Removal of polychlorinated biphenyls from water by sorption onto polymers

BOŽENA SKLÁRŠOVÁ - PETER ŠIMKO - PETER ŠIMON - BEATA DROBNÁ

Summary

Water and rapeseed oil were spiked with six polychlorinated biphenyls (PCBs), filled into polyethylene terephtalate (PET) as well as polystyrene (PS) cylindrical shape receptacles and PCB concentrations were followed within 72 h. As found, PCB concentration in water decreased considerably due to the sorption of PCBs onto walls of the receptacles. From the treatment of experimental data, diffusion and the distribution coefficients were obtained for all studied compounds. Comparing the area of contact surfaces of the receptacles and the calculated area of PCB films composed of PCB molecules it was derived that the PET surface was occupied by 30.4% while the PS surface by 52.7% of PCB film, what indicate better applicability of PS for removal of PCBs from water in comparison to PET. The results show that the mechanism of PCB removal can be characterised as a monolayer adsorption taking place on surfaces of the polymers. Regarding rapeseed oil it was found that PET and PS are inappropriate materials for the removal of PCBs from this non-polar matrix, because no distinct PCB adsorption was observed in this case.

Keywords

polychlorinated biphenyls; rapeseed oil; polyethylene terephtalate; polystyrene; adsorption, removal, diffusion, water

Polychlorinated biphenyls (PCBs) are a group of 209 man-made organic chemicals containing carbon, hydrogen and differing amounts of chlorine atoms. The commercial production of PCBs started in 1929 but their use had been banned or severely restricted in many countries since the 1970s and 80s because of serious risks to human health and the environment. PCBs have been used in a wide range of products such as polymers, paints, and adhesives. Since PCBs are resistant to acids and bases as well as to heat, they have mainly been used in electric equipment as heat transfer fluids, or lubricants, respectively. Disposal of waste that contains PCBs in landfills or incinerators can lead to serious environmental contamination. PCBs were first detected in environmental samples in 1966 [1]. PCBs can persist in the environment and accumulate in animals and along the food-chain. A human organism may be exposed to PCBs by ingestion of contaminated food and water, or in-

haling contaminated air, respectively. PCBs have been shown to cause cancer as well as a number of serious non-cancer health effects in animals, including effects on the immune system, reproductive system, nervous system, endocrine system, more frequent infections, and changes of the skin, particularly rashes and chloracne. Their harmful effects to man and the environment are well documented in a number of reviews [2-7]. Therefore, the elimination of PCBs from foods and the environment is coveted as much as possible. Adsorption of organic contaminants on polymer packaging materials is a promising way of decreasing levels of organic contaminants in foods [8-13]. For example, on the basis of interactions with polymer package, the concentrations of polycyclic aromatic hydrocarbons (PAHs) in a liquid smoke flavour stored in low density polyethylene (LDPE) bottles were lowered by two orders during 14 days [8]. As found [14], the rate-limiting step was diffusion in

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the liquid media. PAHs were primarily adsorbed on the LDPE surface, with subsequent migration into the bulk of the polymer what intensified the effectiveness of the removal process [15]. This process of elimination is also efficient for removal of PAHs from solid media, e.g. benzo[*a*]pyrene content in duck meat was lowered by 75% after 24 hours of interaction with LDPE [16]. The ability of polyethylene terephtalate (PET) to decrease PAH concentrations in polar and non-polar liquid media has already been unambiguously proven [9]. However, the extent of removal processes was limited only to surface adsorption processes which led to equilibrium between liquid and solid phase. Moreover, this process was also affected also by other compounds (vitamins, synthetic antioxidants, phytosterols, etc.) to be present in such liquid media as vegetable oils [12]. The aim of this work was to study the possibilities of PCB removal from water and rapeseed oil by adsorption onto PET and polystyrene (PS) receptacles.

MATERIALS AND METHODS

Rapeseed oil

Commercially available rapeseed oil was produced by Palma-Tumys (Bratislava, Slovakia) and purchased in a local market in Bratislava. The oils were stored in PET bottles with volume of 4 l.

PET receptacles

In the experiment, pre-bubbled PET receptacles of cylindrical shape with i.d. of 21.4 mm and height 150 mm were used. The receptacles were provided by Palma-Tumys. The company uses them for oil and fruit syrup packaging after blowing to volume of 2 l.

PS receptacles

PS tubes with i.d. of 23 mm and height 120 mm were supplied by Čechvalab (Bratislava, Slovakia).

PCB

PCB congeners:
- PCB 28 (2,4,4'-trichlorbiphenyl);
- PCB 52 (2,2',5,5'-tetrachlorbiphenyl);
- PCB 101 (2,2',4,5,5'-pentachlorbiphenyl);
- PCB 103 (2,2',4,5',6-pentachlorbiphenyl);
- PCB 138 (2,2',3,4,4',5'-hexachlorbiphenyl);
- PCB 153 (2,2',4,4',5,5'-hexachlorbiphenyl);
- PCB 174 (2,2',3,3',4,5,6'-heptachlorbiphenyl);
- PCB 180 (2,2',3,4,4',5,5'-heptachlorbiphenyl)

were purchased from Labservice (Spišská Nová Ves, Slovakia) each with the concentration of 100 μg.ml^{-1} in hexane.

Solvents

Methanol, dichloromethane and hexane of analytical grade were purchased from Merck, Darmstadt, Germany. The solvents were rectified just before use in a distillation apparatus.

Other chemicals and materials

Anhydrous Na$_2$SO$_4$, alumina, Florisil, silica gel and H$_2$SO$_4$ were also purchased from Merck.

Experiment

Water

Distilled water was spiked with six PCB congeners solutions diluted in acetone to obtain final concentration in water between 1–7 μg.l^{-1}. Then, the water was heated to 40 °C for 1 hour and occasionally shaken to evaporate the residual acetone. After cooling to 19.0 °C, the water was sampled for initial PCB concentration. Then, the PET and PS receptacles were filled with the water and placed into a polystyrene box to protect them from light and to keep the constant temperature of 19.2 °C. The temperature was monitored and recorded by thermometer Logger S 0121 (Comet System, Rožnov pod Radhoštěm, Czech Republic). The samples for analysis were taken after 1; 3; 5; 7; 11; 24; 72 h. To maintain the same static conditions, a new set of receptacles was taken for each analysis.

Rapeseed oil

100 g of the rapeseed oil was spiked with six PCB congeners in hexane in 2 l volume glass flask and the solvent left to evaporate spontaneously. To accelerate the evaporation of the solvent, the oil was stirred up occasionally. Then roughly 900 g of the oil was added and the flask content was stirred thoroughly. At this stage, the oil was sampled to determine the initial PCB concentration. Then, the PET and PS receptacles were filled with the spiked oil and placed into a polystyrene box to protect them from light and to keep at a constant temperature of 18.2 °C. The samples for analysis were taken after 1; 3; 5; 7; 11; 24; 72 h. To maintain the same static conditions, a new set of receptacles was taken for each analysis.

Sample preparation

Water

5 ml of water were extracted with hexane for four times. Hexane layers were combined, dried with anhydrous Na$_2$SO$_4$ and evaporated until nearly dryness. Remaining solvent was evaporated at room temperature just before analysis. The residuum was dissolved in a known volume of standard solution of PCB 103 and analysed by GC.

Rapeseed oil

A known amount of standard solution of PCB 174 was added to rapeseed oil (cca 0.100 g) and weighted to the nearest 0.001 g to determine the extraction recovery. The sample was dissolved in 1 ml of hexane and cleaned up in the combined Florisil-silica gel column (0.5 g Florisil, 1 g 44% H_2SO_4 on silica gel, 0.5 g Florisil and 1 g anhydrous Na_2SO_4). The column was eluted with 10 ml of 10% (v/v) dichloromethane in *n*-hexane. The eluate was evaporated to about 0.5–1 ml and transferred by Pasteur pipette into a vial. Evaporation continued under nitrogen until nearly dry. Remaining solvent was evaporated at room temperature just before analysis. The residuum was dissolved in a known volume of sampling standard solution of PCB 103 and analysed by GC.

GC analysis

Analysis were performed on gas chromatograph Agilent Technologies 6890N equipped with elec-

tron capture detector using capillary GC column DB-5, 60 m, 0.25 mm (i.d.), 0.25 μm film thickness (purchased from J&W Scientific, Folsom, California, USA) using splitless technique with temperature program as follows: isothermal at 110 °C for 1.5 min, then temperature elevation to 200 °C at 30 °C.min^{-1}, hold for 0.2 min, then temperature elevation to 300 °C at 2,5 °C.min^{-1}. Helium was used as a carrier gas with a constant flow rate of 0.8 ml.min^{-1}.

RESULTS AND DISCUSSION

At first, the experiment was carried out with the spiked water filled in PET and PS receptacles. Concentrations of PCBs started to decrease immediately after filling the receptacles in both systems studied as seen from Figs. 1 and 2. The observed dependences of PCB concentrations versus time were treated using the kinetic equation (1), which
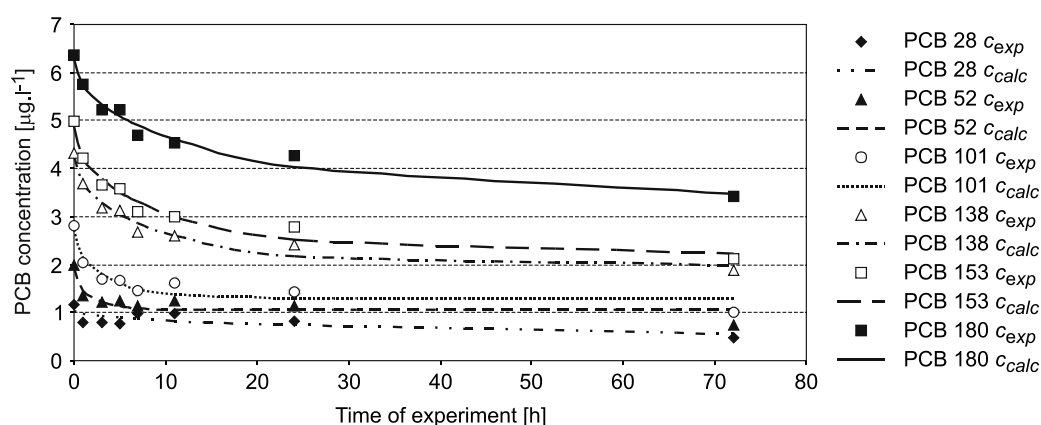

Fig. 1. Changes in PCBs concentration in water stored in PET receptacles.
Experimentally obtained data versus calculated data using kinetic equation of adsorption (1).
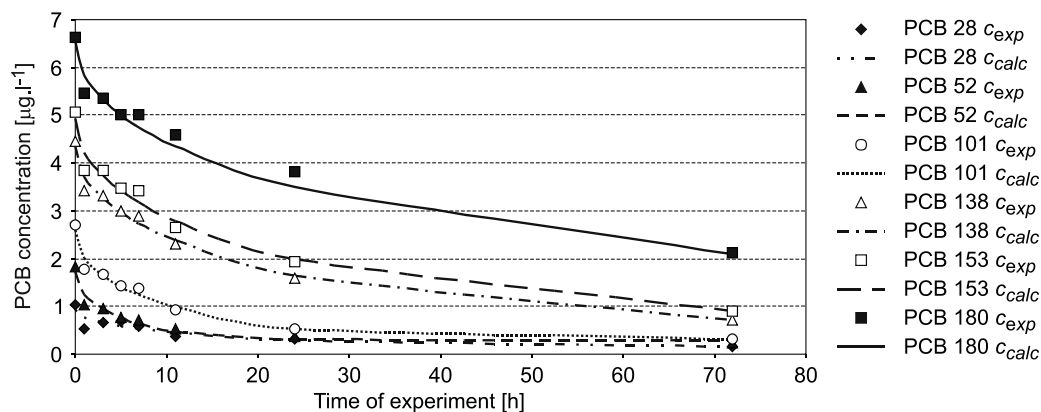

Fig. 2. Changes in PCBs concentration in water stored in PS receptacles.
Experimentally obtained data versus calculated data using kinetic equation of adsorption (1).

Tab. 1. Values of the identified model parameters,
diffusion and distribution coefficients of PCB congeners in the water - PET system.

	PET			
	c_∞ [μg.l^{-1}]	c_0-c_∞ [μg.l^{-1}]	D [cm^2.h^{-1}]	β
PCB 28	0.16	0.86	1.3 × 10^{-3}	5.368
PCB 52	1.07	0.87	8.8 × 10^{-2}	0.818
PCB 101	1.30	1.43	4.5 × 10^{-2}	1.102
PCB 138	1.98	2.29	1.7 × 10^{-2}	1.157
PCB 153	2.23	2.65	1.6 × 10^{-2}	1.188
PCB 180	3.42	2.87	9.6 × 10^{-3}	0.839

Tab. 2. Values of the identified model parameters,
diffusion and distribution coefficients of PCB congeners in the water - PS system.

	PS			
	c_∞ [μg.l^{-1}]	c_0-c_∞ [μg.l^{-1}]	D [cm^2.h^{-1}]	β
PCB 28	0.14	0.78	1.2 × 10^{-2}	5.571
PCB 52	0.30	1.43	3.4 × 10^{-2}	4.847
PCB 101	0.30	2.30	1.8 × 10^{-2}	7.616
PCB 138	0.50	3.86	8.1 × 10^{-3}	7.800
PCB 153	0.62	4.32	7.6 × 10^{-3}	6.966
PCB 180	1.45	5.09	4.6 × 10^{-3}	3.508

has been derived for the diffusion of PAHs in non-stirred liquids placed into cylindrically shaped receptacles [9]:

$$c_t = c_\infty + (c_0 - c_\infty)\sum_{n=1}^{\infty}\frac{4}{a^2\alpha_n^2}\exp\left[-D\alpha_n^2 t\right] \quad (1)$$

where c_0 is the initial concentration of PCBs in water, c_t is the concentration of PCBs in the medium at time t, and c_∞ is the concentration of PCBs corresponding to infinite time (equilibrium), a is the radius of the cylinder, α_n are the roots of the zero-order first-kind Bessel function and D is the diffusion coefficient of PCB in water. The parameters c_∞, c_0-c_∞ and D were obtained by the non-linear least squares method by minimizing the sum of squares of differences between the PCB concentrations measured experimentally and those calculated by equation (1). The values of minimized parameters are listed in Tables 1 and 2.

The extent of PCBs removal can be characterized by the distribution coefficient expressed by the formula

$$\beta = \frac{c_0 - c_\infty}{c_\infty} \quad (2)$$

The higher is the value of β, the greater part of PCBs is removed from water after reaching the equilibrium. The values of β are also listed in Tables 1 and 2. The values of β for PS are much higher than the corresponding values for PET. This implies a much higher affinity of PCBs to PS in comparison with PET. A comparison of "total PCB area" to contact area of the polymer receptacles is really interesting. Surfaces of congener molecules were calculated using the Savol program (Tripos, St. Louis, Missouri, USA) and they are summarised in Tab. 3. Extent of coverage of the polymer surface was calculated from differences between initial and equilibrium PCB concentrations in water using the modified formula derived in [9]

$$C = \frac{N_A\,a\,(c_0 - c_\infty)S}{2M} \quad (3)$$

where C is extent of coverage by PCB film on polymer surfaces, M is the molar mass of the PCB, N_A

Tab. 3. Surface area of PCBs molecules and area of PCB monolayer on polymer surfaces.

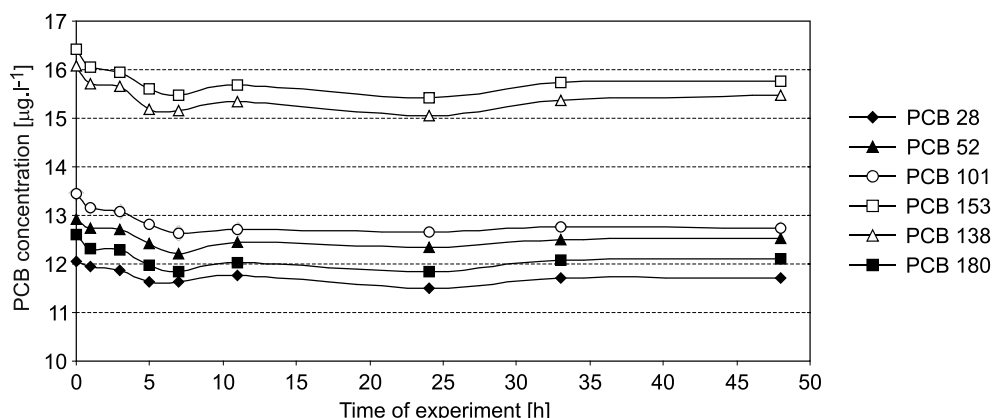| Compound	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	Total
Surface area [nm^2]	2.634	2.741	2.886	3.014	3.031	3.159	–
Molar mass [g.mol^{-1}]	257.559	292.008	326.457	360.906	360.906	395.355	–
PET coverage [%]	2.9	2.6	4.1	6.2	7.2	7.4	30.4
PS coverage [%]	2.8	4.6	7.0	11.6	12.6	14.1	52.7

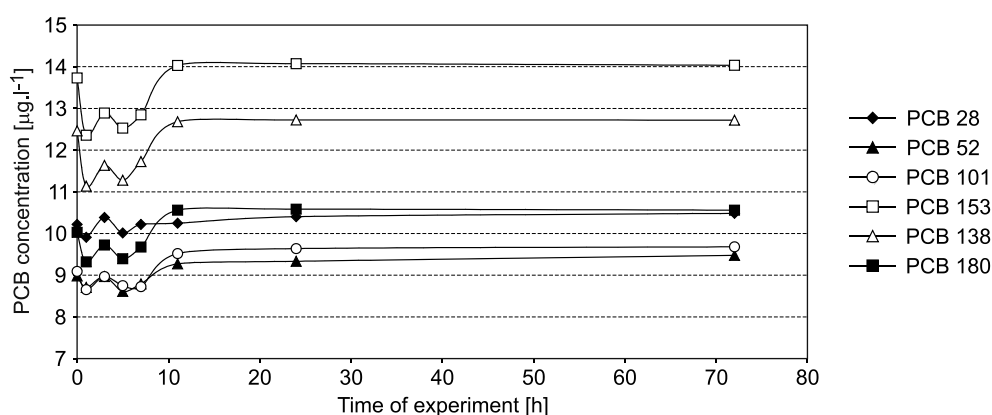**Fig. 3.** PCB concentration in rapeseed oil stored in PET receptacles.

Fig. 4. PCB concentration in rapeseed oil stored in PS receptacles.

is the Avogadro number, S is the surface of PCB congener molecule calculated by the Savol program and the other symbols have the same meaning as above. Results showed that the area of polymers to be covered by PCBs composed from individual congener areas adsorbed onto PET is equal to 30.2% of total PET area, while the total area adsorbed onto PS is equal to 50.7% of total PS area. These values indicate that the PCBs removal from water could be classified as monomolecular adsorption on the polymer surfaces. As follows from Tab. 3, the extent of adsorption increased with number of Cl atoms in PCB molecule. The values of PCB diffusion coefficients in water, calculated from equation (1) for both experimental systems are not very different which indicates that the same physicochemical processes take place in the PCB removal process (Tab. 1 and 2). The curves of PCB concentrations versus time are quite scattered so that the values of D convey great errors. However, the general trend seen in Tables 1 and 2 is that D decreases with the increasing molar mass. Different situation has been observed in

the case of rapeseed oil, where the concentrations at the beginning of experiment decreased only slightly exhibiting oscillations with subsequent return to original concentrations, as shown in Figs. 3 and 4. This indicates that the affinity interactions between the oil and PCBs are much stronger than the interactions between the polymers and PCBs. For this reason the both polymers, PET and PS, are applicable to eliminate PCBs from polar aqueous media, but not from rapeseed oil.

CONCLUSIONS

The results and findings of this work lead to the following conclusions:
1. The PCB concentration in the water filled into PET and PS receptacles decreases considerably due to affinity interactions between PCBs and surface of the polymers.
2. The interactions between PCBs and polymer can be classified as a monomolecular adsorption of PCBs on the polymer surface so than

it can be expected that the adsorption equilibrium will obey the Langmuir isotherm.

3. The values of diffusion coefficients obtained enable to predict the rate of PCB elimination at any time of the interaction; the values of distribution coefficients characterize the extent of the PCBs removal.

4. Although both polymers are suitable for PCB removal, PS is a more efficient material in comparison with PET. However, both materials to be used frequently in food packaging can considerably lower PCB concentrations in foods and such way to protect consumer against exposition of these hazardous compounds

5. It was found that PET and PS are not applicable for elimination of PCBs from rapeseed oil as the non-polar matrix.

Acknowledgement

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