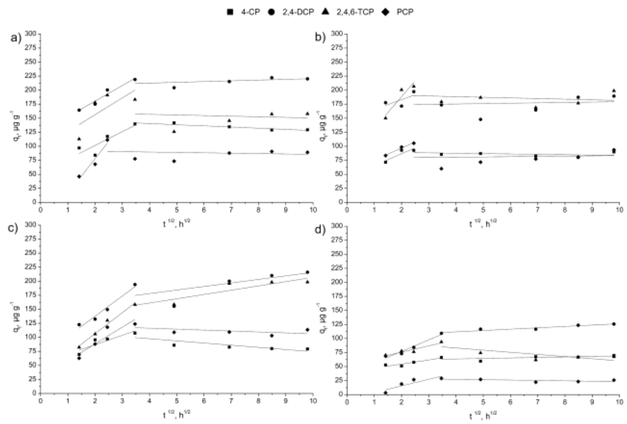


Fig S5. Linear plots of sorption modelled with intraparticle diffusion kinetics for 2,4-DCP, 2,4,6-TCP and PCP on a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET

Table S2. Theoretical and experimental q_e values obtained with pseudo-second-order model

Compounds	**Sorbents**	k_1 **(h^{-1})**	R^2	q_e *(theoretical)*	q_e *(experimental)*	***SD***
4-CP	**PE**	0.0064	0.998	142.9	141.6	0.88
	PE_PCPs_1	0.0120	0.994	84.50	89.85	3.76
	PE_PCPs_2	0.0130	0.987	77.40	79.33	1.36
	PET	0.0140	0.998	69.69	69.71	0.01
2,4-DCP	**PE**	0.0045	0.999	222.2	223.2	0.66
	PE_PCPs_1	0.0054	0.995	188.7	189.6	0.69
	PE_PCPs_2	0.0044	0.992	223.7	226.1	1.68
	PET	0.0080	0.998	126.3	125.6	0.44
2,4,6-TCP	**PE**	0.0066	0.991	156.3	157.7	1.03
	PE_PCPs_1	0.0057	0.998	175.4	176.8	0.95
	PE_PCPs_2	0.0053	0.999	199.0	207.9	6.29
	PET	0.0153	0.998	65.57	67.43	1.32
PCP	**PE**	0.0110	0.998	90.09	90.66	0.40
	PE_PCPs_1	0.0130	0.995	81.30	80.66	0.45
	PE_PCPs_2	0.0100	0.992	104.1	103.0	0.74
	PET	0.0430	0.990	23.94	25.75	1.28

Table S3. Freundlich and Langmuir parameters for adsorption of CPs on MPs

Compounds	**Sorbents**	**Freundlich model**					
		R^2	n	K_F / (µg g^{-1}/µg l^{-1})^n	log K_d 0.01 S_w	log K_d 0.05 S_w	log K_d 0.5 S_w
4-CP	**PE**	0.967	0.60	4.02	1.51	1.18	0.95
	PE_PCPs_1	0.967	0.94	1.65	1.28	1.05	0.71
	PE_PCPs_2	0.982	0.75	3.88	1.29	1.02	0.63
	PET	0.999	0.90	1.29	1.86	1.69	1.45
2,4-DCP	**PE**	0.969	0.63	0.94	1.63	1.35	1.16
	PE_PCPs_1	0.985	0.58	3.45	1.59	1.30	0.86

	PE_PCPs_2	0.977	0.75	1.02	1.29	1.12	0.86
	PET	0.971	0.92	0.29	2.10	2.05	1.96
2,4,6-TCP	**PE**	0.947	0.66	1.39	1.82	1.58	1.24
	PE_PCPs_1	0.961	0.6	1.69	1.67	1.40	0.99
	PE_PCPs_2	0.99	0.6	1.50	1.61	1.32	0.92
	PET	0.989	0.85	0.99	2.41	2.31	2.16
PCP	**PE**	0.959	0.57	1.78	2.34	2.04	1.61
	PE_PCPs_1	0.931	0.53	1.57	2.18	1.85	1.38
	PE_PCPs_2	0.945	0.54	0.63	1.81	1.49	1.02
	PET	0.953	0.94	0.93	2.84	2.79	2.73

Compounds	**Sorbents**	**Langmuir model**			
		R^2	**q_{max} / µg g^{-1}**	**K_L / l µg^{-1}**	**R_L**
4-CP	**PE**	0.997	63.30	0.0530	0.203-0.972
	PE_PCPs_1	0.974	282.9	0.0059	0.210-0.965
	PE_PCPs_2	0.967	86.90	0.0058	0.745-0.997
	PET	0.999	335.5	0.0030	0.828-0.998
2,4-DCP	**PE**	0.921	44.90	0.0066	0.624-0.996
	PE_PCPs_1	0.992	55.30	0.0339	0.267-0.986
	PE_PCPs_2	0.967	86.90	0.0058	0.668-0.996
	PET	0.973	104.7	0.0023	0.826-0.998
2,4,6-TCP	**PE**	0.984	22.90	0.0391	0.223-0.974
	PE_PCPs_1	0.974	38.70	0.0186	0.377-0.989
	PE_PCPs_2	0.993	27.80	0.0294	0.276-0.984
	PET	0.990	198.4	0.0039	0.763-0.998
PCP	**PE**	0.949	15.60	0.1354	0.077-0.937
	PE_PCPs_1	0.948	23.70	0.0243	0.306-0.985
	PE_PCPs_2	0.939	7.70	0.0691	0.130-0.951
	PET	0.956	309.9	0.0027	0.825-0.999