Chapter 4

MOF-assisted membrane process for removal of radionuclides and other hazardous elements from aqueous solutions

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Abstract

This paper presents research on the application of the sorption-assisted membrane process for the removal of hazardous elements from aqueous solutions. As adsorbent in this process, metal-organic-framework compounds (MOFs) have been tested. The hybrid process was carried out in the Amicon-stirred cell and in the Couette-Tylor helical flow membrane contactor equipped with a metallic tubular membrane.

1. Introduction

Membrane processes are widely used in environmental protection technologies, especially in the treatment of industrial wastewater and treatment of surface and groundwater (Konieczny, Wszelaka-Rylik & Macherzyński 2019:20–29; Racar, Dolar, Špehar & Košutić 2017:386–392). They have also been successfully employed for liquid radioactive waste treatment (Zakrzewska-Trznadel 2013:119–130; IAEA Technical Report 2004). The main advantages that make membrane processes more widely used include, the variety of membrane techniques, low energy consumption, no need to add chemical additives, (i.e. waste reduction), easy scale-up (by the modular system), and continuous separation. Moreover, membrane systems are flexible, and it is simple to combine them with other treatment methods to perform hybrid processes, which are efficient and selective for particular components that we want to recover. One of the possibilities of creating such an effective hybrid unit is to combine pressure membrane techniques, i.e. microfiltration (MF), ultrafiltration (UF), or nanofiltration (NF) with the sorption process in sorption-assisted membrane filtration. Such a hybrid arrangement is very attractive because of its high removal efficiency while consuming low energy. A sorption-assisted UF process has been studied as a potential method for water purification and the treatment of wastewaters of different types (Hilbrandt, Shemer, Ruhl, Semiat & Jekel 2019:23–28; Vaziri, Ghomsheh, Azimi & Mirzaei 2021:1–7; Maimoun, Djafer, Djafer, Marin-Ayral & Ayral 2020:001–011; Cojocaru, Zakrzewska-Trznadel & Jaworska 2009:599–609; Cojocaru, Zakrzewska-Trznadel & Miskiewicz 2009:610–620). Recently, such a hybrid process has been used to treat liquid radioactive waste (Miśkiewicz & Zakrzewska-Kołtuniewicz 2021). The paper presents research on the application of a biosorption-assisted ultrafiltration process using alginic acid and sodium alginate for the removal of selected radionuclides (^{60}Co, ^{85}Sr and ^{137}Cs from radioactive liquid waste). Various types of sorbents can be used in the assisted filtration processes. Low-cost abundantly available compounds, for example, agricultural and household wastes, industrial by-products, sludge, soil, and ore materials are of great interest in wastewater treatment processes (De Gisi, Lofrano, Grassi & Notarnicola 2016:10–40). The current research, presented in this work, includes the use of MOF sorbent in the sorption-assisted microfiltration to remove hazardous compounds from aqueous solutions such as mercury in the form of Hg^{2+} ions.

In the current experiments, we focused on the separation of mercury, a toxic element whose emissions harm ecosystems and threaten human health. Global mercury pollution is caused by human activities like mining and the combustion of fossil fuels. When mercury gets into air and water, it is transformed by micro-organisms into methylmercury, especially the toxic form, which accumulates in fish, shellfish, and other animals that feed on fish. Due to its toxicity, mercury should be controlled and removed from the environment.

2. Methodology

2.1. Sorption-assisted microfiltration

Sorption-assisted microfiltration (SMF) is a combination of classical MF with sorption of ions (including metallic element and radionuclide ions) on sorbent dispersed in solution, as it is shown schematically on Figure. 4.1. Such a hybrid process causes a more effective separation of small ions, which are bound with sorbent forming bigger particles.

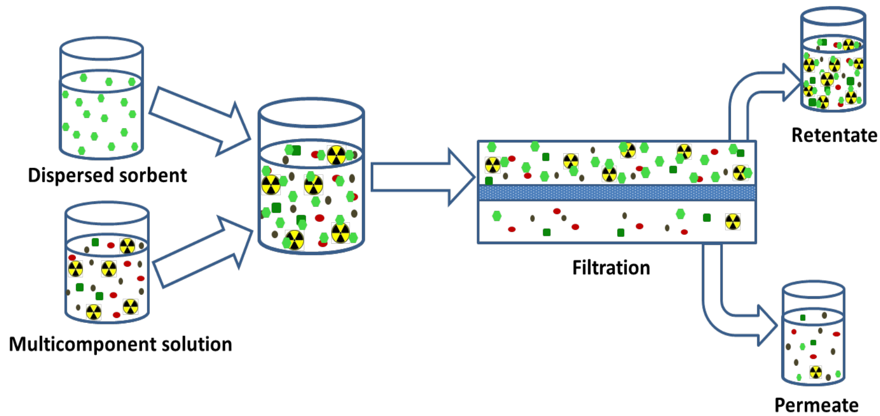

Figure 1: A scheme of sorption-assisted microfiltration process.

The MOFs can be used in the SMF process, and proper functionalisation of the sorbents can ensure high partition coefficients for elements present in the solution. The extensive literature on the subject, including the experience of the team from the Council for Scientific and Industrial Research (CSIR), Republic of South Africa, as well as research conducted at the Institute of Nuclear Chemistry and Technology (INCT) have shown that it is possible.

2.2. Metal-organic-framework (MOF) sorbent

For the sorption of Hg^{2+} from water UiO-66, metal-organic-framework sorbent functionalised with mercaptoacetic acid (thioglycolic acid, $C_2H_4O_2S$) was synthesised. The synthesis was performed in dimethylformamide using terephthalic acid, zirconium chloride, and mercaptoacetic acid under reflux at 120°C. The mercaptoacetic acid was chosen for its -SH group and its affinity for mercury. The content of mercaptoacetic acid in the reaction mixture was fixed at 50 equivalents of zirconium. The SEM picture of synthesised sorbent l showing aggregates of small nanocrystals is presented in Figure. 4.2.

On the basis of analysis by Energy-dispersive X-ray spectroscopy (EDS) made by the MOF's manufacturer, the atomic ratio of -SH group to zirconium was estimated at 0.32. The estimated size of the produced MOF's crystals was about 50 nm, but they formed larger agglomerates, which could be retained by the MF or UF membrane.

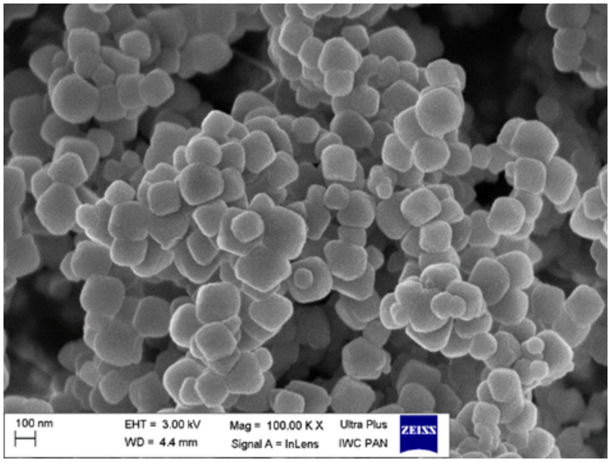

Figure2: SEM image of sorbent made using the Scanning Electron Microscope Zeiss Ultra Plus.

2.3. Membrane fouling

Membranes used in sorption-assisted filtration processes are susceptive to fouling due to deposition of the dispersed sorbent on the membrane. This is followed by continuous permeate flux decline, therefore, the efficiency of the entire separation process diminishes over time. It is important to suppress all negative phenomena that occur in the vicinity of the membrane by adjusting process parameters that avoid the sorbent layer development. An alternative method is to promote the turbulence in the membrane module by introducing movable parts, special baffles which improve mass exchange conditions or by application of pulse flow. In present studies, a Couette-Taylor flow (CTF) creating the vortices by use of a movable part inside the module that results in a self-cleaning effect of the membrane surface was applied. CTF is a combination of the axial Poiseuille flow and the rotating Couette flow with axisymmetric Taylor vortices. Such a combination results in limited axial dispersion coefficients in relation with dispersion coefficients in other directions, independence of mixing intensity on residence time of medium in the apparatus, and good transport parameters (Zakrzewska-Trznadel, Harasimowicz, Miskiewicz, Jaworska, Dłuska & Wroński 2009:108–116).

2.4. Radiotracers method

In this work, the use of the radiotracer method to assess the efficiency of Hg^{2+} sorption on MOF and the efficiency of retention of these ions on the membrane was proposed. Radiotracers provide a convenient tool to study the behaviour of metal ions in aqueous solutions (Petroni, Pires, & Munita 2004:239–243; Badillo-Almaraz, Solache-Ríos, Badillo-Almaraz, Zarate-Morales & Flores-Moreno 2017:113–118). An important advantage of the radiotracer method is that it is often possible to add carrier-free isotopes to the sample without disturbing the concentration of the ion of interest. Radioisotope tracers can be used at very low concentrations as radiation detectors are extremely sensitive. In general, measurements of radiation of gamma/beta emitting nuclides of high precision and sensitivity can be made relatively rapidly with minimal sample processing.

3. Experimental

3.1 Materials

Mercury nitrate ($Hg(NO_3)_2 \cdot H_2O$), Sigma-Aldrich, was used as a metal ions source. The radiolabelled compound $^{197}Hg(NO_3)_2$ was used as a radiotracer in all experiments. To obtain the ^{197}Hg radioisotope, a sample of nonradioactive $Hg(NO_3)_2$ with a mass of 1.2 mg was irradiated for one hour in a stream of $5 \cdot 10^{14}$ neutrons/s·m^2 in the Research Nuclear Reactor (MARIA) (National Centre for Nuclear Research, Świerk, Poland). The obtained radiotracer with an initial activity of approx. 25 MBq was dissolved in 0.6 cm^3 of 2% HNO_3 and then used as a radiolabeling solution. The MOF sorbent type MAA3(4) was applied in the SMF filtration experiments. Sodium hydroxide obtained from CHEMPUR, Poland was used for adjusting the pH of the reaction mixture. Distilled water was used in all experiments.

3.2. Membrane apparatuses

For the preliminary investigation of MOF-assisted filtration for removal of Hg^{2+} ions from water solutions, a stirred membrane cell was used. The experimental system consisted of an AMICON 8400 stirred membrane cell (Merck Millipore, Merck Sp. z o.o., Poland) with a polyethersulfone (PES) flat-sheet membrane (molecular weight cut-off = 10 kDa; diameter = 0.067 m) provided by Merck Millipore (Merck Sp. z o.o., Poland) and compressed nitrogen as a pressure source.

In further experiments, the Couette-Tylor Flow (CTF) membrane contactor was used. The membrane installation is schematically presented in Figure. 4.3. The tubular metal membrane used in the installation was made by sintering of metals such as 16-18% Cr, 10-14% Ni, 2-3% Mo, and 65-72% Fe. For experiments with MOF sorbents, a membrane with pore size of 0.1 µm, was selected.

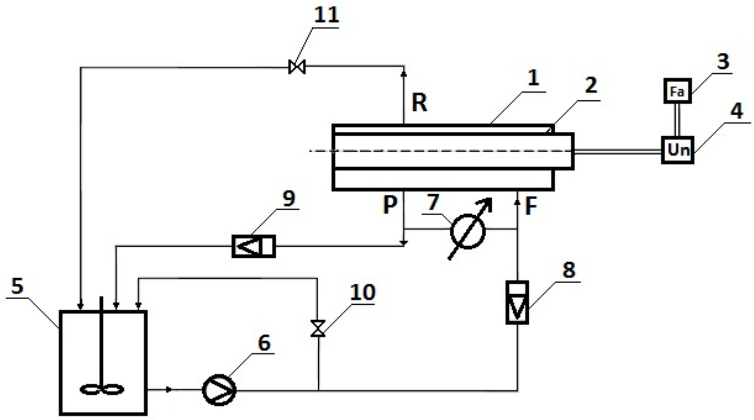

Figure 3: Experimental set-up: 1- membrane contactor, 2 – rotation shaft, 3 – power inverter, 4 – motor, 5 – feed tank with mechanical a stirrer, 6 – pump, 7 – manometer, 8, 9 – flowmeters, 10, 11 – valves.

This set-up worked in a closed system, meaning that the permeate and concentrate streams were returned to the feed tank (5) after exiting the membrane contactor. Feed solutions for filtration experiments were prepared by mixing the appropriate amount of 0.01 M Hg^{2+} stock solution with a certain amount of MOF sorbent to receive its concentration of 0.5-2 g/L in the feed solution and a small amount (10-30 µL) of tracer solution. Prior to the filtration experiment, the pH was adjusted with NaOH and the feed solution was stirred for one hour (experimentally determined to be sufficient time for Hg^{2+} ions adsorption on MOF particles). During the tests performed in the Amicon filtration cell, a transmembrane pressure was maintained at 0.5 to 2 bar. In the case of the CTF membrane module process parameters were as follows:

- transmembrane pressure, p: in the range of 0.3 – 0.5 bar,
- feed flow rate, Q_s: in the range of 1.2 – 2.2 L/min, and
- rotation frequency of the inner shaft, Ω: 2100 rpm.

The parameters of filtration were selected using the experiment design technique and after the optimisation procedure, which enables full observation of the effects of mutual interactions of the variables characterising the system.

During the filtration, permeate samples were collected periodically and analysed in relation to the Hg^{2+} content. The Hg^{2+} contents in the feed solution and the permeate were determined by measuring the radioactivity of $^{197}Hg^{2+}$ radiotracer using the gamma counter LG-1b (INCT, Poland). The Hg^{2+} retention coefficient was then calculated according to the formula (1):

$$R = 1 - \frac{A_P}{A_F} \tag{1}$$

where A_P and A_F represent the activity of radiotracer in the permeate and feed, respectively.

4. Results and discussion

4.1 Preliminary investigation on sorption-assisted filtration for Hg2+ removal from aqueous solutions

Tests with flat microfiltration membranes were performed to determine the parameters of the SMF process and to initially assess the effectiveness of the method and the obtained retention coefficients. These experiments also allowed the rate of deposition of the sorbent on the membrane to be observed and the prediction of membrane fouling that could interfere with the process performed later in the target flow system. Prior to key investigations, the influence of pH and reagents ratio on the retention coefficient (R) of Hg^{2+} ions were determined. The reagents were mixed for one hour and then placed in the Amicon filtration cell with a PES flat membrane with an MW cut-off of 10 kDa. The obtained permeate was analysed for the content of Hg^{2+} and then the retention coefficients (R) of these ions were calculated. Results of these investigations are presented in Table 4.1 and in Fig. 4.4 and 4.5.

As it turned out, the highest retention coefficients were obtained for the ratio of the reagents equal to 1/1 (R = 86%). On the other hand, when the lower concentration of sorbent was used, that is, the ratio of 2/1 and 4/1, R was lower and amounted to 51% and 45%, respectively. Bearing in mind the possibility of significant membrane fouling in the case of using a high concentration of sorbent (2 g/L), it was decided to carry out further research at its average concentration, 1 g/L, which gives the reagent ratio (Hg/MOF) equal to 2/1.

As for the influence of pH, studies have shown that it is most advantageous to conduct the process at a pH of approx. 5 (Figure.4.4). Further experiments were carried out at pH 5.5.

Table 1: The results of the study of the influence of the reagent ratio on the retention coefficient (R) of Hg^{2+} ions.

Hg^{2+} concentration, mol/L	Sorbent concentration, g/L	Reagents mass ratio (Hg/MOF), g/g	R, %
0.01	0.5	4/1	45.67
0.01	1	2/1	51.38
0.01	2	1/1	86.23

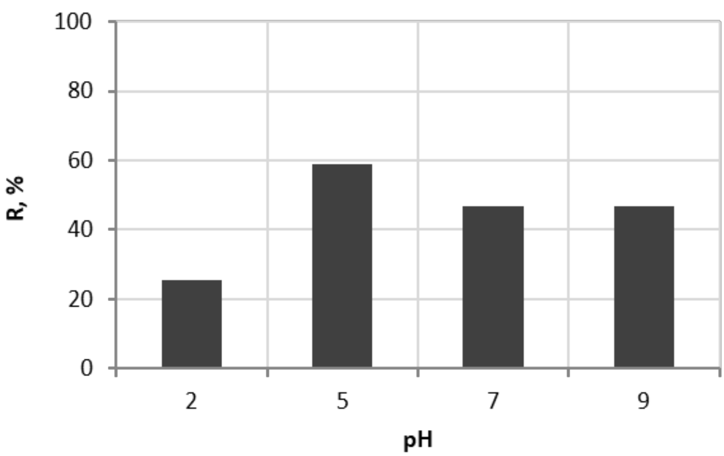

Figure 4: The pH influence on the retention coefficient (*R*) of Hg^{2+} ions; reagent ratio: 2/1.

An example of the MOF-assisted filtration process run carried out in the Amicon cell is shown in Figure 4.5 As evident, at the beginning of the process, the retention coefficient of Hg^{2+} increases and then, after ca 20 minutes, it stabilises at the level of about 51%.

Maintaining the parameters of the Hg^{2+} sorption on the MOF sorbent, established in the above-described experiments (pH = 5.5, Hg/MOF = 2/1), the process was transferred to a continuous membrane installation, namely to a system with a CTF flow module (Figure. 4.3).

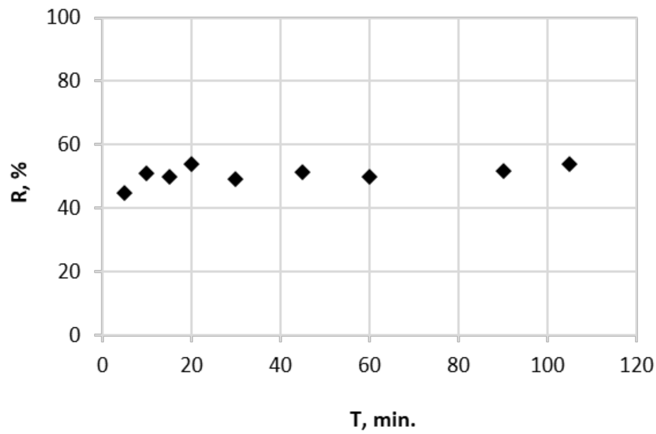

Figure 5: The change in the retention coefficient (*R*) of Hg ions during the MOF-assisted filtration process, carried out in the Amicon filtration cell; pH: 5.5, reagent ratio: 2/1.

4.2 MOF-assisted MF for Hg2+ removal from water solution in CTF membrane contactor

The MOF-assisted microfiltration carried out in the membrane installation with CTF membrane contactor was performed with the various process parameters, namely feed flow rate (Q_S: 1.2, 1.5 and 2.2 L/min) and transmembrane pressure (*p*: 0.3 and 0.5 bar). The influence of the feed flow rate on the retention factor of Hg^{2+} is illustrated in Figure. 4.6. As can be seen, when the feed flow increases, the retention ratio increases slightly. Regardless of the feed flow rates used, there is a noticeable increase in the retention coefficient during the process. After two hours, *R* reached high values: 93-99%.

When considering the influence of transmembrane pressure (Figure. 4.7), it should be stated that the higher the pressure, the higher the retention coefficient of Hg^{2+} ions have been achieved.

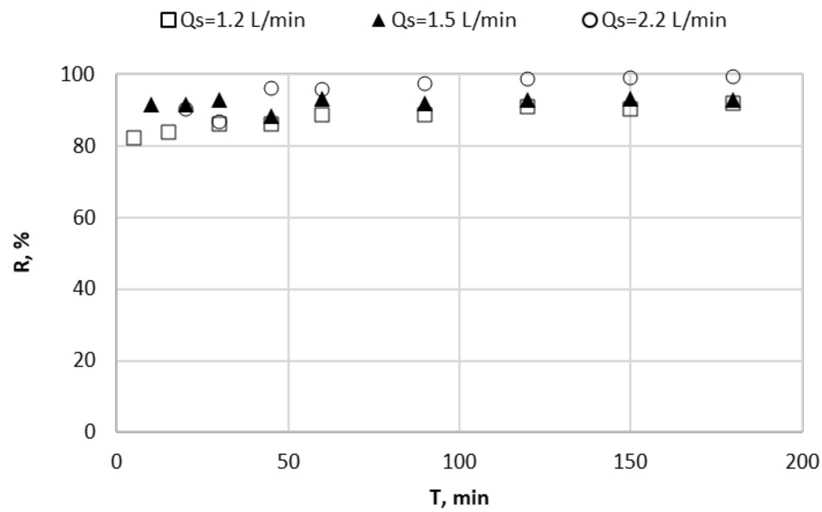

Figure 6: The influence of the feed flow rate (Q_S) on the retention factor of Hg^{2+}.

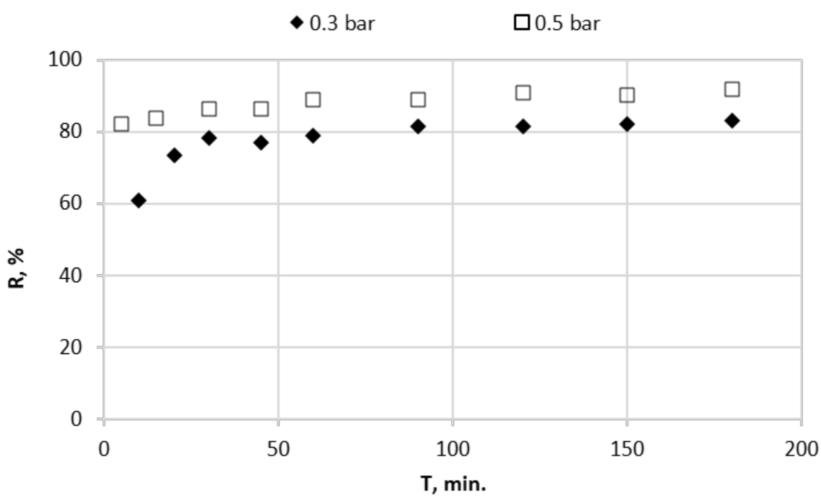

Figure 7: The influence of the transmembrane pressure (*p*) on the retention factor of Hg^{2+}.

Summarising the results obtained during sorption-assisted microfiltration carried out in the membrane module (CTF) with helical flow, it should be stated that Hg^{2+} ions can be effectively removed by the SMF method. Depending on the applied process parameters, R changed in the range of

83–99%. These results are much better than those obtained when running the process in the dead-end membrane cell (see section 4.1).

5. Conclusions

The process of separation of Hg^{2+} from water solutions can be effectively performed in the MF system with the membrane contactor with helical flow. The use of MOF sorbent results in sufficient separation of Hg^{2+} ions with over 80 % efficiency at 2:1 (Hg/MOF) ratio. The process parameters such as transmembrane pressure and the feed flow rate, affect the efficiency of Hg^{2+} ions separation. The process of Hg^{2+} ions sorption on MOF is significantly influenced by the pH and the reagent concentration ratio.

6. Acknowledgement

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