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Application of biosorbents in hybrid ultrafiltration/sorption processes to remove radionuclides from low-level radioactive waste

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ABSTRACT

This paper presents research on the application of a biosorption-assisted ultrafiltration process for the removal of selected radionuclides from radioactive liquid waste. Alginic acid and sodium alginate were used as binding agents owing to their availability and excellent sorption capacities for various metal ions. The first stage of investigations involved kinetic and adsorption studies using model solutions that contained non-radioactive surrogates of the ^{60}Co, ^{85}Sr, and ^{137}Cs radionuclides. After determining the optimal binding conditions for these ions (e.g., reagent ratio, pH, reaction time), the hybrid process was tested using the optimal biosorbent (i.e., sodium alginate) in a hybrid system equipped with a ceramic tubular membrane. The obtained results confirmed the high efficiency of the proposed method for removing radionuclides from model solutions and raw radioactive wastewater. The application of such a hybrid process in a waste treatment plant would allow for the generated concentrate to be further concentrated and then solidified, while the permeate could be safely discharged into the environment or used as process water.

Keywords: Ultrafiltration; Hybrid process; Biosorbent; Radioactive waste

1. Introduction

Nuclear power plants are the main source of radioactive waste; they generate waste during both operation and decommission. The development of nuclear reactor technology and new generation reactors, such as very-high-temperature reactors (VHTR), molten salt reactors (MSR), and supercritical-water-cooled reactors (SCWR), has reduced the amount of waste generated during their operation. However, it is not possible to completely eliminate waste production. In general, radioactive wastes differ in terms of form, radioactive concentration, and type of contamination depending on their origin. They can exist in a solid, liquid, or gaseous state, and the concentration levels of radioactivity can range from very high (e.g., in spent fuel and waste from its reprocessing) to very low (e.g., from the decommissioning of nuclear power plants) [1]. Radioactive waste must be carefully processed to reduce its volume. This is especially important in the case of liquid radioactive waste, which must be solidified in the next step of treatment to produce an appropriate form that enables safe long-term disposal. Various methods for concentrating radioactive matter from liquid low- and medium-level radioactive waste are commonly employed, e.g., chemical precipitation, ion exchange, thermal evaporation, solvent extraction or membrane processes [2–4]. However, there is still a need to find methods that are simpler and more economical, without sacrificing effectiveness. One potential option is to use a combination of membrane filtration techniques with sorption processes involving low-cost sorbents, e.g., biosorbents. Hybrid strategies, such as ultrafiltration (UF)/sorption processes are very attractive because of their high removal

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efficiencies and low energy consumption. A hybrid UF/sorption process can be applied for water purification [5–7] as well as treatment of wastewaters of different types [8,9].

Biosorption has received significant attention recently owing to its potential applications in waste treatment processes requiring the removal of toxic heavy metals from contaminated aqueous environments. The use of biosorbents to remove heavy metals from wastewater merits special attention because their biological origin makes them inexpensive to produce, and the resulting solid waste is easy to process (e.g. by incineration). Adsorbent biomass is advantageous because it contains a nearly unlimited number of binding sites (e.g., carboxylic acid, hydroxyl, and amino groups), a high affinity for various metals, and high retrievability of metal ions. In general, surface chemical reactions, such as metal complexation by carboxylic, amino, hydroxyl, or phenolic sites, allow for the selective removal of pollutants from complex media, whereas for instance activated carbons adsorb solutes in a generally non-specific way. The selectivity and use of low-cost biomass make biosorption an economic alternative to commercial activated carbons. Numerous types of low-cost biosorbents, such as yeast [10] or vegetable wastes [11,12] have been employed for metal ion removal and processing. Biosorbents also have potential for removing radioactive elements [13–15], rare-earth elements [16,17], and precious metals [18,19]. Their efficiency for removing metals from solutions is comparable to that achieved by physical means. As a result, biosorption represents an interesting alternative to conventional technologies based on ion-exchange processes or solvent extraction. Among the established biosorbents, alginic acid and its derivatives have been used extensively as sorbents for removing pollutants from wastewater owing to their hydrophilicity, excellent binding ability, low cost, high biocompatibility, and renewability [20–22].

This study aimed to investigate the application of biosorbents in liquid radioactive waste processing by implementing a hybrid process that combined biosorption with ultrafiltration to remove selected radionuclides from low-level radioactive waste. To our knowledge, there are only a limited number of publications describing the use of membrane filtration assisted by alginates [23,24]. Those reports described the use of alginic acid or its derivatives to remove heavy metal ions from water. The presence of carboxylic acid groups in both monomeric units allowed alginates to interact with various low-molecular weight species, which can capture heavy metal ions during the water purification process.

The present work describes the application of two biosorbents (alginic acid and sodium alginate) in a hybrid UF/sorption process for the removal of ^{60}Co, ^{85}Sr, and ^{137}Cs from model solutions and raw liquid low-level radioactive waste. The aforementioned radionuclides were selected because they commonly exist in liquid radioactive waste generated from uranium fission or activation of reactor structural elements. They are also often found in wastewater generated following the use of radionuclides in industry and medicine. In order to process this radioactive waste, a hybrid UF/sorption method was used due to its advantages, including high efficiency of ion removal, including radioactive ions, and low energy consumption. Compared to reverse osmosis, often used in the nuclear industry, ultrafiltration is more convenient; it does not require the use of high pressures, and hence expensive equipment. In the case of using the hybrid UF/sorption process, it is not less effective in removing radioactive ions than RO. The economy of the process is enhanced by the use of a cheap sorbent, a natural polymer extracted, for example, from algae biomass. In addition, with this method it is possible to carry out the entire process in one apparatus, which is essential in the case of radioactive waste as it minimizes the amount of contaminated equipment that would then have to be decontaminated, generating secondary waste.

In the literature, we can find descriptions of different hybrid processes that combine membrane methods with chemical or physical processes, enabling the earlier capture of radioactive substances through sorbent particles or substances binding them into larger agglomerates or macromolecules, which can then be separated by membrane filtration [25,26]. Methods supporting membrane filtration include such processes as complexation, particle sorption, coagulation, flocculation, or chemical modification of the separated ions by regulating process parameters (e.g. pH). Hybrid processes offer great flexibility in deciding on their purpose; the possibility of optimizing their individual components allows for a wide range of applications, both in front and back ends of the fuel cycle.

2. Materials and methods

2.1. Chemicals

Alginic acid from brown algae, sodium alginate, and metal salts, i.e., $CoCl_2{\cdot}6H_2O$, $SrCl_2{\cdot}6H_2O$, and CsCl, were obtained from Sigma Aldrich. The average particle diameter determined by sieve analysis using laboratory sieve shaker (Multiserw-Morek, Poland) was 0.07 and 0.2 mm for alginic acid and sodium alginate, respectively. The $NaNO_3$ used to increase the ionic strength of the solutions was provided by POCH S.A., Poland. All radionuclides used in the experiments, i.e., $^{60}Co(NO_3)_2{\cdot}6H_2O$ in aqueous solution (^{60}Co: $t_{1/2}$ = 5.24 years), $^{85}SrCl_2{\cdot}6H_2O$ in aqueous solution (^{85}Sr: $t_{1/2}$ = 65 days), and ^{137}CsCl in a solution of 0.1% HCl (^{137}Cs: $t_{1/2}$ = 30.2 years), were purchased from POLATOM Radioisotope Centre, Poland. All reagents were of analytical grade and were used as received.

2.2. Experimental methods

First, the impacts of the reagent ratio, pH, and ionic strength parameters on the removal of cobalt, strontium, and cesium ions (as non-radioactive surrogates of the ^{60}Co, ^{85}Sr, and ^{137}Cs radionuclides) were evaluated. Additionally, the sorption kinetics of these ions on two selected biosorbents (alginic acid and sodium alginate) were investigated. The flow sheet of this part of experiments is shown in Fig. 1.

Ultrafiltration equipment used in this work included an AMICON 8050 stirred membrane cell (Merck Millipore, Merck Sp. z o.o., Poland) with a polyethersulfone (PES) ultrafiltration membrane (molecular weight cut-off = 10 kDa; diameter = 0.043 m; effective active area = 1.34×10^{-3} m^2) provided by Merck Millipore (Merck Sp. z o.o., Poland) and compressed nitrogen as a pressure source.

Feed solutions for the experiments were prepared by adding an appropriate amount of sorbent to the stock solution of each target ion (Co^{2+}, Sr^{2+}, or Cs^{+}) at a concentration of 0.1 g/L. The biosorbent-to-metal concentration ratio applied in the experiments was 1:10. The pH was held within the range of 3–9 range by adding 0.1 M NaOH or a 0.1% solution of HNO_3. The solutions were stirred intensely with a magnetic stirrer for 30 min (for Co and Sr ions) or 120 min (for Cs ions). Preliminary studies indicated that these reaction times were sufficient to allow for the adsorption of each metal ion on a given biosorbent. The solutions prepared in this way fed the membrane cells. During the UF tests, a transmembrane pressure of 0.3 MPa was applied. The permeate collected from the membrane cell during the filtration process was analyzed to determine the concentration of metal ions. Based on these measurements, the retention coefficient (R) of each ion was calculated using Eq. (1):

$$R = 1 - \frac{C_P}{C_F} \tag{1}$$

where C_P and C_F represent the metal ion concentrations in the permeate and feed, respectively.

A DR2000 HACH spectrophotometer was used to measure the cobalt ion concentration (absorbance reading at l = 620 nm). The strontium and cesium ion concentrations were determined using a Dionex 200i/SP ion chromatograph (Thermo Fisher Scientific Inc., USA) equipped with an Ion Pac CS12A cation-exchange column connected to a CG12A guard column, using a solution of 18 mM methanesulfonic acid (MSA) as the eluent (eluent flow rate = 1 mL/min). Conductometric detection (using a CDM II detector) coupled with the use of a suppressor (Thermo CRS 300 4 mm) was employed.

The second phase of this work focused on increasing the scale to evaluate the applicability of the proposed method for industrial implementation. This involved experiments conducted in a continuous membrane system (shown schematically in Fig. 2). The membrane installation was equipped with 10 kDa molecular weight cut-off flat tubular ceramic membrane made from a-Al_2O_3 and TiO_2 (Atech Innovations, GmbH). The membrane was 0.25 m long, with a 0.01 m external diameter, and a 4.71×10^{-3} m^2 active area. This system also contained a centrifugal pump (GE Motors & Industrial Systems). A high-precision flowmeter (MIK-6FT10AC34P, Kobold, GmbH)

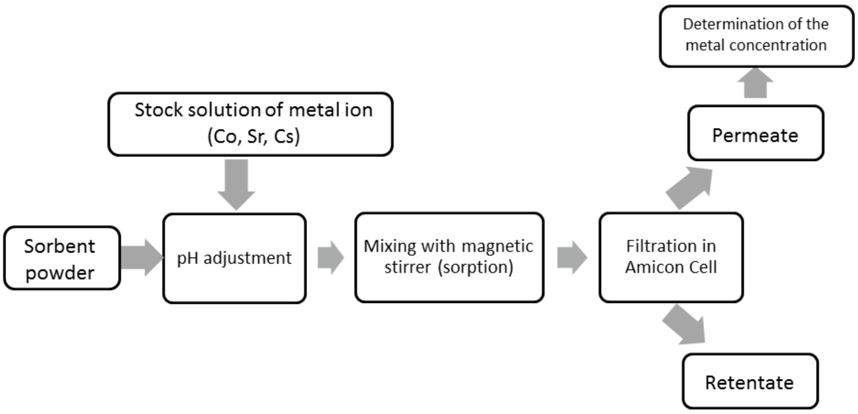

Fig. 1. The flow sheet of the first part of the research.

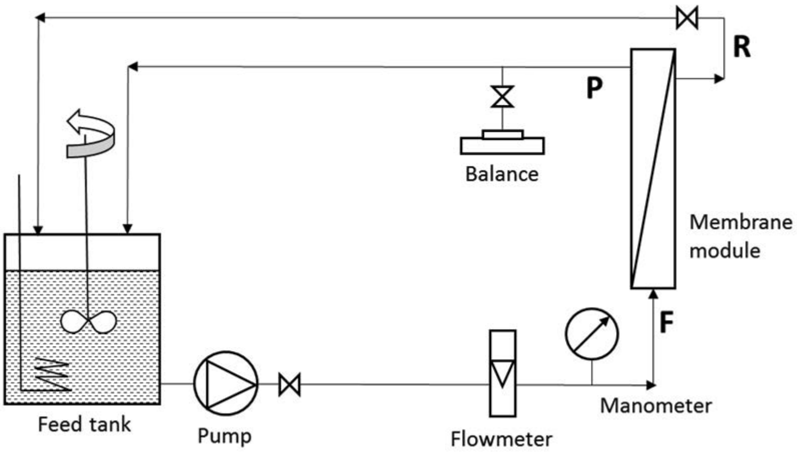

Fig. 2. Schematic diagram of the ultrafiltration setup.

was installed to measure the feed flux (60 L/h), and the permeate flow rate was determined gravimetrically with a balance. The pressure in the feed line (0.2 MPa) was measured using a MS-100K manometer supplied by Aplisens.

The feed solution for this system was prepared as follows: an appropriate amount of selected biosorbent was introduced into 2 L of the radioactive solution containing ^{60}Co or ^{85}Sr. The level of radioactivity in each solution was measured using a gamma counter (LG-1b, INCT, Poland) and varied from 14 to 18 imp/s, which was approximately four times the value of the radiation background. After adjusting the pH, each solution was agitated to reach an equilibrium state and then filtered through the membrane. This setup worked in a closed system, meaning that the permeate and concentrate streams were returned to the feed tank. The membrane system operated under 0.2 MPa pressure and a 60 L/h feed flow rate. Samples of the permeate and retentate were collected for analysis every 10 min in the beginning of the experiment, and then every 60 min once sorption equilibrium was reached. The radioactivities of the retentate and permeate samples were analyzed using a gamma counter. The results of these measurements were used to calculate the decontamination factor (DF) with Eq. (2):

$$\mathrm{DF} = \frac{A_f}{A_p} \tag{2}$$

where A_f and A_p are the radio activities (imp/s) of the feed solution and permeate, respectively.

Additionally, the permeate flux was measured during the experiments to evaluate the normalized permeate flux (J_v/J_w), where J_v represents the permeate flux, and J_w is the water flux. The water flux was determined experimentally prior to the UF/sorption process under identical conditions (transmembrane pressure = 0.2 MPa). The measured J_w values were in the range of 298.09–317.20 L/(m^{2}h).

3. Results and discussion

This study investigated the ability of an ultrafiltration process assisted by two biosorbents (alginic acid and sodium alginate) to remove three radionuclides (^{60}Co, ^{89}Sr, and ^{137}Cs) from aqueous solution. First, model solutions containing surrogates of these isotopes were tested, and the influence of the pH and ionic strength on the binding efficiency of Co^{2+}, Sr^{2+}, and Cs^{+} was examined in those model solutions. The kinetics of each metal adsorption onto a given biosorbent were also evaluated. Sodium alginate and other monovalent cation (K^+, NH_4^+) salts of alginic acid are partially soluble in water, whereas alginic acid is not. Therefore, these biosorbents may differ in terms of their adsorption capacity for the tested isotopes. However, under the applied experimental conditions, both sorbents could be dispersed in aqueous solutions.

3.1. Effect of pH

Upon examining the effect of pH on the retention coefficient of Co^{2+}, Sr^{2+}, and Cs^{+} ions, it was determined that the highest R values for the tested ions were obtained at pH 5–8, regardless of the biosorbent. Both alginic acid and sodium alginate are more stable in this range of pH. Moreover, below pH of 5, the free carboxylate ions in the alginate polymer chains start to become protonated, whereas the higher pH involved a greater dissociation of carboxylic functional groups and enabled the effective binding of metal ions. As shown in Fig. 3a, the R values for Co^{2+} bound by alginic acid and sodium alginate reached 0.85 in this pH range, whereas the R values for Sr^{2+} under the same conditions were 0.98 for alginic acid or 0.96 for sodium alginate (Fig. 3b). In the case of Cs^{+} ions (Fig. 3c), the highest R value achieved for alginic acid was 0.86 at

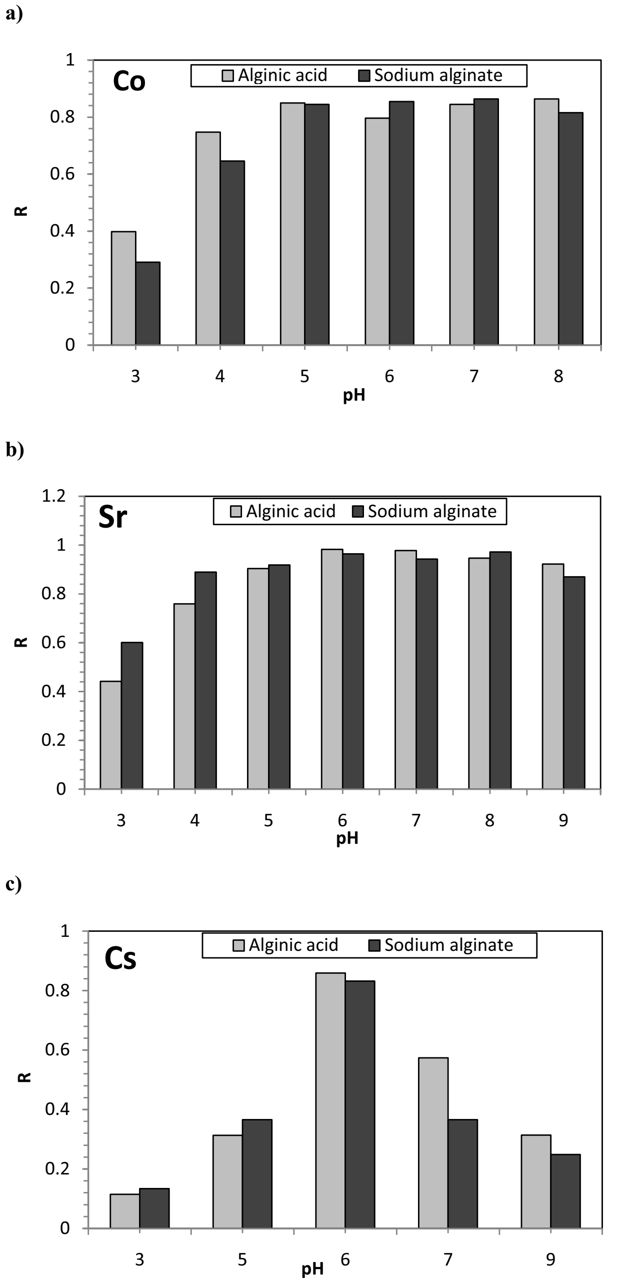

Fig. 3. Effect of pH on the retention coefficient of Co^{2+}, Sr^{2+}, and Cs^{+} achieved using different biosorbents (C_M/C_{sorb} = 1/10).

pH = 6, whereas for sodium alginate under the same conditions, $R = 0.83$. Considering these results, the following conditions were applied in further experiments: pH = 7 for cobalt and strontium ions; pH = 6 for cesium ions.

3.2. Effect of ionic strength on metal ion removal

Liquid radioactive waste is typically very salinated. To evaluate the influence of the ionic strength on the efficiency of metal ion removal using the selected biosorbents, a series of experiments were performed on solutions having various salinities. As presented in Fig. 4, the retention coefficients of all of the tested metal ions decreased significantly as the salinity of the solution increased. The presence of competing cations, e.g. Na^+ in the solution being purified can significantly reduce the effectiveness of Co^{2+}, Sr^{2+} and Cs^+ ions separation. For example, the addition of 75 mmol/L $NaNO_3$ to a solution of sodium alginate in the presence of cobalt ions led to a decrease in R from 0.90 to 0.35 (Fig. 4a). Additionally, the observed reduction in the R value of cobalt ions following the increase in salinity was slightly greater with sodium alginate than with alginic acid. Nevertheless, both the largest and the fastest decline in retention coefficient was observed for the adsorption of cesium ions on alginic acid (Fig. 4c). In this case, R decreased from 0.86 to 0.22 after adding 50 mmol/L $NaNO_3$. It can be also noticed, that, in case of cesium ions the two biosorbents showed a clear difference in the rate of decrease in R with increasing solution salinity; there was a much greater decrease in R with increasing salinity when using alginic acid relative to sodium alginate. The effect of competing ions such as Na^+ on the sorption of Cs^+ by alginic acid is more important than on the sorption of two other ions because the sorption kinetics of Cs^+ is much slower than for Co^{2+} and Sr^{2+} (see subsection 3.3). Sodium ions, present in excess in the solution, easily react with the carboxyl groups of the acid and remain in equilibrium with them, making it difficult for relatively large cesium ions to bind to the sorbent. Therefore, the retention of cesium ions in the UF/sorption process with alginic acid under high salinity conditions is so low. In the case of sorption of cesium ions on sodium alginate, the effect of increased salinity on the retention of these ions is similar to that of other ions (Co and Sr). The slower kinetics of the sorption reaction is not so important here, because sodium cations are already in the solution - they come from the dissociation of alginate and are in equilibrium with carboxylic anions. In the case of strontium ions, the differences in retention coefficients between the two biosorbents upon changing the solution salinity were very small (Fig. 4b).

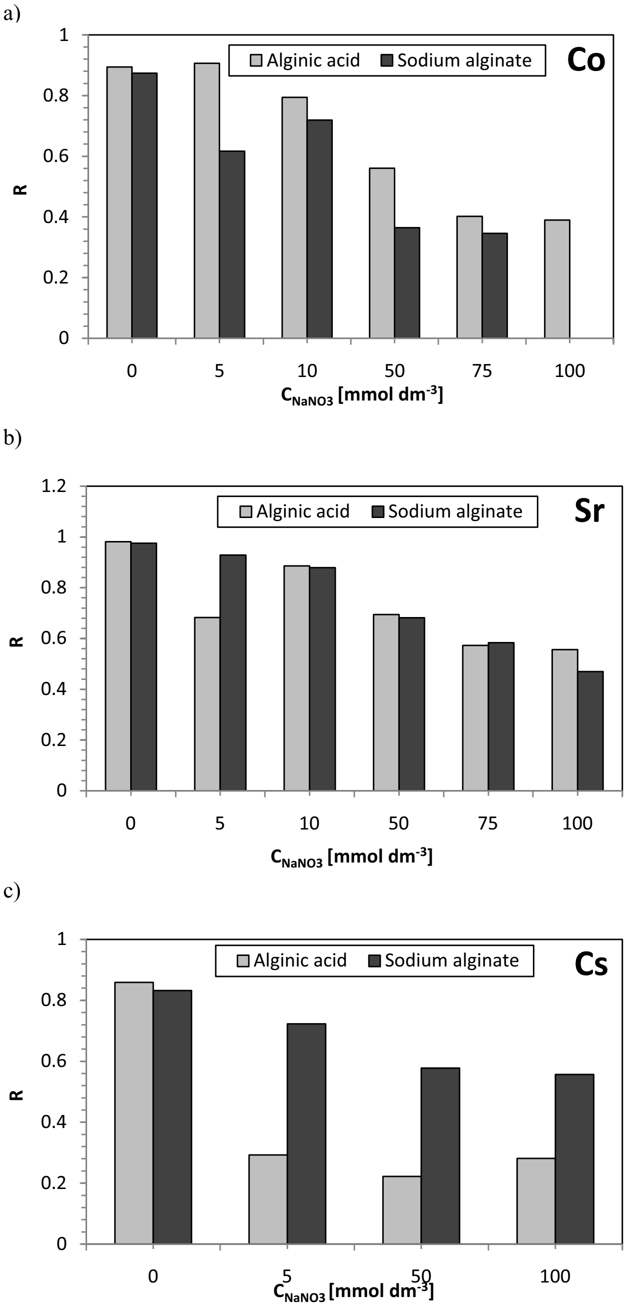

Fig. 4. Effect of salinity on the retention coefficients of different metal ions.

3.3. Kinetic studies of Co^{2+}, Sr^{2+}, and Cs^+ adsorption on alginic acid and sodium alginate.

Figs. 5a-c show the profiles of the cobalt, strontium, and cesium ion adsorptions onto the two studied biosorbents over time. The adsorption of Co^{2+} and Sr^{2+} on the examined sorbents occurred very quickly, and equilibria were reached after only a few minutes. In the case of cesium ions, equilibrium was reached after one hour. The highest retention coefficient was observed for strontium ions, using either the alginic acid and sodium alginate. After reaching an equilibrium state, the R values for Sr^{2+} with both biosorbents were 0.96. The R values for cobalt ions with both tested biosorbents were slightly smaller (0.86). For cesium ions, the retention coefficients obtained with the two biosorbents differed significantly; with alginic acid, R was only 0.57, and with sodium alginate, R reached 0.81.

In summary, strontium ions were most effectively retained using the UF/sorption hybrid process with alginate sorbents, although cobalt ions were also retained with acceptable efficiency under these conditions. In contrast,

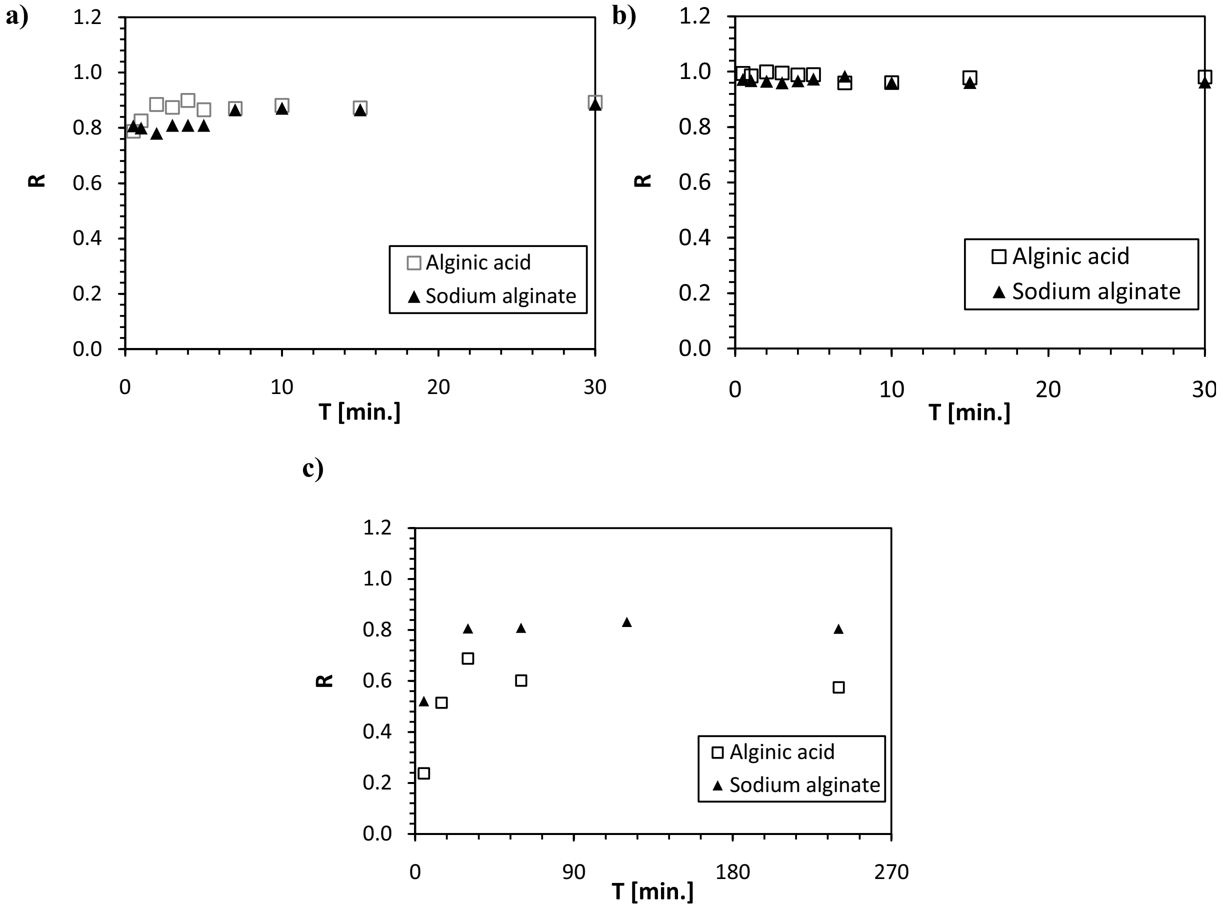

Fig. 5. Influence of contact time on the retention coefficients of (a) cobalt, (b) strontium, and (c) cesium, obtained using the UF/sorption process with alginic acid and sodium alginate

cesium ions were retained the slowest and least effectively. In the case of cesium, the difference in activity of the two biosorbents was clear: sodium alginate achieved more efficient adsorption than alginic acid.

To investigate the kinetics of the adsorption of cobalt, strontium, and cesium ions on the two examined biosorbents, pseudo-first-order and pseudo-second-order models were employed. Both of these kinetic models were based on the kinetics of the chemical reactions involved in the process. The equation describing the pseudo-first-order model is shown in Eq. (3) [27],

$$\log\left(q_{e,\mathrm{exp}} - q_t\right) = \log q_{e,\mathrm{cal}} - k_1 \times \frac{t}{2.303} \tag{3}$$

where q_t is the mass of metal ions adsorbed on the adsorbent (mg/g) at time t (min), $q_{e,\mathrm{exp}}$ is the experimental adsorption capacity (mg/g), $q_{e,\mathrm{cal}}$ is the calculated adsorption capacity (mg/g), and k_1 is the pseudo-first-order rate constant (1/min).

The pseudo-second-order model is expressed by Eqs. (4) and (5):

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_{e,\mathrm{cal}}} \tag{4}$$

$$h = k_2 q_{e,\mathrm{exp}}^2 \tag{5}$$

where h is the initial adsorption rate (at $t = 0$), and k_2 is the pseudo-second-order rate constant (g/mg min).

To evaluate how well the experimental data fit the kinetic models, the correlation coefficients (R^2), kinetic rate constants, and the experimental and calculated adsorption capacities were analyzed (Table 1).

According to the obtained results, the pseudo-second-order model better reflected the adsorption kinetics of the three tested ions on both alginic acid and sodium alginate. This was supported by the obtained correlation coefficients (R^2 values close to 1); for the pseudo-first-order model, these coefficients were between 0.12–0.71 and 0.28–0.93 for sodium alginate and alginic acid, respectively. Considering the second-order model, it is important to note that the highest reaction rate constant of the adsorption process using alginic acid was achieved for strontium ions ($k_2 = 0.3543$ g/mg min). When sodium alginate was used, the highest adsorption rate constant was observed for cobalt ions. Comparing the two tested biosorbents, it was clear that higher k_2 values were achieved for sodium alginate (with cesium and strontium); however, the opposite was true in the case of cobalt, i.e., higher k_2 was achieved for alginic acid. The adsorption capacities of

Table 1
Constants relevant to the applied kinetic models describing alginic acid and sodium alginate biosorption of different ions

Ion	$q_{e,\exp}$ mg/g	C_f^* mg/L	Pseudo-first-order			Pseudo-second-order			
			$q_{e,\mathrm{cal}}$ mg/g	k_1 1/min	R^2	h mg/(g min)	$q_{e,\mathrm{cal}}$ mg/g	k_2 g/(mg min)	R^2
Alginic acid									
Co^{2+}	94.0	11.3	2.6	0.0127	0.284	555.5556	93.5	0.0629	1.000
Sr^{2+}	97.0	1.2	5.3	0.1255	0.934	3333.3333	97.1	0.3543	1.000
Cs^+	75.0	42.8	19.6	0.0016	0.530	6.8681	72.5	0.0012	0.997
Sodium alginate									
Co^{2+}	91.0	14.0	11.9	0.33347	0.711	2000.0000	90.9	0.2415	1.000
Sr^{2+}	98.0	2.5	1.2	0.00530	0.197	1666.6667	97.1	0.1735	1.000
Cs^+	72.0	15.1	2.6	0.00092	0.122	33.2226	72.5	0.0064	1.000

*C_f - the final metal concentration in the solution after UF/sorption process.

both biosorbents calculated at the equilibrium state ($q_{e,\mathrm{cal}}$) were similar. The highest $q_{e,\mathrm{cal}}$ values (90–97 mg/g) were obtained for Co^{2+} and Sr^{2+}, whereas in the case of Cs^+, the adsorption capacity was approximately 72 mg/g for both biosorbents. When considering the degree of removal of individual ions, it can be noticed that when the reaction rate is the highest (values of k_1 or k_2), i.e. in the case of Co and Sr ions sorption (regardless of the sorbent type), the lowest values of metal ion concentration in the solution (C_f) after the process were obtained.

3.4. Hybrid UF/sorption process for treating liquid low-level radioactive waste

In the next stage of this work, the hybrid UF/sorption process was investigated using the continuous-mode apparatus illustrated in Fig. 2. This research represented another step towards examining the applicability of this method in industrial conditions. The experiments were conducted using water solutions containing ^{60}Co or ^{85}Sr, as well as raw radioactive wastewater, whose characteristics are listed in Table 2.

Sodium alginate was selected as the biosorbent for these studies, primarily because of its higher solubility in water, which should minimize membrane fouling. Moreover, the studies described above demonstrated that the use of sodium alginate resulted in higher retention coefficients of cesium ions than the use of alginic acid. For the other examined ions (i.e., cobalt and strontium), no significant difference was observed in terms of the efficiency of their removal depending on the biosorbent used. Therefore, these studies focused on the most effective method for removing cesium ions. Cesium isotopes are one of the components of the liquid waste generated during the operation of nuclear reactors, including high-temperature reactors. Liquid wastes originating from radionuclide applications in medicine, industry, and science also contain large amounts of cesium radionuclides. In some cases, e.g., in the radioactive wastewater sample analyzed in this study, cesium isotopes are the major radioactive component (Table 2). Therefore, as with other radioisotopes, the radionuclides of cesium must be effectively removed from the wastewater and concentrated in a smaller volume, which can be then subjected to solidification.

Table 2
Chemical composition and specific radioactivity of radionuclides in the sample of radioactive wastewater

Parameter	Quantity
^{137}Cs, Bq/L	35,000
^{134}Cs, Bq/L	1,700
^{60}Co, Bq/L	73
^{125}Sb, Bq/L	227
Cl^-, mg/L	26.6
NO_3^-, mg/L	1,800
SO_4^{2-}, mg/L	451.3
Na^+, mg/L	635.5
K^+, mg/L	33.0
Mg^{2+}, mg/L	102.7
Ca^{2+}, mg/L	172.2

The experimental results obtained using the continuous-mode membrane apparatus are summarized in Table 3.

Higher R values were obtained for ^{85}Sr than for ^{60}Co, which confirmed the previous results obtained using model solutions containing non-radioactive surrogates of these radionuclides (see sections 3.1–3.3). The R value for raw radioactive wastewater was based on the total radioactivity of the permeate and the feed solutions; therefore, it should be considered as the retention coefficient of the sum of radionuclides present in the initial solution. Clearly, the decontamination factor calculated according to Eq. (2) for the solution containing ^{85}Sr was much higher than that for the solution containing ^{60}Co. The decontamination factor obtained for raw liquid radioactive wastewater was approximately 9.

The experiments conducted with the continuous-mode apparatus showed that the ultrafiltration process assisted by alginate biosorbents for the removal of radionuclides from radioactive wastewater offered satisfactory results.

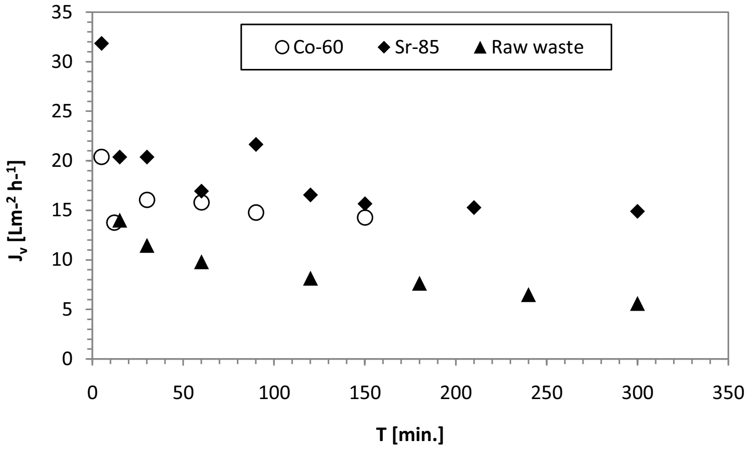

Fig. 6. Time profiles of permeate flux obtained for three different solutions during the hybrid UF/sorption process carried out using a continuous-mode apparatus.

However, in the hybrid process using water-insoluble sorbents, the blocking of the membrane due to the deposition of a filter cake on its surface, could not be ignored. As expected, the resulting decrease in the permeate flux obtained during the continuous UF/sorption process was quite significant. A comparison of the reductions in permeate flux of the tested solutions is shown in Fig. 6, and the values of the normalized permeate fluxes are compiled in Table 3.

The values of the normalized permeate fluxes obtained for ^{60}Co and ^{85}Sr were similar, whereas for raw wastewater, the permeate flux was much smaller. This was likely because of the three-fold increase in sorbent concentration relative to that in the solutions containing ^{60}Co and ^{85}Sr. The biosorbent concentration required for the effective removal of radionuclides from raw radioactive wastewater was estimated based on the radiochemical composition of the treated solution. One of the methods to minimize membrane fouling involves appropriate regulation of the hydrodynamic conditions in the membrane module, e.g., the use of special baffles or movable parts in the apparatus to enhance mass exchange and promote high turbulence in the membrane vicinity. This type of solution was previously tested by our group [25,28], and the results confirmed the effectiveness of this fouling reduction technique. Specifically, we observed an increase in the permeate flux relative to simple cross-flow filtration.

4. Conclusions

This report evaluated the potential applicability of two biosorbents (alginic acid and sodium alginate) for the removal of selected radionuclides from aqueous solutions and liquid radioactive wastes using a hybrid ultrafiltration/sorption process. The research aimed to determine the optimal conditions for the adsorption of Co^{2+}, Sr^{2+}, and Cs^{+} on selected biosorbents. The impacts of the solution pH and salinity level on the retention coefficients of the aforementioned ions were investigated. Additionally, the adsorption kinetics of each of the ions were analyzed, revealing that Co^{2+} and Sr^{2+} reached equilibrium after only a few minutes, while cesium ions required one hour to reach an equilibrium state. Studies of the hybrid UF/sorption process carried out using a continuous-mode apparatus indicated that this strategy offers a very promising approach for treating radioactive wastewater. High radionuclide retention coefficients (0.72–0.97) were obtained for solutions containing single radioactive components (i.e., ^{60}Co and ^{85}Sr), as well as for raw radioactive wastewater. The findings from the studies described herein confirmed that the tested biosorbents used in the employed hybrid UF/sorption process could efficiently remove radioactive substances from liquid low-level radioactive wastes originating from the application of isotopes in the nuclear or medical industry.

Table 3
Results from the treatment of radioactive solutions using the hybrid biosorbent-assisted ultrafiltration process with a continuous-mode membrane apparatus

Type of the solution	R [-]	DF [-]	J_v/J_w
^{60}Co	0.72	3.6	0.0465 – 0.0664
^{85}Sr	0.97	60	0.0485 – 0.0664
Raw radioactive waste	0.89	9.4	0.0183 – 0.0456

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