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Sorption of benzothiazoles onto sandy aquifer material under equilibrium and non-equilibrium conditions

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Abstract: In this study, the sorption behaviour of 1,3-benzothiazole (BT) and 2-(methylthio)benzothiazole (MTBT, 2-methylsulphanyl-1,3-benzothiazole) on Danube geosorbent under equilibrium and non-equilibrium conditions was investigated. All sorption isotherms fitted well with the Freundlich model (R^2: 0.932–0.993). The results showed that the organic matter of the Danube geosorbent has a higher sorption affinity for the more hydrophobic MTBT compared to BT. However, sorption-desorption experiments showed that MTBT was more easily desorbed than BT molecules, which indicates the importance of absorption relative to adsorption in the overall sorption mechanism of MTBT. In general, molecules of BT and MTBT were more easily desorbed in the lower concentration range, which resulted in an increase in the hysteresis indices with increasing concentration. Column experiments revealed that the retention of the investigated compounds on the aquifer material followed the hydrophobicity of the compound. BT showed a lower retention, in accordance with its lower sorption affinity obtained in the static experiments, while MTBT showed a greater sorption affinity, and thus had a longer retention time on the column. Thus during transport, BT represent a greater risk for groundwaters than MTBT. These results improved the understanding of the sorption and desorption processes of benzothiazoles, which represent one of the most important factors that influence the behaviour of organic compounds in the environment.

Keywords: geosorbents; sorption; hysteresis; transport; benzothiazoles.

INTRODUCTION

Sorption of hydrophobic organic compounds on sediment organic matter (SOM) is an essential process that controls the transport and fate of these com-

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pounds in an aquatic environment. Soil, sediments and solid particles suspended in water are called geosorbents. Geosorbents consist of a heterogeneous solid phase consisting of mineral and organic matter, which is the primary sorbent if the content is higher than 0.1 %.[1] There are several mechanisms to explain the sorption behaviour of hydrophobic organic compounds (HOCs) on geosorbent organic matter.[2,3] The most acceptable mechanism is the SOM dual-mode concept. The chemical heterogeneity of SOM affects the rates and equilibrium of sorption and desorption of HOCs in soils and sediments.[4,5] The concept of expanded (flexible, rubbery-like) and condensed (rigid, glassy-like) domains of SOM has been employed to operationally describe the chemical heterogeneity of SOM having two domains with distinctly different degrees of physicochemical condensation and markedly different HOC sorption behaviour.[6–9] The sorption of HOCs in expanded domains of SOM generates linear isotherms due to solid-phase dissolution (absorption), while nonlinear isotherms are observed for the sorption in condensed domains due to a hole-filling (adsorption) process. In a condensed domain, the "holes" are closed internal pores – voids of nanometre dimensions where sorbate molecules undergo an adsorption-like interaction with the polymer strands making up the void walls. Therefore, the total sorption is the sum of sorption in the absorption domain and sorption in the adsorption domain.[10] However, some authors consider that the exact mechanism of the sorption of these compounds on geosorbent has not yet been described.[11,12]

In recent years, great attention has been paid to the identification of specific pollutants in aquatic systems. Monitoring of the water and sediment of the Danube River identified specific organic pollutants, such as compounds from the class of benzothiazoles (BTs).[13]

BTs comprise a group of heterocyclic compounds the molecular structure of which includes benzene condensed with a thiazole ring. Large amounts of BTs are used as vulcanization accelerators in rubber production, where they are added in amounts of over 1 %.[14] Thus, BTs are found in urban run-off, in residential and highway road dust and in urban particulate matter, most probably as a result of vehicle tire wear.[14,15] The daily increase in their use in industrial processes makes them important environmental pollutants listed as emerging pollutants at the European level.[16]

However, data on the behaviour of benzothiazoles in the aquatic environment is scarce, and the results published are not conclusive. One group of authors who investigated the sorption of BTs onto suspended matter and sediments suggested that sorption is the relevant process that affects the fate and behaviour of BTs,[14,17] while the results of other authors suggest that the sorption mechanism is not relevant for BTs.[18] In addition, Ni *et al*.[17] suggest that due to their relatively hydrophilic character (log K_{OW} (partition coefficient) in the range 2.0–3.20), BTs are pollutants relevant for the water phase. Therefore there is a need for further investigation of the sorption behaviour of this class of compounds.

The key objectives of this work were to investigate: 1) the sorption behaviour of 1,3-benzothiazole (BT) and 2-(methylthio)benzothiazole (MTBT, 2-methylsulphanyl-1,3-benzothiazole) on the Danube River geosorbent under equilibrium conditions; 2) the desorption of benzothiazoles and sorption-desorption hysteresis which might give further insights into the sorption mechanism; 3) the transport of BT and MTBT through a column of Danube sandy aquifer material in order to examine the behaviour of BT and MTBT under non-equilibrium conditions.

EXPERIMENTAL

Sorbates and sorbent

BT and MTBT (96%) were obtained from Sigma-Aldrich. Certain physical–chemical properties of the benzothiazoles are listed in Table I. BT is more polar (log K_{OW} = 2.17) and more soluble in water (S_W = 4300 mg·L^{-1}) than MTBT (log K_{OW} = 3.22; S_W = 125 mg·L^{-1}).

TABLE I. Basic characteristic of the selected benzothiazoles; *M* – molecular weight; S_w – water solubility;[18] *ρ* – density;[20] log K_{OW}[18,19] – octanol–water partition coefficient; T_b – boiling point[20]

Compound	M / g mol^{-1}	S_W / mg·L^{-1}	log K_{OW}	ρ / g·cm^{-3}	T_b / °C
BT	135	4300	2.17	1.238	227–228
MTBT	181	125	3.22	1.319	177

The sediment sample was taken from the left bank of the Danube River in the vicinity of the Veliko Ratno Island, which is a drinking water source for the city of Novi Sad. This sediment was used as a sorbent in order to investigate the risk of pollutant infiltration from the Danube into the underground water wells. Danube geosorbent was chosen as it represents a typical sandy aquifer material with a low content of organic carbon (OC). Several samples were taken from different depths ranging from 0 to 30 cm and a composite sample was prepared in order to obtain a representative sample.

The moisture and organic matter contents in the geosorbent sample were determined gravimetrically.[21] The OC content was determined using a total organic carbon (TOC) analyzer (LiquiTOCII, Elementar, Germany) after acid pre-treatment of the geosorbent to remove inorganic carbon. Particle size analysis between 2000 and 63 μm was performed by the wet sieving method (Sieve Shaker mode, PR. 09, CISA), while the analysis articles smaller than 63 μm was performed according to ISO method 13317-2:2001.[22] The precision of the particle size determination expressed as *RSD* was 5 %.

The specific surface area, pore volume and pore size were determined by N_2 adsorption isotherms at 77 K obtained using an Autosorb iQ surface area analyzer (Quantochrome Instruments, USA). The geosorbent sample was out-gassed at 105 °C for 2 h before running the isotherms. The specific surface area was calculated from the N_2 sorption isotherms using the multi-point Brunauer–Emmett–Teller (BET) method. The pore size and pore volume were derived from sorption isotherms using the Barrett–Joyner–Halenda (BJH) model. The micropore volume was calculated using the *t*-test method.

Sorption and desorption experiments

All sorption isotherms were run in duplicate at room temperature (20±2 °C) in 40 mL glass vials with a screw cap with a Teflon-lined silicon septum covered with silver foil. The background solution was 0.01 M $CaCl_2$ in deionised water with 100 mg·L^{-1} NaN_3 as a biocide. Due to the low solubility, before spiking the background solution, stock solutions of BT and MTBT (1000 µg·mL^{-1}) were prepared in MeOH. The initial BT and MTBT concentrations ranged from 50 to 1000 µg·L^{-1}. The volume of the BT and MTBT stock solutions used for background solution spiking was < 0.1% (v/v), which was shown to have no measurable influence on the sorption behaviour of hydrophobic organic compounds.[5]

The amount of geosorbent used in each experiment corresponded to a sample/solution ratio that resulted in 20–80 % uptake of solute. The head space was kept minimal in order to minimize the loss of compounds during the experiment due to evaporation. An equilibration period of 10 days was defined from a preliminary kinetics experiment to determine the time required to reach sorption-desorption equilibrium. The solids were then separated from the aqueous solution by centrifugation at 3000 rpm for 15 min and 30 mL of supernatant was removed using a glass pipette and replaced with the same volume of the fresh solute-free background solution to begin the desorption step by the conventional decant-refill method.[23] The weights of each vial were determined before and after refilling. The vials were further agitated under the same conditions. At the end of the desorption step, the solids were removed by centrifugation under the same conditions and an aliquot of supernatant was withdrawn for BT or MTBT determination. The solid-phase solute concentrations before and after desorption were calculated from a mass balance of the solute between the solid and the aqueous phases.

To determine the initial concentration of BT and MTBT for each point of the sorption isotherm and to account for sorbates losses other than sorption to the sorbent, two control flasks without any sorbent were prepared and treated in the same manner. The recoveries of the initial concentrations of BT and MTBT from the control flasks were in the range of the recoveries for BT and MTBT analysis, indicating no losses of sorbate due to the processes other than sorption to the sorbents (*e.g.*, volatilisation, biodegradation, adsorption on the walls of the glass vials, etc.).

Column experiments

A stainless steel column filled with aquifer material was used and all experiments were realised at room temperature (20±2 °C). The flow direction of the sorbate solution was from bottom to top. Sorbate solutions were prepared in a background solution containing $CaCl_2$ (0.01 M) and NaN_3 (100 mg·L^{-1}) in deionised water. The experiments were performed under sterile conditions as the sorbate solution contained NaN_3 as a biocide. Thiourea, as a non-sorbing solute, was added to the column influent solution to measure tracer breakthrough curves. The column parameters and experimental conditions are given in Table II.

The stainless steel column was packed with aquifer material using the following procedure: a suspension of a specific amount of dried and ground geosorbent and background solution was added to the column from the top, while a peristaltic pump (MasterflexR, Cole--Parmer Instrument Company, USA) connected to the bottom of the column compacted the solid material, giving a homogeneous geosorbent column with minimal entrapped air bubbles and grain size separation. The uniformity of the packing was indirectly reflected by the symmetrical breakthrough curve obtained for the tracer. Accordingly, physical (transport-related) non-equilibrium processes could be excluded.[24]

At the beginning of the experiment, background solution was injected through the column for 24 h at a flow rate of about 2 mL·min^{-1}, in order to have a fully saturated porous medium.[25] Subsequently, the conservative tracer thiourea was applied at a concentration of about 4 mg·L^{-1}. At certain times, the eluate was collected for determination of thiourea by UV spectrophotometry (UV-1800 spectrophotometer, Shimadzu, Japan) at a wavelength of 235 nm. These tracer assays were stopped when the measured thiourea concentration at the outlet of the column became equal to the injected one. The sorbate solution was then passed through the column at a flow rate of about 2.2 mL·min^{-1}. The initial sorbate concentration in solution was 60 µg·L^{-1}. Eluates were collected at regular intervals over 130 h and analyzed for BT or MTBT as described below.

TABLE II. Characteristics of the packed column

Parameter	Value
Length, cm	20.0
Radius, cm	1.00
Cross section area, cm^2	3.14
Volume of column, cm^3	62.8
Density of packed column, g·cm^{-3}	1.35
Porosity	0.48
Flow rate, cm^3·min^{-1}	2.25

Chemical analysis

Supernatants collected after each of the sorption and desorption steps as well as column eluates were quantitatively analyzed for BT and MTBT after liquid–liquid extraction with toluene, using gas chromatography-mass spectrometry (GC/MS, Agilent 7890A/5975C) on a HP-5MS column (J&W Scientific) and quantified according to internal standard calibration using pentachloronitrobenzene as an internal standard. The results of the analytical method performance, obtained from seven measurements at two concentration levels, are presented in Table III.

TABLE III. Data on the performance of the analytical method

Compound	Measurement range, µg·L^{-1}	Detection limit µg·L^{-1}	Quantification limit µg·L^{-1}	Recovery, %	Precision, %
BT	7.50–120	1.90	10.0	97–107	1.71–10.0
MTBT	7.50–120	1.80	9.00	96–117	2.90–7.80

Recoveries of the liquid–liquid extraction and GC/MS determination, measured over a wide concentration range from 7.5–120 µg·L^{-1} for BT and MTBT, ranged from 97–107 % and 96–117 %, respectively. Accordingly, no corrections were made for the analytically determined BT and MTBT concentrations.

Data analysis

All sets of equilibrium sorption and desorption data were fitted using the Freundlich model:

$$q_e = K_F c_e^n \tag{1}$$

where q_e and c_e are the solid phase and aqueous phase equilibrium concentrations (in µg·g^{-1} and mg·L^{-1}, respectively); K_F and the exponent n are the Freundlich sorption capacity coefficient expressed as (µg·g^{-1})/(mg·L^{-1})^n, and the site energy heterogeneity factor indicating isotherm nonlinearity (dimensionless), respectively. K_F and n were obtained from direct nonlinear curve fitting of the sorption and desorption data.

The organic carbon-normalized single point distribution coefficients (K_{OC}) were determined by calculating the q_e values for chosen c_e values from the respective best fit of the Freundlich isotherms according to the following equation:

$$K_{OC} = \frac{q_e / c_e}{f_{oc}} \tag{2}$$

where f_{OC} represents the organic carbon fraction.

Sorption-desorption hysteresis was explored using the Hysteresis Index (*HI*) as proposed by Huang *et al.*:[23]

$$HI = \left.\frac{q_e^d - q_e^s}{q_e^s}\right|_{T,c_e} \tag{3}$$

where q_e^s and q_e^d are solid-phase solute concentrations for single-cycle sorption and desorption experiments, and the subscripts T and c_e specify constant temperature and the residual aqueous phase concentration, respectively.

RESULTS AND DISCUSSION

Geosorbent characterization

The geosorbent consisted mainly of sand (96.2 mass %), in particular with particle sizes over 180 µm (76.1 %). The contents of silt (2–63 µm) and clay (< 2 µm) were 8.17 and 0.78 mass %, respectively. The organic carbon and organic matter contents were 1.21 and 5.61 %, respectively. Based on these results, it could be concluded that the Danube geosorbent represents a typical sandy aquifer material with low organic carbon content. The specific surface area and pore volume of the geosorbent were 3.19 and 0.018 $cm^3 \cdot g^{-1}$, respectively. The geosorbent had an average mesopore radius of about 11.4 nm, while the results of the *t*-test method clearly showed that it did not contain micropores.

Sorption isotherms

The geosorbent exhibited nonlinear isotherms for both BT and MTBT (Fig. 1), meaning that the sorption affinity of the geosorbent decreased as the sorbate concentration increased. The Freundlich model parameters are presented in Table IV.

Slightly higher linearity was obtained for the sorption isotherm of the more hydrophobic MTBT (n = 0.595) compared to BT (n = 0.554). The higher isotherm linearity for MTBT indicates that organic matter of the Danube geosorbent represents a favourable environment for the distribution of this compound. The organic carbon-normalized sorption coefficient (K_FOC) was higher for BT (166) than for MTBT (112.8). However, a direct comparison of K_FOC values could not be made because of their different units as a result of the nonlinearity of the sorption isotherms obtained for the sorbates. The concentration dependent OC-normalized sorption coefficients K_{OC} at three selected equilibrium concentrations (c_e = 1, 5 and 50 % solubility in water) were calculated based on Eq. (2) from the respective best fit Freundlich isotherms, the parameters for which are given in Table IV. In case of both the investigated compounds, the sorption affinity decreased with increasing concentration of sorbate, with log K_{OC} values being higher for MTBT compared to BT, indicating the greater importance of absorption in relation to adsorption in the overall sorption mechanism of MTBT. The obtained log K_{OC} values are in the range of values obtained for the sorption of BT and MTBT on organic matter on suspended particulates.[17]

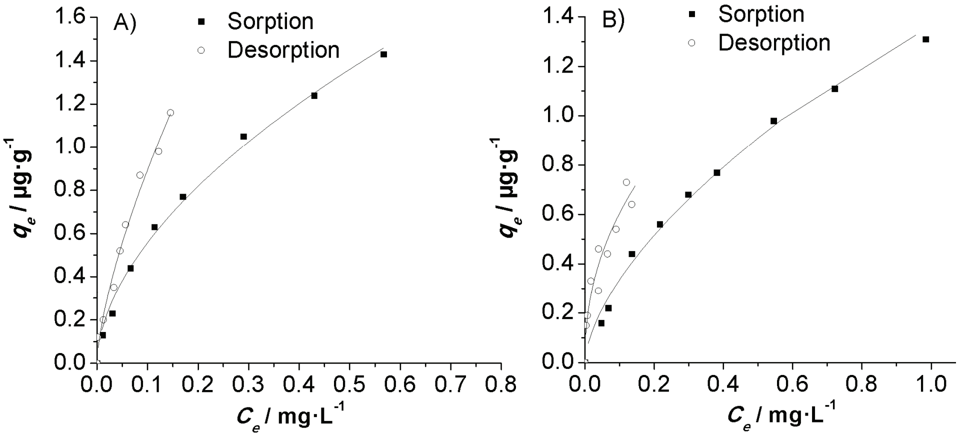

Fig. 1. Sorption and desorption isotherms of A) BT and B) MTBT on the Danube River geosorbent.

TABLE IV. Freundlich sorption and desorption model parameters and hysteresis index

Model	Compd.	R^2	*n*	K_F (μg·g^{-1})/ /(mg·L^{-1})^n	K_FOC^a	log K_{OC}			*HI*		
						c_e / mg·L^{-1}					
						0.01 S_w	0.05 S_w	0.5 S_w	0.01 S_w	0.05 S_w	0.5 S_w
Sorp.	BT	0.993	0.554 (±0.018^b)	1.997 (±0.034^b)	166.6	1.49	1.18	0.73	2.50	3.30	4.90
Desorp.		0.979	0.684 (±0.047^b)	4.321 (±0.213^b)	360.0	2.04	1.82	1.50			
Sorp.	MTBT	0.992	0.595 (±0.090^b)	1.354 (±0.356^b)	112.8	2.01	1.73	1.33	0.90	1.40	2.20
Desorp.		0.932	0.721 (±0.095^b)	2.563 (±0.251^b)	213.6	2.30	2.11	1.83			

[a] $K_FOC = K_F/F_{OC}$; [b] standard deviation

Sorption-desorption hysteresis

Sorption reversibility provides an additional insight into the sorption mechanism. The apparent sorption-desorption hysteresis was quantified for each of the sorption and desorption isotherms using the hysteresis index (Eq. (3)). Hysteresis indices at three sorbate equilibrium concentrations (c_e = 1, 5 and 50 % solubility in water) were calculated using the Freundlich model parameters given in Table IV. The calculated *HI* values are included in Table IV.

Positive values of *HI* indicate that hysteresis exists and is more pronounced as the *HI* value increases. The molecules of BT and MTBT are more easily desorbed in the lower concentration range, which resulted in the hysteresis indices increasing with increasing concentration.

In the case of BT and MTBT, hysteresis could be explained as follows: at low concentrations, sorption may be the result of surface interactions. Surface-bound molecules are probably desorbed much faster. However, as the concentration of sorbate increases, the increased concentration gradient caused the molecules to penetrate deeper into the pores of the geosorbent and organic matter causing pores in which they are trapped to be created, resulting in the pronounced hysteresis. Since the geosorbent has mesopores with an average radius of about 114 Å, the pore volume can be calculated and is equal to 6.20×10^6 Å^3. The volume of one BT molecule is 181 Å^3 and of one MTBT molecule 228 Å^3, which means that "irreversible entrapment" could be the cause of the observed sorption-desorption hysteresis.

In accordance with the dual-mode concept, Sander *et al.*[26] indicated that desorption hysteresis was widely reported for organic contaminants from soils/ /sediments, and was attributed to irreversible pore deformation of the sorbent by the sorbate and the formation of meta-stable states of sorbate in fixed mesopores. The porous structure becomes swollen during sorption and collapses during desorption. Therefore, desorption occurs by a different pathway from that of sorption.

Additionally, it is interesting to note that the organic matter of the Danube geosorbent had a higher sorption affinity for the more hydrophobic compound MTBT compared to BT, with the MTBT molecules more easily desorbed than the BT molecules, which indicates the greater importance of absorption in relation to adsorption in the overall sorption mechanism.

Non-equilibrium sorption of benzothiazoles

Dynamic (column) experiments were used in order to investigate the non-equilibrium sorption of BT and MTBT on the sandy aquifer material. Samples were taken from the column outlet and the measured concentrations plotted *versus* time to obtain a breakthrough curve, which is the basis for estimating the sorption coefficient. The breakthrough curves of the non-sorbing tracer and the selected benzothiazoles are presented in Fig. 2.

The results presented in the Fig. 2 show that in the case of thiourea, the breakthrough curve was a symmetrical S-shaped curve, which indicates the absence of physical non-equilibrium processes in the porous media. Other authors made the same observations.[27]

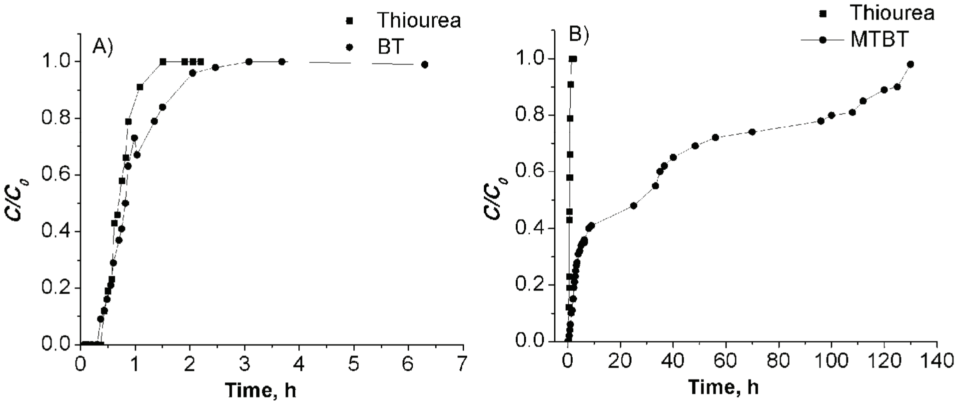

Fig. 2. Breakthrough curves of A) BT and thiourea and B) MTBT and thiourea.

Comparison of the breakthrough curve of thiourea with the breakthrough curve of BT shows a slight asymmetry (Fig. 2A). The breakthrough curve obtained for BT was not fully identical with the breakthrough curve of thiourea, indicating slightly non-equilibrium sorption.

In the case of MTBT, under the same conditions as those applied for BT, as much as 130 h passed before 99 % of the initial concentration was detected in the eluate. It can be seen that the resulting breakthrough curve exhibited a significantly higher asymmetry, which showed a higher degree of non-linear sorption in relation to BT (Fig. 2B).

In order to compare the breakthrough curves of BT and MTBT, c/c_0 = 0.5, the midpoint of the breakthrough curve, was calculated (Table V). The time required to achieve c/c_0 = 0.5 for BT and MTBT was 0.70 and 27.5 h, respectively.

TABLE V. Parameters of transport for BT and MTBT

Compound	Compound in effluent, %	Time (at c/c_0 = 0.5), h
Thiourea	100	0.70
BT	99	0.82
MTBT	99	27.5

If the obtained values for c/c_0 = 0.5 are compared with the log K_{OW} for the two investigated compounds, it could be observed that with increasing molecular hydrophobicity, the time to reach c/c_0 = 0.5 increases. In fact, the polar BT molecule had a relatively short times to c/c_0 = 0.5, whereas the hydrophobic

MTBT molecule reached $c/c_0 = 0.5$ after 28 h, indicating non-equilibrium sorption during the transport (Table V).

Other authors who examined the transport of various phenolic compounds as relatively polar compounds and phenanthrene as a non-polar compound came to similar conclusions.[27]

Comparing the parameters obtained from the column experiments and the parameters of the Freudlich model for the same compounds and the same geosorbent, the following could be concluded: the shorter time to $c/c_0 = 0.5$ for BT is in accordance with the lower sorption affinities obtained from the static experiments for BT compared with MTBT, which shows a greater affinity for sorption on the geosorbent and thus has a longer retention time on the column.

These similarities in the sorption behaviour obtained from static and dynamic experiments have been discussed by other authors.[25] However, a number of authors point to a disparity in their results,[28-30] and suggested explanations, such as the limited availability of sites for sorption in the columns due to the compression of the geosorbent, loss of the sorbent during column conditioning or differences in the experimental conditions.

CONCLUSIONS

In this study, the sorption behaviour of two compounds from the group of the benzothiazoles onto Danube River geosorbent was investigated. The organic matter of the Danube geosorbent had a higher sorption affinity for the hydrophobic compound MTBT compared to BT, which indicates the greater importance of absorption in relation to adsorption in the overall sorption mechanism. Sorption-desorption hysteresis existed for both benzothiazoles. In both cases, the existence of hysteresis may be due to irreversible pore deformation of the geosorbent, which results in the formation of meta-stable states in the mesopores of the sorbate. The obtained transport parameters indicate that with increasing molecular hydrophobicity, the retention time on the column increased, which is consistent with the higher sorption affinity of the hydrophobic MTBT for the Danube geosorbent. Further research should be focused on a more detailed characterization of the organic matter in the geosorbent to better define the sorption behaviour. Understanding these results could be useful for exposure and risk assessment of benzothiazoles in aquifer materials and groundwater.

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ИЗВОД

СОРПЦИЈА БЕНЗОТИАЗОЛА НА ПЕШЧАНОМ МАТЕРИЈАЛУ АКВИФЕРА У РАВНОТЕЖНИМ И НЕРАВНОТЕЖНИМ УСЛОВИМА

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У овом раду испитано је сорпционо понашање 1,3-бензотиазола (BT) и 2-(метилтио)бензотиазола (MTBT) на геосорбенту Дунава. Сорпционо понашање је испитано применом статичких и динамичких експеримената. Све сорпционе изотерме дале су задовољавајуће коефицијенте корелације применом Фројндлиховог модела (R^2: 0,932–0,993). Органска материја геосорбента Дунава има већи афинитет за сорпцију хидрофобнијег једињења MTBT у поређењу са BT. Интересантно је уочити да с молекули MTBT били лакше десорбовани у односу на молекуле BT, што указује на већи значај апсорпције у односу на адсорпцију у укупном механизму сорпције. Додатно, молекули BT и MTBT су лакше били десорбовани при нижим концентрацијама, што указује да су индекси хистерезе расли са повећањем концетрације сорбата. Уколико се добијене c/c_0 = 0,5 вредности упореде са коефицијентом хидрофобности испитиваних молекула (log K_{OW}), може се уочити да са порастом хидрофобности молекула расту и вредности за c/c_0 = 0,5. Ниже c/c_0 = 0,5 вредности добијене за BT у складу са мањим афинитетом за сорпцију добијеним из статичких експеримената, док MTBT показује већи афинитет за сорпцију и тиме и дуже време задржавања на колони. Током транспорта, BT представља већи ризик за подземне воде у односу на MTBT. Добијени резултати доприносе бољем разумевању процеса сорпције и десорпције бензотиазола с обзиром на то да ови процеси представљају један од најзначајнијих фактора који утичу на понашање органских једињења у животној средини.

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