

ADSORPTION OF BIS (2-ETHYLHEXYL) PHTHALATE

Josef Houser, Jan Růžička, Marie Dvořáčková
Department of Environment Protection Engineering, Faculty of Technology,
Tomas Bata University in Zlín, TGM Square 275, 762 72 Zlín, Czech Republic

ABSTRACT

The adsorption of Bis (2-ethylhexyl) phthalate (DEHP) on the carbon adsorbents (Chezacarb S and Chezacarb SH) and polymer adsorbent on basis of polypropylene with polyethylene (Reo Fb) was studied. Efficiency of DEHP adsorption (concentration DEHP to 10 g.L⁻¹, concentration of the adsorbents 1.7 g.L⁻¹) was more than 99.9 %. By the sample from groundwater was efficiency more as 99.7 % in the case of Chezacarb S and Chezacarb SH too and 98.0 % for Rea Fb adsorbent. Adsorption capacity by Chezacarb S was more as 10 g.g⁻¹.

Keywords: Adsorption, Bis (2-ethylhexyl) phthalate, DEHP, Chezacarb S, Chezacarb SH, Reo Fb

1. INTRODUCTION

Bis (2-ethylhexyl) phthalate (DEHP) is used as a plasticizer in polyvinyl chloride products. Its year production reach approx. 1.3 mil tons [1]. Owing to its extremely low solubility in water (data varied from $\mu\text{g.L}^{-1}$ [2, 3] to 11 mg.L^{-1} [4]), efficient removal of this phthalate from contaminated groundwater is relatively troublesome. Adsorption on different types of adsorbents appears to be one of the most promising methods [5]. However, all adsorption isotherms describing equilibrium between adsorbent and adsorbate presuppose two-phase heterogenic system. E.g. Langmuir adsorption isotherm: $\Theta/(1-\Theta) = \beta \cdot c$, where Θ is surface coverage ($\Theta = \Gamma/\Gamma_{\text{max}}$) and corresponds to relation of surface adsorbate concentration on adsorbent " Γ " to maximum concentration " Γ_{max} ", " c " is than equilibrium adsorbate concentration in solution. Adsorption coefficient " β " is than relation of rate constants of adsorption and desorption. By contrast, in the case of emulsion adsorption the system consists of three phases, where adsorbate is continuously supplied from other liquid phase (DEHP). This process is affected by interphase tense between water solution and liquid DEHP and so that the situation is better described by Frumkin adsorption isotherm modified by Kopanica and Novotný [6]: $[\Theta/(1-\Theta)] \cdot \exp \sum A_i \Theta^i = \beta \cdot c$, where " A_i " are interaction coefficients, taking into account the sum of particle – particle interactions as well as other present time-dependent processes (like complexation, chemical or dissociation reactions, etc.). That is why the tests were performed as desorption tests at first and than as the adsorption ones.

2. EXPERIMENTAL

Chemicals

Bis (2-ethylhexyl) phthalate (DEHP, for GC) was purchased from Fluka.

n-hexane: for LC, was purchased from Merck

Chezacarb S: Carbon-based adsorbent. Powder weight max. 160 g.L^{-1} , adsorption of dibutylphthalate 3,7 - 4,5 mL.g^{-1} . Producer: Unipetrol RPA, Litvínov, Czech Republic.

Chezacarb SH: Carbon-based adsorbent, hydrophilised surface. Powder weight max. 160 g.L^{-1} , adsorption of dibutylphthalate 3,7 - 4,5 mL.g^{-1} . Producer: Unipetrol RPA, Litvínov, Czech Republic.

Reo Fb: Adsorption Shears on the polymer basis (55 % polypropylene + 35 % polyethylene + 10 % CaCO_3). Producer: REO Amos s.r.o., Ostrava, Czech Republic.

Groundwater (GW): Groundwater obtained from a well in the area of plastic producer. DEHP concentration approx. 5 g.L⁻¹. At first the phthalate phase (PP) was separated by flotation and so that water phase (WP) containing <10 µg.L⁻¹ DEHP was obtained. By GC-MSD method was found that PP contained more than 99 % DEHP.

Experimental conditions

Preliminary testing of carbon-based adsorbents

1 gram of adsorbent was dosed to Erlenmayer flask of 1000 ml volume and 2 (3, 4, 5, 10) mL of pure DEHP was added. The mixture was thoroughly shaken and after 20 minutes 600 mL of distilled water was added and thoroughly shaken again. After that the mixture was shaken on laboratory shaker for 6 hours and then the adsorbent was removed by filtration through glass filter. 100 ml of solution (emulsion) was transferred to separation funnel and DEHP was extracted twice by 20 mL n-hexane. Hexane phase was separated, dried using anhydrous NaSO₄ and measured in UV spectrum range at 224 nm [7]. The blanks without added adsorbate were done too.

Application of all adsorbents

Application tests were performed using both pure DEHP and real components originating from groundwater. 5 grams of adsorbate (pure DEHP or PP or WP) was dosed to Erlenmayer flask of 1000 ml volume and 600 ml of distilled water (W) or groundwater (GW) was added. After thorough shaking 1 gram of adsorbent was added and shaken again for 6 hours. Separation of adsorbent was done by filtration and after extraction by n-hexane DEHP concentration was by GC determined.

3. RESULTS AND DISCUSSION

Table 1. Results of preliminary adsorbents testing using DEHP as adsorbate. Adsorbent concentration 1.67 g.L⁻¹.

Adsorbent	Initial DEHP concentration [mg.L ⁻¹]	Equilibrium DEHP concentration [mg.L ⁻¹]	Adsorption efficiency [%]	Adsorption capacity [mg.g ⁻¹]
Chezacarb SH	3 333	7.8	99.77	1 995
Chezacarb SH	5 033	3.8	99.92	3 017
Chezacarb SH	5 033	2.5	99.95	3 018
Chezacarb SH	5 033	3.0	99.94	3 018
Chezacarb SH	7 233	8.5	99.88	4 334
Chezacarb SH	8 383	10	99.88	5 023
Chezacarb SH	8 383	8.5	99.90	5 024
Chezacarb SH	8 383	7.7	99.91	5 024
Chezacarb SH	16 667	127	99.24	9 922
Chezacarb S	3 550	2.3	99.93	2 128
Chezacarb S	3 550	3.8	99.89	2 127
Chezacarb S	3 550	2.2	99.94	2 128
Chezacarb S	5 000	4.5	99.91	2 997
Chezacarb S	5 000	4.3	99.91	2 997
Chezacarb S	5 000	4.5	99.91	2 997
Chezacarb S	6 783	5.3	99.92	4 066
Chezacarb S	6 783	5.2	99.92	4 066
Chezacarb S	6 783	5.2	99.92	4 066
Chezacarb S	9 000	17	99.81	5 389
Chezacarb S	9 000	10	99.89	5 393
Chezacarb S	16 800	30	99.82	10 060
Chezacarb S	16 800	37	99.78	10 056
Chezacarb S	16 800	42	99.75	10 053

Preliminary testing of carbon-based adsorbents

As shown in Table I, in all tests with DEHP concentrations under 10 g.L^{-1} the adsorption efficiencies of 99,8 – 99,9% were found. When high concentration of 16 g.L^{-1} DEHP was used, better results in Chezacarb S (99,8 %) then in Chezacarb SH (99,2 %) were obtained. Surprisingly, adsorption capacities of both carbon materials were very high (approx. 10 g.g^{-1}).

Application of Adsorbents

The results adsorption and desorption tests with determination of DEHP concentrations by gas chromatography (GC) are given in Table II. In most cases they correspond with previously obtained results presented in Table I. Equilibrium (final) concentrations of DEHP were even in the cases of adsorption tests lower than in desorption tests (that were performed according to method used in preliminary testing; compare first six lines of the Table II). Efficiency of Reo Fb adsorbent was comparable as in both Chezacarbs in these tests. Favourable results were found when real phthalate phase (PP) was used as adsorbate instead DEHP. On the other hand, slightly lower adsorption efficiency was determined if PP was present in GW (real system). In such case Chezacarb SH revealed to be most efficient material (efficiency 99.88%), whilst Reo Fb was able to adsorb below 98% DEHP. It was probably done by a presence of hydrated ferric oxide flocs in groundwater and by contamination of Reo Fb by the flocs, so that this adsorbent showed to be the least suitable material.

Table 2. Characteristics and Results of Experiments with Gas chromatography determination of Bis (2-ethylhexyl) phthalate (DEHP) concentration.

Process	Adsorbent	Adsorbent quantity [g.L ⁻¹]	Adsorbate	Initial adsorbate concentration [mg.L ⁻¹]	Equilibrium DEHP concentration [mg.L ⁻¹]	Adsorption efficiency [%]
Desorption	Reo Fb	1.75	DEHP in W	8 633	25	99.71
Desorption	Chezacarb S	1.52	DEHP in W	8 400	37	99.56
Desorption	Chezacarb SH	1.77	DEHP in W	8 417	28	99.67
Adsorption	Reo Fb	1.87	DEHP in W	8 450	6.0	99.93
Adsorption	Chezacarb S	2.00	DEHP in W	8 400	3.0	99.96
Adsorption	Chezacarb SH	1.88	DEHP in W	8 400	1.0	99.99
Blank	-	0	DEHP in W	1 733	1 600	-
Blank	-	0	DEHP in W	1 700	1 700	-
Blank	-	0	DEHP in W	233	200	-
Adsorption	Reo Fb	1.83	PP in W	8 700	3.0	99.97
Adsorption	Chezacarb S	1.70	PP in W	8 383	3.7	99.96
Adsorption	Chezacarb SH	1.78	PP in W	8 333	2.2	99.97
Blank	-	0	PP in W	167	190	-
Adsorption	Reo Fb	1.88	WP in W	9 033	19	-
Adsorption	Chezacarb S	1.65	WP in W	9 100	< 1	-
Adsorption	Chezacarb SH	1.85	WP in W	8 850	< 1	-
Blank	-	0	WP in W	1 000 000	< 1	-
Adsorption	Reo Fb	1.69	PP in GW	8 367	170	97.97
Adsorption	Chezacarb S	1.69	PP in GW	8 417	29	99.66
Adsorption	Chezacarb SH	1.73	PP in GW	8 400	9.8	99.88
Adsorption	Chezacarb SH	1.72	PP in GW	233	< 1	>99.57
Blank	-	0	PP in GW	167	170	-
Blank	-	0	GW	1 000 000	< 1	-

4. CONCLUSION

The high DEHP adsorption on carbon-based adsorbents Chezacarb S and especially Chezacarb SH was found. Adsorption efficiency of the later one for DEHP from real contaminated groundwater reached nearly 99,9 %. Adsorption capacity of both Chezacarbs for DEHP up to 10 g.g^{-1} was determined, so that these materials revealed twice higher capacity for the DEHP adsorption then for dibutylphthalate. Adsorbent Reo Fb revealed to be less suitable for groundwater decontamination due to high content of ferric flocs present in it. Besides it, both Chezacarbs offer further important advantage for their further disposal: adsorbed DEHP may be released by thermal desorption or it is possible to burn the used adsorbents including phthalate adsorbed on it. The problem of rest DEHP concentration in water phase should be solved by continual arrangement of adsorption process. The price of Chezacarb SH, that is able to adsorb 10 kg DEHP per kg, is 2-3 €/kg so that it appears to be relatively cheap material for effective removal of the pollutant from contaminated groundwater.

Acknowledgements: The work was supported by the Research project of Ministry of Education, Youth and Sports of the Czech Republic, No. MSM 7088352101.

5. REFERENCES

- [1] Mihovec-Grdič M., Šmit Z., Puntarič D., Bošnjir J.: Phthalates in Underground Waters of the Zagreb area. Croatian Medical Journal, Vol. 43, Issue 4, pp. 493-497, 2002, ISSN 0353-9540.
- [2] Staples C.A., Peterson D.R., Parketon T.F., Adams W.J.: The environmental fate of phthalates esters: A literature review. Chemosphere, Vol. 35, Issue 4, pp. 667-749, 1997, ISSN 0045-6535.
- [3] Prokūpková G., Holadová K. Poustka J. Hajslová J.: Development of a solid-phase microextraction method for the determination of phthalic acid esters in water. Anal. Chim. Acta, Vol. 457, Issue 2, pp. 211-223, 2002. ISSN 0003-2670.
- [4] Fang H.H.F. and Zheng H.: Adsorption of phthalates by activated sludge and its biopolymers. Environmental technology, Vol. 25, pp. 757-761, 2004.
- [5] Research Thesis: Studie k problematice změkčovadel na bázi dialkylftalátů. Zlín 2008. (Czech only)
- [6] Kopanica M. and Novotný L.: Determination of trace of arsenic (III) by anodic stripping voltammetry in solution, natural waters and biological material. Anal.Chim.Acta, Vol. 368, Issue 3, pp. 211-218, 1998. ISSN 0003-2670.
- [7] Dvořáčková M., Vyskočilová J., Houser J.: Photodegradation of di (2-ethylhexyl) phthalate in aqueous medium. 12th International Research/Expert Conference „Trends in the Development of Machinery and Associated Technology“ TMT 2008, Istanbul, Turkey 26-30 August, 2008. pp. 329-332. ISBN 978-9958-617-41-6.