



Heavy metal decontamination by ion exchange polymers for water purification: counterintuitive cation removal by an anion exchange polymer

Emanuela Sgreccia^{1,*}, Celina Rogalska^{1,2}, Francia Sarhaly Gallardo Gonzalez¹, Paolo Proposito¹, Luca Burratti³, Philippe Knauth⁴, and Maria Luisa Di Vona^{1,*} 

¹ Department of Industrial Engineering, University of Rome Tor Vergata, 00133 Rome, Italy

² Faculty of Chemistry, Wrocław University of Science and Technology, Norwida 4/6, 50-373 Wrocław, Poland

³ Department of Sciences, Roma Tre University of Rome, Via della Vasca Navale 79, 00146 Rome, Italy

⁴ Aix Marseille Univ, CNRS, MADIREL (UMR 7246) and International Laboratory: Ionomer Materials for Energy, Campus St Jérôme, 13013 Marseille, France

Received: 3 October 2023

Accepted: 4 January 2024

Published online:
12 February 2024

© The Author(s), 2024

ABSTRACT

Ion exchange polymers were used for mercury and lead ions removal in water. The heavy metal ion concentration was analyzed by two independent methods: inductively coupled plasma–optical emission spectroscopy (ICP-OES) and gravimetry. The studied cation exchange polymer (CEP) was sulfonated poly(ether ether ketone) (SPEEK), and the anion exchange polymer (AEP) was poly(sulfone trimethylammonium) chloride (PSU-TMA). The removal capacity was connected with the ion exchange capacity (IEC) equal to 1.6 meq/g for both polymers. The concentration ranges were 0.15–0.006 mM for Hg²⁺ and 10.8–1.0 mM for Pb²⁺. SPEEK achieved 100% removal efficiency for mercury and lead if the concentration was below the maximum sorption capacity (Q_{\max}), which was about 210 mg/g for Pb²⁺ with SPEEK. For PSU-TMA, the surprising removal efficiency of 100% for Hg²⁺, which seemed incompatible with ion exchange, was related to the formation of very stable complex anions that can be sorbed by an AEP. Langmuir adsorption theory was applied for the thermodynamic description of lead removal by SPEEK. A second-order law was effective to describe the kinetics of the process.

Handling Editor: Annela M. Seddon.

Address correspondence to E-mail: emanuela.sgreccia@uniroma2.it; divona@uniroma2.it

E-mail Addresses: 252571@student.pwr.edu.pl; franciasarhaly.gallardogonzalez@students.uniroma2.eu; proposito@roma2.infn.it; luca.burratti@uniroma2.it; philippe.knauth@univ-amu.fr

Introduction

Ion exchange polymers (IEPs) consist of a backbone grafted with pendant ionic groups; in water they present a peculiar morphology with hydrophobic polymer domains combined with hydrophilic regions containing dissociated ionic groups and water, thus forming hydrated nanometric channels [1, 2]. This nanostructure allows widespread applications, ranging from membranes for ultrafiltration or separation, ion exchange resins, to membranes for advanced energy applications [3–8]. The process of heavy metal ion removal from contaminated water can benefit from the use of IEPs for various reasons: the specific interaction between the metal ion and the ionic group, the adsorption on the IEP surface, and the accessibility of the IEP bulk through the exchange inside the nanometric channels.

Environmental pollution by heavy metals is an urgent social problem and much attention has been paid to their removal from industrial and domestic wastewater in recent decades. Their tendency to accumulate in living organisms and to induce harmful effects has led the scientific community to investigate different methods of removal [9–11]. Among the common heavy metals, lead and mercury present many human health issues and their sources span from fossil fuel combustion to chemical industries [9, 12]. The values established by the World Health Organization (WHO) for drinking water are 0.01 and 0.006 mg/L for Pb and Hg, respectively [13].

Various polymers are used for heavy metal ion removal, e.g., polyethersulfone, polysulfone, or polyphenylsulfone with added carbonaceous materials (carbon nanotubes, graphene oxide, etc.) [14–16]. The adsorption technique using ionomers is considered a very promising method for this purpose due to the low cost, easy handling, and high affinity of ionomeric materials toward heavy metal ions [17]. Some examples are reported in the literature for cation (CEP) and anion exchange polymers (AEP) [18–21] or for nanocomposite IEPs with nanoparticles [22].

The removal ability of IEPs can be attributed to ion exchange [23], to specific interactions between IEPs and heavy metals, as, for example, those of the Hofmeister series [24] or to other sorption phenomena [25]. Another potential benefit of IEPs is their pH-responsive property, exchanging the counterion as a function of the media [26, 27]. The ion exchange capability is connected to the valence and the size of

the ions. Ions with a higher valence, or with the same valence, but a greater ionic radius, are preferentially retained in the IEPs [28].

Aromatic polymers are a family of high-performance, engineering thermoplastic polymers characterized by an unusual combination of properties, ranging from high temperature performance to mechanical strength and excellent chemical resistance [29]. IEPs based on aromatic polymers maintain a relatively low cost and avoid toxic fluorine.

In this paper, we therefore study aromatic ion exchange polymers with grafted cationic or anionic groups: the CEP sulfonated poly(ether ether ketone) (SPEEK) and the AEP poly(sulfone trimethylammonium) chloride (PSU-TMA). SPEEK or composite SPEEK was already used for dyes or uranium removal, water desalination, and ultrafiltration [30–35]. We also explore the surprising quantitative removal of mercury cations by the AEP. The adsorption of cations by anion exchange polymers was already observed, but controversial explanations were given [18, 36]. In the following, we investigate the sorption properties of SPEEK for Hg^{2+} and Pb^{2+} ions at different concentrations and times that were not reported before and analyze the sorption thermodynamics using Langmuir adsorption theory. The origin of the counterintuitive cation removal by PSU-TMA is examined, and the kinetics of heavy metal ion sorption are also investigated.

Materials and methods

PEEK was purchased from Victrex (450P, MW = 38,300 g/mol), polysulfone from Solvay (PSU, MW = 55,500 g/mol). Stannic chloride (SnCl_4), paraformaldehyde, $((\text{CH}_2\text{O})_n)$, trimethylchlorosilane (Me_3SiCl), trimethylamine (TMA, 4.2 M in EtOH), H_2SO_4 , $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and other chemicals were purchased from Merck. All of them were reactant grade and used as received.

Synthesis

Synthesis yield, casting conditions, ion exchange capacity (IEC), and water uptake (WU) of the polymers are reported in Table 1.

Table 1 Synthesis yield, casting conditions, IEC, and water uptake (WU) of the polymers

Sample	Yield (%)	Casting solvent	Casting temperature(°C)/ time (h)	IEC (meq/g)	WU (%)
SPEEK	100	acetone/H ₂ O = 80:20 vol%	50/15	1.65	30
SPEEK	98	acetone/H ₂ O = 80:20 vol%	50/15	2.16	45
SPEEK	100	DMSO	80/48	1.65	23
PSU-TMA	98	DMSO	80/48	1.60	53
PSU	-	DMAc	80/48	0	–

Sulfonated poly(ether ether ketone) (SPEEK)

The synthesis was adapted from ref [37]. H₂SO₄ (96%, 150 mL) was preheated at 45 °C then PEEK (3 g) was slowly added under vigorous stirring. The system was left to react for 14 h and then allowed to cool to room temperature. The solution was poured into an excess of ice water obtaining a white precipitate. The precipitate was filtered and washed with water in a dialysis membrane (Sigma-Aldrich D9402) until pH = 7 to completely eliminate the residual sulfuric acid. The sulfonated polymer (SPEEK) was dried for 12 h at 80–85 °C. The degree of sulfonation (DS) and the IEC were determined by ¹H NMR spectroscopy and by titration (Table 1). The chemical structure and the ¹H NMR spectrum are reported in Fig. 1.

SPEEK membrane preparation

Membranes were prepared by the solution casting method. As a general procedure, 250 mg of SPEEK was dissolved in 30 mL of DMSO or acetone/H₂O = 80:20 vol% (Table 1). The resulting solution was stirred for 4 h, evaporated at 80 °C to 5 mL, cast onto a Petri dish, and heated to dryness at different temperatures depending on the casting solvent.

Poly(sulfone trimethylammonium) chloride (PSU-TMA).

The synthesis of PSU-TMA was described in the reference [38]. In short, the chloromethylation route was followed using paraformaldehyde, trimethylchlorosilane and SnCl₄ in a molar ratio PSU/Me₃SiCl/(CH₂O)_n/SnCl₄ = 1:10:10:0.2. The mixture was left under stirring at 50 °C for 4 days. The solution was then cooled to RT and the polymer precipitated in methanol. The product was dried overnight at 60 °C and analyzed

by ¹H NMR. The final degree of chloromethylation (DCM) was 1 [39]. Chloromethylated PSU (PSU-CH₂Cl) reacted with TMA in DMSO at 70 °C for 72 h in an anhydrous medium (molar ratio PSU-CH₂Cl/TMA = 1:2). The resulting solution was heated under high vacuum to remove the excess of amine for 3 h at 85 °C. The solution of PSU-TMA in DMSO (0.05 M) was directly used for the casting procedure. A little quantity was dried and analyzed by ¹H NMR and by titration. The IEC is given in Table 1; the chemical structure and the ¹H NMR spectrum are reported in Fig. 1.

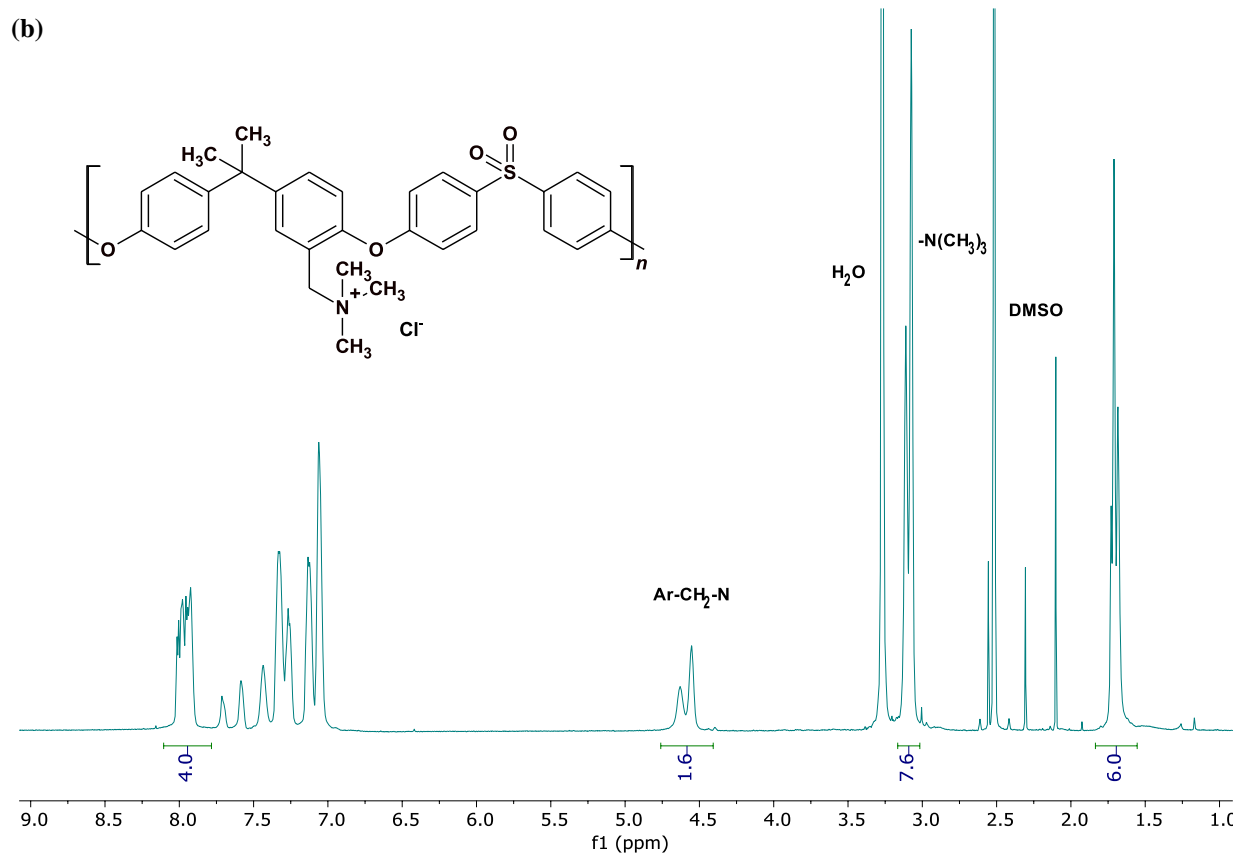
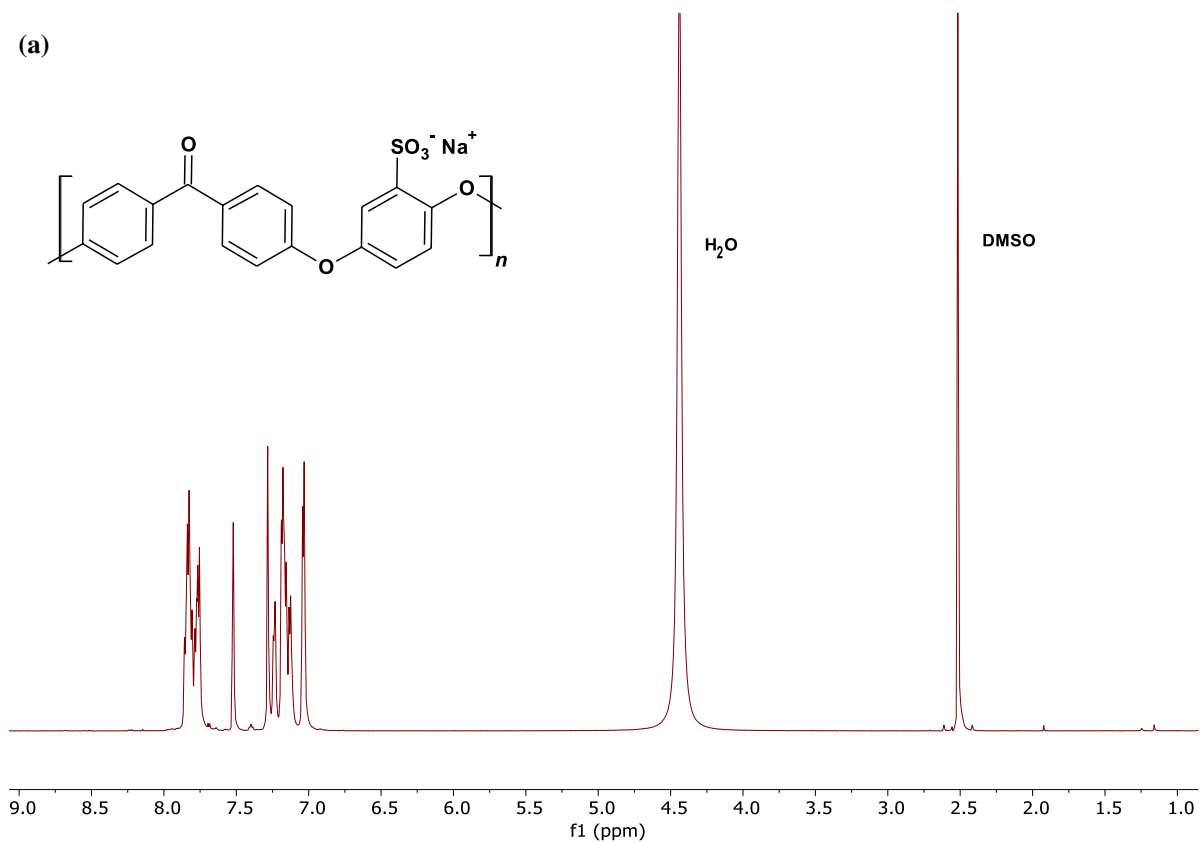
PSU-TMA and PSU membrane preparation.

Ten milliliters of the 0.05 M polymer solution in DMSO was transferred to a Petri dish and left in an oven at 80 °C for 2 days. For PSU, 250 mg of polysulfone was dissolved in 30 mL of DMAc.

Batch adsorption studies

Metal ion solutions with different concentrations were prepared from Pb(NO₃)₂ and Hg(NO₃)₂·H₂O (see Tables 2 and 3). Prior to the use, all polymer samples were inserted into 1 M NaCl solution and kept under stirring overnight; after this time, the samples were washed with deionized water. They were immersed in heavy metal solutions (10 mL) under stirring for different times. After that, the polymers were removed and the water analyzed by ICP-OES and compared with the initial solutions. The multi-ion adsorption of SPEEK was studied with a concentration of 0.15 and 0.22 mM for mercury and lead, respectively. Furthermore, the lead removal was tested in the presence of 10 mM NaCl in the solution.

The sorption of Pb²⁺ was also analyzed by gravimetry [40]. After the selected time in Pb(NO₃)₂ solution, the membrane was removed and 2 mL 0.5 M sulfuric acid



◀**Figure 1** Repeat units and ^1H NMR spectra in DMSO (d_6) of (a) SPEEK and (b) PSU-TMA.

were added. The solution was left under stirring for 2 h, and then the precipitate (lead sulfate) was filtered on a disk of ultrafiltration paper. The filtrate was rapidly washed with water and ethanol, dried, and weighed.

Kinetic measurements were performed at room temperature with a sample mass of 30 mg and a solution volume of 10 mL. Concentrations were measured by ICP-OES.

A preliminary membrane regeneration experiment was carried out using SPEEK acetone/water with two different IEC (2.16 and 1.65 meq/g). After adsorption in $\text{Pb}(\text{NO}_3)_2$ solution, the membranes were quickly washed with water, dried under P_2O_5 for 2 days and weighed. The samples were then immersed in 1 M NaCl for 48 h, washed, dried, and weighed (Table 6).

Characterization

^1H NMR spectroscopy

NMR spectra were recorded with a Bruker Avance 400 spectrometer operating at 400.13 MHz using deuterated solvents ($\text{DMSO}-d_6$).

Ion exchange capacity (IEC)

SPEEK. Acid-form membranes were immersed in 1 M NaCl solution for one day to exchange H^+ with Na^+ , and the solution was back-titrated with 0.02 M NaOH. The IEC was calculated using the dry weight of the sample and the quantity of exchanged protons. The dry weight was measured after exposition of the samples for 3 days over P_2O_5 .

PSU-TMA. The IEC was measured by Mohr titration as described in Ref. [41]. The samples in chloride form were dried over P_2O_5 for 3 days and then weighed. The Cl^- ions were exchanged with SO_4^{2-} by immersion in 1 M Na_2SO_4 solution during 24 h. The solution containing Cl^- ions was titrated using 0.02 M AgNO_3 and K_2CrO_4 as indicator.

Water uptake (WU)

The water uptake (%) was determined at 25 °C from the mass of dried sample after 24 h over P_2O_5 and

the mass of wet sample after immersion in bidistilled water for 48 h. Before weighing, the excess of water on the sample surface was carefully removed with absorbing paper.

Inductively coupled plasma–optical emission spectroscopy (ICP-OES)

Inductively coupled plasma–optical emission spectroscopy (ICP-OES, Perkin Elmer Avio 200) was employed to measure the solution concentration. The reported values of Hg^{2+} and Pb^{2+} concentrations correspond to an average of three independent measurements.

Results

The formulas and the NMR spectra of cationic and anionic membranes are reported in Fig. 1.

The yields of polymer synthesis are almost quantitative (Table 1), meaning that the process is highly efficient, and the majority of the starting materials is successfully converted into the desired polymer product.

Cation and anion exchange polymers were synthesized with a similar relatively low IEC. It is well known that an increase in ionic exchange capacity causes an increase in the water uptake (WU) [42]. While this effect is desired in electrochemical applications to enhance the phase separation within membranes and their conductivity, it could be a deterrent in water treatment applications due to the mechanical instability of the ionomer [43]. On the other hand, an increase of IEC causes an increase in the sorption capacity of IEPs. The selected IEC, around 1.60 meq/g, is a compromise between the two conflicting factors.

The results of the heavy metal ion sorption measurements are reported in Tables 2 and 3. The removal efficiency (RE) of each system is evaluated using the formula:

$$\text{RE}(\%) = \frac{c^{\circ} - c}{c^{\circ}} * 100 \quad (1)$$

where c° and c are the initial concentration, i.e., before sorption by the IEPs, and the final concentration, i.e.,

Table 2 Heavy metal removal by cation exchange polymers after 24 h

Sample	Initial concentration, mg/L (mM)	Mass of IEM, mg	RE, %	Residual metal in water, mg/L
Hg(II)				
SPEEK (DMSO)	30 (0.15)	30	98	0.7
SPEEK (acetone/water)	30 (0.15)	30	95	1.6
Pb(II)				
SPEEK (DMSO)	2237 (10.8)	30	28	1612
	1015 (4.9)	30	55	466
	207 (1.0)	30	100	0.004
	2237 (10.8)	55	53	1058
+ NaCl 10 mM	207 (1.0)	30	99	1.3
SPEEK (acetone/water)	2237 (10.8)	30	26	1649
	2237 (10.8)	84	74	588
Hg(II) + Pb(II)				
SPEEK (DMSO)	Hg 30 (0.15)	27	100	<0.001
	Pb 46 (0.22)	27	100	<0.001

Table 3 Heavy metal removal for anion exchange polymers after 24 h

Sample	Initial concentration, mg/L (mM)	Mass of IEM, mg	RE, %	Residual metal in water, mg/L
Hg(II)				
PSU-TMA (DMSO)	16.2 (0.08)	18	100	0.002
	11.0 (0.055)	18	99	0.087
	5.5 (0.027)	18	98	0.088
	1.2 (0.006)	18	92	0.096
Pb(II)				
PSU-TMA (DMSO)	208 (1.02)	20	0*	208
	217 (1.05)	30	7	201
PSU (DMAc)	2239 (10.8)	30	0*	2239
	217 (1.05)	30	0	217

*Gravimetric data

Table 4 Pb(II) ion exchange as a function of time for SPEEK membranes

Time (h)	Concentration, mg/L (mM)	RE (%)
0	1015 (4.9)	0
0.5	642 (3.1)	37
1	601 (2.9)	41
2	580 (2.8)	43
4	538 (2.6)	47
8	518 (2.5)	49
24	456 (2.2)	55

Table 5 Hg(II) ion exchange as a function of time for PSU-TMA membranes

Time (h)	Concentration, mg/L (μM)	RE (%)
0	16.2 (80)	0
1	0.731 (3.6)	95.5
2	0.009 (0.45)	99.9
4	0.005 (0.025)	100
8	0.004 (0.020)	100

after sorption by the IEPs, respectively. The concentration of Hg²⁺ was limited by the poor solubility of the mercury salt.

Table 6 Regeneration test after immersion in 10.8 mM Pb(II): m_{Pb} (sample mass after Pb sorption), m_{Na} (sample mass after exchange with NaCl)

Sample	IEC (meq/g)	Sample mass m (mg)	m_{Pb} (mg)	m_{Na} (mg)	Regeneration (%) [*]
SPEEK	2.16	76.2 ± 0.1	88.3 ± 0.1	80.2 ± 0.1	68 ± 1
SPEEK	1.65	94.0 ± 0.1	107.1 ± 0.1	98.0 ± 0.1	69 ± 1

* Regeneration: $100 \cdot (m_{Pb} - m_{Na}) / (m_{Pb} - m)$

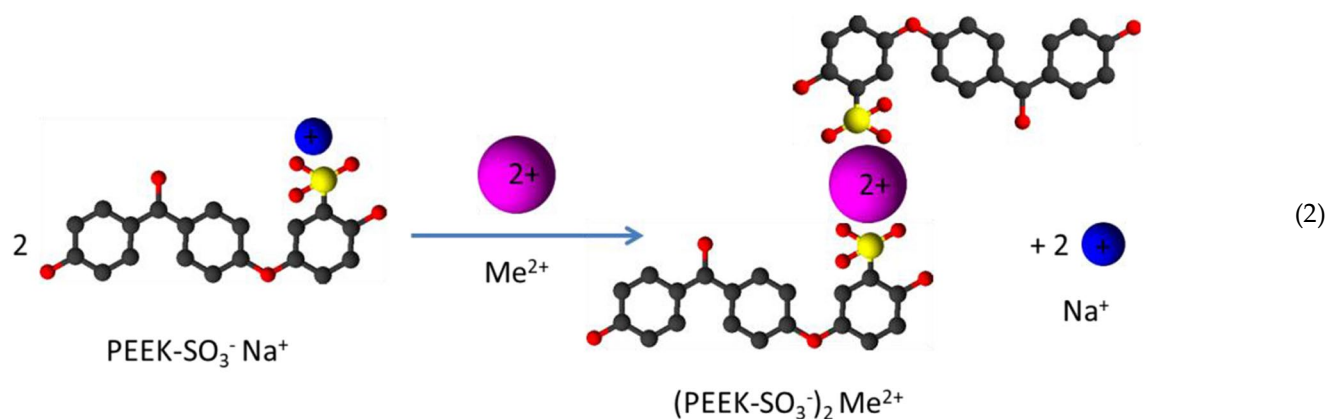
The kinetic data for lead and mercury removal by SPEEK and PSU-TMA, respectively, are reported in Tables 4 and 5.

Table 6 reports experiments on the regeneration of SPEEK membranes.

Discussion

Cation exchange polymer (CEP)

The removal of heavy metal ions by a CEP can be schematized by the following reaction:



The undesired divalent metal ion is captured by the ionomer and replaced with two safe monovalent ones. The ionic radius is an important factor for ion exchange. Considering the ionic radii of lead(II) (Pb^{2+} 133 pm) and mercury(II) (Hg^{2+} 116 pm), the exchange with smaller monovalent ions is quantitative if the IEC is sufficiently high. In the presence of NaCl in the solution, to simulate a more realistic environment, the lead removal efficiency is slightly lower, but still above 99% (Table 2).

Table 7 corroborates that when the ratio of mmol of metal cation and half mmol of SO_3^- is lower than one (see Eq. 2), the removal capacity is around 100%.

PSU without ion exchange groups is not able to remove lead as shown in Table 2, confirming that the process takes place by ion exchange.

Our multi-ion sorption experiments prove that mercury and lead in diluted solution (0.15 and 0.22 mM for Hg and Pb, respectively) can be totally removed by SPEEK.

The reusability and regeneration of IEPs is a complex and critical aspect involving sorption/desorption processes [44–46]. Preliminary regeneration tests were carried out using a simple desorption process with a NaCl solution. The results indicate a recovery of approximately 70%. The incomplete recovery might

be attributed to the ionic crosslink that immobilizes divalent metal ions which cannot occur with monovalent Na ions. Further studies are needed to understand

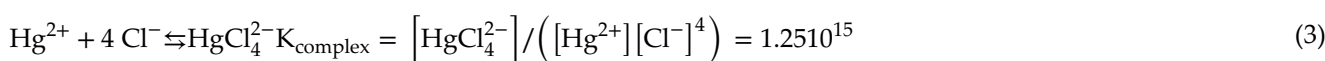
Table 7 Ratio between mmol of SO_3^- (for 30 mg of SPEEK with IEC = 1.65 meq/g) and mmol of heavy metal cations for different salt concentrations

SPEEK (DMSO)	mM	mmol $\text{M}^{2+} / 0.5$ mmol SO_3^-	RE, %
Hg(II)	0.15	0.06	98
Pb(II)	10.8	4.34	28
	4.9	1.96	55
	1.0	0.40	100

the regeneration mechanism in more detail, e.g., by studying the desorption process with different agents, concentrations, temperatures, and durations.

Anion exchange polymer (AEP)

The quantitative removal of mercury ions by an AEP is surprising at first sight (Tables 3 and 5). In reality, the affinity of Hg^{2+} for the formation of $HgCl_4^{2-}$ complexes is very high. The equilibrium constant for mercury cation complexation by Cl^- can be established from the literature [47].



The chloride ions in the solution are provided by ion exchange of the chloride form AEP with nitrate ions; the chloride concentration in solution can be calculated from the mass m of the AEP and its ion exchange capacity IEC according to the equation:

$$[Cl^-] = \frac{IEC \cdot m}{V} = 1.6 \frac{mmol}{g} \cdot 0.03g/0.01L = 4.8mmol/L \quad (4)$$

At all used mercury concentrations ($[Hg^{2+}] < 0.15$ mmol/L), one can deduce from the equilibrium constant (Eq. 3) that the mercury ions are quantitatively transformed into $[HgCl_4^{2-}]$. These complex anions can then be captured by the AEP and removed quantitatively. Given the used volume of solution $V = 0.01$ L, the amount of mercury is below $1.5 \mu mol$, much lower than the amount of available ion exchange sites of $48 \mu mol$ in 0.03 g AEP.

In the case of lead ions, the complexation constant of $[PbCl_3]^-$ is much lower, reported to be around 10^6 [48]. Accordingly, the lead removal by the AEP is very low (Table 3).

Lead ion sorption by SPEEK: Langmuir-type isotherm

The sorption capacity of IEPs can be written as:

$$Q = (c^\circ - c) \cdot \frac{V}{m} \quad (5)$$

Here, c° is the initial cation concentration and c the concentration after sorption. V is the volume of treated solution and m the mass of IEP.

The Langmuir adsorption isotherm describes the relation of the surface coverage Θ with the adsorption equilibrium constant $K_{ads}(T)$ at temperature T and the thermodynamic activity of the adsorbate. In the case of very diluted solutions, the cation activity can be expressed by the equilibrium concentration c . The interfaces between hydrated channels and polymer domains that contain the ionic groups are considered as internal surfaces of the IEP. The surface coverage Θ can then be expressed as the ratio

of the sorption capacity Q and the maximum sorption capacity Q_{max} , giving the Langmuir adsorption isotherm:

$$\frac{Q}{Q_{max}} = \theta = \frac{K_{ads}(T) \cdot c}{1 + K_{ads}(T) \cdot c} \quad (6)$$

This equation can be transformed to give a linear relation between c/Q and the equilibrium cation concentration c :

$$\frac{c}{Q} = \frac{c}{Q_{max}} + \frac{1}{Q_{max}K_{ads}(T)} \quad (7)$$

A plot of the experimental data according to Eq. 7 is shown in Fig. 2.

The experimental data for lead ion removal by SPEEK are in excellent agreement with the Langmuir adsorption isotherm.

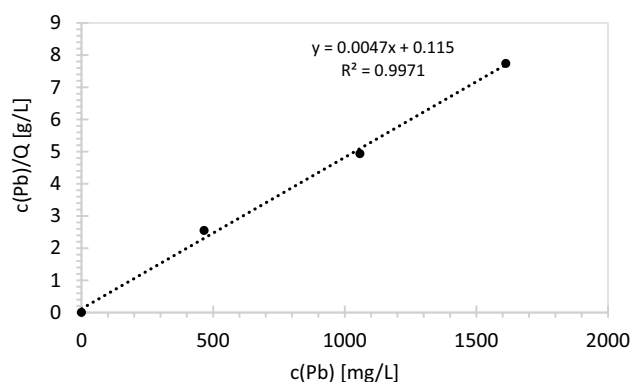


Figure 2 Langmuir adsorption plot according to Eq. 7 for the case of lead ion removal by SPEEK with data from Table 2.

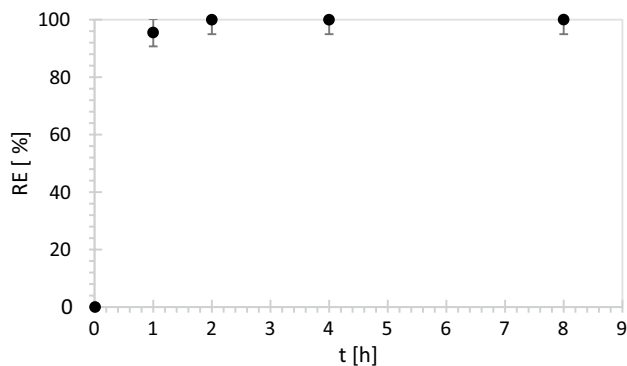


Figure 3 Time dependence of removal efficiency for mercury ions of PSU-TMA anion exchange polymer.

From the slope and ordinate of the straight line, values of $Q_{\max} = 210$ mg/g and $K_{\text{ads}}(T) = 0.04$ can be determined. In the literature it is possible to find very different maximum adsorption capacity values depending on the removal system used; focusing on the ion exchange method, the values range from 30 mg/g for Pb^{2+} and Hg^{2+} , using zeolite as active material [21], to 300 mg/g for Pb^{2+} using stratified silicate [49]. One can conclude that the Langmuir adsorption theory provides a good base for the description of the cation removal by IEPs.

Lead ion sorption kinetics by SPEEK: pseudo-second-order law

The kinetic data of mercury sorption on PSU-TMA are shown in Fig. 3.

Figure 4 shows the kinetics for the case of lead with SPEEK.

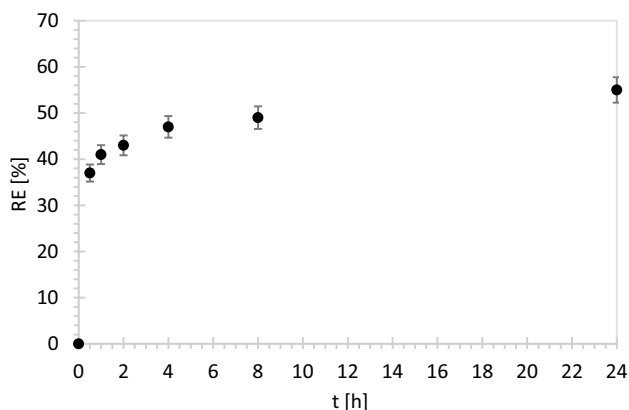


Figure 4 Time dependence of removal efficiency for lead ions of SPEEK cation exchange polymer.

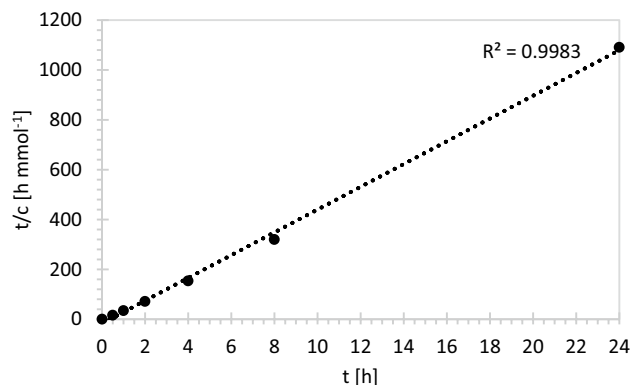


Figure 5 Second-order kinetic plot of lead concentration vs time.

The sorption kinetics can be described by a pseudo-second-order law:

$$\frac{dc}{dt} = k_2(c^\circ - c)^2 \quad (8)$$

k_2 is the second-order kinetic constant and c° is the initial concentration. One obtains after integration:

$$\frac{1}{c^\circ - c} = \frac{1}{c^\circ} + k_2 t \quad (9)$$

This equation can be rearranged into:

$$\frac{t}{c} = \frac{1}{k_2 c^\circ^2} + \frac{t}{c^\circ} \quad (10)$$

The plot of t/c as function of t for lead ion sorption by SPEEK (Fig. 5) provides an excellent description of the experimental data. This pseudo-second-order kinetic law can be interpreted by a similar change of the metal concentration in solution and the concentration of available ionic sites in the IEP. The quantity of lead ions (Table 4) and of ionic sites (about 0.045 mmol) is indeed quite comparable, so that the variation of $(c^\circ - c)$ is similar for both and a square law can be written.

Altogether, the kinetic and equilibrium data are in good agreement with a mechanism by adsorption of metal cations or complex metal anions on CEP or AEP, respectively.

Conclusions

The removal of toxic heavy metal ions is fundamental for water purification. Ion exchange polymers are very effective for this purpose, as shown in this study for mercury and lead. A classic cation exchange polymer (CEP), sulfonated poly(ether ether ketone) (SPEEK), shows a very good removal efficiency. The maximum sorption capacity (Q_{\max}) is related to the IEC; its value is around 210 mg/g for lead with SPEEK. If the ratio between the concentration of bivalent metal ions in solution and sulfonate ions in the membrane is above 0.5, the removal is not quantitative.

Interestingly, a typical anion exchange polymer (AEP), poly(sulfone trimethylammonium) chloride (PSU-TMA), can also be used for Hg^{2+} removal in apparent contradiction with the Donnan effect. This process is related to the formation of very stable complex anions in solution, such as HgCl_4^{2-} . The complex anions can be captured quantitatively by AEPs.

The removal process can be described by Langmuir adsorption theory. For IEPs the adsorption can occur not only at the outer surface but also at internal surfaces along nanometric hydrated ionic channels. The kinetics of lead sorption by SPEEK can be well represented by a second-order law due to similar concentrations of metal ions in solution and ionic groups in the IEPs.

Acknowledgements

Not Applicable. This research was funded by Regione Lazio (Italy) by “Gruppi di ricerca 2020” –POR FESR (Regional Operational Programs financed with the European Regional Development Fund) Lazio 2014–2020 for the project FACS (Filtraggio di acque contaminate tramite sistemi nano strutturati, Grant Agreement: A0375-2020-36521, Codice Unico di Progetto, CUP: E85F21002440002).

Author contributions

ES performed investigation, data curation, formal analysis, and visualization. CR, LB, and FSGG performed investigation and data curation. P.P. contributed to investigation, data curation, and project administration. PK contributed to conceptualization

and writing—review and editing. MLDV contributed to conceptualization, supervision, and writing—review and editing.

Funding

Open access funding provided by Università degli Studi di Roma Tor Vergata within the CRUI-CARE Agreement.

Data and code availability

Not applicable.

Declarations

Conflicts of interest The authors declare no conflicts of interest or competing interests.

Ethical approval Not applicable.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- [1] Kreuer K, Paddison S, Spohr E, Schuster M (2004) Transport in proton conductors for fuel-cell applications:

- simulations, elementary reactions, and phenomenology. *Chem Rev* 104:4637–4678
- [2] Paddison SJ (2003) Proton conduction mechanisms at low degrees of hydration in sulfonic acid-based polymer electrolyte membranes. *Annu Rev Mater Res* 33:289–319
- [3] Hickner MA (2010) Ion-containing polymers: new energy & clean water. *Mater Today* 13:34–41
- [4] Xu TW (2005) Ion exchange membranes: state of their development and perspective. *J Membr Sci* 263:1–29
- [5] Matindi CN, Hu M, Kadanyo S, Ly QV, Gumbi NN, Dlamini DS, Li J, Hu Y, Cui Z, Li J (2021) Tailoring the morphology of polyethersulfone/sulfonated polysulfone ultrafiltration membranes for highly efficient separation of oil-in-water emulsions using TiO₂ nanoparticles. *J Membr Sci* 620:118868
- [6] Narducci R, Di Vona ML, Knauth P (2014) Cation-conducting ionomers made by ion exchange of sulfonated poly-ether-ether-ketone: Hydration, mechanical and thermal properties and ionic conductivity. *J Membr Sci* 465:185–192
- [7] Nekouei RK, Pahlevani F, Assefi M, Maroufi S, Sahajwalla V (2019) Selective isolation of heavy metals from spent electronic waste solution by macroporous ion-exchange resins. *J Hazard Mater* 371:389–396
- [8] Chen YG, Sofinska-Chmiel W, Lv GY, Kolodynska D, Chen SH (2021) Application of modern research methods for the physicochemical characterization of ion exchangers. *Materials* 14:7067
- [9] Qasem NAA, Mohammed RH, Lawal DU (2021) Removal of heavy metal ions from wastewater: a comprehensive and critical review. *npj Clean Water* 4:36
- [10] Joseph L, Jun B-M, Flora JRV, Park CM, Yoon Y (2019) Removal of heavy metals from water sources in the developing world using low-cost materials: a review. *Chemosphere* 229:142–159
- [11] Burratti L, Zannotti M, Maranges V, Giovannetti R, Duranti L, De Matteis F, Francini R, Proposito P (2023) Poly(ethylene glycol)diacrylate hydrogel with silver nanoclusters for water Pb(II) ions filtering. *Gels* 9:133
- [12] Briffa J, Sinagra E, Blundell R (2020) Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon* 6:e04691
- [13] WHO (2022) Guidelines for drinking-water quality: fourth edition incorporating the first and second addenda. ISBN: 978-92-4-004506-4
- [14] Alosaimi AM (2021) polysulfone membranes based hybrid nanocomposites for the adsorptive removal of Hg(II) ions. *Polymers* 13:2792
- [15] Nayak MC et al (2020) Polyphenylsulfone/multiwalled carbon nanotubes mixed ultrafiltration membranes: fabrication, characterization and removal of heavy metals Pb²⁺, Hg²⁺, and Cd²⁺ from aqueous solutions. *Arab J Chem* 13:4661–4672
- [16] Chen H, Wu H, Wang QW, Ji L, Zhang TT, Yang HM (2019) Separation performance of Hg²⁺ in desulfurization wastewater by the graphene oxide polyethersulfone membrane. *Energy Fuels* 33:9241–9248
- [17] Santiago AA, Ibarra-Palos A, Cruz-Morales JA, Sierra JM, Abatal M, Alfonso I, Vargas J (2018) Synthesis, characterization, and heavy metal adsorption properties of sulfonated aromatic polyamides. *High Perform Polym* 30:591–601
- [18] Vinodh R, Padmavathi R, Sangeetha D (2011) Separation of heavy metals from water samples using anion exchange polymers by adsorption process. *Desalination* 267:267–276
- [19] Zhao JH, Yuan WZ, Xu AH, Ai F, Lu YW, Zhang YM (2011) Perfluorinated sulfonic acid ionomer/poly(N-vinylpyrrolidone) nanofiber membranes: Electrospinning fabrication, water stability, and metal ion removal applications. *React Funct Polym* 71:1102–1109
- [20] Dutta K, De S (2017) Aromatic conjugated polymers for removal of heavy metal ions from wastewater: a short review. *Environ Sci Water Res Technol* 3:793–805
- [21] Dbrowski A, Hubicki Z, Podkościelny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere* 56:91–106
- [22] Lofrano G, Carotenuto M, Libralato G, Domingos RF, Markus A, Dini L, Gautam RK, Baldantoni D, Rossi M, Sharma SK, Chattopadhyaya MC, Giugni M, MERIC S (2016) Polymer functionalized nanocomposites for metals removal from water and wastewater: an overview. *Water Res* 92:22–37
- [23] Cumbal L, SenGupta AK (2005) arsenic removal using polymer-supported hydrated Iron(III) oxide nanoparticles: role of donnan membrane effect. *Environ Sci Technol* 39:6508–6515
- [24] Okur HI, Hladílková J, Rembert KB, Cho Y, Heyda J, Dzubielia J, Cremer PS, Jungwirth P (2017) Beyond the Hofmeister series: ion-specific effects on proteins and their biological functions. *J Phys Chem B* 121:1997–2014
- [25] Vo TS, Hossain MM, Jeong HM, Kim K (2020) Heavy metal removal applications using adsorptive membranes. *Nano Conver* 7:1–26
- [26] Musarurwa H, TawandaTavengwa N (2022) Recent progress in the application of pH-responsive polymers in separation science. *Microchem J* 179:107503
- [27] Sgreccia E, Pasquini L, Ercolani G, Knauth P, Di Vona ML (2019) Stimuli-responsive amphoteric ion exchange polymers bearing carboxylic and amine groups grafted to a cross-linkable silica network. *Eur Polym J* 112:255–262

- [28] Luo T, Abdu S, Wessling M (2018) Selectivity of ion exchange membranes: A review. *J Membr Sci* 555:429–454
- [29] Shukla D, Negi YS, SenUppadhyaya J, Kumar V (2012) Synthesis and modification of poly(ether ether ketone) and their properties: a review. *Polym Rev* 52:189–228
- [30] Hizal J, Kanmaz N, Yilmazoglu M (2021) Adsorption efficiency of sulfonated poly (ether ether ketone) (sPEEK) as a novel low-cost polymeric adsorbent for cationic organic dyes removal from aqueous solution. *J Mol Liq* 322:114761
- [31] Arthanareeswaran G, Thanikaivelan P, Jaya N, Mohan D, Raajenthiren M (2007) Removal of chromium from aqueous sulfonated poly(ether ether ketone) solution using cellulose acetate and blend ultrafiltration membranes. *J Hazard Mater* 139:44–49
- [32] Yilmazoglu M, Hizal J (2023) Highly efficient sulfonated poly (ether ether ketone) (sPEEK) adsorbent for removal of uranium (VI) from aqueous solution. *Process Saf Environ Prot* 174:848–855
- [33] Rajput A, Raj SK, Sharma J, Rathod NH, Maru PD, Kulshrestha V (2021) Sulfonated poly ether ether ketone (SPEEK) based composite cation exchange membranes for salt removal from brackish water. *Colloids Surf Physicochem Eng Asp* 614:126157
- [34] Cimbru AM, Rikabi A, Oprea O, Grosu AR, Tanczos SK, Simonescu MC, Pascu D, Grosu VA, Dumitru F, Nechifor G (2022) pH and pCl operational parameters in some metallic ions separation with composite chitosan/sulfonated polyether ether ketone/polypropylene hollow fibers membranes. *Membranes* 12:833
- [35] Arthanareeswaran G, Thanikaivelan P (2012) Transport of copper, nickel and zinc ions across ultrafiltration membrane based on modified polysulfone and cellulose acetate. *Asia-Pac J Chem Eng* 7:131–139
- [36] Bekchanov D, Mukhamediev M, Lieberzeit P, Babonova G, Botirov S (2021) Polyvinylchloride-based anion exchanger for efficient removal of chromium (VI) from aqueous solutions. *Polym Adv Technol* 32:3995–4004
- [37] Knauth P, Di Vona ML (2012) Sulfonated aromatic ionomers: analysis of proton conductivity and proton mobility. *Solid State Ionics* 225:255–259
- [38] Knauth P, Pasquini L, Narducci R, Sgreccia E, Becerra-Arciniegas RA, Di Vona ML (2021) Effective ion mobility in anion exchange ionomers: relations with hydration, porosity, tortuosity, and percolation. *J Membr Sci* 617:118622
- [39] Di Vona ML, Narducci R, Pasquini L, Pelzer K, Knauth P (2014) Anion-conducting ionomers: study of type of functionalizing amine and macromolecular cross-linking. *Int J Hydrogen Energy* 39:14039–14049
- [40] Erdey L (2013) Gravimetric analysis: international series of monographs on analytical chemistry, vol 7. Elsevier, Amsterdam
- [41] Becerra-Arciniegas RA, Narducci R, Ercolani G, Sgreccia E, Pasquini L, Di Vona ML, Knauth P (2020) Model long side-chain PPO-based anion exchange ionomers: properties and alkaline stability. *J Phys Chem C* 124:1309–1316
- [42] Wang XH, McClure JP, Fedkiw PS (2012) Transport properties of proton- and hydroxide-exchange membranes for fuel cells. *Electrochim Acta* 79:126–132
- [43] Banerjee S, Kar KK (2017) Impact of degree of sulfonation on microstructure, thermal, thermomechanical and physicochemical properties of sulfonated poly ether ether ketone. *Polymer* 109:176–186
- [44] Gohari RJ, Lau WJ, Matsuura T, Halakoo E, Ismail AF (2013) Adsorptive removal of Pb(II) from aqueous solution by novel PES/HMO ultrafiltration mixed matrix membrane. *Sep Purif Technol* 120:59–68
- [45] DuChanois RM, Cooper NJ, Lee B, Patel SK, Mazurowski L, Graedel TE, Elimelech M (2023) Prospects of metal recovery from wastewater and brine. *Nature Water* 1:37–46
- [46] Gherasim CV, Bourceanu G, Timpu D (2011) Experimental and modeling studies of lead (II) sorption onto a polyvinylchloride inclusion membrane. *Chem Eng J* 172:817–827
- [47] Liang RN, Wang QW, Qin W (2015) Highly sensitive potentiometric sensor for detection of mercury in Cl-rich samples. *Sens Actuators B Chem* 208:267–272
- [48] Luo Y, Millero FJ (2007) Stability constants for the formation of lead chloride complexes as a function of temperature and ionic strength. *Geochim Cosmochim Acta* 71:326–334
- [49] Chen Z, Liang Y, Jia D, Chen W, Cui Z, Wang X (2017) Layered silicate RUB-15 for efficient removal of UO₂²⁺ and heavy metal ions by ion-exchange. *Environ Sci Nano* 4:1851–1858

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.