Batch studies on adsorptive removal of Co ions by CoTreat® in acidic media

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Abstract

The kinetics of Co ions sorption on CoTreat® was investigated in the 5–40 mg/L concentration range at a bulk temperature of 30 °C in HNO_3 (pH 2.6). A pseudo-second order kinetic model best describes the sorption kinetics at low Co ion concentrations, while a pseudo-first order kinetic model was the best fit at higher concentrations. The equilibrium data were examined using the three models, viz. the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. The Langmuir and the D-R isotherms were the best fits to data from which the monolayer sorption capacity (Q_0) and mean sorption energy (E) can be determined. The estimated values of Q_0 and E were calculated to be 3.20 mg/g and 8.45 kJ/mol respectively at 30 °C. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ were determined to be +32.52 kJ/mol and 0.19 kJ/(mol·K) in the temperature range 30–60 °C respectively, yielding negative values of the Gibbs free energy ($\Delta G°$), indicating the spontaneous nature of the process. The competitive sorption study of Co, Ce, Ru, Sb and Sr ions revealed that the CoTreat® exchanger can effectively remove all the elements concurrently.

Keywords

Co ions, CoTreat®, HNO_3 media, sorption kinetics, sorption isotherms, pH effect

Introduction

Liquid radioactive waste is commonly generated from nuclear fuel cycle operations. These operations include spent fuel reprocessing, routine clean-up operations at nuclear installations and after nuclear accidents such as Fukushima, production and application of radioisotopes in nuclear medicine, operations of hot chemistry laboratories, and treatment of reactor coolant water. Treatment and solidification of these liquid waste effluents are crucial to decrease radioactivity exposure and to obtain acceptable waste forms for final disposal.

Ion exchange is routinely used in light water reactors (LWRs) to purify circulation coolant water and treat effluent. This processing method is economically competitive with the older technologies based on evaporation, and yields the required volume reduction. Because of the potential hazards caused by the accumulation of radioactive materials, it is crucial to design a waste management system to remove radioactivity from the reactor process streams to concentrate and contain the radionuclides with minimal release to the environment. A well-designed ion exchange process can result in effluent which can be easily recycled or safely disposed.

Owing to their good selectivity, as well as high thermal and radiation resistance, inorganic ion exchangers are normally favoured over their organic counterparts for use in the nuclear industry. The major classes of inorganic exchangers utilized in waste treatments include zeolites [1,2], sodium titanates [3-5], hexacyanoferrates [6,7], titanosilicates [8,3], oxides and hydrous oxides [9-11]. CoTreat® is a highly selective ion exchanger material based on titanium oxide. It was originally developed by a research group in the Laboratory of Radiochemistry of the University of Helsinki and is selective for ^{60}Co and other activated corrosion products such as ^{54}Mn, ^{55}Fe and ^{63}Ni [12]. This exchanger material has been tested in the Thermal Oxide Reprocessing Plant (THORP) (Sellafield, United Kingdom) as a precoat to FUNDA filters for the removal of ^{60}Co from LWR fuel [13-16]. It has also been used for radiocobalt removal from nuclear power plant (NPP) waters [12].

^{60}Co, a known corrosion product in cooling water systems of research reactors, was selected as a target radionuclide in this study because of its radiological toxicity and contaminating nature. An optimized ion exchange process could purify the coolant waters of this corrosion product. The main objectives of this study were to investigate the equilibrium and kinetic parameters of CoTreat® as sorbent material for the removal of Co ions. The parameters that impact the sorption behaviour (such as initial metal concentration, pH, contact time and temperature) were investigated to explain the mechanism of the ion exchange process. Competitive sorption of different elemental ions onto the exchanger was studied as well. CoTreat® could serve as alternative to the organic resins mostly used to purify reactor coolant waters of fission products and actinides.

Limited data are available in the literature on the sorption mechanism employed by CoTreat® for cobalt ions. Harjula *et al*. [17] reported that at pH less than 6.5, cobalt species exist as unhydrolysed metal cations but are adsorbed as hydrolysed species due to the alkaline nature of the surface of the CoTreat® material. Their results also indicated that, surface complexation is the prevailing mechanism rather than ion exchange for a Co^{2+}/H^+ system.

The results presented in this study provide additional understanding of the fundamental sorption behaviour of CoTreat® for cobalt removal for a 3-component system ($Co^{2+}/H^+/Na^+$). This study specifically focused on a lower pH range than the previous studies reported in literature.

Experimental

Material

The chemicals used in this study were CoTreat® (Fortum Powder and Heat Oy, Finland) and nitric acid (ACE, platinum line), 1000 mg/L Co, 1000 mg/L Ce, 1000 mg/L Ru, 1000 mg/L Sb and 1000 mg/L Sr metal AA standards (Laboratory Consumables & Chemical Supplies CC).

Sorption of Co ions on CoTreat®

Sorption experiments were conducted via a batch technique using a Labex platform incubator shaking at 250 rpm. A CoTreat® mass of 0.2 g weighed in a polyethylene bottle was contacted with 20 ml Co solution of known concentration and pH for a specified length of time and at a specified temperature. After the specified contact time was achieved, the solutions were centrifuged at 30000 G (Thermo Scientific™ Sorvall™ LYNX 6000 Superspeed centrifuge) for 20 minutes to achieve complete phase separation (the ultracentrifugation phase separation process is recommended by the CoTreat® supplier). The concentration of Co ions in solution was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (instrument: Spectro Arcos), which is based on the measurement of light emitted by elements contained in sample introduced to the plasma.

The effect of pH on sorption capacity was determined in the pH range of 0.5–2.6 at 5 mg/L Co ions concentration. The CoTreat® material was kept in contact with the Co solution for 3 hours at 30 °C. The effect of contact time on the sorption capacity was investigated in the time range of 5–240 minutes at the Co solution concentration range of 5–40 mg/L. The temperature (30 °C) and pH (2.6) were kept constant. The effect of initial Co ions concentration on the equilibrium sorption capacity was studied at the 10–40 mg/L concentration range. The effect of temperature on the Co ions removal by CoTreat® was investigated at 10 mg/L Co ions concentration at pH 2.6. The temperature was varied between 30 and 60 °C. The solution used in the competition study contained 2 mg/L Ce, 2 mg/L Co, 2 mg/L Ru, 2 mg/L Sb and 2 mg/L Sr. The solution (pH 2.6) was contacted with CoTreat® for 3 hours at 30 °C.

All the batch experiments were conducted in triplicates/duplicates to ensure the accuracy, reliability and reproducibility of the data collected. The average values are presented in the results section. The error bars shown in the plots (results section) represent the standard error of the data sets.

Results and discussion

Sorption kinetics

The sorption of different concentrations of Co ions on CoTreat® was studied as function of contact time. The amount of Co ions sorbed on CoTreat® (q_t (mg/g)) after contact time t (min) can be calculated from Eq. (1), where C_i (mg/L) is the initial concentration of the Co ions in solution, C_t (mg/L) is the concentration of Co ions in solution after contact time t, V (mL) is the volume solution and m (g) is the mass of CoTreat® weighed out.

$$q_t = C_i - C_t \times \frac{V}{m} \tag{1}$$

The results obtained are given in **Fig. 1**. A sharp initial rise can be observed at the lower Co concentrations (5 and 10 mg/L) followed by complete Co removal after 10 and 30 minutes contact time respectively. A slower initial rise can be observed for the higher Co concentration (30 and 40 mg/L) followed by complete saturation after 4 hours contact time. The uptake rate decreases with increasing initial concentration of Co. At the concentrations 5, 10 and 30 ppm, complete Co removal from solution was attained, whereas at 40 mg/L initial Co concentration, partial Co removal (~77 %) was obtained after 4 hours contact time. This is due to the saturation of exchanger material. At lower concentrations, adequate binding sites were available for complete removal of the Co ions in solution. The amount of Co ions retained on CoTreat® at equilibrium increases from 0.512 to 3.310 mg/g with increase in Co ions concentration from 5 to 40 mg/L. This observed relationship is due to the fact that there are more free Co ions available to be sorbed at high concentrations.

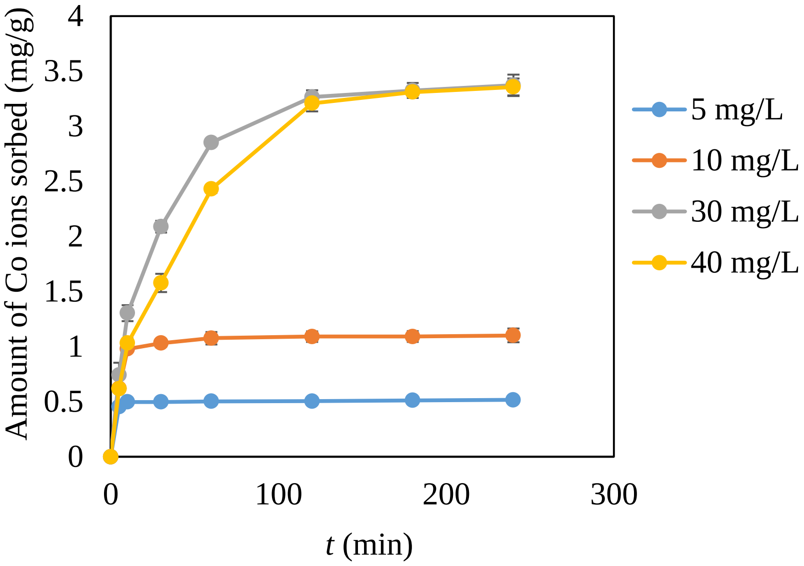

Fig. 1 Trend in uptake of Co by CoTreat® in nitric acid (pH 2.6) at various concentrations of Co and time intervals at 30 °C

Various sorption systems have been explained using the pseudo-first order kinetic model proposed by Lagergren [18-20]. The linear expression for the pseudo-first order kinetic model is given in Eq. (2)[21], where q_e (mg/g) is the amount of Co ions sorbed on CoTreat® at equilibrium, k_1 (min^{-1}) is the pseudo-first order rate constant, q_t is as described previously.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

The kinetic treatment of the data produced linear plots (not shown). The kinetic parameters derived from the model for the data obtained at 30 and 40 mg/L are given in **Table 1**.

Table 1 Calculated values of the constants derived from the pseudo-first order kinetic model for Co removal by CoTreat® in HNO_3 (pH 2.6) at 30 °C

Co ions solution concentration (mg/L)	5	10	30	40
k_1 (min^{-1})	0.351	0.064	0.032	0.028
q_e (mg/g)(calculated)	0.443	0.533	3.059	3.500
r^2	0.9801	0.866	0.998	0.976
q_e (mg/g) (experimental)	0.512	1.092	3.325	3.310

The pseudo-second order kinetic model is also widely used to explain sorption systems in the literature [22-24]. Its linear expression is given in Eq. (3) [21], where k_2 (g/(mg·min)) is the pseudo-second order rate constant, q_e and q_t are as described previously.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

The time dependent data was fitted to the pseudo-second order kinetic model, producing linear plots (not shown). The kinetic parameters obtained from the kinetic model are given in **Table 2**.

Table 2 Calculated values of the constants derived from the pseudo-second order kinetic model for Co removal by CoTreat® in HNO_3 (pH 2.6) at 30 °C

Co ions solution concentration (mg/L)	5	10	30	40
k_2 (g/(mg·min))	5.373	0.306	0.012	0.007
q_e (mg/g)(calculated)	0.504	1.131	3.888	3.962
r^2	0.9998	0.9982	0.997	0.966
q_e (mg/g) (experimental)	0.512	1.092	3.325	3.310

Judging by the differences between the experimental and calculated q_e; the results show that the sorption process conforms to the pseudo-first order kinetic model at high concentrations of Co ions (30 and 40 mg/L) while at lower concentrations (5 and 10 mg/L) the pseudo-second order kinetic model is a better fit. The results are in agreement with the theoretical predictions presented by Azazian [25], which show that the adsorption reaction equation converts to the pseudo-first order model at high solute concentrations and converts to the pseudo-second order at low initial concentrations. The obtained CoTreat® equilibrium sorption capacity (q_e) of 3.310 mg/g for Co ions is lower than that obtained on hydrous titanium oxide [26]. The sorption capacity of CoTreat® for Co ions is expected to be higher in alkaline conditions.

Effect of solution pH

The effect of solution pH on the sorption capacity was studied within a narrow acidic pH range of 0.5–2.6. The results obtained are presented in **Fig. 2**, which reveal that a solution pH of 2 and greater is required for high Co sorption on CoTreat®. Even though Tusa *et al.* [27] reported that the best results are obtained at pH 6–8, the results given by Harjula *et al.* [17] and those presented in this study reveal that CoTreat® is highly effective in removing Co ions from acidic aqueous solution as well.

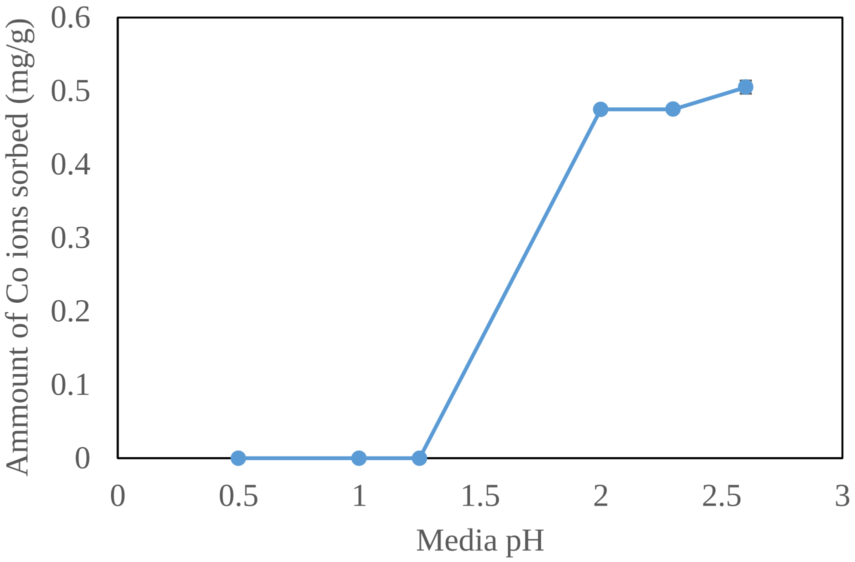

Fig. 2 The sorption extent of CoTreat® for Co ions in varying nitric acid pH at 30 °C (5 mg/L initial Co concentration)

Sorption isotherms

Sorption isotherms are curves that relate the sorption extent to the residual concentration at equilibrium. They can be used to evaluate the effectiveness of a sorption process and to describe how the solute interacts with the ion exchanger surface. The equilibrium data were subjected to three well known isotherm models namely the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. The linear Freundlich isotherm is given in Eq. (4), where q_e is as described previously, and c_e (mg/L) is the residual concentration of Co ions in solution at equilibrium, k_f (mg/g)(L/g)^n and n are Freundlich constants relating to sorption capacity and intensity of adsorption respectively.

$$\log q_e = \log k_f + \frac{1}{n}\log c_e \tag{4}$$

A value of $1/n$ greater than 1 indicates cooperative adsorption while a value less than 1 indicates chemisorption and favourable adsorption. The closer the value of $1/n$ is to 0, the more heterogeneous the sorption surface is [28,29]. The Freundlich plot of $\log q_e$ vs $\log c_e$ gave a non-linear plot (not shown), thus invalidating the applicability of the model to explain the mechanism of Co ions sorption on CoTreat®.

It was determined that the concentration dependent data fitted the Langmuir isotherm best, as shown in **Fig. 3**, suggesting that the surface sorption sites of the CoTreat® material are identical and equivalent. The Langmuir linear expression is given in Eq. (5), where c_e, q_e are as described previously, b (mL/g) is the Langmuir constant and Q_0 (mg/g) is the maximum monolayer sorption capacity. The parameters derived from the Langmuir isotherm model are given in **Table 3**. The Q_0 value is in good agreement with the saturation sorption capacity determined in the kinetics data, which was 3.31 mg/g. For a monolayer sorption process this correspondence is expected. The value of b can be used to calculate the separation factor (R_L) given by (6), which can be used to describe the nature of a sorption process as either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$) [29]. At the four studied concentrations (10, 20, 30 and 40 mg/L Co), the calculated values of R_L were less than 1 indicating that sorption of Co ions on CoTreat® is a favourable process.

$$\frac{c_e}{q_e} = \frac{1}{bQ_0} + \frac{c_e}{Q_0} \tag{5}$$

$$R_L = \frac{1}{1 + bC_i} \tag{6}$$

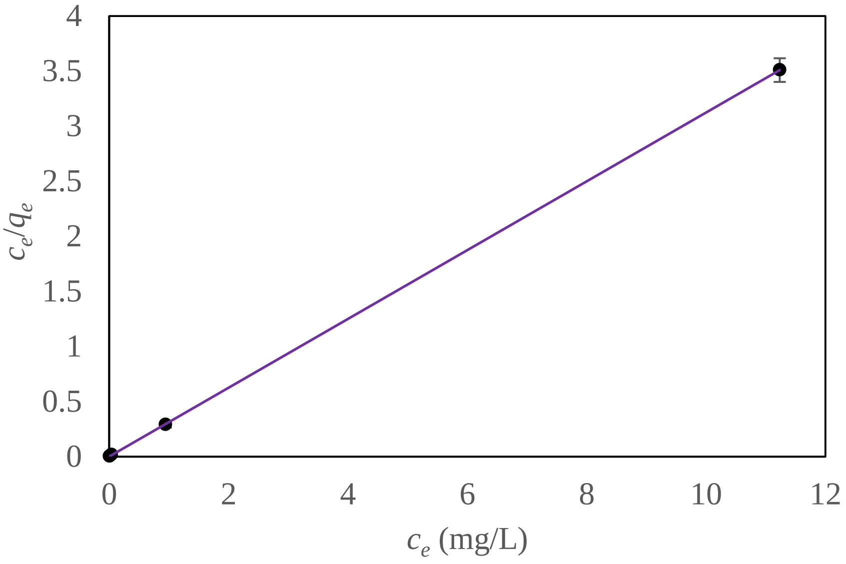

Fig. 3 Langmuir isotherm for Co ions sorption of CoTreat® in HNO_3 (pH 2.6) at 30 °C

The D-R isotherm is normally used to distinguish between physical and chemical adsorption [30]. The linear mathematic description of the model is given Eq. (7), where c_e and q_e are as described previously, q_s (mg/g) is the theoretical isotherm saturation capacity, β ($\mathrm{mol^2/kJ^2}$) is the activity coefficient related to sorption energy and ε given in Eq. (8), is the Polanyi potential.

$$\ln q_e = \ln q_s - \beta \varepsilon^2 \tag{7}$$

$$\varepsilon = RT\ln(1 + \frac{1}{c_e}) \tag{8}$$

From the slope (β) of the linear plot of ln q_e vs ε^2, the sorption energy (E in kJ/mol) can be calculated using equation (9). The value of E can be used to categorize the sorption process as either physisorption ($E < 8$ kJ/mol), ion exchange ($8 \leq E \leq 16$ kJ/mol) or chemisorption ($E > 16$ kJ/mol) [31]. The D-R isotherm plot obtained from the equilibrium data is presented in **Fig. 4**. The parameters derived from the D-R isotherm are given in **Table 3**. The q_s value is in good agreement with the experimentally determined saturation capacity. The value of E was determined to be 8.45 kJ/mol, which suggests that the mechanism of Co removal by CoTreat® conforms to ion exchange.

$$E = \frac{1}{\sqrt{-2\beta}} \tag{9}$$

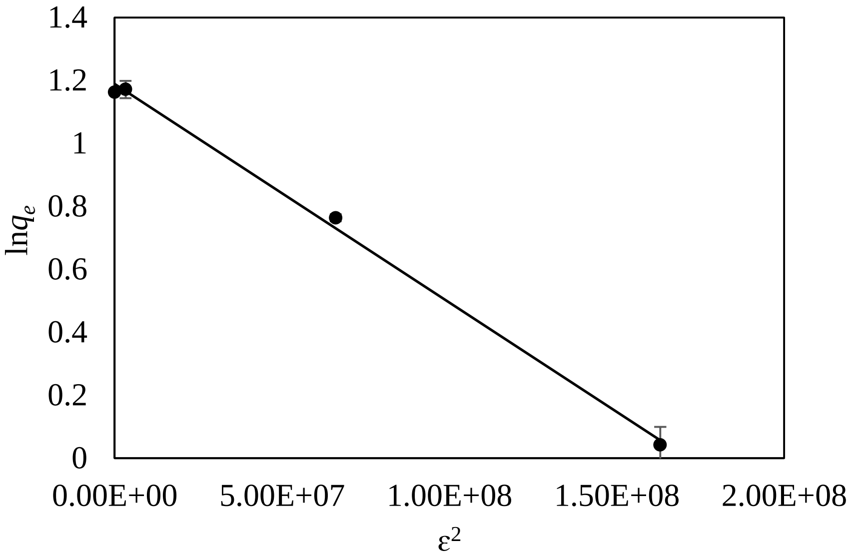

Fig. 4 D-R isotherm for Co sorption on CoTreat® in HNO_3 (pH 2.6) at 30 °C

Table 3 Sorption isotherm constants for Co ions sorption on CoTreat®

Langmuir		D-R	
Q_0 (mg/g)	3.20	q_s (mg/g)	3.28
b (mL/g)	107.6	β (mol^2/kJ^2)	$7*10^{-9}$
r^2	1	r^2	0.9976

Effect of temperature

The sorption enthalpy ($\Delta H°$) and entropy ($\Delta S°$) can be derived from the linearized expression, given by Eq. (10), relating the distribution coefficient to the Gibbs function [32], where k_d (ml/g) is the distribution coefficient at equilibrium, R is the gas constant and T is the bulk temperature in Kelvin. The distribution coefficient can be calculated using Eq. (11), where C_i, C_t, V and m are as described previously.

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

$$k_d = \frac{C_i - C_t}{C_t} \cdot \frac{V}{m} \tag{11}$$

Based on the sign of the ΔH°, the sorption process can be deemed as endothermic (+) or exothermic (-). Based on the value of ΔH°, the sorption process can be inferred to be either physisorption (ΔH° < 80 kJ/mol), ion exchange (ΔH° < 40 kJ/mol) or chemisorption (ΔH° > 80 kJ/mol) [31]. The Gibbs free energy of sorption (ΔG°) can be calculated using Eq. (12), the sign of the calculated value can be used to deduce whether the sorption process is spontaneous or not.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

A plot of ln k_d vs 1/T yielded a linear plot presented in **Fig. 5**. The estimated ΔH° value obtained from the plot is given in **Table 4** along with the other thermodynamic parameters. The results obtained indicate that the sorption of Co ions on CoTreat® is an endothermic and spontaneous ion exchange process, which agree with the results obtained from the isotherm models. The change in the Gibbs energy is negative, thus the process is entropy driven. The positive entropy change may be attributed to the increase in the number of species in solution with each Co^{2+} replacing two cations, either H^+ or Na^+.

Table 4 Thermodynamic parameters for Co ions sorption on CoTreat® (10 mg/L initial Co concentration, pH 2.6)

Bulk temperature (°C)	ΔG° (kJ/mol)	ΔS° (kJ/mol K)	ΔH^o (kJ/mol)
30	-25.37	0.19	+32.52
45	-28.24		
60	-31.10		

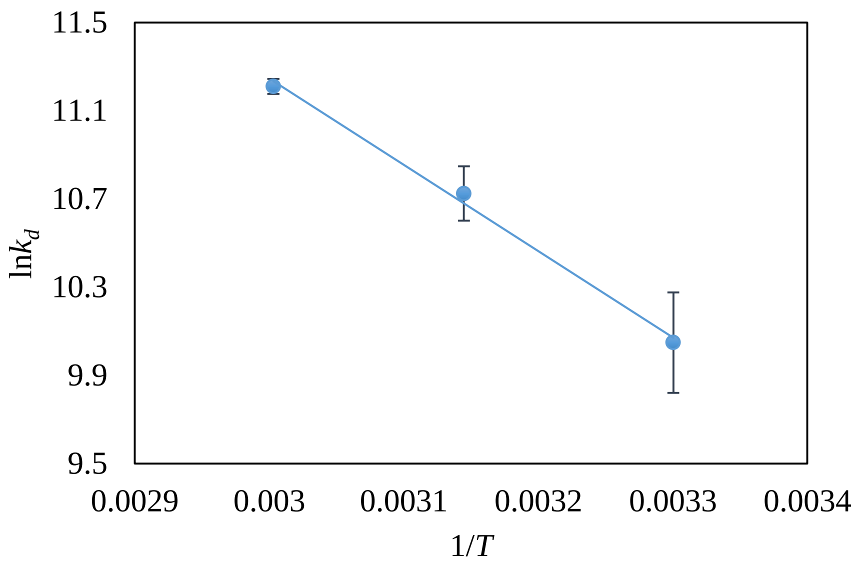

Fig. 5 The influence of temperature on the sorption equilibrium distribution coefficient (k_d) of Co ions on CoTreat® (10 mg/L initial Co concentration, pH 2.6)

Competitive sorption

Removal of coexisting (Co, Ce, Ru, Sb and Sr) metal ions by CoTreat® was studied. The results obtained are given **Fig. 6**, which show that under the defined experimental conditions the CoTreat® material does not specifically target Co ions only in a pool of nuclides, but effectively removes significant amounts of Ce, Ru, Sb and Sr ions as well. The capability of CoTreat® to remove Ce, Ru, Sb and Sr ions is new information which was not previously known and is a positive feature for processing streams where these metal ions are present.

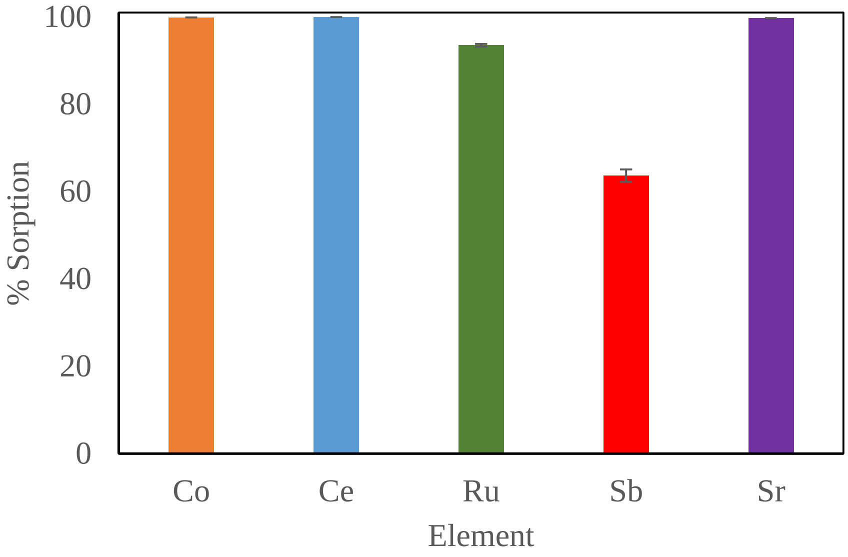

Fig. 6 The sorption extent of Co, Ce, Ru, Sb and Sr ions on CoTreat® (2 mg/L initial metal concentration, pH 2.6, 30 °C)

Conclusions

A comparison of the pseudo-first order and pseudo-second order kinetic models on the overall sorption process revealed that the sorption of Co ions on CoTreat® was best explained by the pseudo-first order kinetic model at high concentrations of Co ions and by the pseudo-second order kinetic model at low concentrations. High sorption capacities are obtained at solution pH of 2 and greater. The sorption process obeyed the Langmuir and the D-R isotherms in the concentration range studied. The value of the free energy of sorption (E) obtained from the D-R isotherm suggested that the Co ions are sorbed predominantly by an ion exchange process. The values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ were calculated using the Arrhenius equation. The values of these thermodynamic parameters indicated the ion exchange of process is endothermic and spontaneous. The presence of co-existing metal ions did not affect the efficacy of CoTreat® to remove Co ions from solution.

Overall, the results presented by this study suggests that CoTreat® can be utilized to remove Co ions from low level radioactive waste to yield less toxic waste forms. The application of CoTreat® is expected to be efficient and economical.

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Conflict of interest

The authors wish to declare that there is no conflict of interest.

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