

Removal of benzene from water by adsorption on polymer materials

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Summary

Water was spiked with benzene at the level of $109 \mu\text{g.l}^{-1}$, filled into low density polyethylene (LDPE) and polyethylene terephthalate (PET) cylindrical shape receptacles and the benzene concentrations were followed for 262 h by GC-MS working in selected ion monitoring mode. During this time, the benzene concentrations decreased to $20.5 \mu\text{g.l}^{-1}$ in PET and $14.9 \mu\text{g.l}^{-1}$ in PE due to the interaction of benzene with plastics. Using a modified diffusion equation, the diffusion coefficients of benzene in water for both studied systems were calculated. In spite of different character of the polymers, both ones are able to remove effectively benzene from water as follows from values of diffusion coefficients ($2.29 \times 10^{-2} \text{ cm}^2.\text{h}^{-1}$ for the system water/PE; $2.17 \times 10^{-3} \text{ cm}^2.\text{h}^{-1}$ for water/PET) as well as distribution coefficients ($\beta = 4.32$ for LDPE; $\beta = 4.68$ for PET). With regard to extensive usage of the plastics in packaging technology, both ones could play important role in protection of consumer health against benzene exposition from packed table water and soft drinks.

Keywords

benzene; water; polyethylene; polyethylene terephthalate; adsorption; removal

A presence of various contaminants in food chain is permanent problem due to industrial activities of mankind. One of the most important pollutants is benzene, which is produced extensively during fossil fuel processing and followingly being used in chemical industry including production of materials (colorants, coatings, plastics, food synthetic additives, etc.) coming directly or indirectly into contact with foods. Moreover, benzene can also be formed directly in foods under special conditions e.g. decarboxylation of benzoic acid in preserved soft drinks at elevated temperatures and exposition to the day light [1]. After entering an organism, benzene targets organs viz. liver, kidney, lung, heart, brain, etc. It is metabolized mainly in the liver by cytochrome P450 multifunctional oxygenase system. Benzene causes haematotoxicity through its phenolic metabolites able to form DNA strand breaks, chromosomal damage, sister chromatid exchange, inhibition of topoisomerase II and damage to mitotic spindle. The carcinogenic and myelotoxic effects of benzene are associated with the free radical formation either as benzene metabolites or lipid peroxidation products

[2]. With regard to these effects, World Health Organisation has adopted limit of $10 \mu\text{g.l}^{-1}$ benzene for drinking water, while Food and Drug Administration in USA has limited benzene concentration to $5 \mu\text{g.l}^{-1}$ and tolerable limit of European Union is confined to $1 \mu\text{g.l}^{-1}$. As the analysis of benzene presence in drinking water in Mexico showed, benzene appeared in 88% of samples (although rarely at the concentration $>0.66 \mu\text{g.l}^{-1}$ apart from 4 sites, where the levels varied between $12.7\text{--}38.5 \mu\text{g.l}^{-1}$), possibly through leaks of petroleum products into water sources [3]. Benzene and toluene were also determined in all of 60 soft drinks (20 cola, 10 light cola and 15 carbonated beverages, together with 15 soft drinks made from orange juice) tested by gas chromatography - mass spectrometry. As concluded, both compounds can either be formed in foods or contaminate raw materials as environmental contaminants [4]. Notable is, that all these drinks were filled into glass bottles. An efficient way for elimination of organic contaminants from liquid media is their sorption into polymer plastics. In this way, concentrations of polycyclic aromatic hydrocarbons (PAHs) in a liquid smoke flavour

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filled in low density polyethylene (LDPE) bottles were lowered by two orders during 14 days [5]. As found later [6], the rate-limiting step of the PAHs sorption from liquid LDPE was the diffusion in a liquid media. PAHs were primarily adsorbed on LDPE surface, with subsequent migration into bulk polymer what increased the effectiveness of the process [7]. The ability of polyethylene terephthalate (PET) to decrease PAH concentrations in polar and non-polar liquid media has already been unambiguously proven [8]. 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 is affected also other compounds to be present in liquid media [9]. The aim of this work was to study the possibilities of benzene removal from water to be filled into LDPE and PET receptacles.

MATERIALS AND METHODS

Water

Water used in experiments was of table quality obtained from local duct in Bratislava, Slovakia. Before the experiment, water was rid of impurities by distillation in glass apparatus.

PET receptacles

Pre-bubbled PET receptacles of cylindrical shape were used with i.d. of 2.14 cm. The receptacles were provided by Palma-Tumys, Bratislava, Slovakia. The company uses them for oil and fruit syrup packaging after blowing to volume of 2 or 4 l, respectively.

LDPE receptacles

LDPE cylindrical shape receptacles with i.d. of 4.5 cm were supplied by Čechvalab, Bratislava, Slovakia.

Benzene

Benzene of p. a. purity was purchased from Lachema, Brno, Czech Republic. Deuterised benzene-d₆ was purchased from Sigma-Aldrich, Steinheim, Germany.

Solvents

Ethanol was purchased from Sigma-Aldrich, Steinheim, Germany.

Experiment

First of all, water was bubbled by nitrogen for 15 min and followingly analyzed for the presence of benzene. Subsequently, ethanolic solution of benzene was added to water to get initial concen-

tration of benzene at the level 109 µg.l⁻¹ and LDPE and PET receptacles were filled with this water, sealed and maintained at the constant temperature 21.3 °C. The samples for analysis were taken after 6, 24, 48, 72, 96, 166, 188, 212, and 262 h. To maintain equal static conditions during the experiments, new receptacles were taken for each analysis. After sampling, the contents of receptacles were followingly discharged. All measurements were carried out in triplicate with average value of RSD_{PET} = 5.2%, or RSD_{LDPE} = 2.8%, respectively.

GC analysis

Agilent Technologies G188 Network Headspace Sampler (Agilent Technologies, Palo Alto, USA), Agilent Technologies 6890 gas chromatograph equipped with an Agilent Technologies 5973 inert mass selective spectrometer was used for the determination of benzene concentrations. The samples of water were inserted into 20 ml head space vials, sealed with rubber stoppers and protected with a Teflon sheet and aluminum crimp caps. 1 µl of benzene-d₆ with concentration of 593 mg.l⁻¹ in ethanol was added as an internal standard. The head space auto-sampler Agilent G188 was operated under the following conditions: sample loop 0.5 ml, oven temperature 70 °C, switching valve and sample loop temperature 90 °C, transfer line temperature 110 °C, sample equilibrium time 15 min, pressurize 50 kPa 0.2 min, pressurize equilibrate time 0.2 min; loop fill time 0.2 min; loop equilibrate time 0.05 min; injection time 0.25 min. Splitless mode was used in all experiments. The separations were performed using Agilent 19091P-Q04 HP-PLOT Q 30 m × 0.32 mm × 20 µm fused silica capillary column coupled with the 2.5 m × 0.32 mm Particle Trap. The column was held at 80 °C for 1 min, then heated to 220 °C at a rate of 10 °C.min⁻¹. The carrier gas (helium) flow was maintained at 0.8 m.min⁻¹ by an electronic control. The MS detector was operated in SIM mode under the following conditions: ion source EI was 70 eV, interface temperature 230 °C, ion source temperature 230 °C, monitoring ions in SIM mode m/z 51 and 78 for benzene, m/z and 56 and 84 for benzene-d₆, respectively. The dwell time was 100 ms.

RESULTS AND DISCUSSION

Concentration of benzene started to decrease immediately after filling the receptacles in both systems studied as seen in Figs. 1 and 2. Since the static conditions were maintained during the experiments, it was possible to use the diffusion equation for calculation of diffusion coefficients, which has been

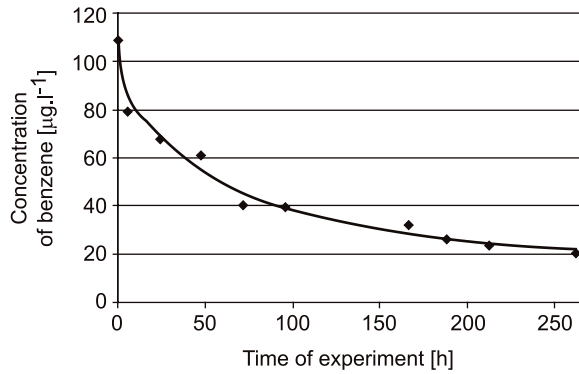


Fig. 1. Changes of benzene concentration in water stored in PET receptacles.
(♦) - experimentally obtained data, (—) - calculated data using the equation of diffusion (1).

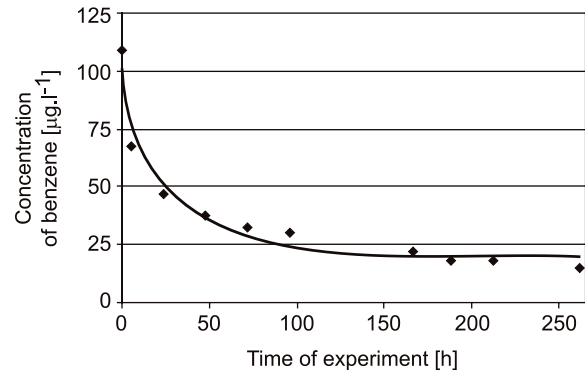


Fig. 2. Changes of benzene concentration in water stored in PE receptacles.
(♦) - experimentally obtained data, (—) - calculated data using the diffusion equation (1).

derived for the description of PAHs's behaviour in non-stirred liquid media in the form

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

where c_0 , c_t and c_∞ are the initial concentration, concentration at time t and equilibrium concentration, respectively, D is the diffusion coefficient, a is the radius of the cylinder, and α_n are the roots of the equation

$$J_0(a \alpha_n) = 0 \quad (2)$$

where J_0 is the zero-order first-kind Bessel function.

Diffusion coefficients of benzene were calculated by the non-linear least squares method by minimizing the sum of squares of differences between the concentrations of benzene measured experimentally and those calculated by eq. (1). The minimization was carried out by the simplex method. Minimized parameters were c_∞ , $c_0 - c_\infty$ and D and they are summarized in Table 1. In calculations, the first 20 terms of eq. (1) were taken into account. The values of α_n were taken from tables [10]. The agreement between experimental and calculated values is fairly good as it can be seen from Figs 1 and 2.

As follows from the values of diffusion coefficients, the benzene removal is much more quickly by LDPE than by PET since its diffusion coefficient is greater by an order of magnitude than that for PET. The difference in diffusion coefficients indicates that the coefficients are composite quantities and, beside the diffusion of benzene in water, they comprise also the effects of an adsorption on the polymer surface and conceivably the subsequent diffusion into the polymer bulk in the case of LDPE, as has been proven for PAHs [7]. The PET is a less efficient material for organic contaminant removal since only the surface adsorption comes into account [8]. The efficiency of benzene removal can be characterized by the distribution coefficient expressed by the formula

$$\beta = \frac{c_0 - c_\infty}{c_\infty} \quad (3)$$

The higher is the value of β , the greater part of benzene is removed from water. The values of β are also listed in Table 1. As it follows from the values presented, there was no great difference between LDPE and PET distribution coefficient values at given experimental conditions, e.g. capacities of both plastics to remove benzene from water were comparable.

Tab. 1. Minimized parameters, distribution and diffusion coefficients of benzene in the studied systems.

	c_∞ [$\mu\text{g.l}^{-1}$]	$c_0 - c_\infty$ [$\mu\text{g.l}^{-1}$]	β	D [$\text{cm}^2.\text{h}^{-1}$]
PET	18.6	87.1	4.68	2.17×10^{-3}
LDPE	19.5	84.3	4.32	2.29×10^{-2}

CONCLUSIONS

Summarizing the results and findings obtained in this work, the following conclusions could be drawn:

1. The concentration of benzene in water can be efficiently lowered by the interaction between benzene contained in the liquid phase and LDPE or PET as a solid phase.
2. This way of benzene elimination could be useful especially in the cases where the use of other procedures or techniques is impossible.
3. This way of benzene removal from water is especially suitable for a longer time of interaction, e.g. during storing the filled PET or PE bottles which are also frequently used for packing table water, or soft drinks, respectively; in this case the plastic packaging can efficiently protect consumers against benzene exposure.
4. While LDPE is more efficient with regard to the rate of benzene removal, extend of removal is comparable for both plastics.
5. The rate of decrease of benzene concentration can be described by the modified diffusion equation.
6. The values of diffusion coefficients obtained enable to predict the benzene concentration at any time of the interaction; the values of distribution coefficients characterize the efficiency of the benzene removal.
7. Known values of diffusion coefficients make possible to use the equation of diffusion also for prediction of benzene concentrations in plastics with different geometry.
8. The results obtained indicate that the interaction of benzene with polymers could be a prospective way of removal also for other organic contaminants (e.g. toluene, xylenes, etc.) from water and aqueous media in order to improve considerably the consumer health protection against industrial environment contaminants.

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