

Evaluation of permutite for removal of radiocobalt from nuclear wastewater

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Received: 28 May 2014
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Abstract A synthetic zeolite, commercially available as permutite was tested for removing radiocobalt from aqueous solutions by sorption. The sorption process was studied as a function of contact time, pH, ionic strength and solid content by batch technique. The results revealed that the process is dependent on the pH and ionic strength under ambient conditions. The kinetic sorption was fitted well by a pseudo-second-order rate equation. The thermodynamic parameters (ΔH^0 , ΔS^0 , ΔG^0) suggested that sorption behavior of Co(II) is a spontaneous and endothermic process. The study shows that permutite has excellent potential for disposal of wastewaters containing radiocobalt.

Keywords Sorption · Co(II) · Permutite · Kinetics · Thermodynamic parameters

Introduction

Discharge of aqueous radioactive waste from nuclear industry has become a major concern all over the world due to its potential to pollute portable water sources. In particular, this issue is of great interest in china because of the expanding nuclear industry. Radionuclide ^{60}Co is one of the most problematic radionuclides in the radioactive effluent because of its long half-life ($t_{1/2} = 5.27$ y) and

high energy decay photons [1]. Exposure to such ionizing radiation increases the risk of developing radiation induced illness such as cancer. Furthermore, acute cobalt poisoning can cause other health problems such as asthma or damage to vital organs [2]. Therefore, to minimize health risks and maintain ecosystem stability, it is imperative that the level of ^{60}Co in nuclear discharge is reduced to permissible limits (2 $\mu\text{g/L}$) [3].

With a better awareness of this problem, the removal of ^{60}Co from wastewater has been the focus of many research studies [1, 4–8]. In these studies, sorption is widely adopted and different clay minerals are applied. Zeolites, one of clay minerals, are nanoporous aluminosilicate materials. They have a framework structure with enclosed cavities and tunnels, which provide a conducive environment for sorption. A variety of these materials have been generated for sorption purposes [9]. However, these natural zeolites do not often perform optimally in industrial applications. Because of the high efficiency required in nuclear wastewater treatment, low impurity synthetic zeolites with better cation exchange capacity can be good alternative sorbents.

The aim of this work was to test the ^{60}Co sorption capacity of permutite, a synthetic zeolite manufactured by a chinese company, Sinopharm Chemical Reagent, and further assess its potency for nuclear wastewater treatment. In all experiments, the stable cobalt was chosen as an adsorbate to simulate the sorption of radioactive cobalt. This approach was adopted on the basis that stable cobalt has similar chemical characteristics as radiocobalt. The influence of contact time, pH, ionic strength and solid content factors on radionuclide $^{60}\text{Co(II)}$ sorption on permutite were investigated. From the measurements, sorption isotherms were determined and the thermodynamic parameters of $^{60}\text{Co(II)}$ sorption on permutite were calculated.

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Materials and methods

Materials

Permutite which was applied as the raw material of the sorbent was obtained from a Chinese company, Sinopharm Chemical Reagent. According to the information from the manufacturer, permutite was made by fusing argil, siliceous sand and sodium carbonate, and its particle size ranges from 0.18 to 0.25 mm. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was used as the raw material of adsorbate, while distilled water (18 M Ω) was used as the solvent. Xylenol orange was used as color developing agent while a solution of acetic acid and sodium acetate (HAc-NaAc) was used as buffer medium. All chemicals were purchased in analytical purity and used without any further purification.

Experimental apparatus

The light absorbance of cobalt complex was measured by UV-1800 spectrophotometer, the technical specifications of the equipment are shown in Table 1. Other equipments used in this work include pH meter, Centrifuger, Orbital shaker and Electrical thermostatic oscillation tank.

Experimental procedures

All the experiments were carried out in polyethylene centrifuge tubes (15 ml) under ambient conditions by batch technique. Clay suspensions, sodium chloride solutions and distilled water were pre-equilibrated for 24 h to achieve Na^+ sorption equilibration on permutite. Then, Co(II) stock solution was added to achieve the desired concentrations of different components. After the addition of the above components, the solution in the test tubes achieved final volume of 10 ml. Each test solution was adjusted to desired pH by adding negligible volumes of 0.01 or 0.1 mol/L HCl or NaOH. The suspensions were oscillated under orbital shaker or electrical thermostatic oscillation tank for 24 h to achieve sorption equilibrium. After equilibrium, all the suspensions were centrifuged at 8,000 rpm for 30 min to separate the liquid phase. The supernatant solution (2 ml), HAc-NaAc

buffer solution (5 ml), color developing agent (4 ml) and distilled water were mixed in the volumetric flask (25 ml), and then heated 10 min at 328.15 K in the electrical thermostatic oscillation tank. At last, the light absorbance of cobalt complex was measured at 578 nm by Uv-vis spectrophotometer.

To study the kinetics of cobalt sorption on permutite, an initial cobalt concentration of 10 mg/L was used. The temperature was at 298.15 K and solution pH was about 6.35. The suspensions were oscillated under orbital shaker for 0–24 h. The concentration of sodium chloride was kept at 0.01 mol/L while the solid content was 0.3 g/L.

To investigate the effect of pH and ionic strength on sorption, the pH was adjusted from 4 to 12, while the concentration of NaCl was varied (0.001, 0.01 and 0.1 mol/L, respectively). A contact time 24 h was used. The other parameters were the same as for the kinetic studies. To further investigate the effect of solid content on sorption, the solid content was varied from 0.1 to 1.1 g/L, but other parameters were the same as those used in the pH and ionic strength investigations.

For equilibrium sorption isotherm, the initial concentration of cobalt was varied from 4 to 24 mg/L. The suspensions were oscillated for 24 h under electrical thermostatic oscillation tank at 298.15, 318.15 and 338.15 K. The solid content was 0.3 g/L, but other parameters were the same as for the investigation of solid content.

Sorption isotherm models

A nonlinear fitting of the Langmuir and Freundlich models was used to determine the sorption isotherms. The Langmuir model assumes that sorption cannot proceed beyond monolayer coverage and the sorption sites are equivalent. It also assumes that solute immobilization occurs without mutual interaction between the neighboring sorbed molecules. Equation 1 describes the model.

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (1)$$

where C_e is the equilibrium concentration of Co(II) remaining in the solution (mol/L); q_e the amount of Co(II)

Table 1 The specifications of UV-1800 spectrophotometer

Parameter	Value	Parameter	Value
Wavelength range:	190–1,100 nm	Absorbance range:	–0.3–3 Abs
Spectral bandwidth:	2 nm	Wavelength accuracy:	±0.5 nm
Wavelength repeatability:	<0.2 nm	Photometric accuracy:	±0.5 %T (0 ~ 100 %T)
Photometric repeatability:	<0.2 %T (0 ~ 100 %T)	Stray light:	<0.05 %T at 220,360 nm
Baseline flatness:	±0.002 Abs	Baseline stability:	0.001 Abs/h at 500 nm (1 h after light source turned on)

sorbed after equilibrium (mol/g); q_{max} , the maximum sorption capacity, is the amount of sorbate at complete monolayer coverage (mol/g), and b (L/mol) is a constant related to the heat of sorption. The characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless parameter R_L , (also called separation factor), which has been defined as the isotherm shape to predict whether an sorption system is favorable or not. The relationship between R_L and isotherm parameter b is shown in Eq. 2.

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where C_0 is the initial concentration of Co(II) in solution (mol/L). The value of R_L indicates the sorption process to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [10, 11].

The Freundlich model is based on an exponential distribution of active sites and their energies, heterogeneous surface for ion exchange and possible mutual interaction between sorbed molecules [12, 13]. The model is represented by Eq. 3:

$$q_e = k_F C_e^n \tag{3}$$

where k_F ($\text{mol}^{1-n} \text{L}^n/\text{g}$) represents the sorption capacity when metal ion equilibrium concentration equals to 1, and n refers to the Freundlich sorption intensity parameter.

Calculation

The sorption of Co(II) was expressed in terms of distribution coefficient (K_d) [14] and sorption percentage(%) [15], which were calculated by the following equations:

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \tag{4}$$

$$\text{Adsorption}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{5}$$

where C_0 is the initial concentration, C_e is the equilibrium concentration in supernatant after centrifugation, m is the mass of permutite, and V is the volume of the suspension. All the experiments were completed in triplicate and the average uncertainties were below 5 %.

Results and discussion

Sorption kinetics

Figure 1 shows the influence of contact time on the removal of Co(II) by permutite. As shown in the figure, the sorption of Co(II) on permutite increases rapidly at the initial contact time and then reaches a plateau, which

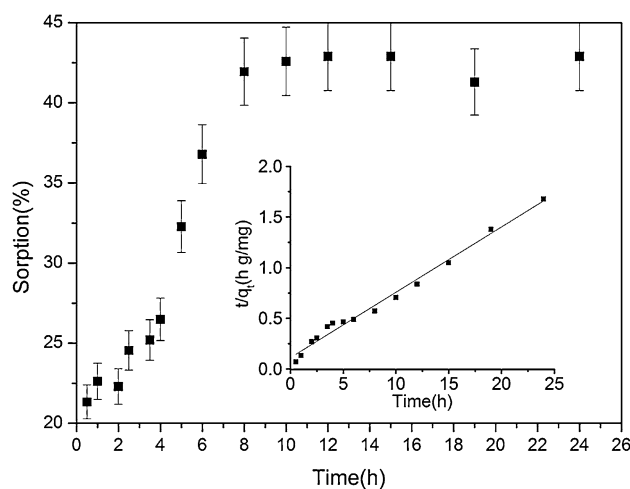


Fig. 1 Effect of contact time on Co(II) sorption on permutite and the pseudo-second-order rate equation fit (inset). $T = 298.15 \text{ K}$, $\text{pH} = 6.35 \pm 0.2$, $m/V = 0.3 \text{ g/L}$, $I = 0.01 \text{ mol/L NaCl}$, $C_{\text{Co(II) initial}} = 1.67 \times 10^{-4} \text{ mol/L}$

indicates that the sorption of Co(II) on permutite is mainly dominated by chemical sorption rather than physical sorption [16–19]. Sorption process proceeds in two steps: a initial fast step, followed by a much slower step. The first step is attributed to the chemical reaction with the functional groups, while the second step could be attributed to the exchange with cations in the inner surface of permutite and the longer range of diffusion through the particle pores. On the basis of the above results, the shaking time was fixed to 24 h to ensure the complete sorption equilibrium.

To determine the kinetic parameters of the sorption process, a pseudo-second-order rate equation was used to simulate the kinetic sorption [20, 21]:

$$\frac{t}{q_t} = \frac{1}{2Kq_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_t (mg/g) is the amount of Co(II) sorbed on the surface of permutite at time t (h), and q_e (mg/g) is the equilibrium sorption capacity. While K ($\text{g}/(\text{mg h})$) is the pseudo-second-order rate constant of sorption. The correlation coefficient ($R^2 = 0.9867$) of the linear plot of t/q_t versus t (the inserted figure in Fig. 1) is very close to 1, which indicates that the kinetic sorption of Co(II) on permutite agrees with the pseudo-second-order model.

Effect of pH

Figure 2 shows Co(II) sorption on permutite as a function of pH under 0.001, 0.01, 0.1 mol/L NaCl solutions at 298.15 K, respectively, while Fig. 3 shows the distribution species of Co(II) as a function of pH. From Fig. 2, it is clear that the efficiency of Co(II) removal by permutite is pH dependent. Furthermore, the function profile takes three

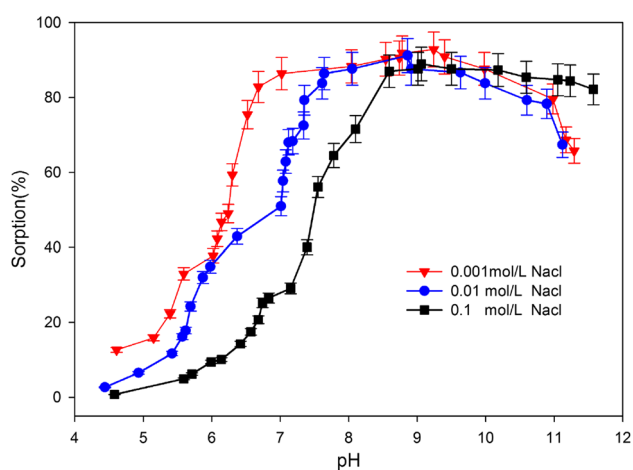


Fig. 2 Effect of ionic strength on Co(II) sorption on permutite as a function of pH, $T = 298.15$ K, $m/V = 0.3$ g/L, $C_{\text{Co(II) initial}} = 1.67 \times 10^{-4}$ mol/L

phases: slow sorption at low pH ($\text{pH} < 5.5$), followed by a sharp increase in the pH range from 5.5 to 8.5, and then a slight decrease at $\text{pH} > 8.5$. At low pH, this phenomenon can be attributed to the coulombic repulsion between Co^{2+} and the positively charged edge groups ($\equiv \text{SOH}_2^+$) since surface protonation reaction. For the second phase, as the pH increasing, the positive charge density of sorption edges reduces by the deprotonation reaction and some surface binding sites becomes negatively charged (such as $\equiv \text{SO}^-$), enhancing the sorption of positively charged Co(II) ions through electrostatic attraction. At high pH ($\text{pH} > 8.5$), Co(II) ions start to precipitate in the form of the insoluble hydroxide $\text{Co}(\text{OH})_2$ and the species of $\text{Co}(\text{OH})_3^-$ competes with negatively charged surface of permutite, which contribute to the slight decrease of sorption percentage. The results are similar to the sorption of Co(II) on Ca-rectorite [5], electrospun meso-hydroxylapatite nanofibers [16], magnetic multiwalled carbon nanotube/iron oxide composites [22] and bagasse pith based sulphurised activated carbon [23].

Effect of ionic strength

As shown in Fig. 2, the removal of Co(II) is significantly affected by ionic strength at $\text{pH} < 8.5$, however there is no drastic change in adsorption beyond this pH for all the NaCl solutions. This is possibly due to the influence of ionic strength on the thickness and interface potential of the double electrode layer, which could affect the binding of sorbed species [24]. The sorption of Co(II) on permutite increases as the ionic strength decreases at $\text{pH} < 8.5$. There are three possible explanations for this phenomenon: Firstly, the Co(II) ions form outer-sphere complexes with the permutite, favoring the sorption when the electrolyte

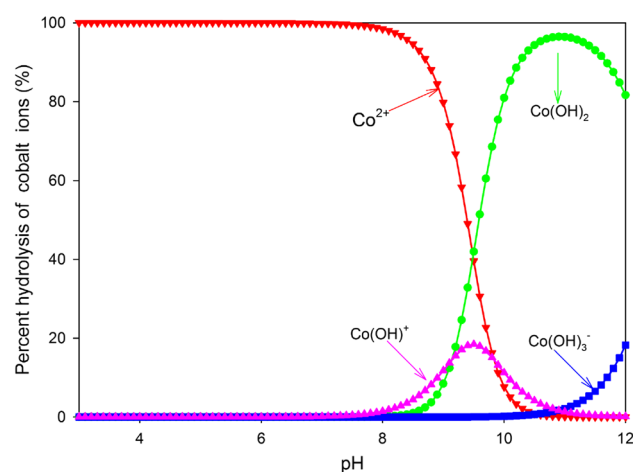


Fig. 3 Relative proportion of Co(II) species as a function of pH, $T = 298.15$ K, $I = 0.01$ mol/L NaCl, $C_{\text{Co(II) initial}} = 1.67 \times 10^{-4}$ mol/L

concentration decreases. This suggests that the sorption between the functional groups of permutite and Co(II) ions involves ionic interaction, which is consistent with an ion exchange mechanism [25]. Secondly, the influence of ionic strength on the activity coefficient of the Co(II) ions limits their transfer to permutite surfaces [26]. Thirdly, the electrostatic repulsion reduces with the increase of ionic strength, leading to increase in permutite particle aggregation. This would further reduce the amount of available binding sites [24].

In order to establish the relationship between C_e , pH and q_e for Co(II) sorption on permutite, the experimental data of Co(II) sorption in 0.001, 0.01 and 0.1 mol/L NaCl were plotted as three dimensional plots of C_e , pH and q_e , as shown in Fig. 4. On the pH- q_e plane, one can see that the sorption of Co(II) on permutite is greatly dependent on pH values, which is similar to the results shown in Fig. 2. The projection on the pH- C_e plane is just the inverted image of the projection on the pH- q_e plane; On the C_e - q_e plane, all experimental data lie in a straight line. Equation 7 describes the relationship of C_e - q_e :

$$VC_0 = mq_e + VC_e \quad (7)$$

where V is the volume of solution and m is the mass of permutite. The slope ($-V/m$) and the intercept ($C_0 V/m$) calculated from C_e to q_e line are -3.33 and 33.33 , which are in good agreement with the values of m/V and $C_0 V/m$ selected for the experiment shown on the caption of Fig. 4.

Effect of permutite content

The sorption of Co(II) on permutite as a function of solid content was studied at $T = 298.15$ K and $\text{pH} = 6.35$. From the Fig. 5, the sorption percentage of Co(II) increases

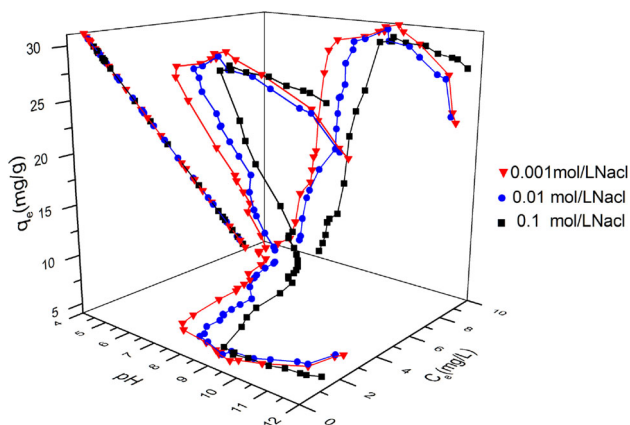


Fig. 4 3D plots of C_e , pH and q_e of Co(II) sorption on permutite, $T = 298.15\text{ K}$, $m/V = 0.3\text{ g/L}$, $C_{\text{Co(II) initial}} = 1.67 \times 10^{-4}\text{ mol/L}$

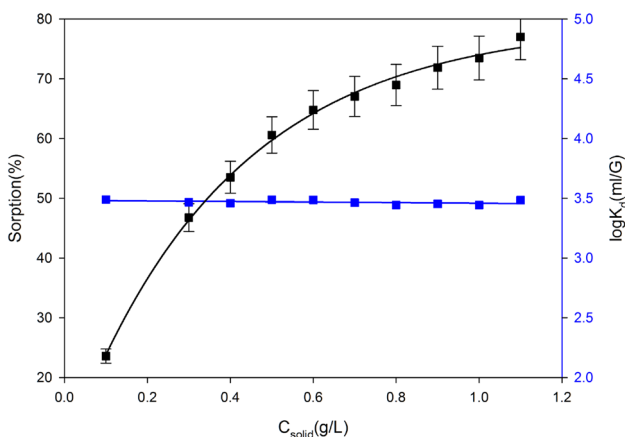


Fig. 5 Effect of solid content on Co(II) sorption on permutite, $T = 298.15\text{ K}$, $\text{pH} = 6.35 \pm 0.2$, $I = 0.01\text{ mol/L NaCl}$, $C_{\text{Co(II) initial}} = 1.67 \times 10^{-4}\text{ mol/L}$

significantly with increasing of permutite contents. A possible explanation for this phenomenon could be that more binding sites on surface of permutite were available with the increase of solid content, enhancing the formation of complexes between Co(II) and permutite.

Figure 5 shows the K_d values as a function of solid contents. One can see that the K_d values are constant with increasing solid contents, which is in agreement with the physicochemical property of the distribution coefficient, suggesting that there is almost no competition among the functional groups at permutite surfaces.

Sorption isotherms

Figure 6 shows the sorption isotherms of Co(II) on permutite at 298.15, 318.15 and 338.15 K, respectively. It is clear that the sorption isotherm at high temperature is higher than that at low temperature, which indicates that

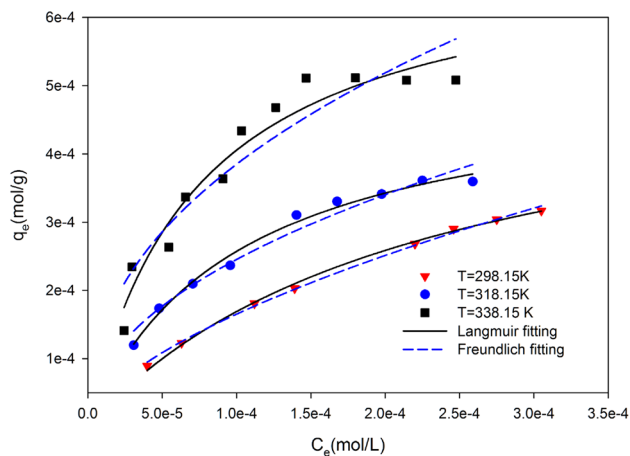


Fig. 6 Sorption isotherms of Co(II) on permutite at three different temperatures, $m/V = 0.3\text{ g/L}$, $\text{pH} = 6.35 \pm 0.2$, $I = 0.01\text{ mol/L NaCl}$

Table 2 The parameters for the two isotherm models at different temperatures

Correlation parameters	$T = 298.15\text{ k}$	$T = 313.15\text{ k}$	$T = 338.15\text{ k}$
Langmuir			
$b(\text{L/mol})$	4.44×10^3	1.01×10^4	1.36×10^4
$q_{\text{max}}(\text{mol/g})$	5.5×10^{-4}	5.13×10^{-4}	7.03×10^{-4}
R_L	0.360–0.771	0.199–0.598	0.155–0.523
R^2	0.997	0.989	0.945
Freundlich			
$k_F(\text{mol}^{1-n}\text{ L}^n/\text{g})$	4.30×10^{-2}	1.91×10^{-2}	2.02×10^{-2}
n	0.604	0.473	0.430
R^2	0.997	0.966	0.886

the high temperature promotes Co(II) sorption on permutite.

The experimental data of Co(II) sorption are simulated with the Langmuir and Freundlich models, and the results are shown in Fig. 6. The relative parameters calculated from Langmuir and Freundlich models are listed in Table 2. It can be concluded from the correlation coefficients that the Langmuir isotherm fits the experimental data very well, which suggests almost complete monolayer coverage of sorbent surfaces. The sorption process is favorable on the basis of the values of R_L (in Table 2) in the range 0–1. All the values of n obtained from the Freundlich model are lower than 1, which indicates that a nonlinear sorption took place on the surface of sorbent.

Thermodynamic parameters

Thermodynamic parameters can provide additional in-depth information regarding the inherent energetic changes

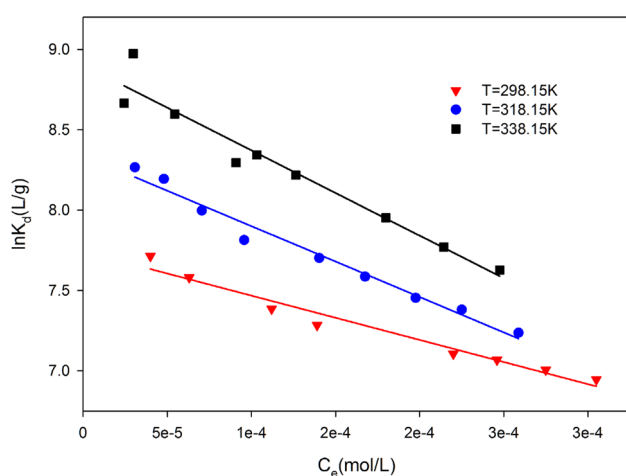


Fig. 7 Linear plots of $\ln K_d$ versus C_e for Co(II) on permutite at three different temperatures, $m/V = 0.3$ g/L, $\text{pH} = 6.35 \pm 0.2$, $I = 0.01$ mol/L NaCl

Table 3 Thermodynamic parameters for the sorption of Co(II) on permutite

$T(K)$	$\Delta G^0(\text{kJ/mol})$	$\Delta H^0(\text{kJ/mol})$	$\Delta S^0(\text{J/(mol K)})$
$T = 298.15$ k	-19.20	24.30	145.9
$T = 313.15$ k	-22.07	24.35	145.9
$T = 338.15$ k	-25.03	24.31	145.9

associated with the sorption process. The thermodynamic parameters, average standard enthalpy change (ΔH^0), standard entropy change (ΔS^0) and Gibbs free energy change (ΔG^0) for Co(II) sorption on permutite can be determined from the temperature-dependent sorption. The Gibbs free energy change can be calculated from the following equation:

$$\Delta G^0 = -RT \ln K^0 \quad (8)$$

where K^0 is the sorption equilibrium constant, R is ideal gas constant (8.315 J/(mol K)), and T is the absolute

temperature in Kelvin (K). The values of $\ln K^0$ are obtained by plotting $\ln K_d$ versus C_e (Fig. 7) and extrapolating C_e to zero, which are 7.74 at 298.15 K, 8.34 at 318.15 K and 8.90 at 338.15 K, respectively. Standard entropy change (ΔS^0) is calculated using the equation:

$$\Delta S^0 = -\left(\frac{\partial \Delta G^0}{\partial T}\right)_P \quad (9)$$

The average standard enthalpy change (ΔH^0) is then calculated from the relationship:

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 \quad (10)$$

The values calculated by Eqs. 8–10 are listed in Table 3. The positive value of ΔH^0 suggests the sorption process is endothermic, probably because the solvated Co(II) ions in water have to partly denude their hydration sheath before its sorption on permutite [16, 27]. This dehydration process needs energy, which exceeds the exothermicity of Co(II) ions to attach to the permutite surface [16]. The positive ΔS^0 value reflects the high affinity of permutite towards Co(II) ions in aqueous solutions, and suggests some structural changes onto permutite surface. The value of ΔG^0 is negative as expected for a spontaneous process under the conditions applied. The ΔG^0 value decreases with an increase of temperature, indicating that spontaneity increases with increasing temperature. At high temperature, cations are readily desolvated, and hence their sorption becomes more favorable [27, 28]. Above all, it can be concluded that the sorption of Co(II) on permutite is an endothermic and spontaneous process.

Comparison of Co(II) sorption capacity of permutite with other sorbents

Several sorbent materials, either naturally occurring or synthetic, can be used to eliminate Co(II) from wastewater. The maximum sorption capacity (q_{max}) of Co(II) simulated by the Langmuir model for the different materials are listed

Table 4 Comparison of sorption capacity of permutite with other sorbents for Co(II)

Sorbents	Solution chemistry conditions	$q_{\text{max}}(\text{mg/g})$	Reference
Oxidized MWCNT	$\text{pH} = 6.4, T = 303.15$ K	8.67	29
Na-rectorite	$\text{pH} = 6.2, T = 298.15$ K	11.82	30
Natural zeolites	$\text{pH} = 6-7, T = 298.15$ K	14.38	31
Ca-rectorite	$\text{pH} = 6.5, T = 298.15$ K	14.4	5
Lemon peel	$\text{pH} = 6.0, T = 298.15$ K	22	32
Na-montmorillonite	$\text{pH} = 6.0, T = 298.15$ K	26.64	7
Permutite	$\text{pH} = 6.35, T = 298.15$ K	32.45	Present study
Fishbone	$\text{pH} = 6.0, T = 298.15$ K	33	33
GMZ bentonite	$\text{pH} = 6.0, T = 298.15$ K	36.84	8
Multiwalled carbon nanotube	$\text{pH} = 6.35, T = 298.15$ K	38.04	34

in Table 4. From the table, it can be observed that the sorption capacity of permutite is better than some sorbents under similar experimental conditions.

Conclusions

As part of an ongoing research in our lab to identify the most appropriate materials for nuclear waste water treatment, we studied the sorption process of Co(II) on permutite, a synthetic zeolite, under different experimental conditions. The sorption is pH and ionic strength dependent. The sorption kinetic results and the separation factor of Langmuir isotherm model reveal that the sorption of Co(II) onto permutite is a favorable chemical sorption process. The thermodynamic parameters indicate the sorption of Co(II) onto permutite is an endothermic and spontaneous process. Compared with other sorbents, it is clear that the permutite has excellent potential for disposal of radiocobalt (II) bearing wastewaters and may be suitable for the uptake other heavy metals and radionuclides. However, the capacity to sorb other heavy metals in different conditions needs further investigation.

Acknowledgments We thank the financial supports by the National Natural Science Foundation of China (Grant No. 11275147) and by Program for Changjiang Scholars and Innovative Research Team in University (No: IRT1280).

References

- Mustafa YA, Zaiter MJ (2011) Treatment of radioactive liquid waste (Co-60) by sorption on Zeolite Na-A prepared from Iraqi kaolin. *J Hazard Mater* 196:228–233
- Rengaraj S, Moon SH (2002) Kinetics of sorption of Co (II) removal from water and wastewater by ion exchange resins. *Water Res* 36(7):1783–1793
- Ahmadpour A, Tahmasbi M, Bastami TR, Besharati JA (2009) Rapid removal of cobalt ion from aqueous solutions by almond green hull. *J Hazard Mater* 166(2):925–930
- Omar H, Arida H, Daifullah A (2009) Sorption of ^{60}Co radionuclides from aqueous solution by raw and modified bentonite. *Appl Clay Sci* 44(1):21–26
- Zong P, Guo Z, He C, Zhao Y, Liu S, Wang H, Pan H (2012) Impact of environmental conditions on the sequestration of radionuclide ^{60}Co (II) at Ca-rectorite/water interface. *J Radioanal Nucl Chem* 293(1):289–297
- Smičiklas I, Dimović S, Plečaš I (2007) Removal of Cs^{1+} , Sr^{2+} and Co^{2+} from aqueous solutions by sorption on natural clinoptilolite. *Appl Clay Sci* 35(1):139–144
- Wen T, Chen Y, Cai L (2011) Impact of environmental conditions on the sorption behavior of radiocobalt onto montmorillonite. *J Radioanal Nucl Chem* 290(2):437–446
- Chen L, Yu S, Zuo L, Liu B, Huang L (2011) Investigation of Co (II) sorption on GMZ bentonite from aqueous solutions by batch experiments. *J Radioanal Nucl Chem* 289(2):511–520
- Frising T, Leflaive P (2008) Extraframework cation distributions in X and Y faujasite zeolites: a review. *Microporous Mesoporous Mater* 114(1):27–63
- Webi TW, Chakravort RK (1974) Pore and solid diffusion models for fixed-bed adsorbents. *AIChE J* 20(2):228–238
- Nassar MM, Ewida KT, Ebrahiem EE, Magdy YH, Mhaedi MH (2004) Sorption of iron and manganese ions using low-cost materials as adsorbents. *Sorpt Sci Technol* 22(1):25–37
- Naeem A, Westerhoff P, Mustafa S (2007) Vanadium removal by metal (hydr) oxide adsorbents. *Water Res* 41(7):1596–1602
- Mamba BB, Nyembe DW, Mulaba-Bafubandi AF (2009) Removal of copper and cobalt from aqueous solutions using natural clinoptilolite. *Water SA* 35(3):307–314
- Zhang QH, Sun S, Li S, Jiang H, Yu JG (2007) Sorption of lithium ions on novel nanocrystal MnO_2 . *Chem Eng Sci* 62(18):4869–4874
- Lu X, Yin Q, Xin Z, Zhang Z (2010) Powerful sorption of silver (I) onto thiol-functionalized polysilsesquioxane microspheres. *Chem Eng Sci* 65(24):6471–6477
- Wang H, Zhang P, Ma X, Jiang S, Huang Y, Zhai L, Jiang S (2014) Preparation, characterization of electrospun meso-hydroxylapatite nanofibers and their sorptions on Co (II). *J Hazard Mater* 265:158–165
- Guo Z, Li Y, Zhang S, Niu H, Chen Z, Xu J (2011) Enhanced sorption of radiocobalt from water by Bi(III) modified montmorillonite: a novel adsorbent. *J Hazard Mater* 192(1):168–175
- Guo Z, Xu D, Zhao D, Zhang S, Xu J (2011) Influence of pH, ionic strength, foreign ions and FA on sorption of radiocobalt on goethite. *J Radioanal Nucl Chem* 287(2):505–512
- Guerra DL, Viana RR, Airoidi C (2009) Sorption of thorium cation on modified clays MTTZ derivative. *J Hazard Mater* 168(2):1504–1511
- Ho YS, Wase DAJ, Forster CF (1996) Kinetic studies of competitive heavy metal sorption by sphagnum moss peat. *Environ Technol* 17(1):71–77
- Órfão JJM, Silva AIM, Pereira JCV, Barata SA, Fonseca IM, Faria PCC, Pereira MFR (2006) Sorption of a reactive dye on chemically modified activated carbons—influence of pH. *J Colloid Interface Sci* 296(2):480–489
- Wang Q, Li J, Chen C, Ren X, Hu J, Wang X (2011) Removal of cobalt from aqueous solution by magnetic multiwalled carbon nanotube/iron oxide composites. *Chem Eng J* 174:126–133
- Krishnan KA, Anirudhan TS (2008) Kinetic and equilibrium modelling of cobalt (II) sorption onto bagasse pith based sulphurised activated carbon. *Chem Eng J* 137(2):257–264
- Yang S, Hu J, Chen C, Shao D, Wang X (2011) Mutual effects of Pb(II) and humic acid sorption on multiwalled carbon nanotubes/polyacrylamide composites from aqueous solutions. *Environ Sci Technol* 45(8):3621–3627
- Reddad Z, Gerente C, Andres Y, Le Cloirec P (2002) Sorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ Sci Technol* 36(9):2067–2073
- Ravat C, Dumonceau J, Monteil-Rivera F (2000) Acid/base and Cu (II) binding properties of natural organic matter extracted from wheat bran: modeling by the surface complexation model. *Water Res* 34(4):1327–1339
- Tahir SS, Rauf N (2003) Thermodynamic studies of Ni (II) sorption onto bentonite from aqueous solution *J Chem Thermodyn* 35(12)
- Qadeer R, Hanif J, Saleem M, Afzal M (1993) Surface characterization and thermodynamics of sorption of Sr^{2+} , Ce^{3+} , Sm^{3+} , Gd^{3+} , Th^{4+} , UO_2^{2+} on activated charcoal from aqueous solution. *Colloid Polym Sci* 271(1):83–90
- Wang Q, Chen L, Sun Y (2012) Removal of radiocobalt from aqueous solution by oxidized MWCNT. *J Radioanal Nucl Chem* 291(3):787–795
- Liu Z, Chen L, Dong Y, Zhang Z (2011) Impact of environmental conditions on the sorption behavior of Co (II) on Na-rectorite

- studied by batch experiments. *J Radioanal Nucl Chem* 289(3):851–859
31. Erdem E, Karapinar N, Donat R (2004) The removal of heavy metal cations by natural zeolites. *J Colloid Interface Sci* 280(2):309–314
32. Bhatnagar A, Minocha AK, Sillanpää M (2010) Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent. *Biochem Eng J* 48(2):181–186
33. Park Y, Shin WS, Choi SJ (2013) Removal of cobalt and strontium from groundwater by sorption onto fishbone. *J Radioanal Nucl Chem* 295(1):789–799
34. Li K, Hu J, Liu Z, Chen L, Dong Y (2013) Sorption of radio-cobalt (II) onto MWCNTs: effects of solid content, contact time, pH, ionic strength, humic acid and temperature. *J Radioanal Nucl Chem* 295(3):2125–2133