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SUPPLEMENTARY MATERIAL TO

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

MAJA LONČARSKI#, ALEKSANDRA TUBIĆ*#, MARIJANA KRAGULJ ISAKOVSKI#, BRANISLAV JOVIĆ#, TAMARA APOSTOLOVIĆ#, JASMINA NIKIĆ# and JASMINA AGBABA#

*University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia*

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## ANALYTICAL PROCEDURE, QUALITY ASSURANCE AND QUALITY CONTROL

Chlorinated phenol concentrations were determined by gas chromatography with mass spectrometry detection (GC/MSD), requiring an acetylating step prior to analysis. For acetylation of chlorinated phenols, $K_2CO_3$ and acetanhydride were added to the aqueous solution and stirred for 15 min to ensure complete acetylation of the phenols. The acetylated phenols were extracted using hexane (J. T. Baker, for organic residue analysis) with shaking for 15 min. The acetylated phenols were analyzed using an Agilent 7890A/5975C GC/MSD on a HP-5MS column (J&W Scientific) using the following conditions: helium carrier gas at a flow rate of 1.5 ml $min^{-1}$ in the column; injector temperature 200 °C; initial oven temperature 40 °C for 2 min, then 40 °C/min to 100 °C for 0.5 min, then 2 °C $min^{-1}$ to 140 °C and 30 °C $min^{-1}$ to 300 °C; detector temperature 150 °C. The sample volume injected was 2 μL. Blank and control experiments were performed in parallel to the sorption experiments. Blank tests, containing the same amounts of background solution and solid particles as the samples, but without the addition of chlorinated phenols, were performed using conditions similar to those described previously, and no target compound was found. Control tests were performed 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 walls of the glass bottles. Recovery of selected CP after derivatisation 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 (*MDL*s) of the applied analytical methods ranged between 0.11–0.53 μg $L^{-1}$. 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 standard.

* Corresponding author. E-mail: aleksandra.tubic@dh.uns.ac.rs

TABLE S-I. Physicochemical properties of the investigated chlorophenols; *MW* – molecular weight; $K_{ow}$, octanol–water partition coefficient; $V_i$ – McGowan volume

| Compound | *MW*, g mol$^{-1}$ | log $K_{ow}$ | $V_i$ / cm$^3$ mol$^{-1}$ 10$^{-2}$ | $S_w$ / mg L$^{-1}$ | p$K_a$ |
|---|---|---|---|---|---|
| 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 |

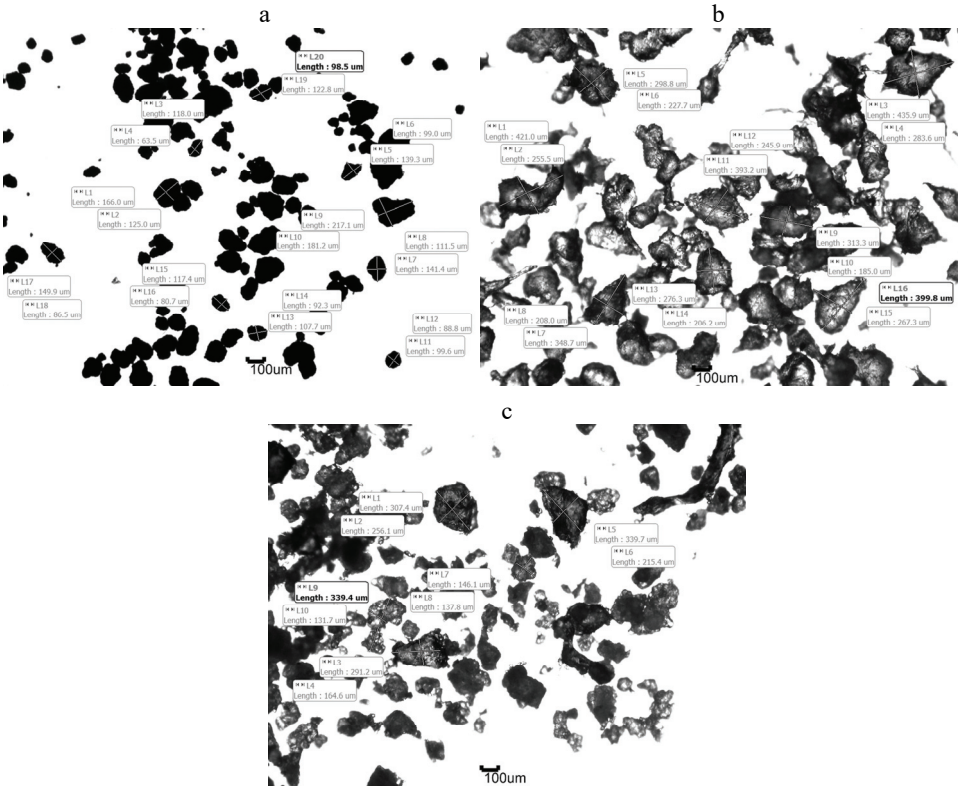


Fig. S-1. Images of the microplastic particles used in the experiments: a) PE, b) PE_PCPs_1 and c) PE_PCPs_2.

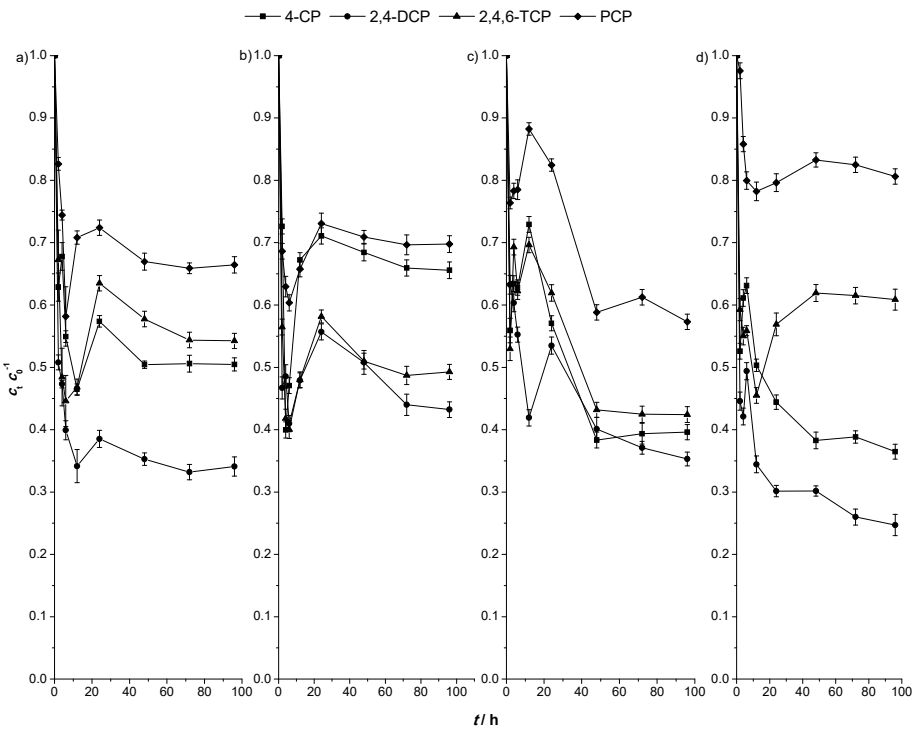


Fig. S-2. Kinetic study results of 4-CP, 2,4-DCP, 2,4,6-TCP and PCP on a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET (during 96 h, pH 6.8±0.5, initial CPs concentration 100 μg $L^{-1}$).

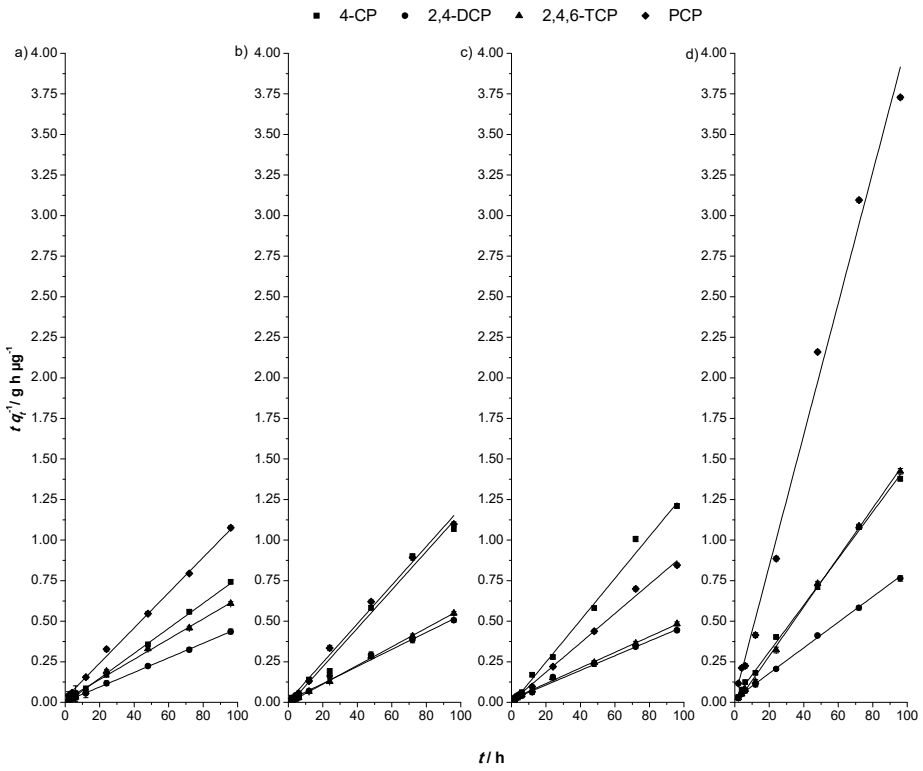


Fig. S-3. Linear plots of sorption pseudo-second-order kinetic model for 2,4-DCP, 2,4,6-TCP and PCP onto a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET.

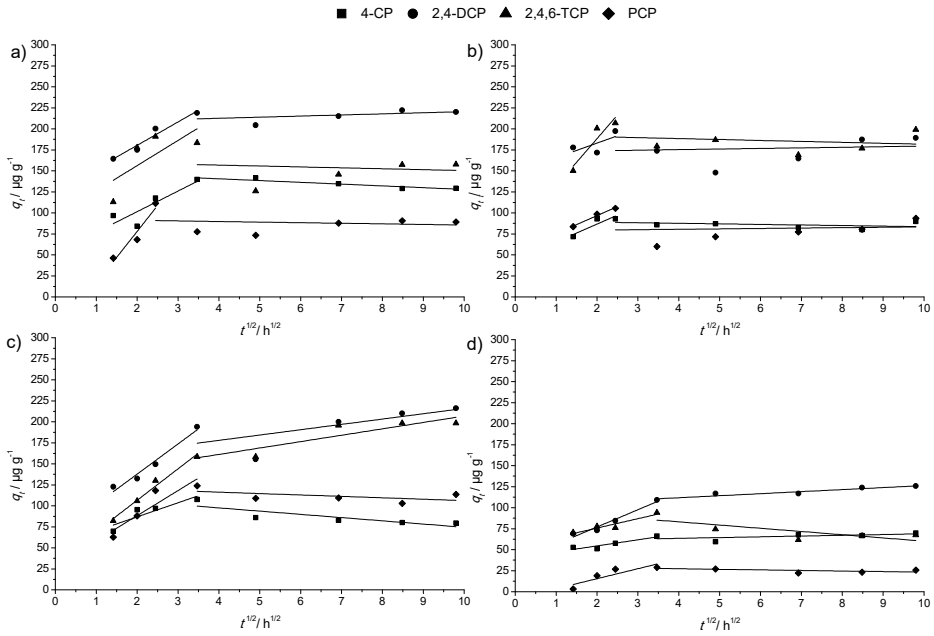


Fig. S-4. Linear plots of sorption modelled with intraparticle diffusion kinetics for 2,4-DCP, 2,4,6-TCP and PCP on a) PE, b) PE_PCPs_1, c) PE_PCPs_2 and d) PET.

TABLE S-II. Theoretical and experimental $q_e$ values obtained with the pseudo-second-order model

| Compound | Sorbent | $k_1$ / h$^{-1}$ | $R^2$ | $q_{e\ (theoretical)}$ / μg g$^{-1}$ | $q_{e\ (experimental)}$ / μg g$^{-1}$ | *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 S-III. Freundlich and Langmuir parameters for adsorption of CPs on MPs

| Compound | Sorbent | Freundlich model | | | | | |
|---|---|---|---|---|---|---|---|
| | | $R^2$ | $n$ | $K_F$ / (μg g$^{-1}$/μg l$^{-1}$)$^n$ | log $K_d$ | | |
| | | | | | 0.01$S_w$ | 0.05$S_w$ | 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 |

| Compound | Sorbent | 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 |

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