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Influence of the type of polymer and plasticizer on the properties and efficiency of membranes containing acetylacetone carrier for the removal of Cd(II) ions from aqueous solutions

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ABSTRACT

A series of polymer membranes containing various polymers such as: poly(vinyl chloride) (PVC), cellulose triacetate (CTA), polyethylene (PE), and poly(lactide) (PLA), and plasticizers (bis(2-ethylhexyl) adipate) (ADO) or 2-nitrophenyl octyl ether (2-NPOE), and acetylacetone (Acac) as a carrier were applied for the removal of cadmium(II) ions from aqueous solutions. The surface wettability of the obtained membranes and their chemical composition (determined by wavelength-dispersive X-ray fluorescence spectroscopy) were characterized. The obtained results indicate that the adsorption of Cd(II) ions on all examined polymer membranes (PM-1: PVC/ADO/Acac, PM-2: PE/ADO/Acac, PM-3: CTA/2-NPOE/Acac, PM-4: PLA/2-NPOE/Acac) occurred very quickly, and after 10 min of the processes, the percentage of bound cadmium(II) ions reached about 70%. The best result for the removal of cadmium(II) ions (86%) was obtained after 3h of the process conducted using the PM-3. The application of the PM-4 membrane, containing PLA enabled removal of 85% of Cd(II) ions after 0.5 h of the process. The possibility of using a biodegradable PLA as a membrane matrix is part of the so-called “Green Chemistry”, and the results obtained using membranes containing synthetic polymers and natural PLA are similar. The estimated production costs of PLA-based membrane are higher than membranes containing synthetic PVC, CTA or PE.

Keywords: Membrane separation; Cadmium(II) ions; Acetylacetone; Synthetic and biodegradable polymers

1. Introduction

Cadmium, which belongs to the group of toxic heavy metals, occurs in the environment as a result of natural processes (e.g., weathering of rocks, forest fires, etc.) but mainly due to human activity related to the development of various industries (e.g., electroplating, tanning, agriculture) [1,2]. Cd(II) present in the natural environment may pose a serious threat to aquatic organisms, plants, animals and consequently also to humans, for whom it may negatively affects the functioning of, among others, the liver, kidneys or thyroid gland. This element introduced into the human body with contaminated food or water possess the ability to bioaccumulate and has a long half-life, but all of the molecular mechanisms related to the effect of Cd(II) on individual organs are not yet fully understood [3,4]. Due to the potential hazards associated with the presence of cadmium in the environment, intensive research is being carried out to develop methods to effectively remove Cd(II) from sewage and waste. This is particularly important because wastewater treatment plants are now considered to be one of the sources of cadmium released into the environment [5].

Currently, various techniques are used to remove cadmium(II) ions from different types of aqueous solutions, including, but not limited to, chemical precipitation, ion

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exchange, adsorption, biological methods based on the use of various microorganisms and membrane techniques [5–9]. Each of the methods used has certain limitations (e.g., in the case of chemical precipitation, a large amount of sludge is generated, which must be handled appropriately), therefore these methods are systematically modified to increase their effectiveness, reduce costs and the negative impact on the environment. Membrane techniques are of particular interest due to, inter alia, the possibility of introducing various, environmentally friendly modifications, for example, the use of biodegradable or/and non-toxic compounds as membrane components and the reduction of the amount of chemical reagents used in their manufacture. Such modifications are often referred to as "Green" [10,11].

Currently, various types of membranes are used to remove different metal ions from aqueous solutions, for example, polymer inclusion membranes (PIMs) or adsorptive membranes (AMs). The AMs just like PIMs are utilized for the elimination of various substances from the aqueous solutions, for example, heavy metal ions [12], whey proteins [13], and other inorganic water and wastewater pollutants, including ammonia [14]. However, in comparison with PIMs the application of adsorptive membranes is related to significantly less energy consumption [15]. The absorbent in AM is incorporated into the membrane matrix and has the capability of capturing pollutants [16]. This is mainly associated with the presence of a large number of binding sites (functional groups) on the membrane surface [17]. That mechanism relies on a mass transfer process and the pollutants attach to the solid surface via chemical or physical interactions [18]. The adsorption processes take place [19,20]. The AM may be easily regenerated in the reversible process called desorption [21].

The adsorptive membranes can be obtained using various compounds and their compositions. Polymers, nanomaterials, active substances like inorganic (e.g., metal oxides) and organic substances can be used, among others, for membrane preparation. These kinds of membranes can be categorized into: polymer membranes (PMs), polymer-ceramic membranes (PCMs), electrospun nanofibrous membranes (ENMs), nano-enhanced membranes (NEMs), and mixed matrix membranes [22,23].

Modifications made to polymer membranes most often relate to their composition, both the type of chemical compounds used and their amounts, and thus the weight ratio of individual components. For example, poly(vinyl chloride) and cellulose triacetate are usually used as main polymer matrices in PIMs, but they are increasingly being replaced by non-conventional linear homopolymers (e.g., PVDF: poly(vinylidene fluoride)), copolymers (e.g., PVDF-HFP: poly(vinylidene fluoride-co-hexafluoropropene)) and cross-linked polymers (e.g., PVDF-HFP/PEG-DMA, where PEG-DMA: poly(ethylene glycol) dimethacrylate). Changes to the polymer matrices used are often made in order to obtain a membrane that is resistant to harsh environmental conditions and can be used several times after regeneration [24]. However, there is also increasing interest in the use of naturally occurring polymers (e.g., cellulose, chitin, starch or poly(lactide)) as a biocompatible and environmentally safe alternative for the manufacture of wastewater treatment biodegradable membranes [25,26]. Because the plasticizer affects the workability and flexibility of the membrane structure and should be compatible with the other membrane components, numerous studies have been conducted on the possibility of using various compounds for this purpose (e.g., ADO, 2-NPOE, 2-NPPE), but it has also been shown that the addition of plasticizer does not always improve the properties and effectiveness of the membranes [27]. Carriers contained in polymer membranes play an important role in the processes of separation and transport of metal ions, and the proper selection of the carrier has a key impact on the efficiency of the process. Various basic, acidic, neutral, macrocyclic and macromolecular carriers are used to remove different metal ions from aqueous model and real solutions [28]. Simple chemical compounds with known metal ion binding properties, which were previously applied as extractants in solvent extraction processes, are often used for this purpose. For example, 1-alkylimidazoles have been applied both as extractants and carriers (for transport through PIMs with cellulose triacetate (CTA) polymer and o-NPPE plasticizer) for the separation of Cd(II) ions [29]. 1-alkyl-triazole (alkyl = hexyl, octyl, decyl) and new reactive ionic liquids (RILs) based on the imidazole derivatives were also successfully used as carriers in separation processes involving PIMs (CTA/o-NPPE and CTA/o-NPOE, respectively) [30,31]. However, since the efficiency of polymer membranes depends on many factors, including the composition of the membranes (qualitative and quantitative), the properties of the separated metal ions and the properties of the solution from which these ions are removed (e.g., wastewater composition), research is systematically conducted on this selection of membrane components, so that its efficiency is as high as possible in relation to specific metal ions and feed solution properties [27,32].

This article describes the results of the first comparison of the properties and effectiveness of polymer membranes containing a composition of various polymers (i.e., PVC, CTA, PE, or PLA), plasticizers (ADO or 2-NPOE) and acetylacetone (Acac) as a carrier, used to remove cadmium(II) ions from model aqueous solutions. Based on the available literature data [23,27,28], the selected polymers and plasticizers were paired in such a way as to ensure the best compatibility of these membrane components (i.e., PVC/ADO, PE/ADO, CTA/2-NPOE, PLA/2-NPOE). Not only synthetic polymers were used in the study, but also natural PLA. As a result of the growing concern about environmental pollution from plastic waste (including synthetic polymer membranes), biodegradable materials such as various PLA-based membranes are increasingly being studied and used in various fields due to their non-toxicity and high mechanical strength [33]. Acetylacetone was used as a carrier in all tested membranes, because this compound is characterized by a simple structure, is commercially available and relatively inexpensive, and it binds various metal ions well. Moreover, both Acac and its derivatives have been successfully used before as carriers in various polymer membranes [34,35]. In addition, attention was paid not only to the effectiveness of the tested membranes with regard to the removal of cadmium(II) ions, but also the approximate production costs of each of them were estimated.

2. Materials and methods

2.1. Reagents

The nitrate standard solution of Cd(II) ions with a concentration of 1,000 mg/L was of analytical grade and was purchased from Sigma-Aldrich (St. Louis, MO, USA).

The ion carrier (Acac) was purchased from POCh (Poland). The polymer matrixes were purchased from, respectively: PVC from Anwil (Włocławek, Poland), PE and PLA from Sigma-Aldrich (St. Louis, MO, USA), and CTA from Fluka (Buchs, Switzerland). The other reagents, such as plasticizers (ADO) and solvents, for example, tetrahydrofuran (all of analytical grade), were sourced from Avantor (Gliwice, Poland). The 2-nitrophenyl octyl ether and dichloromethane were also of analytical grade and were purchased from Fluka (Buchs, Switzerland). All reagents were used without further purification.

2.2. Preparation of polymer membranes

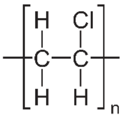
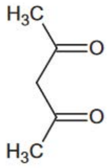
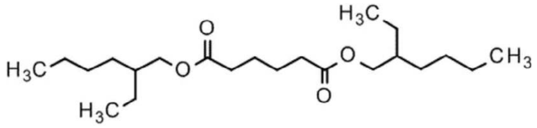
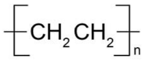
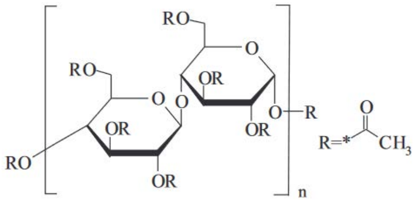
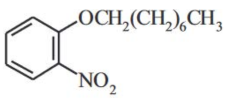
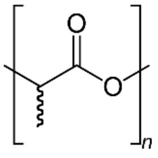
For the preparation of PM-1 - PM-4 polymer materials, solutions containing about 56 wt.% of appropriate polymer (PVC, PE, PLA, or CTA) used as polymer matrix, 22 wt.% of Acac used as ion carrier, and 22 wt.% of appropriate plasticizer (ADO or 2-NPOE) were prepared in 10 mL of tetrahydrofuran. Table 1 shows the composition of the produced polymer membranes.

Each solution prepared in this way was poured into ANUMBRA self-levelling Petri dish with a diameter of 4.5 cm. The dish was covered with filter paper to allow the THF (tetrahydrofuran) to slowly evaporate over 1 d. After complete evaporation of THF, the membrane was carefully separated from the glass plate and conditioned in distilled water for 24 h.

2.3. Surface wettability of polymer membranes

The static water contact angles on the surfaces of the prepared polymer membranes were measured using the sessile drop method at the ambient temperature using a contact angle goniometer (T-1, DSA100E - Drop Shape Analyzer, Krüss). A membrane sample was washed thoroughly with distilled water and wiped with filter paper to remove the moisture prior to the contact angle (CA) measurements. A 5 μL drop of deionized water was placed on the surface of the membrane; within 3 s of adding the water drop, the CA was measured. The measurement temperature was 23°C. The contact angle was measured at three random locations for each sample and the average value was reported.

Table 1
Composition of obtained polymer membranes

Symbols of PMs	Polymer matrix	Ion carrier	Plasticizer
PM-1	 PVC	 Acac	 ADO
Mass (g)	0.509	0.205	0.213
PM-2	 PE	Acac	ADO
Mass (g)	0.516	0.212	0.196
PM-3	 CTA	Acac	 2-NPOE
Mass (g)	0.500	0.195	0.203
PM-4	 PLA	Acac	2-NPOE
Mass (g)	0.500	0.196	0.201

2.4. Characterization of the chemical composition of polymer membranes by X-ray fluorescence spectroscopy method

The chemical composition of polymer membranes PM-1 to PM-4 after sorption of cadmium(II) ions from aqueous solutions was determined by wavelength-dispersive X-ray fluorescence spectroscopy (WD-XRF). A qualitative spectral analysis was performed by identifying spectral lines and determining their possible coincidence. On this basis, analytical lines were selected. Semi-quantitative analysis was developed using the SQX Calculation program (fundamental parameter method). The analysis was performed in the fluorine-uranium (F-U) range and the concentrations of the determined elements were normalized to 100% using CH as the balance.

2.5. Membrane separation processes

The separation of the cadmium(II) ions from the aqueous phase using polymer membranes was conducted as follows: membranes from PM-1 to PM-4 (with the compositions presented in Table 1) were immersed in a beaker containing 10 mL of solution with a concentration of 1,000 mg/L of Cd(II) (pH = 0.898). Samples of the solution were taken at regular intervals throughout the 24 h of the process. Then, the concentration of cadmium(II) ions was determined by atomic absorption spectroscopy (Thermo Scientific iCE 3000, Waltham, Massachusetts, USA).

3. Results and discussion

3.1. Contact angle measurement of the tested PMs

The water contact angle is an indicator of the wettability of film surfaces. An increase in the CA indicates a reduction of hydrophilic properties of surfaces, whereas a decrease in the CA indicates the increase of these properties [36]. Hydrophobicity of a material increases with the increasing water contact angle:

- CA < 90° surface is hydrophilic,
- CA = 90° surface is hydrophilic–hydrophobic,
- 90° < CA ≤ 150° surface is hydrophobic,
- CA > 150° superhydrophobic material [37].

The values presented in Fig. 1 show that the highest contact angle value was recorded for the PM-4 (CA = 108.27°), which indicates its hydrophobic nature. The polymeric membranes: PM-1 (CA = 76.63°), PM-2 (CA = 78.55°) and PM-3 (CA = 68.13°) are hydrophilic. The literature data confirm obtained results, because PVC, PE, and CTA [38] are known as hydrophilic polymers. In the case of poly(lactide), the methyl groups of PLA monomers make this polymer hydrophobic [39]. The greater hydrophilicity of a polymer membrane is advantageous to hinder the membrane contamination [40]. Conversely, the hydrophobicity of a polymer membrane could lead to the deposition of particles on its surface, causing a reduction in membrane efficiency and its lifetime [41].

3.2. Membrane separation of Cd(II) ions over time

The efficiency ($\%R_{\text{ads}}$) of sorption of cadmium(II) ions from aqueous solutions and sorption capacity (q_t) of investigated membranes were determined using Eqs. (1) and (2):

$$q_t = \left(\frac{c^i - c^t}{m}\right) \cdot V \tag{1}$$

$$\%R_{\text{ads}} = \left(\frac{c^i - c^t}{c^i}\right) \times 100\% \tag{2}$$

where q_t – the sorption capacity (mg/g), V – the volume of the solution (L), m – the mass of the used membranes (g), and c^i and c^t – the analytical concentration of cadmium(II) ions in the solution at the beginning and after a determined period of the sorption process (mol/L), respectively.

Changes over time in the percentage adsorption of cadmium(II) ions on polymer membranes PM-1 - PM-4 from the aqueous solution are shown in Fig. 2.

From Fig. 2 it can be seen that adsorption on the polymer membranes tested occurs already at the beginning of the

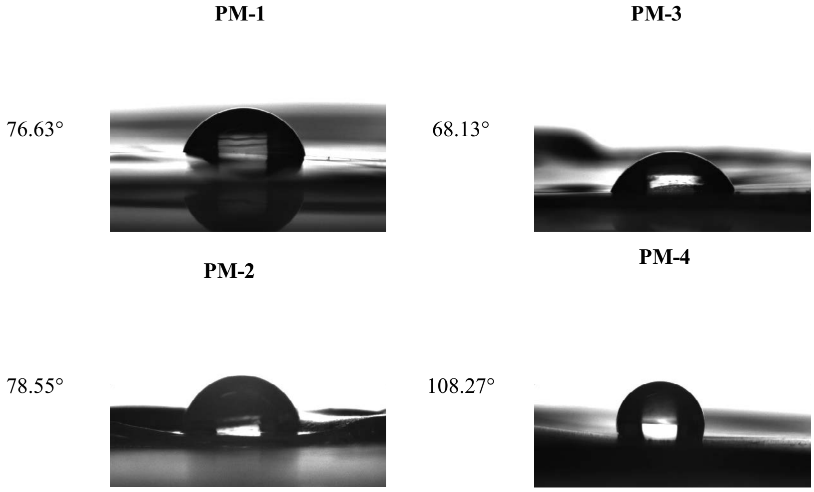


Fig. 1. Contact angle of polymer membranes from PM-1 to PM-4. Images taken with a Krüss DSA100E droplet shape analyzer, T-1 method, 5 μL water, 23°C.

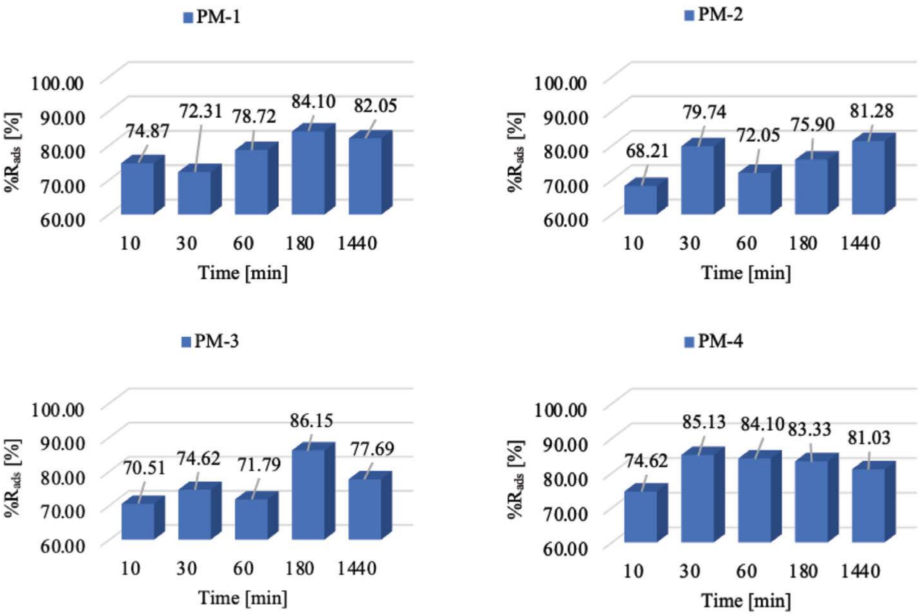


Fig. 2. Changes in the adsorption percentage of cadmium(II) ions on tested polymer materials over time. The values given with tolerance $\%R_{\text{ads}} \pm 0.01$.

process and the percentage of cadmium ion binding reaches values of about 70% after the first 10 min. Similar results were obtained after the same time for PM-1 and PM-4 for which the $\%R_{\text{ads}}$ was approx. 75%, while for PM-2 and PM-3 it was 68.20% and 70.51%, respectively. As time passes, the amount of bound cadmium(II) ions increases, but at the same time fluctuates to some extent.

Evaluating the sorption process carried out only in terms of efficiency, it can be seen that the best result for the removal of cadmium(II) ions from the aqueous solution was achieved after 180 min for PM-3 obtained from CTA and 2-NPOE (86.15%). On the other hand, regarding the running time of the process, it can be concluded that cadmium(II) ions are sorbed the fastest on the PM-4 membrane containing PLA as matrix and 2-NPOE as plasticizer; this membrane showed the highest efficiency and allowed the maximum removal of cadmium(II) ions already after 30 min, with the $\%R_{\text{ads}}$ value reaching 85.13% in this case. The sorption time is thus reduced by as much as six times, with very little difference in the removal of metal ions from the solution (1%). After 30 min, the PE and ADO-based membrane (PM-2) also reaches its maximum efficiency (79.74%). The other two membranes bind their maximum amount of cadmium(II) ions only after 3 h and the $\%R_{\text{ads}}$ obtained for them is 84.10% and 86.15% for PM-1 and PM-3, respectively. After 3h of the process, the order of removal of cadmium(II) ions is thus as follows: PM-3 containing CTA (86.15%) > PM-1 containing PVC (84.10%) > PM-4 containing PLA (83.33%) > PM-2 containing PE (75.90%).

The graph shown also illustrates that it is not necessary to extend the process to 24 h, as the results obtained after this time are even slightly worse than those obtained in the earlier stages. In addition, the economic aspect is also relevant, as increasing the sorption time can have a significant impact on the cost of the process, especially when carried out on a larger scale (e.g., in the case of removal of cadmium(II) ions from wastewater).

The sorption capacity of the studied membranes during the process has also been tested over time. Fig. 3 shows the results obtained with an ion carrier dose of 20% wt. in the membranes PM-1 - PM-4 and an initial cadmium(II) concentration of 1,000 mg/L in the solutions. The maximum values of the sorption capacity were obtained after 3 h of membrane separation processes for each PM. After this time, the sorption capacity of the tested materials decreased slightly, which may indicate the exhaustion of the sorption capacity of the material or the reversal of this process, that is, desorption.

For economic reasons, the processes were carried out at room temperature without mechanical mixing. The high rates of cadmium(II) ion removal from acidic solutions obtained on the polymer membranes tested allow the process to be considered effective and efficient. As it is known that the pH and temperature of the system play an essential role in the sorption process in addition to the composition of the membrane itself, it is likely that optimization of the process conditions will allow even more effective use of the membranes tested.

After the sorption processes the surface of the tested polymer membranes PM-1, PM-2 and PM-3 slightly changed color, whereas the PM-4 membrane had intensive color. These changes indicate the binding of cadmium(II) ions (Fig. 4).

3.3. Characterization of the chemical composition of polymer membranes PM-1 to PM-4 after cadmium(II) ion sorption processes

The chemical composition of the polymer membranes PM-1 to PM-4 was determined using the WD-XRF method. As the apparatus allows determination of the elemental composition in the studied material in the range from fluorine

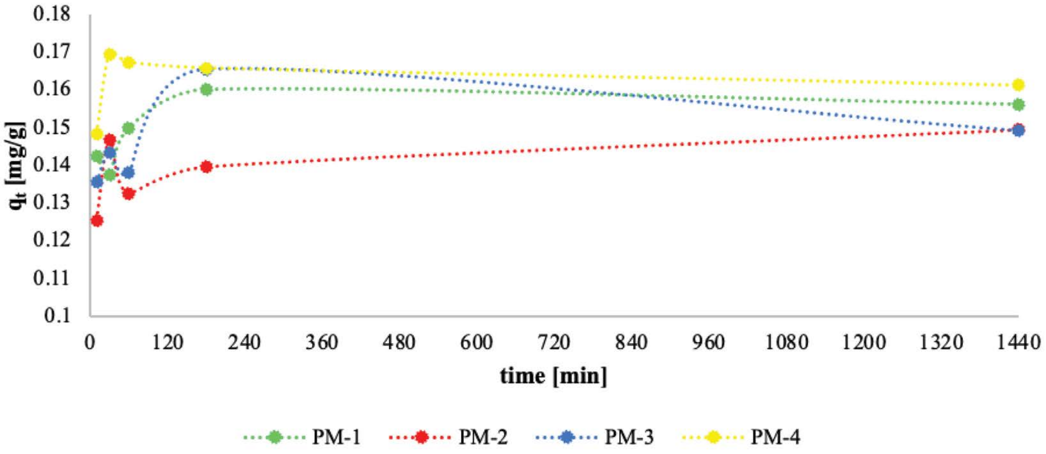
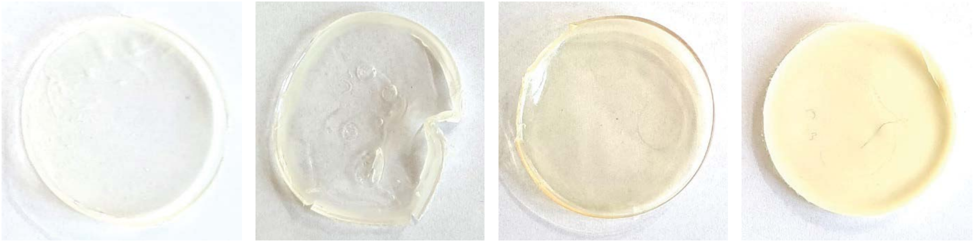


Fig. 3. Effect of time on the sorption capacity of the tested polymer membranes. The values given with tolerance q_t ± 0.01.



PM-1 **PM-2** **PM-3** **PM-4**

Fig. 4. Tested polymer membranes after binding cadmium(II) ions from aqueous solution.

to uranium (F-U), and the concentrations of the determined elements were normalized to 100% using CH as a balance, it was possible to test the polymer membranes already after a 24-h sorption process of cadmium(II) ions from aqueous solutions with a cadmium concentration of 1,000 mg/L. This made it possible to simultaneously assess the correct composition of the membranes, in relation to the substrates used to obtain them, but also to evaluate their ability to bind cadmium(II) ions.

The results of the elemental analysis for the membranes tested are given in Table 2.

The analysis performed confirmed the presence of the key components used to obtain the polymer membranes. Furthermore, it confirmed the ability of the tested materials to bind cadmium(II) ions from solution. The values of percentage adsorption of cadmium(II) ions on polymer materials $\%R_{ads}$ over 24 h were as follows: 82.05% for PM-1 > 81.28% for PM-2 > 81.03% for PM-4 > 77.69 for PM-3. The WD-XRF analysis confirms the obtained results, as the amount of bounded cadmium(II) ions decrease in similar order: PM-4 > PM-1 > PM-2 > PM-3.

3.4. Cost of the membrane separation of Cd(II) ions process

From the data described in section 3.2 – Membrane separation of Cd(II) ions over time, it can be seen that the PM-4 membrane, containing PLA and 2-NPOE, has the best ability to bind cadmium(II) ions from the aqueous solution, as the percentage removal of metal ions $\%R_{ads}$ was already 85% after 30 min of sorption time. An additional advantage of this membrane is that, of all the polymers used in this study, PLA is the only one that is biodegradable. The only disadvantage is its price.

To determine the cost-effectiveness of the process, the estimated average cost of the reagents required to

Table 2
Results of the WD-XRF analysis of polymer membranes PM-1 - PM-4 after 24 h of sorption of Cd(II) ions on their surfaces

Polymer membrane	Component	Unit, mass%	Total, mass%
PM-1	CH_2	77.9717	
	Cl	21.9455	
	Cd	0.0578	
			99.9750
PM-2	CH_2	99.9081	
	Cd	0.0425	
			99.9506
PM-3	CH_2	99.9206	
	Cd	0.0369	
			99.9575
PM-4	CH_2	99.8889	
	Cd	0.0651	
			99.9540

Values given with tolerance mass% ±0.0001.

manufacture each membrane was calculated. The prices quoted apply to the manufacture of polymer membranes according to the procedure described in section 2.2 – Preparation of polymer membranes. The cost of the sufficient quantity of reagents needed to create PM-1 to PM-4 membranes with a diameter of 4.5 cm, which will bind the maximum amount of cadmium(II) ions from a solution of 1,000 mg/L in the time needed, was taken into account. The data are shown in Table 3.

The data in Table 3 shows that the PM-4 polymer membrane is the most expensive of the membranes produced. PM-4 containing PLA is as much as 16 times more expensive than the cheapest membrane, that is, PM-2 (containing PE). It should be noted, however, that PM-2, after the same amount of time as PM-4, that is, after 30 min of sorption of cadmium(II) ions, has only a 5% lower efficiency. Thus, taking into account the cost of the reagents required for the manufacture of the polymer membranes, the PE-based membrane with ADO is by far the most advantageous.

4. Discussion. Application of adsorptive membranes to removal of various pollutants, especially metal ions

One of the most effective method for removing metal ions from the aquatic environment is the adsorption process using AMs. Adsorptive membranes can be potentially used in separation processes, because of their advantages, that is, availability of polymer materials, easy mixing of polymer materials, the possibility of regeneration and reuse of membranes, large contact surface, wide application possibilities, etc. [22].

Adsorptive membranes are widely applied in separation processes, especially in removal of metal ions. PMs enable the effective recovery of metal ions, for example, cadmium(II), nickel(II) or chromium(VI) ions [42,43]. For example, Sahabjamee et al. [43] used a polymer membrane based on chitosan/poly(vinyl alcohol) (CS/PVA), which was modified by polyethyleneimine (PEI) for the removal of heavy metal ions. The authors found that the removal percentage of the investigated metal ions by the modified membranes included 0.5 wt.% PEI was more than 60% higher than for the pure activated carbon and more than 40% higher than for the non-modified polymer membrane. The highest adsorption capacity of the modified membrane (CS/PVA/PEI) was observed for cadmium(II) ions (112.13 mg/g), but the lowest for nickel(II) ions (75.5 mg/g). The polymer-ceramic membranes also belong to adsorptive membranes. For example, the cheap ceramic membrane coated by cellulose acetate (CA) was used for the removal of heavy metal ions (Cu^{2+}, Cr^{6+}, and Ni^{2+}) by the ultrafiltration process. The membrane was highly effective in the removal (above 99.7%) of investigated metal ions [44]. On the other hand, the electrospun nanofibrous membranes and nanoenhanced membranes were used to remove heavy metal ions (e.g., Cu^{2+}, Pb^{2+}, Cr^{6+}, and As^{5+} etc.) from aqueous solutions [45,46]. For example, Zia et al. [47] developed a nanofibrous porous chitosan-grafted poly(L-lactic acid) (P-PLLA) membrane using polydopamine (PDA) as an interlayer. Because of the high active surface area of P-PLLA membranes and presence of many amine groups in PDA and chitosan, the obtained PMs were used to remove copper(II) ions from the wastewater. The adsorption capacity of P-PLLA/PDA-6 and P-PLLA/PDA-6/chitosan membranes for Cu^{2+} ions was about 90% and 80% after two and three regeneration cycles, respectively. Other electrospun nanofibrous membranes based on poly(vinyl alcohol/poly(acrylic) acid (PVA/PAA) can be an effective adsorbent to separate lead ions. The maximum separation efficiency of an investigated ENM was observed at pH = 7 in tested tap water. The highest adsorption capacity was 288 mg/g with the initial Pb(II) concentration of 1 mg/L [48]. The nanofibrous membranes based on PVDF-HFP coated polyaniline (PANI), which were obtained by electrospinning of PVDF-HFP, can be successfully used in separation chromium(VI) ions. The coating by PANI influenced the growth of chromium removal efficiency, the maximum adsorption capacity was 15.08 mg/g at pH = 4.5. It was found that, the membrane PVDF-HFP/PANI efficiency after 5 cycles of usage reached above 70% [49]. The NEMs obtained by surface modification of Fe_3O_4 nanoparticles due to immobilizing silica, metformin, and amine were used to eliminate copper(II) ions from aqueous solutions. A mixed matrix nanofiltration membrane was prepared by embedding various concentrations of the modified Fe_3O_4- based nanoparticles. The iron oxide nanoparticles in membranes caused a significant rise in the pure water flux. The better hydrophilicity of the membrane and the presence of nucleophilic functional groups on nanoparticles were influenced by an effective sorption capacity. The membrane containing 0.1 wt.% metformin-modified silica coated Fe_3O_4 nanoparticles allowed the removal of about 92% of Cu^{2+} [50].

Due to these separating properties of AMs, the adsorptive membranes are commonly used to remove of dyes, for example, methylene blue (MB), safranin O (SO), rhodamine B (RH), methyl red (MR), methyl orange (MO), rose Bengal (RB), Congo red (CR) etc.) and pharmaceuticals (e.g., diclofenac, ibuprofen, and sulfamethoxazol [51–53] from aqueous

Table 3
Estimated cost of the reagents needed for the preparation of the polymer membranes

Polymer membrane	Medium cost of reagents used, EUR	Maximum percentage of removal of cadmium(II) ions, %	Time of sorption process needed to obtain maximum percentage removal of cadmium(II) ions, min
PM-1	0.36	84	180
PM-2	0.36	81	30
PM-3	5.14	86	180
PM-4	5.80	85	30

Values given with tolerance $\%R_{ads}$ ± 1.

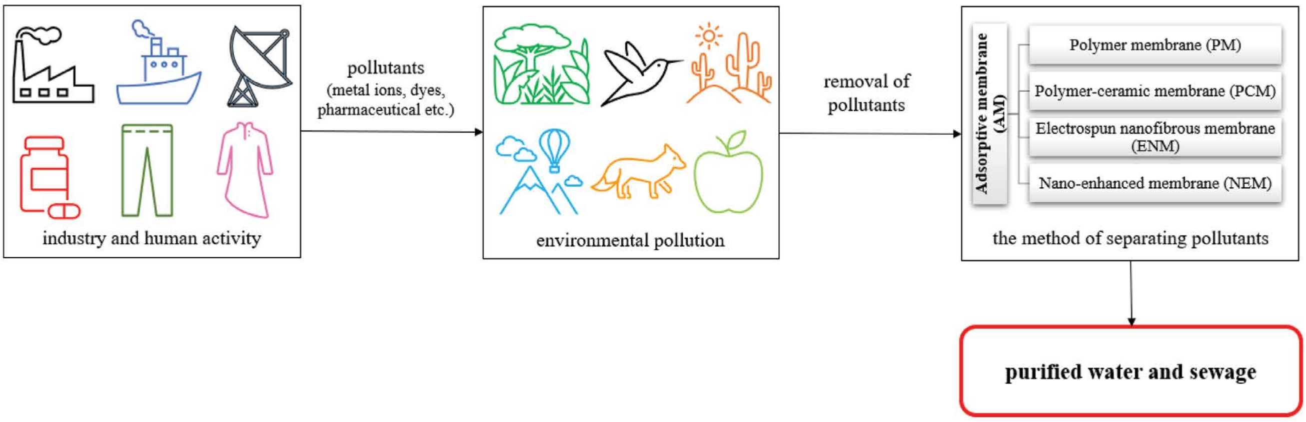


Fig. 5. Application of adsorptive membranes to remove metal ions, dyes and pharmaceuticals from aqueous solutions [51–53].

solutions (Fig. 5), which is confirmed by the latest literature data. The literature examples presented show the effectiveness of adsorptive membranes in removing various pollutants. Therefore, in this work, an attempt was made to remove cadmium ions using different composition AMs.

5. Conclusions

Four types of membranes containing the same metal ion carrier, acetylacetone, were obtained. However, the membranes differed in the polymer matrix (PVC, PE, CTA, or PLA) and plasticizer (ADO or 2-NPOE) used. The maximum percentage removal of cadmium ions from the aqueous solution calculated for the materials used after 24 h of the sorption process did not differ significantly between the membranes (ranging between 78%–82%). However, the results obtained confirmed that the use of different polymers and plasticizers to obtain membranes not only has a significant effect on the hydrophilicity or hydrophobicity of their surface, but above all on the reduction of the required sorption time. In this case, the highest efficiency was demonstrated for a membrane made of PLA and 2-NPOE (PM-4), with which up to 85% of the cadmium(II) ions present in the solution were removed after only 30 min. The disadvantage of this membrane, however, is its estimated unit price, as the cost of the reagents needed to manufacture it is 16 times higher than the cost of the substances needed to manufacture the cheapest PE membrane.

The WD-XRF analysis confirmed both the composition of the polymer membranes resulting from the use of specific components to obtain them and the ability of the membranes tested to bind cadmium(II) ions from solution.

Symbols

Acac – Acetylacetone
ADO – Bis(2-ethylhexyl) adipate
AC – Contact angle
CS – Chitosan
AM – Adsorptive membrane
CA – Cellulose acetate
CR – Congo red
CTA – Cellulose triacetate
MB – Methylene blue
MG – Malachite green
MO – Methyl orange
MR – Methyl red
ENM – Electrospun nanofibrous membrane
NEM – Nano-enhanced membrane
2-NPPE – o-nitrophenyl pentyl ether
2-NPOE – 2-nitrophenyl octyl ether
PAA – Poly(acrylic) acid
PAN – Polyacrylonitrile
PANI – Polyaniline
PCM – Polymer-ceramic membrane
PDA – Polydopamine
PE – Polyethylene
PEI – Polyethyleneimine
PEG-DMA – Poly(ethylene glycol) dimethacrylate
PLA – Poly(lactide)
P-PLLA – Poly(L-lactic acid)
PM – Polymer membrane
PVA – Poly(vinyl alcohol)
PVC – Poly(vinyl chloride)
PVP – Polyvinylpyrrolidone
PVDF – Poly(vinylidene fluoride)
PVDF-HFP – Poly(vinylidene fluoride-co-hexafluoropropene)
RB – Rose Bengal
RH – Rhodamine B
RIL – Reactive ionic liquid
SO – Safranin O
THF – Tetrahydrofuran
WD-XRF – Wavelength-dispersive X-ray fluorescence spectroscopy

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