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Removal of selected heterocyclic organic compounds from water and possibilities of system optimization

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ABSTRACT

Benzotriazoles (BTs) harm the life of organisms due to their chemical, physical and biological properties. It is essential to remove them from the natural environment without introducing additional chemical compounds into it. Benzotriazoles are difficult to remove from water because they are resistant to classic technological processes used for water treatment, for example, chlorination, biodegradation, or ozonation. To extend the methods of removing benzotriazoles from water, a membrane process was used – nanofiltration. The research was carried out at a small nanofiltration station with a spiral aromatic polyamide membrane. Four compounds were selected for the study: 1H-benzotriazole (BT), 4-methyl-1H-benzotriazole (4MBT), 5-methyl-1H-benzotriazole (5MBT), and 5-chlorobenzotriazole (5ClBT). The tests were carried out using surface water enriched with a standard solution of the tested compounds. As a result of the research carried out at this stage, data were obtained which indicate the dependence of the treatment efficiency on the transmembrane pressure.

Keywords: Benzotriazoles; Water; Nanofiltration; Molecular weight

1. Introduction

Recently, the pollutants of the aquatic environment include insufficiently studied endocrine heterocyclic organic compounds from the benzotriazole group (BTs) [1–3]. Due to their chemical properties, these compounds have been used in many industries. They are used in the production of detergents, tires, rubber, and medicines. They are used as corrosion inhibitors and UV stabilizers, among others in plastics and paints. Likewise, they are also added to petroleum products, de-icing, and anti-freeze agents. In the past, they were used in the photographic industry [4–8].

Benzotriazoles are biologically active compounds, which is why they are widely used. Benzotriazole compounds are not biodegradable and oxidized, which causes their accumulation in the environment for a long time [8–12]. The results of the conducted research confirmed the negative influence of benzotriazoles on plants and microorganisms. Additionally, the carcinogenic properties of BT micropollutants towards humans have been demonstrated [9,11–16].

Benzotriazoles are resistant to chlorination, biodegradation, sorption Reemtsma et al. [17], and conventional water treatment. They can be removed by ozonation and advanced as well as high-pressure membrane methods or photochemical degradation [7–10,18–20]. There is a danger that the use of high doses of UV radiation to remove benzotriazoles can result in the formation of intermediates that can be much more toxic.

The presence of organic compounds in drinking water means that the current treatment methods are not fully

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effective. Research upon new, more effective solutions in water purification processes is essential. Książek et al. [1] have shown that bank filtration used in the purification of raw water for the production of drinking water from surface waters is not efficient. After several months of water treatment using the infiltration process, the presence of 1H-benzotriazole (BT) at concentrations of several hundred ng/L was still found [4,9–11].

Studies conducted at wastewater treatment plants (WWTP) in Berlin on the removal of BT, 5-methyl-1H-benzotriazole (5MBT), and 4-methyl-1H-benzotriazole (4MBT) showed that the removal efficiency of these compounds varied from 20% to 70% for 5MBT and 30% to 55% for BT, to negligible one for 4MBT. The BT concentration in sewage was 7–18 μg/L, 4MBT 1–5 μg/L, and 5MBT 0.8–1.2 μg/L. It was also found that in the surface water in the 600–700 km section of the Rhine and Labe rivers, the BT concentration was from <0.05 μg/L to about 0.5 μg/L BT and 4MBT from 0.2 to 0.5 μg/L. The BT and 4MBT are typical examples of polar and poorly degradable trace pollutants [1,9–11].

The solubility of BT is 19.8 g/L, and 5MBT is 3.1 g/L. In contrast, the octanol-water partition coefficients (log K_{OW}) are 1.23 and 1.82 for BT and 5MBT, respectively. A number of these compounds exhibit allergenic and irritating properties and, due to their octanol-water partition coefficient, are prone to be absorbed by the skin [1,8,9,19–22].

New techniques are urgently demanded to remove organic micropollutants (OMPs) such as endocrine-disrupting compounds, pharmaceuticals and pesticides from our drinking water sources [22,23]. Scientific reports confirming the danger of benzotriazoles have prompted research on the removal of compounds from this group in the nanofiltration process. The effectiveness of removing impurities from water in the nanofiltration (NF) process is influenced, among others, by membrane permeability, ionic strength of compounds, pressure molecular weight and length of the molecule. The research focused on determining the effect of pressure and particle size on the effectiveness of BT removal from water with NF.

2. Research methodology

2.1. Technological research

The semi-technical pilot plant was designed by SWD and realized by Cornelsen Umwelttechnologie GmbH, Essen, Germany. The LPRO unit was constructed by Grünbeck Wasseraufbereitung GmbH, Höchstädt an der Donau (Höchstädt), Germany (GENO-Nano RKF1800 S). In the conducted tests, the NF process was carried out in a continuous system with partial recirculation of the concentrate on a small nanofiltration (NF) station (Fig. 1). The research system used a spiral module made of aromatic polyamide with an area of 2 m^2 with NF-70, cut-off Da 200, by FilmTec. The process was carried out at a pressure of 0.9, 0.6, and 0.5 MPa with a recovery of 75%. Sand filter filtration was used as a pretreatment to remove iron and manganese before nanofiltration. Before the actual measurements, deionized water was passed through the membrane to stabilize the membrane and determine the permeate flux, followed by the actual tests. Then, the research began on filtration in a cross-pattern of model water prepared on the basis of redistilled water with the addition of BT. After the tests, the membrane was rinsed again with deionized water, thus determining the change in transport properties of the membrane after the operation. The effectiveness of the water filtration process was assessed based on the measurement of the volumetric permeate flux (J_v) and its chemical analysis.

The model water was the surface water with added compounds from the benzotriazole group (BT, 4MBT, 5MBT, 5ClBT). Data on physical and chemical properties are included in Table 1, and the concentration of the tested compounds in the model water is presented in Table 2.

The presented values of BTR concentrations (Table 2) in the feed were adopted to the approximate values found in the environment [21].

The quantification of compounds from the benzotriazole group was carried out by gas chromatography.

2.2. Analytical methodology

Spectrophotometric, pH-meter, and conductometric determinations were performed according to the applicable standards or based on analytical methodologies commonly recognized and recommended by the scientific literature [6,7]. The test results presented in the paper are the average of at least three determinations performed simultaneously.

Table 2
Concentrations of tested compounds

Compound	Model water (μg/L)	
	Series 1	Series 2
BT	1.846	2.894
4MBT	1.660	2.159
5MBT	0.884	1.096
5ClBT	0.684	1.591

*own research

Table 1
Chemical and physical properties of the analyzed compounds [20,21]

Compounds	Molecular weight (Da)	Solubility in water (g/L)	log K_{OW}
BT	119.14	19.8	1.23
4MBT	133.15	3.1	1.60
5MBT	133.15	3.1	1.60
5ClBT	153.57	Soluble in hot water	2.17

2.3. Procedure of benzotriazole microextraction with in situ derivatization

For the simultaneous extraction and derivatization of target benzotriazoles, an aliquot of 5-mL of the examined liquid sample was placed in 10-mL glass centrifuge test tubes. The extraction solvent (chlorobenzene, 80 μL) and the derivatization reagent (acetic anhydride, 125 μL) were added to such prepared samples and mixed. Then, tubes were immersed in an ultrasonic bath (Polsonic, Sonic-3, Poland). Extractions were performed at 42 kHz of ultrasound frequency and 230 W of power for 5 min at room temperature. Emulsions were disrupted by centrifugation at 6,000 rpm for 6 min in an MPW-250 Med. Instruments (Poland) laboratory centrifuge. The organic phase was settled at the bottom of the conical tube, removed using a 50 μL Hamilton syringe (USA), and transferred into a chromatographic vial.

2.4. Chromatographic analysis

Analysis was performed with an HP 6890 gas chromatograph with a mass spectrometric detector MSD5973 and HP 7673 autosampler (Agilent Technologies, USA). This device was equipped with an HP-5MS column with dimensions 30 m × 0.25 mm with 0.25 μm film thickness and split/splitless injector. The injector worked in splitless mode; injection volume was 1 μL. The helium of 99.999% purity was used as carrier gas at a flow rate of 1.2 mL/min; the injector temperature was 250°C, the oven temperature was programmed at 80°C, increased by 10°C/min to 180°C and 20°C/min to 280°C. The electron impact source temperature was 230°C with an electron energy of 70 eV. The quadrupole temperature was 150°C, and the GC interface temperature was 280°C. The MS detector worked in Selected Ion Monitoring (SIM) mode.

3. Results and discussion

Analysis for the main components in the surface water during experiments was performed, and the data are listed in Table 3. The surface water tested (Table 3) was characterized by significant color with relatively low turbidity, variable content of organic substances expressed as chemical oxygen demand, and average salinity. During the preliminary purification on a sand filter, the color was removed in 96%, the turbidity in 78%, the total iron in 88.3%, and the manganese in 72.4%. The sand bed filtration process significantly improved the quality of surface water, and at the same time, protected the nanofiltration membrane against fouling and scaling.

It was found (Fig. 2) that with increasing transmembrane pressure in series 1 from 0.5 to 0.9 MPa, the increased retention coefficient. In all tested compounds, the treatment efficiency was the highest for the pressure of 0.9 MPa. The most effective nanofiltration process turned out to be for 5ClBT at a pressure of 0.9 MPa, obtaining over 72% retention coefficient, and the least effective for 5MBT. The BT and 4MBT at the pressures tested were removed at a similar level, achieving about 55% removal at 0.9 MPa, at 0.6 MPa from 47% to 51%, and at 0.5 MPa from 28% to 31%. Regardless of the pressure used, the weakest removal of 5MBT was achieved, at a pressure of 0.9 MPa, a retention coefficient of 42%, and at the lowest pressure of 0.5 MPa, only 28%.

When examining the removal of BT, 4MBT, 5MBT, 5-chlorobenzotriazole (5ClBT) in series 2 (Fig. 3), a significant reduction in the retention rate was found over series 1 for all compounds. In series 2, 5MBT was the least removed, while BT and 4MBT have about 15% lower retention coefficient than series 1, while 5ClBT at a pressure of 0.5 MPa was removed only in 15%.

Analysis of the influence of molecular weight (MW) of the tested benzotriazoles (Figs. 4 and 5) on the removal process in nanofiltration showed that 5ClBT has the highest mass among the tested compounds and is the best removed. The influence of the concentration of compounds in water on the efficiency of nanofiltration is described by Steinle-Darling et al. [9,10] who stated that the compound with a higher molecular weight shows higher nanofiltration efficiency in removal from water [9,10,16,18,].

On the other hand, 4MBT and 5MBT compounds with the same molecular weight (MW), log K_{OW} did not remove with the same efficiency, which may indicate different mechanisms influencing this process. There is likely a

Table 3
Quality of surface water used in the research

Parameters	Unit	Surface water					Removal (%)
		Values				Standard deviation	
		Min.	Max.	Mean	Median		
Color	mg Pt/L	10.0	22.0	16.9	12.0	1.77	96.1
Turbidity	NTU	0.90	2.00	1.20	1.30	0.79	78
Conductivity	μS/cm	312	410	379	388	21.7	58.4
pH		7.19	7.60	7.27	7.26	0.11	
Calcium	mg Ca^{2+}/L	79.2	89.5	83.53	84.1	2.70	28.2
Manganese	mg Mn/L	0.02	0.04	0,02	0.02	0.05	72.4
Iron	mg Fe/L	0.08	0.19	0.13	0.38	0.16	88.3
COD_{Mn}	mg O_2/L	6.60	14.6	10.5	10.4	1.96	40.3

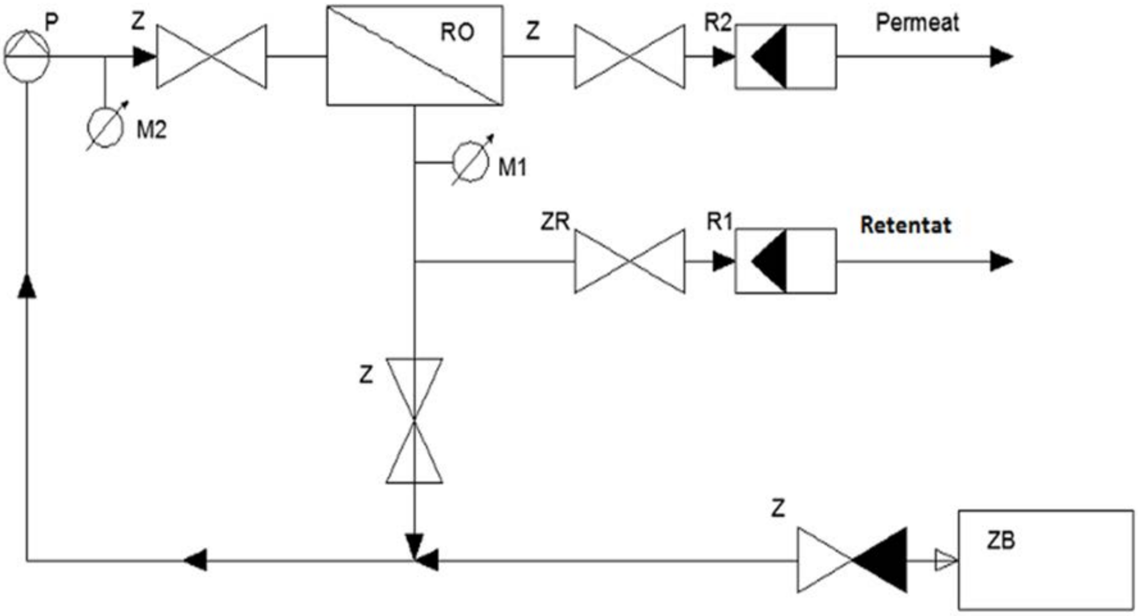

Fig. 1. Installation diagram of the nanofiltration process used for research: P – pump; Z – control valves; NF – spiral nanofiltration membrane; R1, R2 – rotameters; M1, M2 – manometers; ZB – pressure water tank.

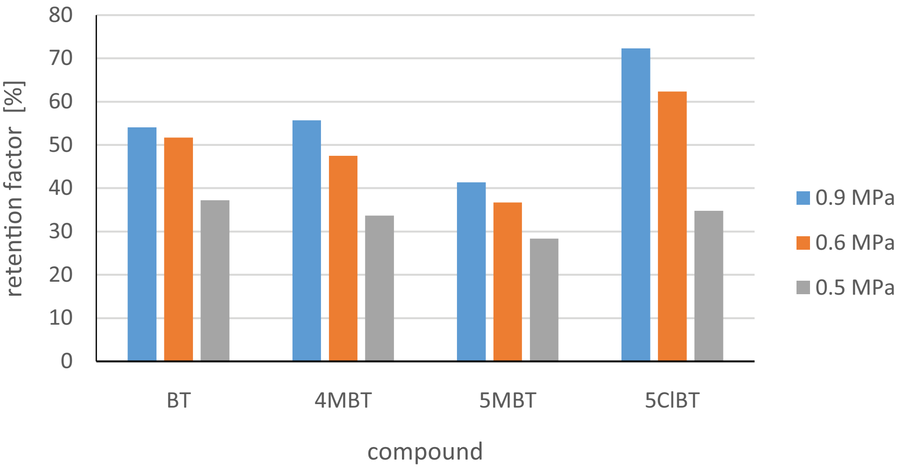

Fig. 2. Effectiveness of removing compounds from the benzotriazole group in series 1.

rearrangement of the 4MBT compound to 5MBT, indicating that one of the compounds (4MBT) is cleared better than 5MBT. The 4MBT is less stable than 5MBT and may be rapidly transformed into other compounds.

The poor effect of removing BT and its methyl derivatives at the level of 51% was also noted in the process of water purification on reverse osmosis by Leo et al. It was also observed that in RO, there is a correlation between removal and the number of methyl groups [9,11,17,19] for benzotriazoles and its methyl derivatives 80% retention factor. On the other hand, other researchers found a strong inverse correlation between the size and the removal of the neutral charge of organic micropollutants, including benzotriazoles. This correlation was weaker for moderately hydrophobic organic micropollutants. The removal efficiency observed for organic micropollutants ranged from less than 1%–25%. To assess the relationship between the physicochemical properties and performance, a statistical analysis was performed. The effect of the permeate flux was more pronounced in the case of small neutral organic micropollutants.

By increasing the pressure to 0.9 MPa in the tested process, higher were achieved at the level from 1.3÷1.45 Jv^{-10} (m^3/m^2 s) for series 1 and 2 (Fig. 6). However, at a transmembrane pressure of 0.5 MPa, the volumetric permeate flux was about 10% lower than at 0.9 MPa for both series.

The authors [23–27] found a visible dependence of the pressure value on the permeate flux in the range from 1 to 3 atm. Their research concluded that with the

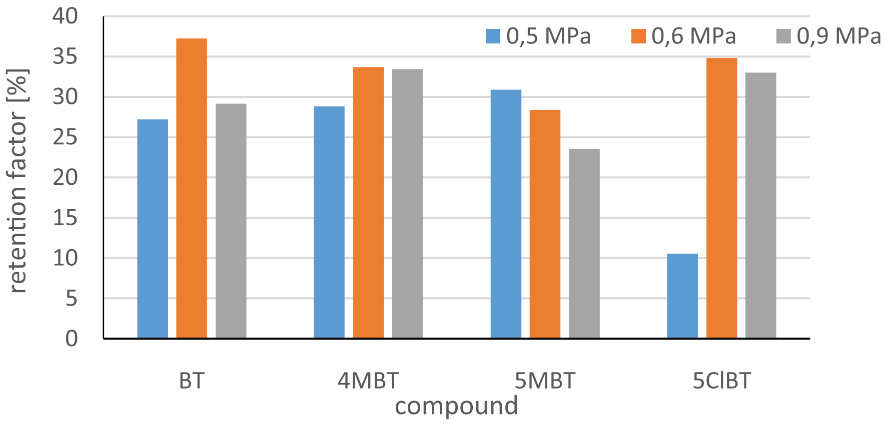

Fig. 3. Effectiveness of removing compounds from the benzotriazole group in series 2.

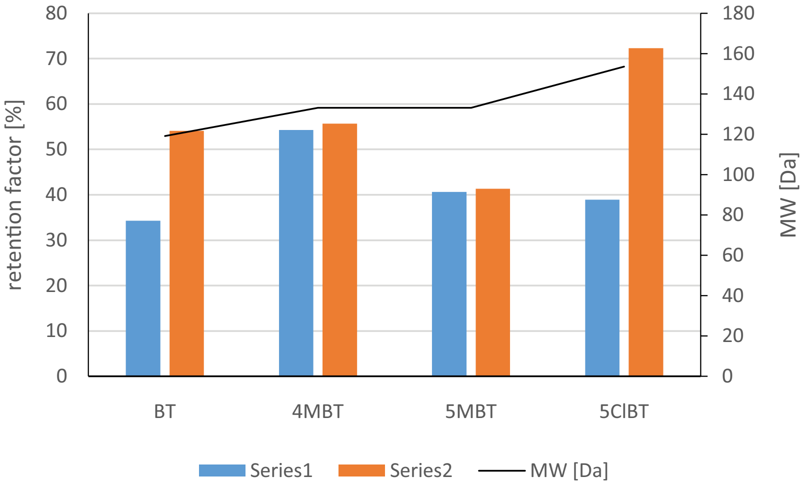

Fig. 4. Effectiveness of removing compounds from the benzotriazole group at a pressure of 0.9 MPa, series 1.

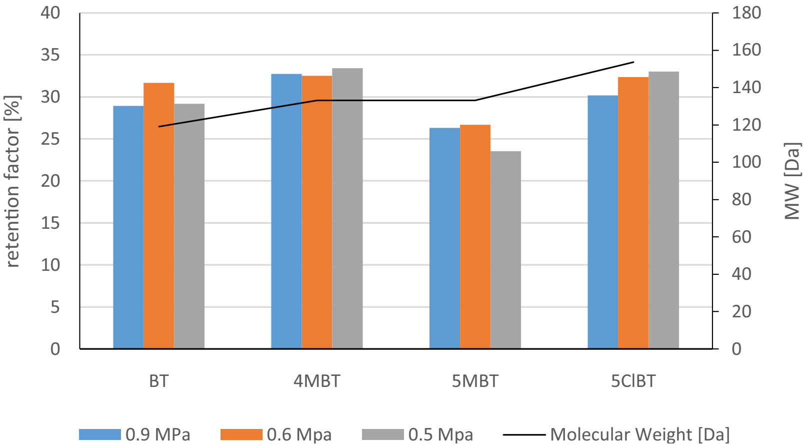

Fig. 5. Effectiveness of removing compounds from the benzotriazole group in series 2, at variable pressures.

increase in the pressure difference on both sides of the membrane, the flux value increases, but the relationship is not linear. The higher the pressure of the nanofiltration process, the greater the efficiency of glycerol nanofiltration; with the higher this process parameter, the retention coefficient slightly increases by a few percent [27]. On the other hand, Woźniak-Budych [25] in the doctoral dissertation "Dicarboxylic acid separation by membrane techniques (NF and EDBM)" shown that the pressure used in nanofiltration for sodium fumarate, succinic acid,

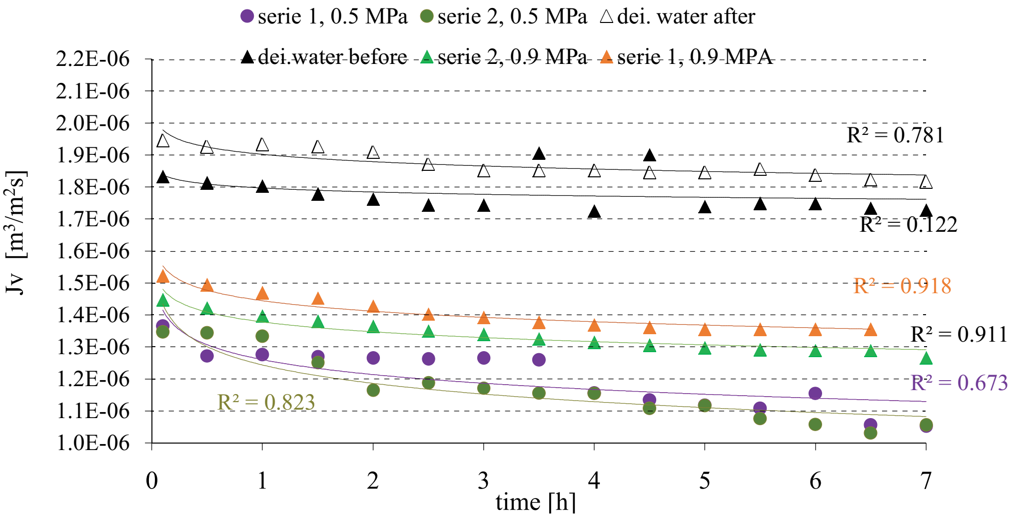

Fig. 6. Dependence of the volumetric stream of redistilled water and model water on time.

and citric acid affects the process of retaining these molecules on membranes. The applied pressure has little effect on the degree of sodium fumarate retention, and in the case of acids, the higher the value, the more effective the process. This dependence may be related to forming a boundary layer at the surface of the membrane, which was created due to convective transport of the separated components, which is greater resistance, and the nanofiltration retention coefficient decreases [12,16,26]. Dudziak and Bodzek [27] and found that increasing the transmembrane pressure enables an increase in efficiency, which may inhibit the removal of low molecular weight organic compounds.

4. Conclusions

The paper presents a comprehensive analysis of model water purification of compounds from the benzotriazole group on a polyamide membrane in the nanofiltration process. Based on the research, the following conclusions were drawn:

- The nanofiltration process can be an effective way to eliminate BT, 4MBT, 5MBT, and 5ClBT from aqueous solutions
- Removal of compounds from the group of benzotriazoles from water requires further nanofiltration and detailed identification of the mechanisms influencing the removal efficiency.
- The tested benzotriazoles did not significantly reduce the permeate flux.

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