Rhenium(VII) and technetium(VII) separation from aqueous solutions using a polyethylenimine–epichlorohydrin resin

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Abstract The ReO_4 and $^{99}TcO_4$ removal from aqueous solutions using a polyethylenimine–epichlorohydrin resin was investigated in absence and presence of background electrolyte (0.01 and 0.50 M NaCl). Re(VII) and Tc(VII) sorption isotherms were obtained for solutions with $2.3 \leq pH \leq 8.9$ and concentration 0.21–26.9 mmol Re/L and $5 \times 10^{-3} - 5 \times 10^{-2}$ mmol ^{99}Tc/L. The highest uptake for both elements ($R_d \approx 10^4$ mL/g) was observed for solutions with $pH \leq 4$ and $C_{NaCl} \leq 0.01$ M, hinting towards the existence of protonated groups contributing to the sorption of anions under acidic conditions and to the competition of Cl^-. The sorption data were modeled using the Langmuir and Freundlich equations.

Introduction

Rhenium (Re) is one of the rarest elements in Earth's crust with an average concentration of less than 1 ng/g. The natural occurrence of rhenium is still uncertain, but it is found in small concentrations (up to 0.2 %) in the mineral molybdenite (MoS_2). Rhenium appears in a wide variety of oxidation states (from $-I$ to $+VII$) and its chemistry resembles this of manganese and technetium. For this reason, it is very frequently used as chemical analogue for the study of the behavior of the β-emitting radioactive technetium-99 isotope (^{99}Tc, $T_{1/2} = 2.13 \times 10^5$ years). Rhenium appears under oxidizing and anoxic conditions in the form of perrhenate ion ($Re^{VII}O_4$), whereas several oxidation states ($-I$ to $+IV$) exist under reducing conditions [1].

^{99}Tc is a fission product of ^{235}U and ^{239}Pu formed during the operation of nuclear reactors (fission yield: 6.161 and 6.205 %, respectively). Although the radiotoxicity of ^{99}Tc is relatively low, it is a radionuclide of environmental concern due to its very long half-life and redox-sensitive character. ^{99}Tc shows high solubility and low sorption potential ($K_d < 1$ mL/g) under oxidizing and sub-oxic conditions [2, 3]. The oxidized form of ^{99}Tc (pertechnetate anion, TcO_4^-) migrates in the subsurface at nearly the same velocity as groundwater. In reducing environments, pertechnetate is reduced to Tc(IV) yielding the sparingly soluble $TcO_2 \cdot nH_2O$ solid ($[Tc]_{aq} \sim 10^{-8.2}$ M at $3 \leq pH \leq 11$) [4–6]. The heterogeneous surface-mediated reduction reaction has been reported to occur significantly faster than the homogenous one [7, 8].

A number of raw and modified natural [9–16] as well as synthetic materials [17–29] have already been investigated as technetium and rhenium sorbents and extractants from aqueous solutions. Biomaterials and modified biomaterials were also studied for the removal of Re(VII) from waters [30–32].

An especially interesting family of materials used for the separation of rhenium and technetium are those containing amino groups (e.g., [15, 31, 32]). These groups can both chelate cationic and adsorb anionic metal species through electrostatic interactions or hydrogen bonding (e.g., [33,

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34]). In this context, polyethylenimine arises as an attractive material possessing a large number of ternary and quaternary amine groups. Among other applications, this polymer has been studied as modifier of lignin-based anion sorbents for the separation of Re(VII) [31].

In this work, the uptake of Re(VII) and Tc(VII) from aqueous solutions by a polyethylenimine–epichlorohydrin (PEI) resin was investigated as a function of initial metal concentration, pH and concentration of background electrolyte (NaCl). The results are systematized in the form of sorption isotherms (Langmuir and Freundlich) in order to assess the analogies between Re(VII) and Tc(VII) and the possible use of PEI resin for the removal of the highly mobile ^{99}Tc from aqueous solutions. Special efforts were also dedicated to the appropriate characterization of the resin.

Experimental part

Preparation and characterization of the resin

A polyethylenimine–epichlorohydrin resin was prepared using a high molecular weight polyethylenimine (M.W. $\sim$25,000, Sigma-Aldrich, Fig. 1) according to a modification of a previously described synthesis method [35]. The main modifications of the resin synthesis consisted in the selection of a lower preparation temperature (60 °C) and the use of another surfactant (in our case IGEPAL BC/6, nonylphenol ethoxylate, supplied by Rhodia).

The resin was characterized by different techniques before testing its Re(VII) and Tc(VII) sorption ability. The water content of the resin was determined after equilibration of a precisely weighted amount in a constant humidity chamber for 30 days over a saturated aqueous solution of $Ca(NO_3)_2$ (relative humidity at 25 °C: 55 % [36]) and subsequent heating at 110 °C to constant weight.

In order to examine the influence of the pH on the resin, the latter was treated with aqueous solutions of pH 2–10, embedded in an epoxy resin, cut and carefully polished. The inside of the particle sections was then examined by
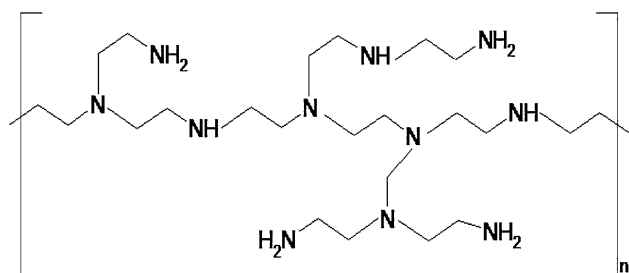
Fig. 1 Chemical formula of the high-molecular weight polyethylenimine used in this work for the synthesis of the PEI resin

scanning electron microscopy (SEM) using a JEOL 840A SEM (acceleration voltage: 20 kV) equipped with an OXFORD ISIS 300 energy dispersive spectroscopy (EDS) analyzer. Additionally, 156.5 mg of the resin were added to 50 mL of water, and the suspension sequentially titrated with 0.05 M NaOH and 0.1 M HCl to assess the reversibility of the alkali-based processes affecting the resin.

The crystallinity of the resin was examined by X-ray diffraction (XRD) using a Philips PW 1710 diffractometer with Ni-filtered CuK_α radiation (scanning region $3 \leq 2\theta \leq 63°$, scanning rate 1.2°/min). The morphology was complementary evaluated by SEM. The particle size distribution of the resin was determined using the SEM images and the program UTHSCSA Image Tool 3.00.

The thermal stability of the resin was evaluated by thermogravimetric analysis (TG) using a thermo-balance SETSYS 1618 TG–DTA by SETARAM in N_2 atmosphere. The temperature range considered was 20–500 °C and the heating rate 10 °C/min.

The specific surface area of the resin was determined using an automatic volumetric sorption analyzer (Autosorb-1MP by Quantachrome Instruments). The pretreatment was performed at 80–90 °C for 6 h under vacuum $5 \cdot 10^{-9}$ Torr and the adsorption/desorption of nitrogen at liquid nitrogen temperature.

The N- and O-functional groups in the resin were investigated using X-ray photoelectron spectroscopy (XPS) using a PHI 5600ci equipment (Physical Electronics). The C 1s (C_xH_y) signal at 284.8 ± 0.15 eV binding energy was taken as charge reference for the measurements.

pH measurements

The hydrogen ion concentration ($pH_c = -\log[H^+]$) was measured using combination pH electrodes (Re: Metrohm; Tc: type ROSS, Orion) calibrated against standard pH buffers (pH 1–12, Merck). The values of $pH_c = pH_{exp} + A_c$ were calculated from the operational "measured" pH_{exp} using empirical correlation factors (A_c), which include both the liquid junction potential and the activity coefficient of H^+. A_c values determined as a function of NaCl and $MgCl_2$ concentration are reported in the literature [37]. In the case of 0.5 M NaCl, $A_c = -0.01$. For samples at lower ionic strength, the measured electrode potential directly related to a thermodynamically meaningful pH value.

Rhenium(VII) sorption experiments

All Re-sorption experiments were performed at room temperature. 30 mg of the resin were contacted in polypropylene tubes for 24 h with 10 mL of rhenium solutions of initial concentration (C_{init}) 0.2–26.9 mmol Re/L. No pH

buffers were used for these tests. The pH before contacting the resin was adjusted to 3 and 7 with HCl and NaOH. The rhenium solutions were prepared by dilution of an NH_4 ReO_4 stock solution (Aldrich, 99+ %) with bi-distilled water. After separation of the solid and liquid phases by centrifugation, the pH was measured and the rhenium concentration in the liquid phase was photometrically determined using the hydrochloric hydroxylamine method at 300 nm [38]. After the completion of this series of sorption experiments, the surface and the interior of the resin particles were also examined by SEM.

In a second series of sorption tests, the Re(VII) uptake by the PEI resin was investigated in the presence of increasing concentrations of background electrolyte (0, 0.01 and 0.50 M NaCl). 50 mg of the resin were contacted in polypropylene tubes for 24 h with 9 mL of tri(hydroxylmethyl)-aminomethane–buffered solution (TRIZMA, Sigma-Aldrich) at pH 9. To this suspension, 1 mL of Re solution of the appropriate concentration was added aiming at concentrations of 0.2–8.6 mmol Re/L. The system was left to equilibrate for 24 h, and the solid and liquid phases were separated by centrifugation. The pH of the supernatant solution was measured and the rhenium concentration in the liquid phase was photometrically determined using the method described above.

The Re uptake (mmol/L) was calculated from the data obtained. Further, these data were used to derive the corresponding sorption isotherms. Sorption coefficients (R_d) in each of the individual samples were calculated as $R_d = [Re]_s/[Re]_{aq}$.

Regeneration of the Re-loaded resin

The regeneration of the resin was investigated in two series of sequential experiments. In the first one, 30 mg of the Re-loaded resin were treated for 24 h with 10 mL of 0.033 M Na_2SO_4 solution at pH 6. After this resin depletion, the rhenium released in the liquid phase was determined using the hydrochloric hydroxylamine method. The resin was rinsed with bi-distilled water and further contacted with 10 mL of an non-buffered 26.9 mmol Re/L solution of pH 3. After 24 h contact time, the amount of rhenium remaining in the aqueous phase was photometrically determined.

In the second experiment, 30 mg of the Re-loaded resin treated with 0.033 M Na_2SO_4 solution were additionally contacted for 24 h with 10 mL of 0.10 M NaCl solution with the aim of exchanging the strongly bound sulfate by the weakly bound chloride ions. The pH of Na_2SO_4 and NaCl solution was ca. 6. The solid phase was then used for a second Re-uptake test using the same approach as described above.

Technetium(VII) sorption experiments

The technetium experiments were performed at the controlled area of KIT–INE under inert gas (Ar) atmosphere (glove-box) at 22 ± 2 °C. A purified and radiochemically well-characterized ^{99}Tc stock solution (1.30 M $Na^{99}TcO_4$) was used for the experiments. 50 mg of the PEI resin were contacted for 60 h with 50 mL of a solution 0.50 M NaCl and 5 mmol ^{99}Tc/L. The pH of the aqueous solution was initially adjusted to 3–11 with HCl and NaOH, but no pH buffers were used. The pH in the sample solutions were measured again after equilibration with the resin. The measurement of the ^{99}Tc concentration was performed by liquid scintillation counting (Wallac, Perkin-Elmer QUANTULUS).

Sorption isotherms were obtained with solutions containing 5×10^{-2}, 1×10^{-2} and 5×10^{-3} mmol ^{99}Tc/L and increasing concentration of background electrolyte (0, 0.01 and 0.50 M NaCl). A series of samples were prepared without any pH buffer, whereas the pH of a second series was fixed at 8.9 using 0.05 M 2-(cyclo-hexylamino)ethanesulfonic acid) buffer (CHES, Sigma-Aldrich).

Results

Characterization of the resin

The water content of the PEI resin equilibrated at constant humidity for 30 days was 18.5 %. This value can be directly related to the open porosity of the resin. The addition of 30 mg of the PEI resin into 10 mL of aqueous solutions of pH 2–10 for 24 h caused a shift of the pH to values between 2.5 and 5, reflecting a certain buffering capacity of the functional groups in the resin.

The titration (0.05 M NaOH) and backtitration (0.1 M HCl) curves of the resin are shown in Fig. 2. The shape of the titration curve with 0.05 M NaOH indicates the presence of a number of functional groups potentially contributing to the sorption of anionic species. In contrast to the titration with 0.05 M NaOH, the backtitration with 0.1 M HCl shows one single equivalent point at pH ~ 8, hinting at a non-reversible behavior of the resin.

The XPS analysis of the resin shows N 1s binding energies at 399.2 and 401.4 eV (Fig. 3), indicating the existence of both ternary and quaternary amino-groups with a ratio 45 ± 5 % to 55 ± 5 %. The predominance of these groups in the investigated resin could explain the anion-sorption properties of the material. In principle, quaternary amine groups can exchange anions in a very large pH range due to their permanent positive charge, whereas ternary amines can only exchange anions in the pH-range where they are protonated.

Fig. 2 Titration of 156.5 mg of resin in 50 mL of water with 0.05 M NaOH and 0.1 M HCl
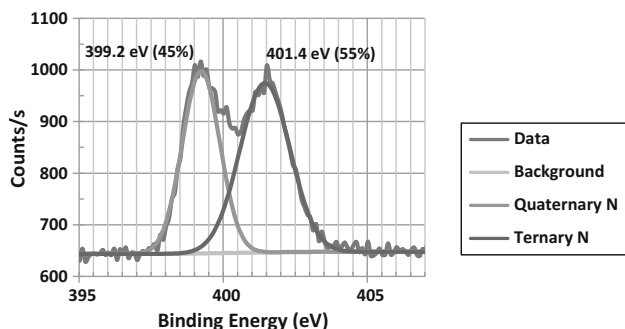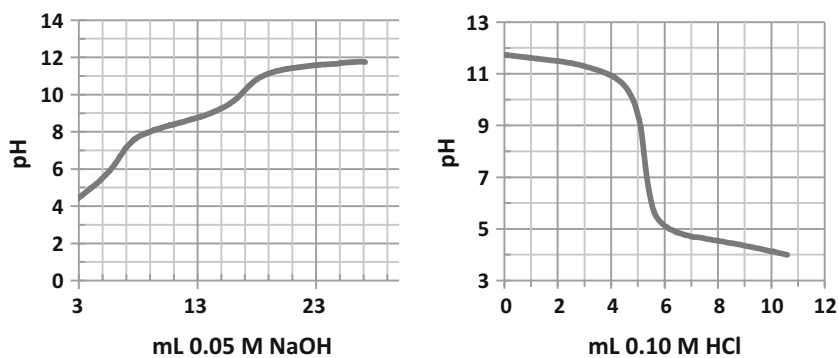
Fig. 3 Quaternary and ternary nitrogen contribution to the N1s X-ray photoelectron spectrum of the PEI resin

The presence of oxygen assigned to hydroxyl-groups (O 1s binding energy: 532.6 eV), chlorine (Cl $2p_{3/2}$ binding energies: 197.4 eV (86 %) and 198.6 eV (14 %)) and a small number of COO^--groups (C 1s binding energy: 287.5 eV ca. 8 %) were also observed in the X-ray photoelectron spectrum of the resin. These observations highlight the variability of functionalities available in the resin, and the capacity of adsorbing a certain amount of cationic species provided by the carboxylate groups.

Microphotographs of the resin taken before the Re/Tc sorption are presented in Fig. 4. These microphotographs show that the resin particles do not have a uniform size. It can also be observed that the particles do not show an entirely compact structure and have a porous interior. SEM

pictures were also used to assess the particle size distribution, which resulted in an average particle size of 80 ± 5 μm. No significant morphological changes were observed during the exposure of the resin to acidic and alkaline solutions (pH 2–10). The XRD characterization of the resin did not show any well-defined pattern, thus reflecting the amorphous character of the resin (data not shown).

The TG shows a weight loss around 100 °C, which is attributed to the water content of the resin (data not shown). The resin remains stable up to 180–200 °C, where its decomposition begins. The specific surface area of the resin as quantified by BET is 0.410 m^2/g. The resin appears to be macroporous and therefore the calculation of the pore size distribution by the above mentioned method is not possible.

The examination of sections of the Re-loaded resin particles by SEM/EDS revealed that rhenium was evenly distributed throughout the bulk of the resin and not only bound to their external surface (Fig. 5). This observation indicates that the interior of the resin particles and not only their external surface is contacted by the Re-solution and thus active in the process of Re uptake.

Sorption of Re(VII)

The evolution of pH_{equil} as a function of the Re concentration in non-buffered solutions with initial pH 3 and 7 is
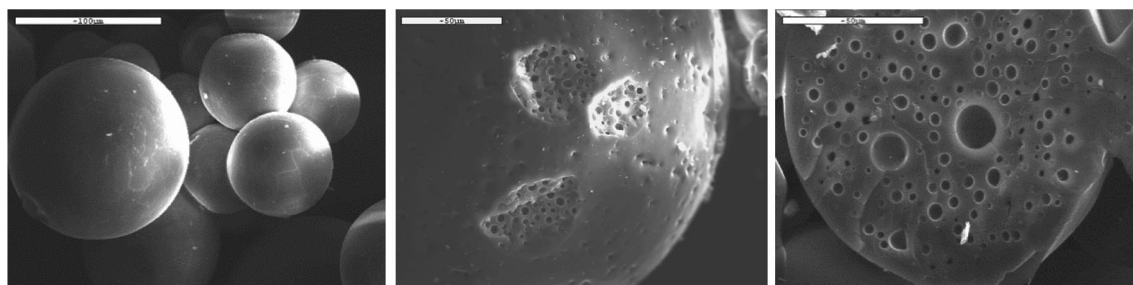
Fig. 4 SEM microphotographs of the resin before the interaction with the Re(VII)/Tc(VII) solutions

Fig. 5 SEM image of a section of the resin after rhenium uptake (*left*) and the corresponding rhenium mapping of the same particle using the Re L_{a1} X-rays (*right*)

Electron Image 1

Re La1
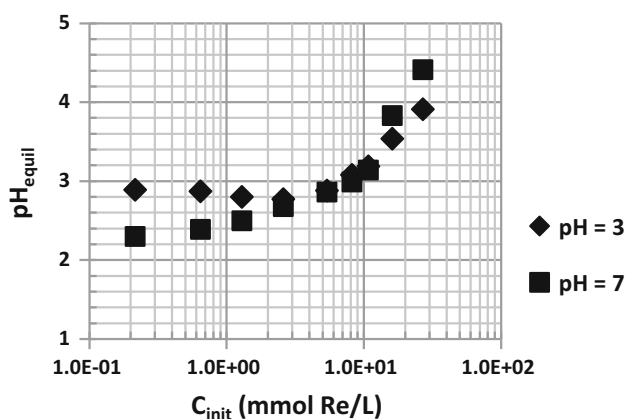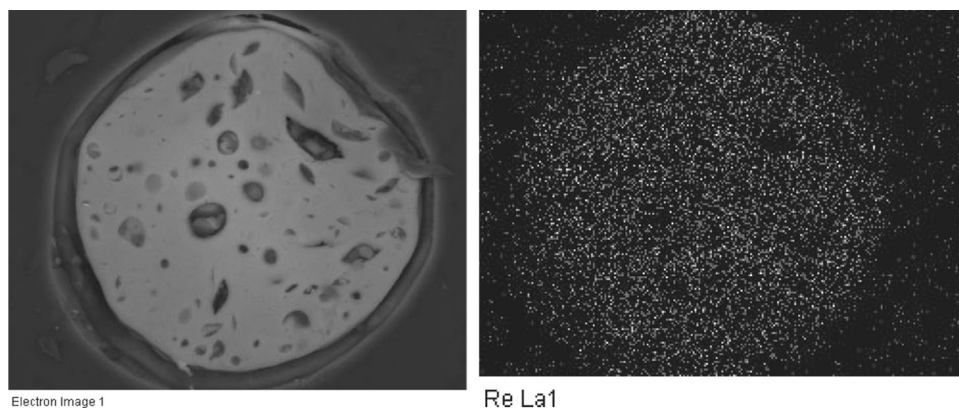
Fig. 6 Equilibrium pH of non-buffered Re solutions of initial pH 3 and 7 after a contact time of 24 h with the PEI resin

given in Fig. 6. This figure shows that the pH_{equil} increases with increasing Re loading, following a very similar pattern independent of the initial pH.

The uptake of Re(VII) by the resin in non-buffered and buffered (TRIZMA, pH 8.6) solutions with increasing concentrations of background electrolyte (0, 0.01, 0.50 M NaCl) is shown in Fig. 7a, b as sorption isotherms and sorption coefficient (R_d) values, respectively. Due to the similar uptake and R_d values observed in the experiments with initial pH 3 ($pH_{equil} = 2.9$–3.9) and pH 7 ($pH_{equil} = 2.3$–4.4), only the latter are used in the following discussion.

Figure 7 shows that the investigated resin is very efficient in removing Re(VII) from aqueous solutions under the conditions of the present study. The highest uptake (4.9 mmol Re/g) is observed under acidic conditions and absence of NaCl. Above pH 4, the uptake of Re(VII) decreases about one order of magnitude, reflecting the presence of functional groups only protonated in these very acidic conditions. Minor differences arise between the uptake in absence of background electrolyte (0 M NaCl) and 0.01 M NaCl. On the contrary, a considerable decrease

in the uptake (again ca. one order of magnitude) takes place in 0.50 M NaCl. This observation reflects the competition of ReO_4^- and Cl^- species for the anion sorption sites of the resin.

Sorption coefficients calculated for the uptake of Re(VII) by the PEI resin range between 10^4 mL/g in dilute and very acidic conditions (pH 2.3) to 10^2 mL/g in 0.50 M NaCl solutions with pH 8.6. These values confirm the affinity of the PEI resin for the uptake of Re(VII) anions, especially under acidic conditions and absence of other competing anions (e.g. Cl^-).

Although various sorbents have previously been tested for the removal of Re from aqueous solutions, the direct comparison with the results obtained in the present study is not straight forward due to the very low Re concentrations (in analogy to Tc) used in the previous studies. The highest Re-removal efficiency among the investigated modified natural sorbents was shown by hexadecyl-pyridinium-modified bentonite (2.3 mmol/g) [13], the polyethylen-imine-modified lignin sludge exchanger (1.3 mmol/g) [31] and the amine-modified corn stalk (0.9 mmol/g) [32]. Among the investigated resins, the 4-amino-1,2,4-trazole resin (1.9 mmol/g) [23] and the anion-exchange resin D318 (1.9 mmol/g) [22] showed high Re-sorption capacity. The Reilex and the poly(4-vinylpyridine) resins were also quite efficient in removing rhenium from acidic solutions [21].

The sorption data collected for Re were modeled using the Langmuir and Freundlich isotherms according with Eqs. (1) and (2), respectively [39].

$$\text{Langmuir } q_{equil} \quad Q_{max} \frac{K_L C_{equil}}{1 + K_L C_{equil}}, \tag{1}$$

$$\text{Freundlich } q_{equil} \quad K_F C_{equil}^{1/n}, \tag{2}$$

where q_{equil} and C_{equil} are the equilibrium concentration in resin and liquid phase, respectively, K_L and K_F the Langmuir and Freundlich constants, n a parameter considering the system heterogeneity and Q_{max} the maximum sorption capacity.

Fig. 7 Uptake of Re(VII) by PEI resin in non-buffered ($2.3 \leq pH \leq 4.4$) and buffered (TRIZMA, pH 8.6) systems with $C_{NaCl} = 0$, 0.01 and 0.5 M. **a** Sorption isotherms fitted by the Langmuir equation; **b** Sorption coefficients as a function of C_{equil} in the aqueous phase
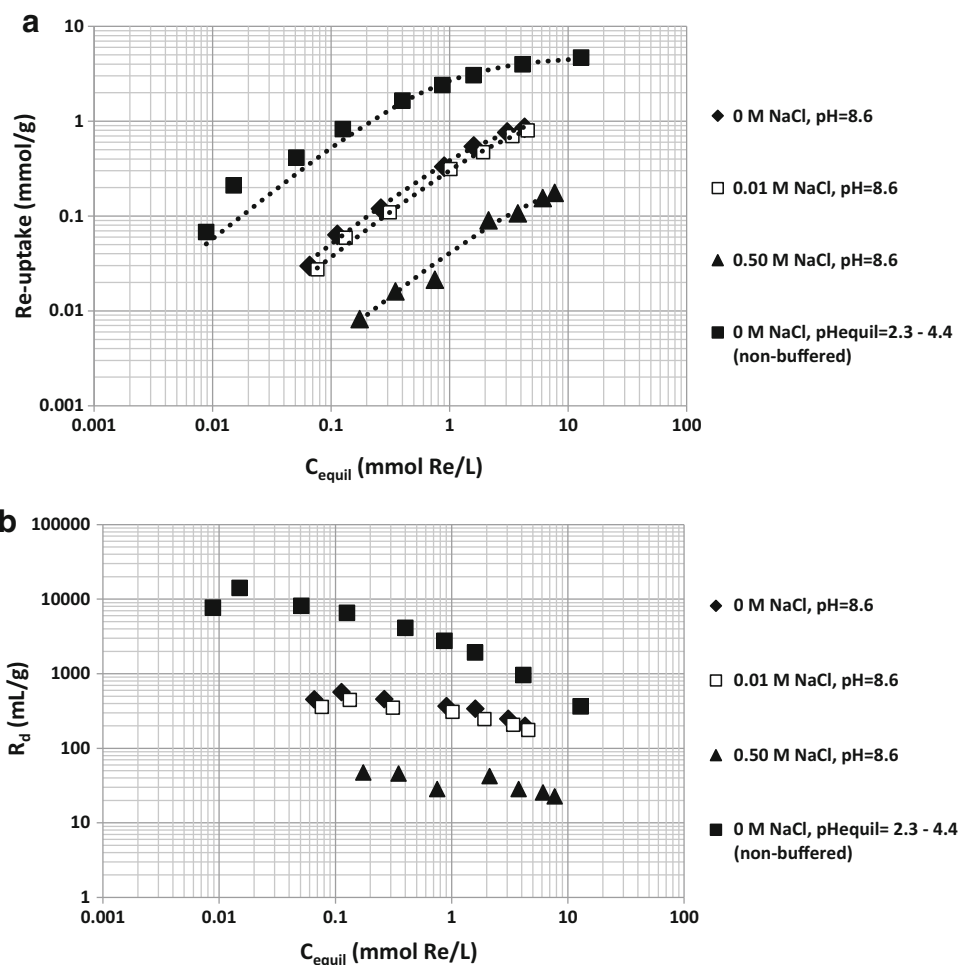
**Table 1** Modeling of the experimental Re sorption isotherms by the Langmuir and Freundlich equations

	Langmuir			Freundlich		
	Q_{max} (mmol/g)	K_L (L/mmol)	R^2	K_F	n	R^2
0 M NaCl, pH 8.6	1.41	0.370	0.998	0.36014	1.587	0.986
0.01 M NaCl, pH 8.6	1.51	0.248	0.999	0.2948	1.468	0.995
0.50 M NaCl, pH 8.6	0.34	0.136	0.987	0.04272	1.419	0.980
0 M NaCl, pH_{equil} = 2.3–4.4 (non-buffered)[a]	4.87	1.191	0.995	2.21884	3.032	0.946

[a] Model data of limited accuracy provided only for comparison purposes

The outcome of the fit of Langmuir and Freundlich isotherms (Q_{max}, K_L, K_F, n and the correlation coefficient R^2) is shown in Table 1 for those systems with buffered pH. In all cases, experimental data could be better fitted by the Langmuir isotherm, as indicated by the greater correlation coefficient R^2 obtained for this model. A comparison of experimental and Langmuir model isotherms is further provided in Fig. 7a. Modelling of isotherms obtained under varying pH_{equil} conditions (e.g.,

non-buffered systems with $pH_{equil} = 2.3$–4.4) is also appended to Table 1, although the resulting parameters can entail significant errors due to the expected decrease of the resin capacity with increasing pH. A qualitative comparison of Q_{max} calculated with the Langmuir equation and including also data in non-buffered systems clearly reflects the increased Re capacity of the PEI resin caused by acidic pH conditions and absence of competing anions.

Fig. 8 Comparison of the Tc(VII)- and Re(VII) sorption isotherms (**a**) and the corresponding sorption coefficients (**b**) as a function of C_{equil} in the aqueous phase. The Langmuir fit of the Re(VII) data extrapolated to lower C_{equil} values in order to show the analogy of the Re and Tc sorption behavior of the resin is also included
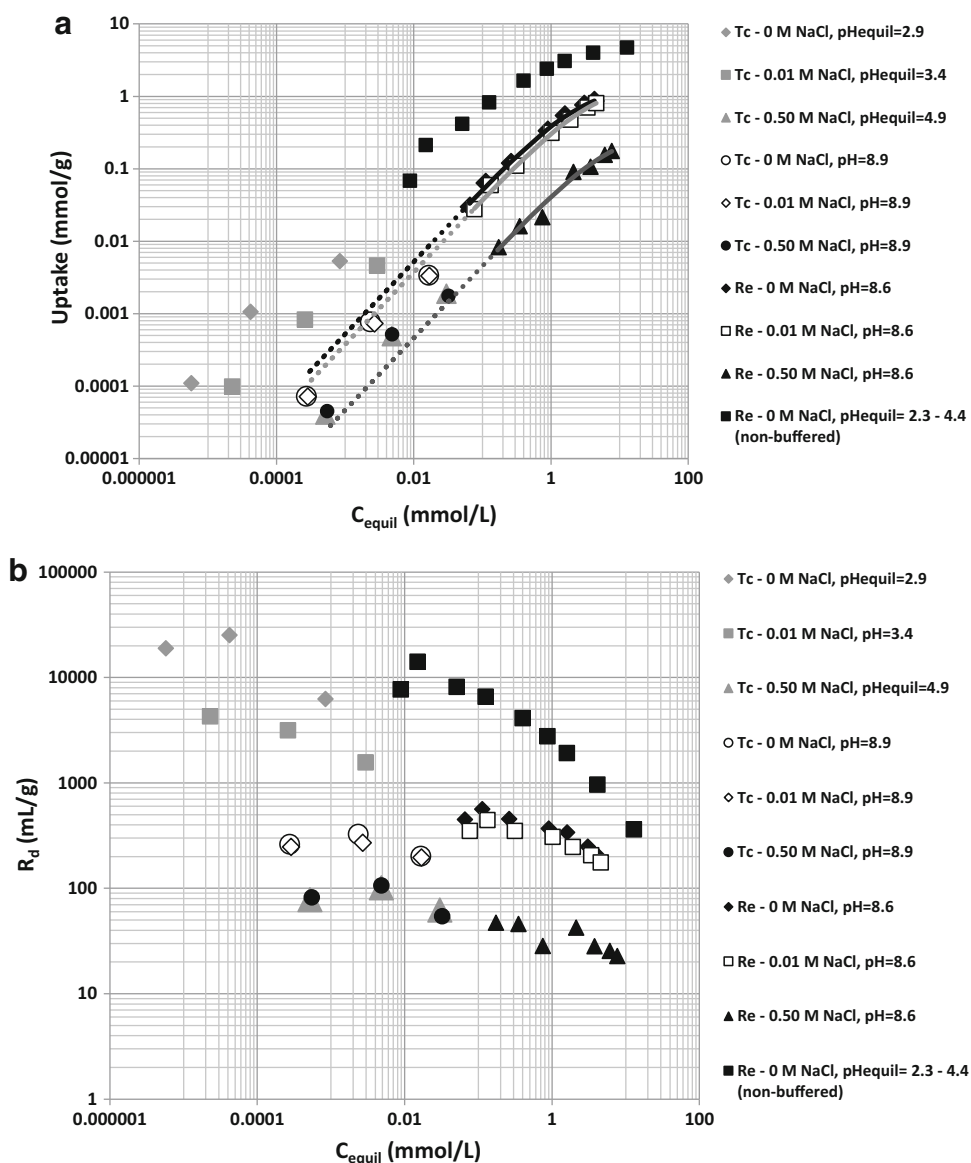
Regeneration of the Re-loaded resin

The regeneration of the resin was based on the ion-exchange of the perrhenate ions sorbed by sulfate- and, in the second attempt, by sulfate and chloride ions.

The regeneration of the Re-loaded resin with 0.033 M Na_2SO_4 removed 96 % of the sorbed Re(VII). After this regeneration step, the sorption capacity of the resin decreased from 4.9 (initial Re-uptake) to 1.3 mmol/g. The loss in the Re capacity results from the higher affinity of the resin towards divalent anions such as SO_4^{2-}. High sulfate affinity was also observed in the case of other anion exchange resins possessing quaternary amines as functional groups (e.g., the polystyrene-based Purolite A-520E) [40].

The second regeneration step with 0.10 M NaCl after Re removal by the sodium sulfate solution led to a comparably

higher sorption capacity (2.3 mmol/g). This observation can be explained by the replacement of the strongly bound sulfate by the easily exchangeable chloride ions. These results show that the quantitative recovery of Re bound to the resin is feasible using Na_2SO_4 as regenerating agent, although at the cost of a significant decrease in the total capacity of the resin (27 % of initial capacity using Na_2SO_4; 47 % of initial capacity using Na_2SO_4 + NaCl).

Sorption of Tc(VII)

As in the case of Re, the contact of the resin with pH non-buffered Tc(VII) solutions of different initial pH (3–11) also leads to a shift in pH again highlighting the buffering capacity of the resin. The pH_{equil} of these non-buffered

samples ranges between 2.9 (in absence of NaCl) and 4.9 (in 0.50 M NaCl).

Figure 8a, b show the sorption isotherms and distribution coefficients, respectively, for the uptake of Tc by the PEI resin under the evaluated conditions. Sorption data gained for Re under analogous pH- and [NaCl]-conditions have been appended for comparison purposes. Note that due to the significantly lower metal concentrations used in the Tc studies compared to the Re experiments, no saturation of the sorption sites is reached and thus sorption isotherms remain linear even for the highest Tc concentrations.

For dilute systems (absence of NaCl), the effect of pH on the uptake is very strong with a decrease of ca. 2 log-units for R_d values at pH 2.9 and 8.9. This effect vanishes for samples with 0.50 M NaCl and pH 4.9 and 8.9, likely indicating that the functional groups responsible for the uptake of anions under acidic conditions are deprotonated above pH 4.9. As in the case of Re, the presence of high chloride concentration in solution induces a significant decrease in the uptake and resulting R_d values. These findings are in agreement with data presented in the literature concerning the effect of salinity on the sorption of technetium in soils [41].

The limited number of experimental sorption data collected for TcO_4^- at low C_{equil} precludes to derive a reliable model isotherm using the Langmuir or Freundlich equations. Instead, the Langmuir fit completed for ReO_4^- has been extrapolated, where plausible, to lower C_{equil} with the aim of assessing the analogies between the sorption of both anions under different experimental conditions (s. dashed lines in Fig. 8a). This exercise confirms the similar sorption behavior of the resin for ReO_4^- and TcO_4^- anions, and supports the use of data gained for Re in the prediction of the sorption properties of Tc under analogous boundary conditions. Note that such analogies apply only in the sub-oxic to oxidizing redox conditions where the +VII redox state of both elements prevail.

The calculated sorption coefficients (R_d) are considerably higher than those observed for the technetium removal by the majority of minerals and soil types investigated under various experimental conditions [3]. Somehow increased Tc-uptake values were only observed in specific cases in the presence of zero valent iron or Fe(II) compounds (e.g., pyrrhotite, $Fe_{1-x}S$ ($x = 0$ to 0.2)) most probably due to the reductive precipitation of Tc(IV)-oxide phases. The R_d values observed during this work were comparable and even higher than those obtained using Purolite A-520E and a number of synthetic resins developed and tested using a 6 μM pertechnetate solution in NaCl, NaNO$_3$, and Na$_2$SO$_4$ (each at 0.06 M) matrix [40]. They were also of the same order of magnitude with those measured for a number of Dowex- and Bio-Rad anion exchange resins [29].

Conclusions

The investigated polyethylenimine–epichlorohydrin resin has shown a strong tendency to remove significant amounts of perrhenate and pertechnetate ions (up to 4.9 mmol/g resin) from aqueous solutions in absence and presence of competing ions ($[Cl^-] \leq 0.5$ M) over a wide pH-range ($2.3 \leq pH \leq 8.9$).

The sorption of ReO_4^- and TcO_4^- anions is pH- and $[Cl^-]$-dependent, with the highest capacity and R_d values observed for pH ≤ 4.4 and $[Cl^-] \leq 0.01$ M. The impact of chloride on the uptake of Re and Tc by PEI resin is especially significant at high metal C_{equil} (≥ 0.1 mmol/L), where 0.5 M NaCl induces a decrease in the resin capacity and log R_d of about one order of magnitude.

The use of Langmuir isotherms derived for ReO_4^- properly reproduces the uptake and R_d values determined for TcO_4^- in a lower concentration range, thus confirming the analogous sorption behavior of both elements under sub-oxic to oxidizing conditions.

The high uptake capacity of the PEI resin together with its high sorption coefficients open application perspectives of this material in the management and disposal of Tc-containing aqueous wastes under oxic conditions, where the highly mobile Tc(VII) is expected to prevail.

References

1. Brookins DG (1986) Appl Geochem 1:513–517
2. Icenhower JP, Martin WJ, Qafoku NP, Zachara JM (2008) The geochemistry of technetium: a summary of the behavior of an artificial element in the natural environment, Pacific Northwest National Laboratory, Report PNNL 18139
3. Söderlund M, Lusa M, Lehto J, Hakanen M, Vaaramaa K, Lahdenperä A-M (2011) Sorption of Iodine, Chlorine, Technetium and Cesium in Soil, POSIVA Report 2011-04, EURAJOKI
4. Guillaumont R, Fanghänel T, Neck V, Fuger J, Palmer DA, Grenthe I, Rand MH (2003) Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. OECD Nuclear Energy Agency, vol. 5. Elsevier, Amsterdam

5. Kobayashi T, Scheinost AC, Fellhauer D, Gaona X, Altmaier M (2013) Radiochim Acta 101:323–332
6. Yalcintas E, Gaona X, Scheinost AC, Kobayashi T, Altmaier M, Geckeis H (2015) Radiochim Acta 103:57–72
7. Cui DQ, Eriksen TE (1996) Environ Sci Technol 30:2259–2262
8. Cui DQ, Eriksen TE (1996) Environ Sci Technol 30:2263–2269
9. El-Wear S, German KE, Peretrukhin VF (1992) J Radioanal Nucl Chem 157:3–14
10. Shen D, Fan XH, Su XG, Zeng JS, Dong Y (2002) J Radioanal Nucl Chem 254:137–142
11. Keith-Roach MJ, Morris K, Dahlgaard H (2003) Mar Chem 81:149–162
12. Vinšová H, Konirova R, Koudelkova M, Jedináková-Křižová V (2004) J Radioanal Nucl Chem 261:407–413
13. Behnsen J, Riebe B (2008) Appl Geochem 23:2746–2752
14. Vinšová H, Jedináková-Křižová V, Ožanova M (2009) J Radioanal Nucl Chem 281:75–78
15. Hudson MJ, Tyler DJ (1990) Hydrometallurgy 24:111–125
16. Kasar S, Kumar S, Kar A, Bajpai RK, Kaushik CP, Tomar BS (2014) J Radioanal Nucl Chem 300:71–75
17. Gu B, Dowlen KE, Liang L, Clausen JL (1996) Sep Technol 6:123–132
18. Kholmogorov AG, Kononova ON, Kachin SV, Ilyichev SN, Kryuchkov VV, Kalyakina OP, Pashkov GL (1999) Hydrometallurgy 51:19–35
19. Kim E, Benedetti MF, Boulègue J (2004) Water Res 38:448–454
20. Lan X, Liang S, Song Y (2006) Hydrometallurgy 82:133–136
21. Jermakowicz-Bartkowiak D, Kolarz BN (2011) React Funct Polym 71:95–103
22. Shu Z, Yang M (2010) Chin J Chem Eng 18:372–376
23. Xiong C, Yao C, Wu X (2008) Hydrometallurgy 90:221–226
24. Ashley KR, Cobb SL, Redzinski SD, Schroeder NC (1996) Solv Extr Ion Exch 14:263–284
25. Kim E, Benedetti MF, Boulègue J (2004) Water Res 38:448–454
26. Ashley KR, Ball JR, Abney KD, Turner R, Schroeder NC (1995) J Radioanal Nucl Chem 194:71–79
27. Popova NN, Bykov GL, Petukhova GA, Tananaev IG, Ershov BG (2013) J Radioanal Nucl Chem 298:1463–1468
28. Ashley KR, Ball JR, Pinkerton AB, Abney KD, Schroeder NC (1994) Solv Extr Ion Exch 12:239–259
29. Liang L, Gu B, Yin X (1996) Separ Technol 6:111–122
30. Mashkani SG, Ghazvini PTM, Aligol DA (2009) Bioresour Technol 100:603–608
31. Chopabaeva NN, Ergozhin EE, Tasmagambet AT, Nikitina AI (2009) Solid Fuel Chem 43:99–102
32. Lou Z, Zhao Z, Li Y, Shan W, Xiong Y, Fang D, Yue S, Zang S (2013) Bioresour Technol 133:546–554
33. Wang L, Liu W, Wang T, Ni J (2013) Chem Eng J 225:153–163
34. Zhao YG, Shen HY, Pan SD, Hu MQ (2010) J Hazard Mater 182:295–302
35. Ebner AD, Ritter JA, Pioehn HJ, Kochen RL, Navratil JD (1999) Sep Sci Technol 34:1277–1300
36. Apelback A (1992) J Chem Thermodyn 4:619–626
37. Altmaier M, Metz V, Neck V, Müller R, Fanghänel T (2003) Geochim Cosmochim Acta 67:3595–3601
38. Borisova LV, Ermakov AN, Ismagulova AB (1982) Analyst 107:495–499
39. Limousin G, Gaudet JP, Charlet L, Szenknect S, Barthes V, Krimissa M (2007) Appl Geochem 22:249–275
40. Gu B, Liang L, Brown GM, Bonnesen PV, Moyer BA, Alexandratos SD, Ober R (1998) A field trial of novel bifunctional resins for removing pertechnetate (TcO₄⁻) from contaminated groundwater, Oak Ridge National Laboratory, Report ORNL/TM-13593. http://web.ornl.gov/sci/casd/csg/pgdp/pgdp.html. Accessed 15 Feb 2015
41. Lieser KH, Bauscher CH (1987) Radiochim Acta 42:205–213