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Application of membrane filtration and adsorption processes in the removal of micropollutants released from microplastics

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ABSTRACT

Microplastics, derived from the decomposition of plastics, can be identified in almost any type of surface water. Various pollutants, which are often toxic and hardly biodegradable, can leach from these particles. For this reason, it is important to know the possibilities of their effective removal from water. The tests carried out were aimed at determining the effectiveness of removing the tested substances from water - isophorone, dimethyl phthalate, and 4-tert-octylphenol in membrane processes using the following membranes: NF270, BX, V5, as well as adsorption on powdered activated carbon. The tests using membrane techniques consisted of passing the feed (water solution of the tested pollutants) under high pressure through the membrane, which was collected as permeate after filtration. The membrane was conditioned before testing. During the test with the use of activated carbon, its sorption properties were tested at varying doses of activated carbon in the samples (and constant concentrations of pollutants in water) and at different times of contact with pollution (at constant doses of activated carbon and constant concentration of pollutants in water). Studies using ultra- and nanofiltration membranes have shown that the type of membrane had a significant impact on the effectiveness of the pollutant removal process. The highest efficiency was obtained using a nanofiltration membrane for all tested substances. The conducted adsorption tests showed that the concentration of the tested pollutants decreases with the increase in the dose of activated carbon and the extension of the contact time of the pollutant with the sorbent. Comparing the effectiveness of the processes used to remove the tested pollutants leached from microplastics, it can be concluded that greater efficiency was obtained in the adsorption process on activated carbon.

Keywords: Microplastics; Isophorone; Dimethyl phthalate; 4-tert-octylphenol; Membrane processes; Activated carbon; Adsorption

1. Introduction

Plastic materials are inherent in many fields of our lives, whether it comes to everyday items, such as plastic bottles, boxes, bags, or vehicle tires; also, plastic can be used in advanced technological processes. Widespread use of this material often leads to its improper disposal. This issue, in conjunction with weather conditions such as wind and rain, might be a reason for transporting plastic items and particles. They can be transferred, for example, to the water environment, where they might decompose into microplastics. These tiny plastic particles can contaminate every water reservoir, and, most importantly, they can be toxic and harmful not only to the water organisms but also may have a bad influence on fauna and flora worldwide [1].

Methods for removing microplastics from the aquatic environment can be divided into physical, chemical, and biological. Physical methods include the following processes:

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filtration, sedimentation, flotation, and adsorption. Chemical methods are often used in combination with physical methods, including, for example, coagulation, flocculation (in combination with sedimentation or flotation), and advanced oxidation methods. Biological processes use the ability of some microorganisms to decompose microplastics, although it was previously assumed that this was not possible [2]. However, it should be noted that these methods used in a conventional wastewater treatment plant only sometimes ensure a sufficiently high degree of removal of microplastics from wastewater (it ranges in a wide range from 16.5% to 98.4%) [3]. When conventional treatment technologies are used, most microplastics from wastewater treatment plants remain in the sludge. To effectively remove microplastics from wastewater, tertiary treatment removals of microplastics should be used, which allows for the removal of microplastics in amounts above 99.9% [4–7].

Microplastics can enter the aquatic environment through various routes. One of the main sources of microplastics in surface waters is sewage outflow from WWTP [8–10]. However, Tang and Hadibarata's [3] research concluded that it is possible to appropriately manage microplastics from treatment plants so that wastewater treatment plants are no longer a significant source of microplastic pollution. However, this requires further research in membrane-based WTPs as well as technologies for removing microplastics.

With a sufficiently long period of contact with water and exposure to other environmental factors (UV radiation, erosion, leaching), microplastic particles present in water may constitute a source of dissolved micropollutants. Due to the possible harmful properties of microplastics and the substances leached from them, it is essential to remove them from water. One such method of eliminating microplastic is the membrane filtration process. It relies on separate different-sized contamination particles in special liquid solutions or gas mixtures. The semi-permeable membrane functions as a hindrance, holding back bigger particles, but it permits smaller molecules to go across the membrane and enter the permeate. The pressure on both sides of the membrane is different, allowing the molecules to flow. Some types of membrane filtration enable effective separation and removal of various pollutants. Microfiltration lets us isolate bacteria; ultrafiltration causes the separation of macromolecular compounds or colloids, whereas nanofiltration is used to separate ions or micromolecular organic compounds. Every kind of membrane has its own size of pores, so it causes differences in substances that each of them can separate. This is why it is important to research whether these membranes are eligible for removing microplastics and which is best suited for it [11]. Another process used to remove parts of microplastics from the water environment is adsorption on powder-activated carbon. This material has a specific structure that consists of pores of different shapes and sizes, so its' specific surface area can be relatively high. That is what makes it nearly perfect pollutant adsorption material. During the process, parts of the microplastic stop at the carbon surface, and then pieces of pollutant stuck in the sorbent pores [12]. Many publications concern the removal of microplastics in membrane processes and adsorption. However, there is a lack of research on the removal of substances leached from microplastics that are dangerous to human health and for which membrane methods and adsorption can be successfully used. The research presented in the article concerns selected substances that can be released from microplastics and whose toxicity to aquatic organisms was demonstrated in the authors' previous unpublished research. The first of them is isophorone. It is a transparent to slightly yellow liquid that possesses a smell reminiscent of camphor. It doesn't dissolve in water but can mix well with a wide range of typical organic solvents [13]. Isophorone is a basic reactant used as a precursor to polymers [14], and isophorone diisocyanate is used to produce polyurethane-based films and foams - high-performance coatings [15]. The second is dimethyl phthalate. This substance is the methyl form of phthalic acid, a clear, oily liquid with a faintly sweet fragrance. This compound has numerous applications, such as being employed in solid rocket fuels and the production of plastics as a plasticizer due to its softening properties. It is also used as a component of fragrances in the production of cosmetics and detergents [16] and even insect repellents [17]. The last test substance is 4-tert-octylphenol. This compound is used as a raw material in the production of phenol-formaldehyde resins (synthetic resins) and the production of non-ionic detergents and pesticides [18]. This compound is also used to produce alkylphenol ethoxylates, which are anionic surfactants. Alkylphenols are used in detergents, emulsifiers, industrial cleaning products and as modifiers in paints, pesticides, textiles, and some personal care products; therefore, according to the authors, they can be released from the plastics to which they were added. Alkylphenols can accumulate in fish. Some of their decomposition products are toxic to aquatic organisms. Human exposure to alkylphenols and alkylphenol ethoxylates occurs through the consumption of contaminated food (e.g., fish) and drinking water and as a result of contact with specific products (e.g., personal care products and detergents) [19].

The main aim of the research is to compare both methods – membrane filtration process and adsorption on powder-activated carbon. It allows us to determine which of the following removal methods is the most effective and should be used to remove the contamination. Moreover, thanks to conducted research, there is a possibility to get to know which kind of tested contamination is the most removable. It should be noted here that, given the multitude of membrane types, the research results presented in this article concern only the membranes used, that is, two ultrafiltration membranes - V5 and BX and one NF270 nanofiltration membrane. This means it is necessary to look for membranes that will be more effective in removing contaminants released from microplastics. Research on the removal of micropollutants leached from microplastics to the authors' knowledge, for the selected substances (isophorone, 4-tert-octylphenol, and dimethyl phthalate) is not described in the available literature. For isophorone, no publications regarding its removal using membrane methods or adsorbents were found. However, for 4-tert-octylphenol and dimethyl phthalate, scientific research was carried out on their removal in membrane processes and adsorbents, but these works concerned only single compounds. For example, Kanaujiya et al. [20] conducted research on the removal of dimethyl phthalate using ceramic membranes integrated with a bioreactor. The results of these studies indicate high efficiency

of dimethyl phthalate removal, but this may be mainly due to the bacteria *Gordonia* sp. According to Constantin et al. [21], membrane processes play a double role in removing dimethyl phthalate for photocatalyst separation and reuse and as a barrier for advanced removal. Thanks to this, it was possible to remove dimethyl phthalate at a level exceeding 98%. A photocatalytic membrane reactor with a suspended photocatalyst seems to be a suitable method of removal of phthalates from the aquatic environment.

This paper presents the research results on removing these substances from a mixture of three chemical compounds. Plastic materials are inherent in many fields of our lives, whether it comes to everyday items, such as plastic bottles, boxes, bags, or vehicle tires; also, plastic can be used in advanced technological processes. Widespread use of this material often leads to its improper disposal. This issue, in conjunction with weather conditions such as wind and rain, might be a reason for transporting plastic items and particles. They can be transferred, for example, to the water environment, where they might decompose into microplastics. These tiny plastic particles can contaminate every water reservoir, and, most importantly, they can be toxic and harmful not only to the water organisms but also may have a bad influence on fauna and flora worldwide [1].

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2. Material and methods

2.1. Tested water solutions

The subject of the research was model water solutions based on tap water with the addition of chemical compounds isophorone, 4-tert-octylphenol, and dimethyl phthalate in a concentration of 0.5 mg/dm^3. Compound standards were purchased from Sigma-Aldrich (Poznań, Poland). The characteristics of the tested compounds are summarized in Table 1. The prepared solutions were subjected to membrane filtration as well as to batch adsorption processes.

2.2. Micropollutant analytical procedure

The removal of the tested micropollutants was calculated based on their concentration in solutions before (C_i) and after membrane filtration and sorption processes (C_p) according to Eq. (1):

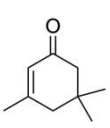
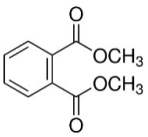
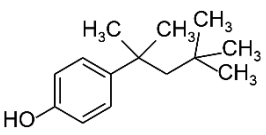
$$\text{Removal} = \frac{C_i - C_p}{C_i} \times 100\% \quad (1)$$

Gas chromatography with mass spectroscopy performed on the 7890B Gas Chromatograph by Agilent Technologies (Santa Clara, United States) was used for the analysis of the compound concentration in extracts after solid–phase extraction (SPE). The SPE procedure was detailed described in [25,26]. Recovery of isophorone, 4-tert-octylphenol, and dimethyl phthalate after the implemented SPE conditions exceeded 99%, 97% and 98%, respectively. The Limit of Detection for isophorone and 4-tert-octylphenol was equal to 0.05 and 0.11 μg/dm^3 for dimethyl phthalate. The LOQ value for isophorone was 7 μg/dm^3, for 4-tert-octylphenol 6 μg/dm^3, while for dimethyl phthalate 18 μg/dm^3, respectively. The gas chromatograph was equipped with an SLB™-5MS (30 m × 0.25 mm of 0.25 μm film thickness) column by Sigma-Aldrich (Poznań, Poland). The temperatures of the key parts of the chromatograph are given in Table 2.

Table 2
Temperatures of the chromatographic analysis

Part of the chromatograph	Temperature (°C)
Injector	250
Oven program	80 (6 min), 5°C/min up to 260, 20°C/min up to 300 (2 min)
Ion trap	150
Ion source	230

Table 1
Chemical formulas and molar masses of the tested compounds [22–24]

	Isophorone	Dimethyl phthalate	4-tert-octylphenol
Summary formula	$C_9H_{14}O$	$C_{10}H_{10}O_4$	$C_{14}H_{22}O$
Chemical structure			
CAS RN	78-59-1	131-11-3	140-66-9
Molar mass (g/mol)	138.21	194.18	206.32
logK_{ow}	1.70	1.60	5.30

The results presented in this study are the arithmetic average of 3 replicates of each experiment. The error bars marked on the columns shown in the figures were calculated using standard deviation, which did not exceed 4.5%.

2.3. Ultra- and nanofiltration processes

The membrane filtration was conducted by the use of three different membranes - two ultrafiltration membranes - V5 and BX, and one NF270 nanofiltration membrane (Table 3). The characteristics of the membranes (Table 4) show that the pH range in which they retain their properties is similar, and this range is wide. All three tested membranes are able to filter feed containing industrial wastewater. All the membranes were cut into the shape of a circle with an active surface equal to 38.5 cm^2. Membrane testing began with their conditioning. For this purpose, deionized water was used, and it was passed through the membranes until set permeate volumetric flux. Membranes prepared in this way were placed in a dead-end stainless steel filtration unit. The membrane cell was equipped with a perforated sinter, which allowed for an even collection of retentate under the entire active surface of the membrane. The ultrafiltration process was carried out at a pressure of 0.2 MPa, while the nanofiltration was operated at 2.0 MPa. The process was carried out to collect 50% of the initial volume of the feed.

2.4. Adsorption process

Batch adsorption studies were conducted to remove isophorone, dimethyl phthalate, and 4-tert-octylphenol. Commercial charcoal powdered activated carbon was used as the adsorbent (Chempur, Chem CWZ-22/w). Adsorption studies included determining the effect of contact time and adsorbent dose on the effectiveness of removing these three compounds from their mixture in an aqueous solution.

Table 3
Characteristics of tested membranes

Membrane symbol	Producer	Type of membrane
NF 270	FilmTec	Nanofiltration
BX	Sterlitech	Ultrafiltration
V5	Sterlitech	Ultrafiltration

Table 4
Properties of tested membranes [27]

Series	BX	V5	NF 270
Feed[a]	IND	IND/WW	IND/WW
Type[b]	CWM, particle	FR	High recovery
pH range[c]	1–11	1–11	2–11
Flux (GFD)/psi	244–375/60	228–350/60	22.9/70
Rej. size	250 K	200 K	–
Pore size/MWCO	250,000 Da	200,000 Da	–
Polymer[d]	PVDF	PVDF+	Polypiperazine

Notes: [a]IND-industrial, WW-wastewater;
[b]CWM-corn wet milling, FR-fouling resistant;
[c]Evaluated at 25°C;
[d]PVDF-Poly(vinylidene fluoride).

The effectiveness of removing individual micropollutants η was calculated from Eq. (2), while the amount of the substance adsorbed by a unit mass of activated carbon q_e was calculated from Eq. (3).

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

$$q_e = \frac{C_0 - C_e}{m} \tag{3}$$

where C_0 – initial concentration of micropollutants (mg/dm^3), C_e – the concentration of micropollutants after the adsorption process (mg/dm^3), m – weight of activated carbon (g/dm^3).

The measurement of the concentration of micropollutants was made using the chromatographic method, similar to what was performed in the membrane separation studies.

The study of the impact of contact time on adsorption efficiency was carried out using constant values of the concentration of micropollutants in their aqueous solution (C_0 = 0.5 mg/dm^3 of each substance) and using a constant dose of activated carbon (0.25 g/dm^3), however changing the contact time in the range from 5 min up to 120 min. Into the conical flasks, 200 cm^3 of an aqueous solution of impurities was introduced, next 0.05 g of activated carbon was added and mixed on a laboratory shaker. After the appropriate contact time, the individual samples were filtered to separate the activated carbon from the solution. Then, the remaining concentration of each micropollutant was determined.

In the case of studies related to the determination of the effect of the adsorbent dose on the effectiveness of micropollutant removal, a constant contact time and a constant concentration of isophorone, dimethyl phthalate, and 4-tert-octylphenol in their aqueous solution were used, while an increasing dose of adsorbent was used in the range from 0.011 to 0.5 g/dm^3. The procedure of conducting the experiments was analogous to that applied in the case of examining the impact of contact time on adsorption efficiency.

Moreover, based on the results of the study, an analysis of three adsorption kinetic models (pseudo-first-order, pseudo-second-order, and Elovich models) was performed, as well as an analysis of four selected models of adsorption isotherms (Freundlich, Langmuir, Jovanovic, and Toth). The parameters of both kinetics and isotherm models were determined by non-linear estimation using the method of minimizing the RMSE error value [Eq. (4)] using the Microsoft Office 365 Solver add-in.

$$\mathrm{RMSE} = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}\left(q_{e,\mathrm{exp}} - q_{e,\mathrm{calc}}\right)_i^2} \tag{4}$$

where $q_{e,\mathrm{exp}}$ – the amount of micropollutant adsorbed during the experiments (mg/g), $q_{e,\mathrm{calc}}$ – the estimated value of the amount of micropollutant adsorbed (mg/g).

The formulas of kinetics models are presented in Table 5, while the isotherm models are listed in Table 6.

Table 5
Adsorption kinetics models

Kinetics model	Formula	References
Pseudo-first-order	$q_t = q_e \cdot \left(1 - \exp\left(-k_1 \cdot t\right)\right)\left[\text{mg/g}\right]$	[28]
Pseudo-second-order	$q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t}\left[\text{mg/g}\right]$	[29]
Elovich	$q_t = \frac{1}{b} \cdot \ln\left(1 + a \cdot b \cdot t\right)$	[30,31]

q_t – the amount of micropollutant adsorbed after each contact time (mg/g), q_e – the amount of the adsorbed micropollutant at equilibrium state (mg/g), k_1 – the constant rate of the pseudo-first-order model (1/min), k_2 – the constant rate of the pseudo-second-order model (g/(mg·min)), a – regarded as the initial sorption rate (mg/(g·min)), b – constant related to the extent of surface coverage, t – contact time (min).

Table 6
Adsorption isotherm models

Isotherm model	Non-linear formula	References
Freundlich	$q_e = K_F \cdot C_e^{1/n}$	[32]
Langmuir	$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	[33]
Jovanovic	$q_e = q_{\max} \cdot \left[1 - \exp\left(-K_J \cdot C_e\right)\right]$	[34]
Dubinin–Radushkevich	$q_e = Q_s \cdot \exp\left(-K_{\text{DR}} \cdot \varepsilon^2\right)$ $\varepsilon = RT \cdot \ln\left(1 + \frac{1}{C_e}\right)$ $E = \frac{1}{\sqrt{2 \cdot K_{\text{DR}}}}$	[35]

K_F - constant related to the sorption capacity of the adsorbent, $1/n$ - the constant in Freundlich isotherm model (–), K_L – the constant related to the energy of adsorption (dm³/mg), q_m - maximum monolayer coverage capacity (mg/g), K_J - constant related to the energy of adsorption (dm³/g), $q_{\max}$ - maximum adsorption capacity (mg/g), Q_S - theoretical isotherm saturation capacity (mg/g), K_{DR} - coefficient constant related to sorption energy (mol²/kJ²), ε - Polanyi potential, E - mean free energy of sorption (kJ/mol), R - universal gas constant (kJ/(mol·K)), T – temperature (K).

3. Results and discussion

3.1. Removal of micropollutants during ultra- and nanofiltration processes

The effectiveness of the use of ultrafiltration membranes (V5 and BX) and nanofiltration membrane (NF270) in removing individual impurities from the solution: isophorone, dimethyl phthalate, 4-tert-octylphenol is shown in Fig. 1. The effectiveness of isophorone removal was low for all tested membranes and did not exceed 20%. Dimethyl phthalate was removed more effectively by the ultrafiltration membrane BX than V5, the removal of this compound was equal to 26.4% and 13.8%, respectively. The highest removal was noted for 4-tert-octylphenol, whose concentration in the solutions after ultrafiltration carried out by the V5 was reduced by over 80%, and by the BX membrane by over 60%. The NF270 membrane allowed for a complete removal of 4-tert-octylphenol. Lim et al. [36] also noted high removal degrees of 4-tert-octylphenol and other phenolic compounds with a similar structure to octylphenol during the filtration process carried out by NF270, NF90 and NF200 membranes.

By analyzing the molecular structure of the three examined substances, we can conclude that 4-tert-octylphenol was the easiest to remove by all types of membranes thanks to the long chains that make up the substance. The same cannot be said for dimethyl phthalate and isophorone [37]. Therefore, dimethyl phthalate and isophorone can easily pass through the membrane and remain in the obtained filtrate. A nanofiltration membrane with a smaller pore size than the NF270 membrane could have a better effect on the removal of micropollutants [38]. Research conducted by Kaminska et al. [39] showed significant efficiency in the removal of micropollutants with various particle geometries using HL (by GE) or NF90 (by Dow FilmTec) membranes characterized by a molecular weight cut off of approximately 150 Da. As research by other researchers indicates, biological and chemical methods of removal alone, cannot

be used as an effective removal process of micropollutants [40]. In some situations, the toxicity of treated wastewater can be unchanged or it becomes more toxic than the original compounds [41].

3.2. Removal of micropollutants during the adsorption process

The experiments showed a significant impact of the dose of activated carbon on the effectiveness of removing the tested micropollutants (Fig. 2). In the case of isophorone, an increase in effectiveness was observed from 0% for a dose of 0.01 g/200 cm^3 to 99.8% for doses equal to or greater than 0.07 g/200 cm^3. In the case of the other two micropollutants, namely dimethyl phthalate and 4-tert-octylphenol, the use of very small doses of activated carbon allowed for very high effectiveness. Increasing the adsorbent dose did not contribute to a significant increase in the effectiveness of these compounds. In the case of dimethyl phthalate, the use of a dose of 0.02 g/200 cm^3 allowed for the adsorption of this compound in 99.4%. The use of higher doses of activated carbon contributed to the complete removal of this compound. However, in the case of 4-tert-octylphenol, a dose of 0.03 g/200 cm^3 contributed to achieving 100% removal efficiency of this compound. Therefore, the research has shown that in order to obtain the highest removal efficiency for all analyzed micropollutants, it is necessary to use a 0.05 g/200 cm^3 dose of activated carbon.

Studies on the influence of the contact time of activated carbon with the mixture of three tested micropollutants were also carried out. The experiments showed that the most significant impact of contact time on the change in removal efficiency was noted in the case of isophorone, and the smallest - for 4-tert-octylphenol (Fig. 3). In the case of isophorone, after the first 5 min of contact, a significant degree of removal of this pollutant was achieved (89.6%), but to achieve its almost complete removal, a contact time of 120 min was needed. At the same time, as the contact time increased, the efficiency of isophorone removal from the solution gradually increased. In the case of dimethyl phthalate, a contact time of 10 min enabled almost complete removal of this compound, and extending the contact time did not significantly change the effectiveness of its removal. In contrast,

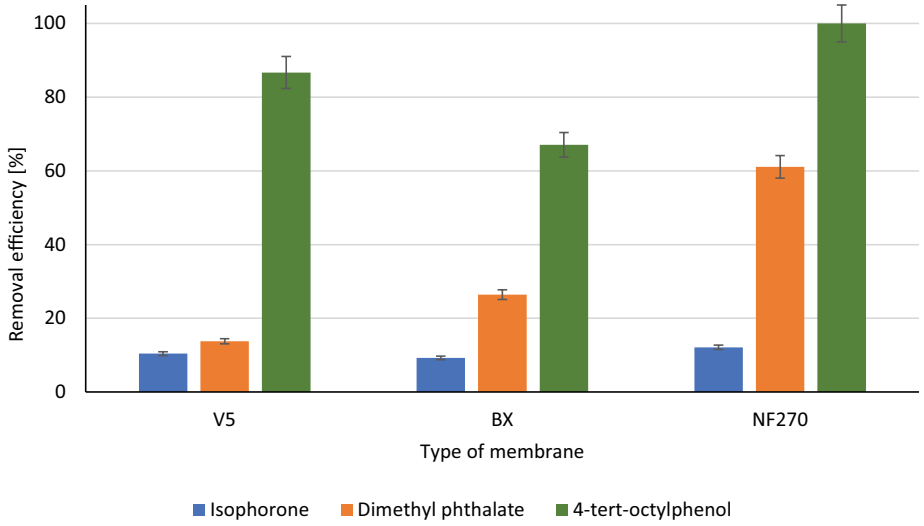


Fig. 1. Removal of tested micropollutants after membrane filtration.

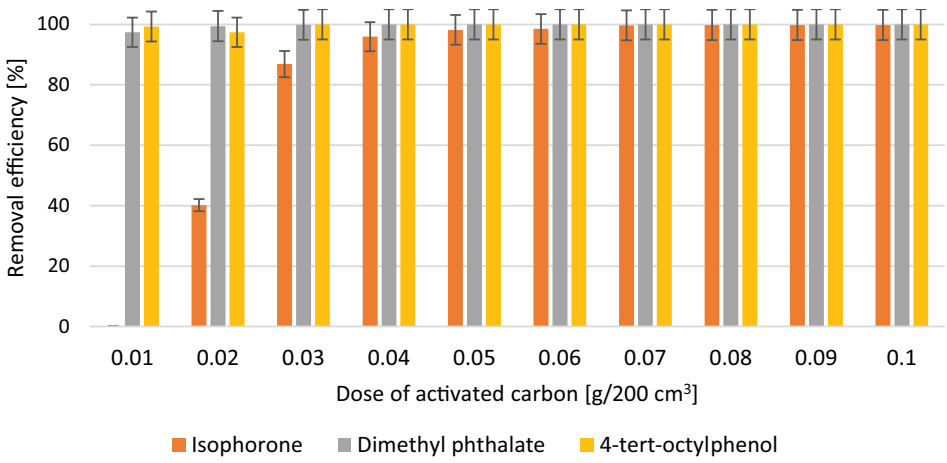


Fig. 2. Impact of activated carbon dose on removal efficiency at constant contact time and constant initial concentration of impurities.

in the case of 4-tert-octylphenol, using only 5 min of contact of the solution with the adsorbent enabled effective (100%) removal of this micropollutant.

3.2.1. Adsorption kinetics

The studies on the impact of contact time on adsorption efficiency and the experimental data were used to determine the parameters of adsorption kinetics for only two tested micropollutants, namely for isophorone and dimethyl phthalate.

The analysis of experimental data showed that for both of these chemical compounds, the best fit to the experimental results was obtained for the Elovich model and pseudo-second-order kinetics (Table 7). This is indicated by the values of the correlation coefficient R^2, which for isophorone were 0.983 and 0.882 for pseudo-second-order and Elovich, respectively. For dimethyl phthalate, the R^2 values were 0.886 and 0.964 for pseudo-second-order and Elovich kinetics, respectively. Much lower values were recorded for the pseudo-first-order kinetics model. Analyzing the estimated values of q_e, it was noted that the values of this parameter were slightly more similar to the experimental data in the pseudo-second-order model than in the pseudo-first-order model.

The tests also showed that the highest rate of adsorption was demonstrated by 4-tert-octylphenol, which was 100% removed from the aqueous solution after the first 5 min of adsorption. However, in the case of the other two micropollutants, analyzing the estimation data of the kinetics models, it can be concluded that dimethyl phthalate has a slightly higher adsorption rate than isophorone. For these two compounds, the adsorption rate constants in the pseudo-second-order kinetics model were 1.21515 and 2.64813 g/(mg·min) for isophorone and dimethyl phthalate, respectively. In the case of the initial sorption rate in the Elovich model, the obtained values also indicate a higher adsorption rate of dimethyl phthalate than isophorone. In addition, based on the Elovich model, it can be observed that in the case of adsorption of both isophorone and dimethyl

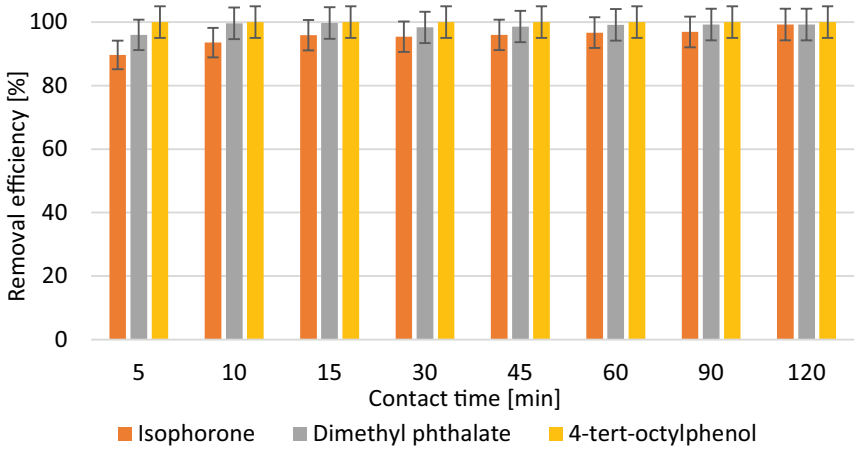


Fig. 3. Impact of contact time on removal efficiency at a constant initial concentration of impurities and a constant dose of activated carbon.

Table 7
Results of kinetics models' estimation

Kinetics model	Parameter	Unit	Type of contaminant	
			Isophorone	Dimethyl phthalate
Pseudo-first-order	k_1	1/min	0.53709	0.61195
	q_e	mg/g	1.92	1.98
	RMSE		0.0230	0.0364
	R^2		0.791	0.497
Pseudo-second-order	k_2	g/(mg·min)	1.21515	2.64813
	q_e	mg/g	1.94	1.98
	RMSE		0.0066	0.0085
	R^2		***0.983***	***0.886***
Elovich	a	mg/(g·min)	3.81 E+16	1.07 E+35
	b	g/mg	23.542	44.796
	RMSE		0.0173	0.00483
	R^2		***0.882***	***0.964***

phthalate, much higher values of initial adsorption rate than the desorption constant were obtained, which indicates that the adsorption process was much faster than desorption [30].

The Elovich model describes the course of chemical adsorption that takes place on a heterogeneous adsorption surface [42]. The pseudo-second-order model also characterizes the course of the chemical adsorption process [43]. In this kinetics model, the adsorption rate depends on the adsorption capacity [43]. Therefore, based on the conducted research, it can be assumed that in the case of isophorone and dimethyl phthalate, the adsorption of these micropollutants on the activated carbon surface followed the kinetics of chemical adsorption.

Moreover, the conducted data analysis in terms of determining the adsorption kinetics of the tested micropollutants correlates very well with the results of the influence of contact time on the effectiveness of the adsorption process. The determined adsorption rate constants are higher for dimethyl phthalate than for isophorone (for all types of kinetics analyzed). This indicates that the adsorption process was faster for the dimethyl phthalate compound than for isophorone, as shown by the results of experiments on the influence of contact time.

3.2.2. Adsorption isotherms

The analysis of experimental data and estimation results showed that in the case of dimethyl phthalate and 4-tert-octylphenol, higher R^2 values were obtained for the Langmuir and Jovanovic isotherm models (Table 8). However, in the case of isophorone the highest value of R^2 was for the Freundlich isotherm model. Such significant discrepancies may indicate that isophorone particles were adsorbed on the activated carbon surface in a different way than dimethyl phthalate and 4-tert-octylphenol particles. The Langmuir isotherm describes single-layer adsorption on an energetically homogeneous adsorbent surface. In this model, it is assumed that all active sites are 'equally active' and that their number is strictly defined and limited [44,45]. The Jovanovic isotherm is based on the same assumptions as the Langmuir isotherm, but it assumes the possibility of some mechanical contact between the retained substance (adsorbate) and the surface of the adsorbent [46,47].

Based on the estimation of activated carbon adsorption capacity for individual micropollutants, they showed that the highest value was obtained for 4-tert-octylphenol (q_m = 44.84 mg/g, q_{max} = 27.20 mg/g, Q_S = 41.6 mg/g) – Table 8. Significantly lower values were recorded for dimethyl phthalate (q_m = 6.74 mg/g, q_{max} = 5.15 mg/g, Q_S = 6.54 mg/g), and the lowest for isophorone (q_m = 2.37 mg/g, q_{max} = 2.24 mg/g, Q_S = 3.37 mg/g). Also, the value of the K_F parameter in the Freundlich model, which corresponds with sorption capacity, indicates that the activated carbon had the highest adsorption capacity for 4-tert-octylphenol (K_F = 48.934) and the lowest for isophorone (K_F = 5.420) [45].

The parameters K_L and K_J are constants related to free energy adsorption in the Langmuir and Jovanovic models, respectively [45,47,48]. The estimation results indicate that the highest value was obtained for isophorone (K_L = 831.65 dm^3/mg and K_J = 649.20 dm^3/g) and the lowest value for 4-tert-octylphenol (K_L = 2.54 dm^3/mg and K_J = 4.10 dm^3/g). These results correspond to the value of adsorption energy determined based on the Dubinin–Radushkevich model, which was the highest for isophorone adsorption (E = 11.22 kJ/mol) and the lowest for 4-tert-octylphenol (E = 3.39 kJ/mol). The obtained values of mean free energy of adsorption indicate that an ion exchange process could have taken place in the case of isophorone (since the E value is in the range of 8–16 kJ/mol). In contrast, in the

Table 8
Results of isotherm models' estimation

Isotherm model	Parameter	Type of contaminant		
		Isophorone	Dimethyl phthalate	4-tert-octylphenol
Freundlich	1/n	0.22386	0.39226	0.74907
	K_F	5.420	8.511	48.934
	R^2	***0.968***	***0.900***	***0.930***
	RMSE	0.101	0.26	1.34
Langmuir	q_m	2.37	6.74	44.84
	K_L	831.65	10.49	2.54
	R^2	***0.830***	***0.948***	***0.952***
	RMSE	0.31	0.18	1.13
Jovanovic	q_{max}	2.24	5.15	27.20
	K_J	649.20	11.11764	4.10
	R^2	***0.710***	***0.967***	***0.956***
	RMSE	0.36	0.15	1.09
Dubinin-Radushkevich	Qs	3.37	6.54	41.63
	K_{DR}	0.00397	0.01879	0.04338
	E	11.22	5.16	3.39
	R^2	***0.958***	***0.945***	***0.937***
	RMSE	0.14	0.16	1.85

case of the other two micropollutants, a physical adsorption process occurred (E value less than 8 kJ/mol) [49,50].

The adsorption process used for the removal of micropollutants was applied in some other research. Staniszewska et al. [51] analyzed the adsorption efficacy of 4-tert-octylphenol onto marine suspended particular sediments and on the nano-TiO_2. In the studies, the efficiency reached the levels of 37% and 66%, for marine sediments and nano-TiO_2, respectively. ALOthman et al. [52] used multi walled carbon nanotubes for 4-tert-octylphenol removal by adsorption process. The effectiveness was achieved at 94%, and a maximum adsorption capacity q_0 (estimated from the Langmuir isotherm adsorption model) was equalled 142.86 μg/g. In contrast, in the case of dimethyl phthalate, Ahmadi et al. [53] used a magnetic zeolite nanocomposite synthesized through a chemical co-precipitation in the adsorption process. In their study, the effectiveness of removal reached even 100%. The adsorption process was conducted according to the pseudo-second-order kinetics model, and the best fit of the isotherm model to experimental data was achieved for the Langmuir model. The maximum sorption capacity from the Langmuir model was 96.026 mg/g in those studies. In other studies described by Zhuang et al. [54], the multi-walled carbon nanotubes were applied as adsorbent for dimethyl phthalate adsorption. The maximum adsorption capacity was 196.85 mg/g, and the process proceeded through a pseudo-second-order kinetics model.

4. Conclusions

The results varied depending on what removal method had been applied. In all cases, 4-tert-octylphenol was the most accessible substance to remove, with all of the removal percentages being 100 or close to that number. Isophorone, however, was the most difficult compound to remove, with membrane filtration efficiency never exceeding 20%. The most effective membrane in removing pollutants was the FilmTec nanofiltration membrane (NF270), which managed to remove a low amount of isophorone, a moderate amount of dimethyl phthalate and all of 4-tert-octylphenol. Compared to membranes, powdered activated carbon produced much better results, varying depending on how much of the carbon was used and how long the adsorption process lasted. The test results show that higher doses of activated carbon lead to higher removal efficiency. Prolonged contact of the test sample with the adsorbate also led to better results since 120 min of the process resulted in almost 100% of the pollutants removed.

Regarding the dosage of the powdered activated carbon, the test results show that adding 0.07 g/200 cm^3 already gives satisfactory effects, thus rendering the addition of even higher doses of the substance economically unviable. In conclusion, the NF270 membrane managed to produce the best result out of all the other membranes, with it being able to reliably remove 4-tert-octylphenol and a portion of the other two pollutants. However, sorption using powdered activated carbon might be a more viable way to remove all of the chemical compounds released from microplastics since prolonged contact with the carbon gave better results than using a smaller dose of the carbon while giving it time to cleanse the water, may be the best way to remove the impurities, while also saving resources. However, the tests carried out on membranes should be treated as preliminary tests. The obtained results indicate the need to conduct further research using other types of nanofiltration and reverse osmosis membranes to determine the optimal process conditions. Different adsorbents made of other materials (e.g., waste) can also be tested. The multitude of types of membranes could allow us to select those that will achieve results similar to those obtained in adsorption.

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References

[1] K. Samsonowska, A. Kaszuba, Microplastic in natural environment (Mikroplastik w środowisku naturalnym), Polimery, 67 (2022) 28–33 (in Polish).
[2] M. Bodzek, A. Pohl, Removal of microplastics in unit processes used in water and wastewater treatment: a review, Arch. Environ. Prot., 48 (2022) 102–128.
[3] K.H.D. Tang, T. Hadibarata, Microplastics removal through water treatment plants: its feasibility, efficiency, future prospects and enhancement by proper waste management, Environ. Challenges, 5 (2021) 100264, doi: 10.1016/j.envc.2021.100264.
[4] S. Ziajahromi, P.A. Neale, L. Rintoul, F.D.L. Leusch, Wastewater treatment plants as a pathway for microplastics: development of a new approach to sample wastewater-based microplastics, Water Res., 112 (2017) 93–99.
[5] L. Yang, K. Li, S. Cui, Y. Kang, L. An, K. Lei, Removal of microplastics in municipal sewage from China's largest water reclamation plant, Water Res., 155 (2019) 175–181.
[6] H. Hidayaturrahman, T.-G. Lee, A study on characteristics of microplastic in wastewater of South Korea: identification, quantification, and fate of microplastics during treatment process, Mar. Pollut. Bull., 146 (2019) 696–702.
[7] M. Pivokonsky, L. Cermakova, K. Novotna, P. Peer, T. Cajthaml, V. Janda, Occurrence of microplastics in raw and treated drinking water, Sci. Total Environ., 643 (2018) 1644–1651.
[8] W. Nocoń, K. Moraczewska-Majkut, E. Wiśniowska, Microplastics in surface water under strong anthropopression, Desal. Water Treat., 134 (2018) 174–181.
[9] K. Moraczewska-Majkut, W. Nocoń, M. Zyguła, E. Wiśniowska, Quantitative analysis of microplastics in wastewater during selected treatment processes, Desal. Water Treat., 199 (2020) 352–361.
[10] E. Wiśniowska, K. Moraczewska-Majkut, W. Nocoń, Selected unit processes in microplastics removal from water and wastewater, Desal. Water Treat., 199 (2020) 512–520.
[11] M. Bodzek, J. Bohdziewicz, K. Konieczny, Membrane Technics in Environmental Protection (Techniki membranowe w ochronie środowiska), Silesian University of Technology Press, Gliwice, 1997 (in Polish).
[12] A. Kobyłka, Zastosowanie adsorpcji na węglu aktywnym w różnych układach technologicznych oczyszczalni ścieków Application of Adsorption on Activated Carbon in Various technological Systems in Sewage Plants, Tech. Issues, (2016) 27–34.
[13] J. Kapp, W. Robert, S. Henry, Toxicological Information Sources and Their Use, CRC Press, 1999.
[14] H. Siegel, M. Eggersdorfer, Ketones, in: Ullmann's Encycl. Ind. Chem., Wiley-VCH, Weinheim, Weinheim, Germany, 2000, pp. 187–207.
[15] Isophorone Diisocyanate, Sigma-Aldrich. Available at: https://www.sigmaaldrich.com/PL/pl/product/aldrich/317624 (Access: 2023-10-09).

[16] A. Woźnica, Dimethyl phthalate determination in workplace air, Pod. i Metod. Oceny Środowiska Pr., 36 (2019) 47–59.
[17] Dimethyl Phthalate, BMT. Available at: https://cargohandbook.com/Dimethyl_Phthalate (Access: 2023-08-08).
[18] D. Błędzka, D. Gryglik, M. Lach, M. Olak, J.S. Miller, Efektywność degradacji ksenoestrogenu 4-tert-oktylofenolu metodami fotochemicznymi, Inżynieria i Apar. Chem., 48 (2009) 28–29.
[19] Biomonitoring Summary, National Biomonitoring Program, 4-Tert-Octylphenol, General Information, 2017.
[20] D.K. Kanaujiya, M. Purnima, G. Pugazhenthi, T.K. Dutta, K. Pakshirajan, An indigenous tubular ceramic membrane integrated bioreactor system for biodegradation of phthalates mixture from contaminated wastewater, Biodegradation, 34 (2023) 1–16.
[21] L.A. Constantin, M.A. Constantin, I. Barrere, M.D. Puiu, Dimethyl phthalate removal from aqueous system using a photocatalytic membrane reactor with suspended photocatalyst, Rom. J. Ecol. Environ. Chem., 4 (2022) 104–111.
[22] National Center for Biotechnology Information, PubChem Compound Summary for CID 6544, Isophorone, 2023. Available at: https://pubchem.ncbi.nlm.nih.gov/compound/Isophorone (Access: 2023-09-14).
[23] National Center for Biotechnology Information, PubChem Compound Summary for CID 8554, Dimethyl Phthalate, 2023. Available at: https://pubchem.ncbi.nlm.nih.gov/compound/Dimethyl-Phthalate (Access: 2023-09-14).
[24] National Center for Biotechnology Information, PubChem Compound Summary for CID 8814, 4-Tert-Octylphenol, 2023. Available at: https://pubchem.ncbi.nlm.nih.gov/compound/4-tert-Octylphenol (Access: 2023-09-14.).
[25] E. Kudlek, Decomposition of contaminants of emerging concern in advanced oxidation processes, Water, 10 (2018) 955, doi: 10.3390/w10070955.
[26] E. Kudlek, Formation of micropollutant decomposition by-products during oxidation processes supported by natural sunlight, Desal. Water Treat., 186 (2020) 361–372.
[27] https://www.sterlitech.com/catalogsearch/result/?q=NF270#gsc.tab=0&gsc.q=NF270&gsc.page=1 (Access: 2023-09-20).
[28] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, K. Sven. Vetenskapsakademiens. Handl., 24 (1898) 1–39.
[29] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.
[30] R.S. Juang, M.L. Chen, Application of the Elovich equation to the kinetics of metal sorption with solvent-impregnated resins, Ind. Eng. Chem. Res., 36 (1997) 813–820.
[31] C. Aharoni, F.C. Tompkins, Kinetics of adsorption and desorption and the Elovich equation, Adv. Catal., 21 (1970) 1–49.
[32] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.
[33] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.
[34] D.S. Jovanovic, Physical adsorption of gases I: isotherms for monolayer and multilayer adsorption, Colloid. Polym. Sci., 235 (1969) 1203–1214.
[35] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, Chem. Rev., 60 (1960) 235–241.
[36] E.Q. Lim, M.Q. Seah, W.J. Lau, H. Hasbullah, P.S. Goh, A.F. Ismail, D. Emadzadeh, Evaluation of surface properties and separation performance of NF and RO membranes for phthalates removal, Membranes (Basel), 13 (2023) 413, doi: 10.3390/membranes13040413.
[37] Y. Ishigaki, T. Shimajiri, T. Takeda, R. Katoono, T. Suzuki, Longest C–C single bond among neutral hydrocarbons with a bond length beyond 1.8 Å, Chem, 4 (2018) 795–806.
[38] A.I. Cirillo, G. Tomaiuolo, S. Guido, Membrane fouling phenomena in microfluidic systems: from technical challenges to scientific opportunities, Micromachines, 12 (2021) 820, doi: 10.3390/mi12070820.
[39] G. Kaminska, M. Dudziak, J. Bohdziewicz, E. Kudlek, Effectivness of removal of selected biologically active micropollutants in nanofiltration, Ecol. Chem. Eng. a-Chemia I Inz. Ekol. A, 23 (2016) 185–198.
[40] A. Khan, J. Ali, S.U.U. Jamil, N. Zahra, T.B. Tayaba, M.J. Iqbal, H. Waseem, Chapter 22 – Removal of Micropollutants, M.Z. Hashmi, S. Wang, Z. Ahmed, Eds., Environ. Micropollutants, Elsevier, Amsterdam, Netherlands, 2022, pp. 443–461.
[41] Z. Derakhshan, M. Mokhtari, F. Babaei, R.M. Ahmadi, M.H. Ehrampoush, M. Faramarzian, Removal methods of antibiotic compounds from aqueous environments - a review, J. Environ. Health Sustainable Dev., 1 (2016) 43–62.
[42] T. Ngulube, J.R. Gumbo, V. Masindi, A. Maity, Calcined magnesite as an adsorbent for cationic and anionic dyes: characterization, adsorption parameters, isotherms and kinetics study, Heliyon, 4 (2018) e00838, doi: 10.1016/j.heliyon.2018.e00838.
[43] T.R. Sahoo, B. Prelot, Chapter 7 – Adsorption Processes for the Removal of Contaminants From Wastewater: The Perspective Role of Nanomaterials and Nanotechnology, B. Bonelli, F.S. Freyria, I. Rossetti, R. Sethi, Eds., Nanomaterials for the Detection and Removal of Wastewater Pollutants: A Volume in Micro and Nano Technologies, Elsevier, Amsterdam, Netherlands, 2020, pp. 161–222.
[44] M. Hadi, M.R. Samarghandi, G. McKay, Equilibrium two-parameter isotherms of acid dyes sorption by activated carbons: study of residual errors, Chem. Eng. J., 160 (2010) 408–416.
[45] C.S.T. Araújo, I.L.S. Almeida, H.C. Rezende, S.M.L.O. Marcionilio, J.J.L. Léon, T.N. de Matos, Elucidation of mechanism involved in adsorption of Pb(II) onto lobeira fruit (*Solanum lycocarpum*) using Langmuir, Freundlich and Temkin isotherms, Microchem. J., 137 (2018) 348–354.
[46] D. Ordonez, A. Valencia, H. Elhakiem, N. Bin Chang, M.P. Wanielista, Adsorption thermodynamics and kinetics of Advanced Green Environmental Media (AGEM) for nutrient removal and recovery in agricultural discharge and stormwater runoff, Environ. Pollut., 266 (2020) 115172, doi: 10.1016/j.envpol.2020.115172.
[47] N. Can, B.C. Ömür, A. Altındal, Modeling of heavy metal ion adsorption isotherms onto metallophthalocyanine film, Sens. Actuators, B, 237 (2016) 953–961.
[48] M.S. Podder, C.B. Majumder, SD/$MnFe_2O_4$ composite, a biosorbent for As(III) and As(V) removal from wastewater: optimization and isotherm study, J. Mol. Liq., 212 (2015) 382–404.
[49] V.S. Munagapati, D.S. Kim, Equilibrium isotherms, kinetics, and thermodynamics studies for congo red adsorption using calcium alginate beads impregnated with nano-goethite, Ecotoxicol. Environ. Saf., 141 (2017) 226–234.
[50] M. Ghasemi, Mu. Naushad, N. Ghasemi, Y. Khosravi-fard, Adsorption of Pb(II) from aqueous solution using new adsorbents prepared from agricultural waste: adsorption isotherm and kinetic studies, J. Ind. Eng. Chem., 20 (2014) 2193–2199.
[51] M. Staniszewska, B. Graca, I. Nehring, The fate of bisphenol A, 4-tert-octylphenol and 4-nonylphenol leached from plastic debris into marine water - experimental studies on biodegradation and sorption on suspended particulate matter and nano-TiO_2, Chemosphere, 145 (2016) 535–542.
[52] Z.A. ALOthman, A.Y. Badjah, I. Ali, Facile synthesis and characterization of multi walled carbon nanotubes for fast and effective removal of 4-tert-octylphenol endocrine disruptor in water, J. Mol. Liq., 275 (2019) 41–48.
[53] E. Ahmadi, B. Kakavandi, A. Azari, H. Izanloo, H. Gharibi, A.H. Mahvi, A. Javid, S.Y. Hashemi, The performance of mesoporous magnetite zeolite nanocomposite in removing dimethyl phthalate from aquatic environments, Desal. Water Treat., 57 (2016) 27768–27782.
[54] S. Zhuang, X. Zhu, J. Wang, Adsorptive removal of plasticizer (dimethyl phthalate) and antibiotic (sulfamethazine) from municipal wastewater by magnetic carbon nanotubes, J. Mol. Liq., 319 (2020) 114267, doi: 10.1016/j.molliq.2020.114267.