



Capture of Co(II) from its aqueous EDTA-chelate by DTPA-modified silica gel and chitosan

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ABSTRACT

The adsorption of Co(II) by diethylenetriaminepentaacetic acid (DTPA)-modified silica gel and chitosan in the presence of EDTA and other interfering species was studied. Co(II) removal ranged from 93% to 96% from the solutions where Co(II) was totally chelated by EDTA. The amount of oxalate or Fe(II) did not affect the adsorption of Co(II) in the case of DTPA-chitosan. However, increasing the amount of oxalate enhanced the adsorption performance of DTPA-silica gel, probably due to the formation of new active sites on the silica gel surface. DTPA-chitosan was also effective in simulated decontamination solutions. For DTPA-silica gel, the rate of adsorption of free Co(II) was controlled by pore diffusion, but the rate of adsorption of Co(II)EDTA was controlled by the surface chelation reaction, which was attributed to the inhibited diffusion of Co(II)EDTA inside the silica gel mesopores. However, the macroporous structure of DTPA-chitosan enabled pore diffusion of both Co(II) and Co(II)EDTA. The equilibrium isotherms of DTPA-silica gel were best described by a BiLangmuir model, in which there are two different adsorption sites on the silica gel surface assigned to different speciations of DTPA. For DTPA-chitosan, the data fit best with a Sips model, which indicates system heterogeneity. Finally, measurements with capillary electrophoresis showed an increase in dissolved EDTA during adsorption, demonstrating the ability of DTPA-modified adsorbents to release Co(II) from its EDTA chelate. This promising result can provide a basis for applying the studied materials to the treatment of water effluents containing Co(II) chelated by EDTA by a simple one-step adsorption process.

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1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that is widely used in industrial cleaning, the nuclear industry, pharmaceuticals, and manufacturing of textile leather, rubber, and paper [1–6]. The main reason for using EDTA in many of these applications is to clear pipes and reactors of metal ions or prevent their precipitation through chelation [7]. Chelating agents and their salts are not toxic as such, but environmental concerns arise due to the potential for EDTA to remobilize the metals from sediments and decrease the efficiency of heavy metal elimination in wastewater treatment processes [8,9]. Moreover, EDTA contains about 10% nitrogen, which causes eutrophication in the aquatic environment.

Low-level radioactive waste (LLRW) arising from the operation of nuclear power plants (NPPs) and medical use of radioactive

isotopes accounts for more than 90% of the volume but only 1% of the radioactivity of all radioactive waste [10]. However, this waste is still hazardous and has to be treated and stored properly. Many of the liquid waste streams from NPPs contain chelating agents, such as EDTA, originating from cleaning solutions used to decontaminate NPP structures [11]. Treatment of radioactive waste containing chelating agents by conventional methods like non-specific ion exchangers, precipitation or mixing with cement produces large amounts of waste to treat and dispose of [12,13]. Combined treatment of radioactive waste involving destruction of chelant before adsorption has been shown to be useful but additional treatment steps usually increase the cost and time spent for the whole process [14]. Thus, a one-step method that is both economical and reduces the amount of LLRW is needed. Selective ion-exchangers may be the most promising solution to this problem.

Various ion exchange materials have been tested for metal adsorption from solutions containing EDTA or other complexing agents. Such materials are, for example, titanium antimonates [11], clay minerals [15], commercial anion exchangers [7,16], commercial cation exchangers [17], copolymers with amino groups

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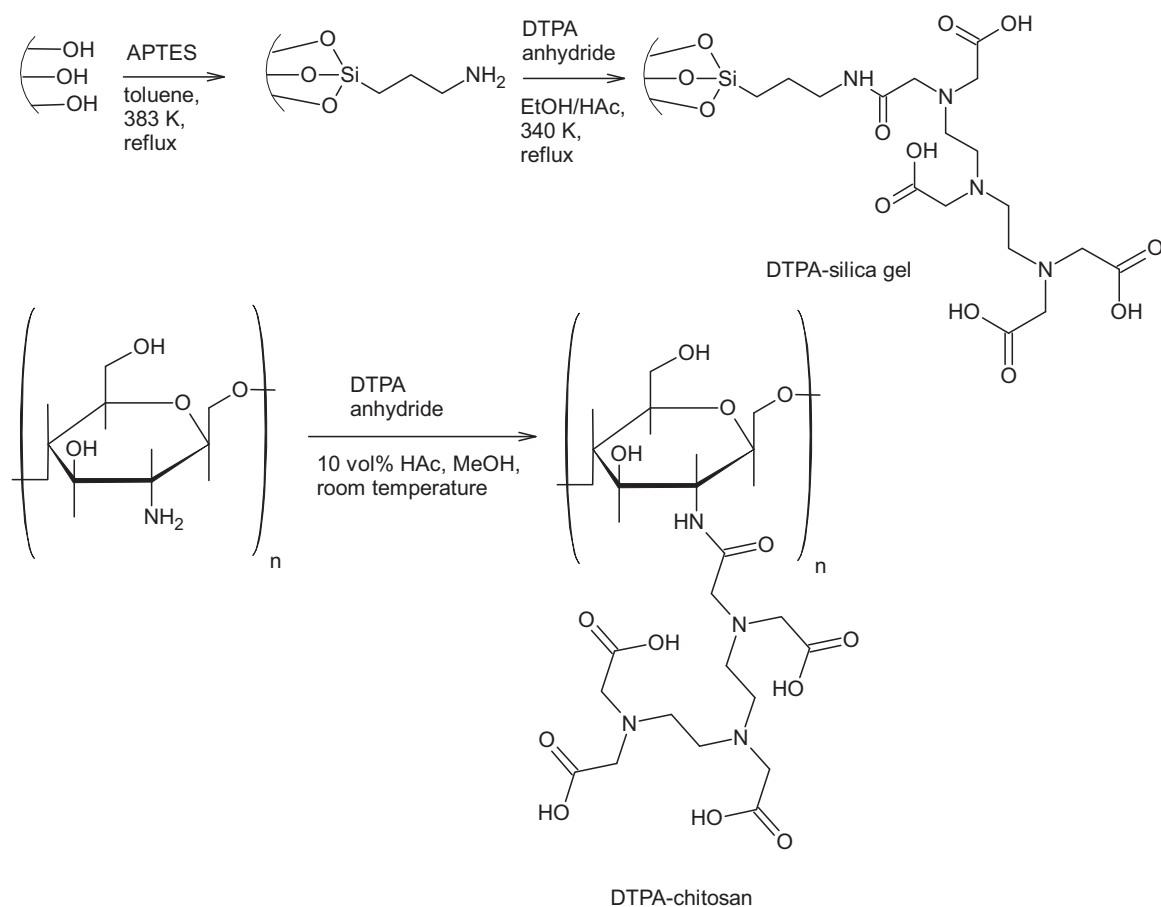


Fig. 1. Synthesis of DTPA-modified adsorbents.

[18], polyethyleneimine-agarose [19], and chitosan [20–23]. The studies above were based on either cation exchange between a dissolved metal–EDTA chelate and the ion exchanger or anion exchange where the whole metal–EDTA chelate was adsorbed. For the treatment of radioactive waste, cation exchange is preferred due to the fact that EDTA may enhance the leaching of radionuclides from the disposal sites. New, effective cation exchangers should contain chelating agents with higher binding affinities towards target metals than EDTA. Such a chelating agent is, for example, diethylenetriaminepentaacetic acid (DTPA).

The aim of this work was to study the applicability of DTPA-functionalized silica gel and chitosan [24,25] to the adsorption of Co(II) in the presence of EDTA. Co(II) was selected as the target metal because its radioactive isotope ⁶⁰Co is one of the most problematic waste nuclides, with quite a long half-life (5.2 years) and high gamma decay energy [11]. DTPA-modified silica gel [24] and chitosan [25] have been found to be effective adsorbents for Co(II) from pure metal solutions. These studies included only fundamental investigations of metal solutions without any interfering species. However, in this work, the adsorption properties of DTPA-modified adsorbents in the Co(II) solutions containing EDTA as a strong chelating agent as well as some other interfering ions such as oxalate, calcium, permanganate, and iron were studied. Moreover, the release of EDTA during the Co(II) adsorption was experimentally confirmed. To the best of our knowledge, there are not many reports about possible separation of metals from their aqueous EDTA chelates using only cation exchange [11,17].

2. Materials and methods

2.1. Materials

As received, silica gel type LiChroPrep® (Merck) was provided in powder form (diameter: 63–200 μm, surface area: 540 m²/g). Chitosan flakes >85% deacetylated (Sigma–Aldrich) had a molecular weight ranging from 190,000 to 375,000 g/mol. All chemicals used in this study were of analytical grade and supplied by Sigma–Aldrich. A Co(II) stock solution of 1000 mg/L was prepared from its nitrate salt. The radioactive tracer, ⁵⁷Co, was obtained from Eckert & Ziegler Isotope products. The ⁵⁷Co concentration in trace solutions was <3 × 10^{−14} M. Before use, prepared solutions were allowed to equilibrate for at least 24 h by mixing in the dark. Adjustment of pH was done using 0.1 M NaOH and 0.1 M HNO₃.

2.2. Methods

2.2.1. Chemical modification of silica gel and chitosan

The silica gel was modified as previously described [24]. Briefly, aminopropyltriethoxysilane (APTES) and silica gel were first allowed to react in toluene in order to attach APTES groups covalently to the silica surface. Then the surface-bound amino groups were allowed to react with DTPA-anhydride in an ethanol and acetic acid solution. Chitosan was also modified as described earlier [25] by allowing chitosan to react with DTPA-anhydride in a solution of acetic acid and methanol (Fig. 1).

The formation of functional groups on the adsorbent surface was confirmed using a FTIR-spectroscopy Nicolet Nexus 8700 (USA). The

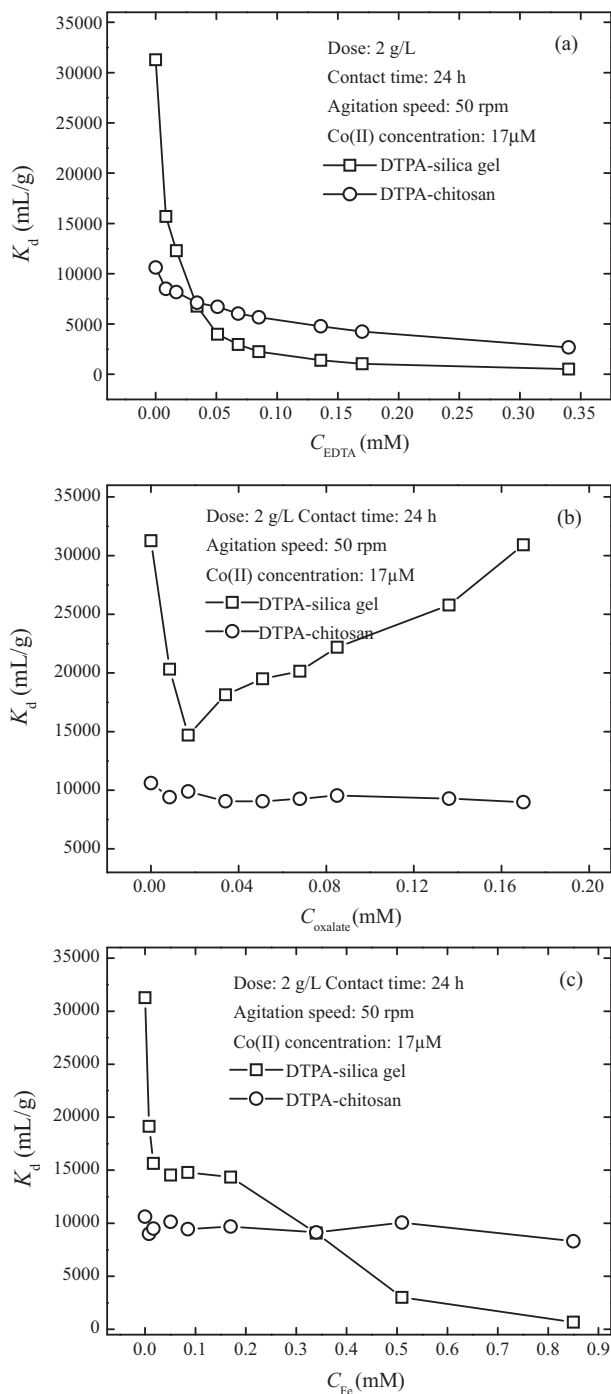


Fig. 2. Effects of (a) EDTA, (b) oxalate, and (c) iron on the adsorption of Co(II) by DTPA-modified adsorbents, pH 3 (DTPA-silica gel) and pH 2 (DTPA-chitosan).

peaks at wavenumbers of 1631 and 1398 cm^{-1} for DTPA-silica gel and 1731 and 1643 cm^{-1} for DTPA-chitosan indicated the formation of carboxylic groups on the adsorbent surfaces. The surface coverages of DTPA-groups analyzed by elemental analysis [24,25] and Boehm titration [26] were 0.22–0.26 mmol/g for DTPA-silica gel and 0.90–0.96 mmol/g for DTPA-chitosan. The specific surface area, total pore volume, and average pore size of DTPA-silica gel were 309 m^2/g , 0.34 cm^3/g , and 49 \AA , respectively, and those of DTPA-chitosan were 0.36 m^2/g , 0.74 $\times 10^{-3}$ cm^3/g , and 552 \AA , as determined by Autosorb-1-C (Quantachrome, The UK).

2.2.2. Studied solutions

The adsorption of Co(II) by DTPA-modified adsorbents was tested in different solution matrices. The effects of EDTA, oxalate, and iron on Co(II) adsorption were separately studied, since these ions are often found in the target waste streams. Other solutions were selected to examine the influence of salts, acids and oxidizing agents (Table 1). The studied solutions were an aqueous solution containing oxalate, EDTA, and calcium (EOC), simulated floor drain water (FDW) [27], and simulated decontamination solutions (DEs). In addition, a few adsorption tests were carried out on the Co(II) solutions with trace radioactive ^{57}Co isotope. In LLRW solutions Co(II) can be found at the nanomolar level, but to get reliable results from ICP analysis, a Co(II) concentration of 17 μM (1 mg/L) was selected for most of the studies. Furthermore, at low Co(II) concentrations, the adsorption efficiency of both modified adsorbents was found to be highly dependent on pH [24,25] and the pH was thus adjusted to 3 for DTPA-silica gel and 2 for DTPA-chitosan to obtain maximum adsorption efficiency.

2.2.3. Batch adsorption studies

Batch experiments were conducted at ambient temperature (22 ± 1 $^\circ\text{C}$) by mixing Co(II) solution and adsorbent (dose: 2 g/L) for a designated time in a rotary shaker, type ST5 (CATM.Zipperer GmbH, Staufen, Germany). The adsorbent was separated from the solution using a 0.45 μm polypropylene syringe filter. The samples were analyzed by an inductively coupled plasma optical atomic emission spectrometer (ICP-OES), model iCAP 6300 (Thermo Electron Corporation, USA). Co(II) concentrations were analyzed at a wavelength of 228.616 nm and the detection limit was 0.007 μM . The amount of radiocobalt (^{57}Co) was determined using an automatic gamma counter (Wallac 1480 WizardTM 3). The quantity of the adsorbed metal per unit mass of modified silica gel (mmol/g) was calculated as follows:

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where C_i and C_e are the initial and the equilibrium concentrations (mmol/L), while M and V represent the weight of the adsorbent (g) and the volume of the solution (L), respectively. The distribution ratio (mL/g), which describes the distribution of adsorbate between the solution and the adsorbent at equilibrium, was calculated using Eq. (2):

$$K_d = 1000 \frac{\text{mL}}{\text{L}} \times \frac{q_e}{C_e} \quad (2)$$

2.2.4. Capillary electrophoresis measurements

Capillary electrophoresis (CE) enables simultaneous detection of EDTA and its metal complexes in aqueous solutions [28]. CE measurements (Beckman Coulter, USA) were conducted to determine the amount of free EDTA in the solution after adsorption experiments [29]. A solution of 25 mM phosphate buffer (pH 7) and 0.5 mM tetradecyltrimethylammonium bromide (TTAB, Aldrich) was used as carrier electrolyte. TTAB changed the direction of the electro-osmotic flow in the fused silica capillary (75 μm diameter, 60 cm length to the detector) by making the wall charge positive. The power supply was changed to negative, generating net fluid movement towards the detector. The injection time of samples was 10 s and the run voltage 19 V. Between runs the capillary was washed with 0.1 M NaOH and water. Between every five samples the capillary was also rinsed with TTAB-buffer solution.

2.2.5. Regeneration studies

The regeneration of DTPA-modified adsorbents was studied previously in pure metal ion solutions [24,25]. Both of the adsorbents lasted several regeneration cycles without losing their adsorption efficiency. However, to study the effect of EDTA on regeneration

Table 1
Co(II) adsorption from waters containing different interfering species.

Solution	Composition	K_d (mL/g)/ads% for DTPA-silica gel	K_d (mL/g)/ads% for DTPA-chitosan
Co1	17 μM Co^{2+} , pH: 3	31270/98.5	
Co2	17 μM Co^{2+} , pH: 2	5726/92.1	10620/95.5
EOC	17 μM Co^{2+} , 51 μM EDTA, 51 μM oxalate, 1.25 mM Ca^{2+} , pH: 3	3946/89.0	5985/92.4
FDW	17 μM Co^{2+} , 34 μM EDTA, 1.74 mM Na^+ , 0.21 mM K^+ , 25 μM Ca^{2+} , 2.3 M H_3BO_3 , pH: 3	4950/90.9	
DE1	17 μM Co^{2+} , 90 μM Fe^{2+} , 0.01 M oxalic acid, pH: 2	1537/75.9	5756/92.1
DE2	17 μM Co^{2+} , 34 μM EDTA, 90 μM Fe^{2+} , 0.01 M oxalic acid, pH: 2	649/57.4	1499/75.5
DE3	17 μM Co^{2+} , 90 μM Fe^{2+} , 1 mM KMnO_4 , 0.01 HNO_3 , pH: 2	241/33.4	316/39.1
DE4	17 μM Co^{2+} , 34 μM EDTA, 90 μM Fe^{2+} , 1 mM KMnO_4 , 0.01 HNO_3 , pH: 2	270/35.5	389/44.5
DE5	17 μM Co^{2+} , 90 μM Fe^{2+} , 0.01 HNO_3 , pH: 2	1219/72.0	8518/94.7
DE6	17 μM Co^{2+} , 34 μM EDTA, 90 μM Fe^{2+} , 0.01 HNO_3 , pH: 2	980/67.1	4554/90.6
R1	10 μM Co(II) and 20 μM EDTA traced with ^{57}Co , 0.01 M NaNO_3 , pH: 3	11730/96.0	
R2	10 μM Co(II) and 20 μM EDTA traced with ^{57}Co , 0.01 M NaNO_3 , pH: 2	3254/86.6	6413/92.8

properties, adsorbents were first mixed with 1 mM Co(II):EDTA (1:2) following regeneration with 2 M HNO_3 .

3. Results and discussion

3.1. Effects of various ions on Co(II) adsorption by DTPA-modified adsorbents

Water effluents to be treated before discharge contain not only target metals but also organic and inorganic compounds that may inhibit the adsorption of metal ions. One of the aims of this study was to investigate the possibility of using DTPA-modified adsorbents in the treatment of LLRW solutions produced by NPPs and the solution matrices were selected accordingly (Section 2.2.2, Table 1). The adsorption efficiencies were compared using both distribution ratio (K_d , Eq. (2)) and percentage removal of Co(II).

3.1.1. Effect of EDTA

The main goal of this study was to investigate how EDTA affects the adsorption of Co(II) by DTPA-modified adsorbents. Fig. 2a shows that when EDTA was not present in the solution or the amount of EDTA was less than two-fold the concentration of Co(II), DTPA-silica gel had a higher K_d value than DTPA-chitosan. However, the effectiveness of Co(II) adsorption decreased steeply in the case of DTPA-silica gel, and in Co(II):EDTA 1:10 solution the K_d was four times higher for modified chitosan. The Co(II) removal efficiencies of DTPA-silica gel and -chitosan in the Co(II):EDTA 1:2 solution were 96.3% and 93.8%, and in 1:10 solution they were 67.8% and 90.2%, respectively. For comparison, 97% removal of Co(II) was achieved by Malinen et al. [11] using titanium antimonates in the Co(II):EDTA 1:2 system, while only 7% removal was obtained using CoTreat in a Co(II):EDTA 1:1 system [30].

Based on the speciation calculations (MINEQL, ver. 2.53), in the Co(II):EDTA 1:10 solution over 99% of Co(II) is chelated by EDTA at pH 3 and over 90% at pH 2. Thus, it is obvious that, besides binding Co(II) ions, DTPA-silica gel and -chitosan were able to bind either Co(II)EDTA-chelates or capture Co(II) from dissolved metal EDTA species (see Sections 3.3 and 3.4). This result is promising because the highly Co(II) specific adsorption material CoTreat can bind Co(II) only in ionic form [11,30].

3.1.2. Effect of oxalate

Besides EDTA, oxalate is a commonly found chemical in NPP liquid waste [31]. Oxalate addition did not show any significant effect on the Co(II) adsorption of DTPA-chitosan (Fig. 2b). However, in the case of DTPA-silica gel, an increasing amount of oxalate at first inhibited but then enhanced the adsorption efficiency of Co(II). This could be explained by oxalate ion adsorption on the surface. A previous study showed that there were still free amino groups on the DTPA-silica gel surface after DTPA immobilization [24]. These

amino groups were positively charged at pH 3 [21] and might have bound negatively charged oxalate ions on the surface, forming more favorable binding sites for Co(II).

3.1.3. Effect of iron

A very common metal contaminant on NPP's reactor walls and piping is iron. That is why the spent decontamination solutions used in cleaning can contain varying amounts of iron. For DTPA-silica gel, increasing the concentration of iron decreased the adsorption efficiency of Co(II) (Fig. 2c). However, DTPA-chitosan adsorbed approximately the same amount of Co(II) when there was no iron as when the Co(II):Fe(II) molar ratio was 1:50. The difference between modified silica gel and -chitosan can be explained by the higher surface coverage of DTPA-ligands on the surface of chitosan compared to silica gel. While DTPA-chitosan had enough adsorption sites for both Co(II) and Fe(II), Fe(II) was able to occupy some of the adsorption sites of DTPA-silica gel. The overall favorable binding of Co(II) over Fe(II) for both DTPA-modified adsorbents can be explained by the higher stability constant of Co(II)DTPA chelate ($\text{p}K = 20.95$) compared to the corresponding Fe(II)DTPA chelate ($\text{p}K = 18.35$) [32].

3.1.4. Solutions with mixed ions

Table 1 shows the distribution ratios and adsorption efficiencies for Co(II) removal by DTPA-modified adsorbents from both pure Co(II) solutions and solutions containing different interfering species. At the optimal pH, for DTPA-silica gel the K_d value was three times higher than that of DTPA-chitosan (Table 1). However, at higher Co(II) concentrations the adsorption efficiency of DTPA-chitosan was better than that of DTPA-silica gel due to its higher ligand loading [24,25]. The unusual behavior at low concentrations was attributed to the crosslinking of DTPA-groups on the surface of chitosan due to its branched structure [25]. When solutions contained high amounts of metals, chelating with the surface groups occurred before crosslinking.

The first solution with mixed ions contained both EDTA and oxalate along with 1.25 mM Ca(II). Table 1 shows that distribution ratios of Co(II) decreased significantly for both modified adsorbents but nonetheless adsorption efficiencies of around 90% were obtained. The adsorption performance of DTPA-silica gel in simulated FDW, where the most abundant interfering agent was boric acid, was also lower than in pure Co(II) solutions, but at pH 3 an adsorption efficiency of around 90% was achieved. However, in real applications the pH of FDW is around 8, where both of the adsorbents studied here were shown to be ineffective. This highlights the importance of pH adjustment.

Decontamination solutions (DEs) are used to clean reactors and pipes in NPPs. These solutions contain, for example, nitric acid, boric acid, or fluoroboric acid and in some cases permanganate as an oxidizing agent. In this study the removal of Co(II) from six different

DE-solutions was studied. DTPA-silica gel had low adsorption efficiency in all of the solutions (Table 1). This is because pH 2 was not optimal for DTPA-silica gel. However, even when the pH was optimal for DTPA-chitosan, the adsorption efficiency was clearly affected by the solution matrix. The most notable effect was seen in the solutions containing permanganate ions. This is not surprising since permanganate is known to oxidize polyaminocarboxylic acids [33], which would result in degradation of surface-bound DTPA groups. The effect of the type of acid was also evident in the case of the DE-solutions. The K_d value was around 1.5 times higher in nitric acid than in oxalic acid for DTPA-chitosan in the solutions without EDTA (DE1 and DE5). In similar solutions with EDTA (DE2 and DE6), the K_d value was three times higher in nitric acid. This can be explained by the chelating ability of oxalate ion, which could have interrupted metal binding on the surface groups.

Finally, the adsorption properties of DTPA-modified adsorbents were tested in solutions containing $10 \mu\text{M}$ Co(II) and $20 \mu\text{M}$ EDTA with ^{57}Co tracer. K_d values obtained were over $10\,000 \text{ mL/g}$ for DTPA-silica gel and over 6000 mL/g for DTPA-chitosan. For comparison, the K_d value for CoTreat was below 580 mL/g in the solution where Co(II) was chelated by EDTA [34]. Thus, the reasonably high adsorption efficiency of both DTPA-modified adsorbents in the $^{57}\text{Co(II)EDTA}$ solutions indicated their potential for use in the treatment of LLRW effluents.

3.2. Effect of EDTA on kinetics of Co(II) adsorption

When Co(II) is chelated by EDTA both its diffusion properties and chemical reactions on surfaces are affected. The best way to study these effects is comparison of adsorption kinetics in both Co(II) and Co(II)EDTA solutions. The kinetics of the chelation reaction was investigated using a pseudo-second-order model, which was previously found to describe Co(II) and Ni(II) adsorption well on both DTPA-silica gel and DTPA-chitosan [24,25]. However, non-linear regression (Origin software version 8.0, Microcal Software) was used here instead of linear regression in order to avoid the changes in error distributions caused by the linearization technique [35]. The non-linear pseudo-second-order model has the following form:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (3)$$

where q_t and q_e (mmol/g) represent the amount of Co(II) adsorbed at time t (min) and at equilibrium, respectively.

The plots of the pseudo-second-order equation are shown in Fig. 3a and estimated parameters in Table 2. Fig. 3a shows that the non-linear pseudo-second-order model did not describe adsorp-

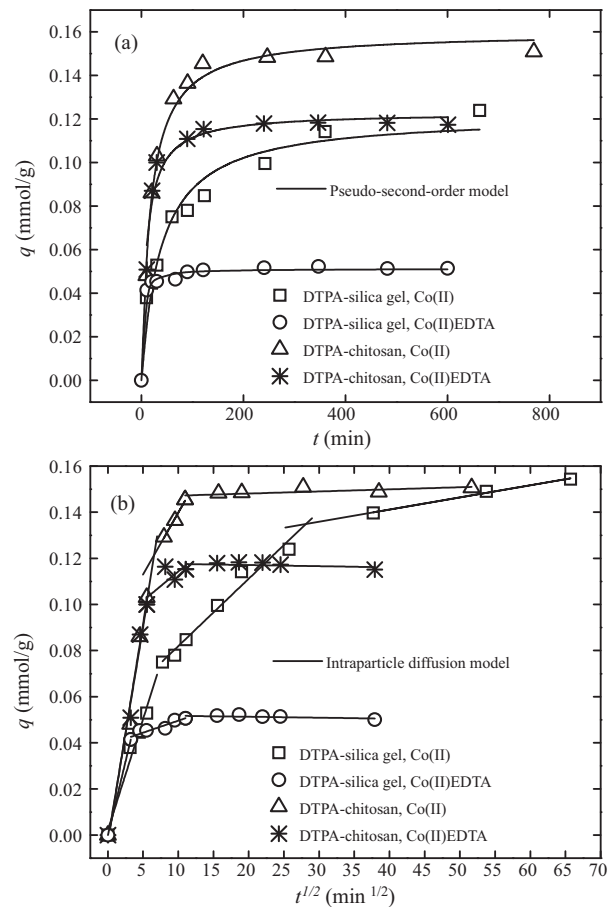


Fig. 3. (a) Adsorption kinetics of Co(II) and Co(II)EDTA (1:2) by DTPA-modified adsorbents. Agitation speed: 50 rpm; Co(II) concentration: 0.34 mM ; dose: 2 g/L ; pH 3 (DTPA-silica gel), pH 2 (DTPA-chitosan). (b) Intraparticle diffusion plots for the results presented in (a).

tion kinetics of Co(II) on DTPA-modified adsorbents from pure Co(II) solutions as well as was expected based on the linear fittings [24,25]. However, the kinetic data obtained from Co(II)EDTA solutions fit better, indicating that the chelation reaction was the rate limiting step (Table 2). A possible explanation is that Co(II)EDTA-chelates reacted with outermost surface groups but could not diffuse inside the pores due to their bulky structure and negative charge. In contrast, the adsorption kinetics of free Co(II) seemed to be limited by diffusion. Despite the goodness of fit, parameters pre-

Table 2
Pseudo-second-order rate constants for DTPA-modified adsorbents in Co(II) and Co(II)EDTA 1:2 solutions: non-linear regression.

$C_{0,\text{Co}}$ (mM)	T ($^{\circ}\text{C}$)	Co(II):EDTA molar ratio	$q_{e,\text{exp}}$ (mmol/g)	q_e (mmol/g)	k_2 (g/mmol min)	R^2
DTPA-silica gel						
0.017	22 ± 1	1:0	0.008	0.008	34.48	0.985
0.017	22 ± 1	1:2	0.008	0.008	17.09	0.988
0.34	22 ± 1	1:0	0.154	0.122	0.24	0.934
0.34	22 ± 1	1:2	0.051	0.051	7.01	0.992
0.14	22 ± 1	1:2	0.036	0.037	2.12	0.987
0.34	35	1:2	0.057	0.056	8.47	0.997
0.34	10	1:2	0.049	0.047	3.23	0.941
DTPA-chitosan						
0.017	22 ± 1	1:0	0.009	0.009	8.55	0.948
0.017	22 ± 1	1:2	0.009	0.009	10.49	0.914
0.34	22 ± 1	1:0	0.151	0.160	0.35	0.976
0.34	22 ± 1	1:2	0.118	0.123	0.78	0.932
0.85	22 ± 1	1:2	0.229	0.233	0.47	0.978
0.34	35	1:2	0.119	0.118	1.50	0.995
0.34	10	1:2	0.116	0.131	0.26	0.950

Table 3
Diffusion rate constants for DTPA-modified adsorbents in Co(II) and Co(II)EDTA 1:2 solutions.

C _{0,Co} (mM)	T (°C)	Co(II):EDTA molar ratio	k _{d,1} (mmol/g min ^{1/2})	k _{d,2} (mmol/g min ^{1/2})	k _{d,3} (mmol/g min ^{1/2})
DTPA-silica gel					
0.017	22 ± 1	1:0	0.0019		4.41 × 10 ⁻⁵
0.017	22 ± 1	1:2	0.0014		3.05 × 10 ⁻⁵
0.34	22 ± 1	1:0	0.0101	0.0029	52.4 × 10 ⁻⁵
0.34	22 ± 1	1:2	0.0128	0.0011	≈ 0
0.14	22 ± 1	1:2	0.0054	0.0029	28.2 × 10 ⁻⁵
0.34	35	1:2	0.0118	0.0023	16.2 × 10 ⁻⁵
0.34	10	1:2	0.0104	0.0011	14.6 × 10 ⁻⁵
DTPA-chitosan					
0.017	22 ± 1	1:0	0.0012		0.85 × 10 ⁻⁵
0.017	22 ± 1	1:2	0.0010		1.02 × 10 ⁻⁵
0.34	22 ± 1	1:0	0.0190	0.0054	50.9 × 10 ⁻⁵
0.34	22 ± 1	1:2	0.0156	0.0025	≈ 0
0.85	22 ± 1	1:2	0.0372	0.0096	8.65 × 10 ⁻⁵
0.34	35	1:2	0.0236	0.0119	30.8 × 10 ⁻⁵
0.34	10	1:2	0.0125	0.0046	≈ 0

sented in Table 2 can be used to compare the adsorption kinetics of Co(II) species on the modified silica gel and chitosan. In most of the cases, the pseudo-second-order rate constant was lower for DTPA-chitosan than for DTPA-silica gel. This could be attributed to the rigid structure of the silica gel where adsorption sites were easily available.

The effect of chelate formation on diffusion was studied using an intraparticle diffusion model:

$$q_t = k_d t^{1/2} + C \quad (4)$$

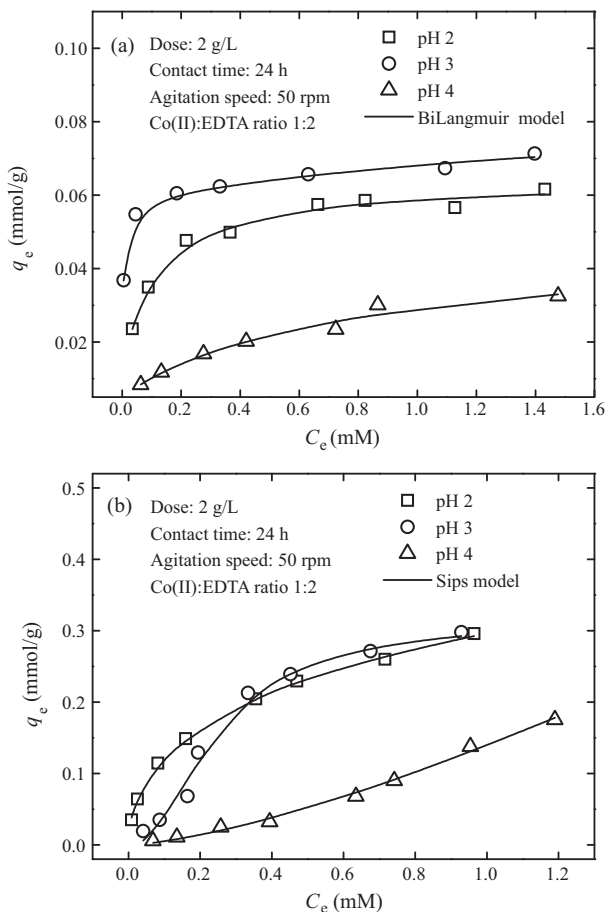


Fig. 4. The effect of pH on the Co(II) adsorption isotherms of (a) DTPA-silica gel and (b) DTPA-chitosan.

where k_d (mmol/g min^{1/2}) is the diffusion rate constant and C (mmol/g⁻¹) represents the thickness of the boundary layer. Fig. 3b shows that an intraparticle model plot had more than one linear region. These regions can be attributed to the different stages of diffusion. The first region, with a steep slope, represented diffusion in the bulk phase to the exterior surface of the adsorbent or film diffusion, the second represents the gradual adsorption stage (diffusion into mesopores or macropores), and the third region represents diffusion into micropores or the equilibrium state [36].

The diffusion rate constants obtained from the slopes of the intraparticle model plots are presented in Table 3. In 17 μM Co(II) and Co(II)EDTA solutions only the linear region prior to the equilibrium state represented diffusion from the bulk phase to the surface of the adsorbent or film diffusion. This is not surprising because the outermost surface areas of both adsorbents contained enough adsorption sites for all the metal ions at low concentrations. The most apparent effect of Co(II) chelation was seen in the case of DTPA-silica gel when the concentration of Co(II)/Co(II)EDTA was 0.34 mM. For free Co(II) more diffusion stages were observed than for Co(II)EDTA. This could be attributed to the fact that Co(II) ions were able to diffuse into the silica gel pores (pore diameter: 49 Å) due to their small size and the attraction of negatively charged carboxyl groups. However, the pore diffusion of Co(II)EDTA was limited due to its size and negative charge. Therefore, it rather reacted with the outermost DTPA groups. In the case of DTPA-chitosan, this effect was not seen due to its higher surface coverage and macroporous structure (pore diameter: 552 Å), and both Co(II) and Co(II)EDTA were equally able to reach the active sites. It is interesting to note that the diffusion rate constants from bulk to surface ($k_{d,1}$, Table 3) of DTPA-chitosan were directly proportional to the initial Co(II) concentration, which is consistent with the concept of surface “film diffusion” [37].

Besides ambient temperature, kinetic experiments were also conducted at 10 and 35 °C. Table 2 shows that adsorption was clearly slower at 10 °C than at the other two temperatures. This further indicates that the chelation reaction had the main role in the adsorption kinetics of Co(II) from EDTA-containing solutions. In the case of DTPA-silica gel the adsorption capacity increased slightly as a function of temperature indicating the endothermic nature of the surface reaction (Table 2 and Supplementary information: Figures S1 and S2).

3.3. Effect of EDTA on Co(II) adsorption isotherms

It is evident that the addition of EDTA affected the adsorption of Co(II) by DTPA-modified adsorbents. In addition, the speciation

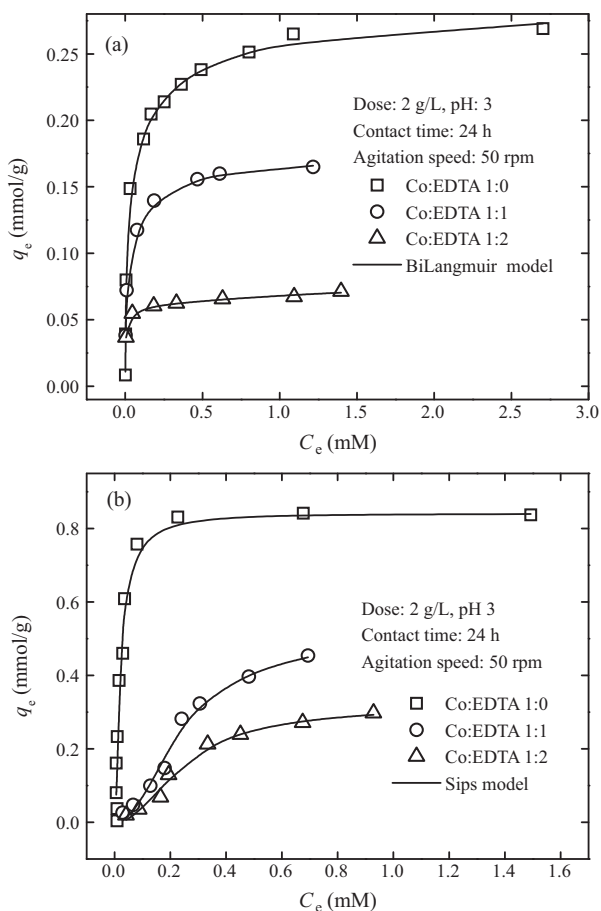


Fig. 5. The effect of EDTA on the Co(II) adsorption isotherms of (a) DTPA-silica gel and (b) DTPA-chitosan.

of both surface bound DTPA and Co(II)EDTA in the solution were pH dependent. Therefore, the adsorption equilibrium was studied in solutions containing Co(II) and EDTA at molar ratios of 1:0, 1:1, and 1:2 and varying in pH from 2 to 4.

It is useful to look first at the overall effects of pH and EDTA on Co(II) adsorption by DTPA-modified adsorbents (Figs. 4 and 5). Fig. 4a shows that in the Co(II):EDTA 1:2 solutions, the best adsorption performance of DTPA-silica gel was obtained at pH 3 and the worst at pH 4. In the case of DTPA-chitosan (Fig. 4b), pH 4 also gave the poorest performance, but near the equilibrium the adsorption capacities were rather similar at pH 2 and pH 3. That the poorest adsorption performance was seen for both materials at pH 4 can be attributed to the speciation of both surface DTPA-groups and Co(II)EDTA-species in the solution (MINEQL, ver. 2.53). At this pH the predominant compound in the solution was Co(II)EDTA²⁻ and the dominant surface compounds were R-NH-H₂DTPA²⁻ and R-NH-HDTPA³⁻ (R = silica gel or chitosan, simplified presentation). Thus, there was electrochemical repulsion between the negatively charged groups. The increase in positive surface charge with decreasing pH allowed a better surface approach of Co(II)EDTA-chelates at pH 2 and pH 3. Fig. 4b also shows that pH had a clear effect on the shape of the isotherm curve, which is discussed later in this section. Furthermore, it should be noted that without EDTA, the pH only slightly affected the maximum Co(II) adsorption (Tables 4 and 5) even if the effect at low Co(II) concentrations was significant.

The effect of Co(II):EDTA molar ratio on the adsorption of Co(II) species is presented in Fig. 5. The adsorption performance of DTPA-modified materials decreased as the EDTA content in the solution

increased, and this was evident over the whole studied pH range (Tables 4 and 5). This was attributed to the enhanced competition for Co(II) ions between dissolved EDTA and surface DTPA-groups.

To obtain a deeper understanding of the adsorption equilibrium, theoretical isotherm models were fitted to the experimental data using non-linear regression (Origin software). The BiLangmuir and Sips models were selected based on previous results [24,25]. The BiLangmuir model is given as

$$q_e = \frac{q_{m1}K_{L1}C_e}{1 + K_{L1}C_e} + \frac{q_{m2}K_{L2}C_e}{1 + K_{L2}C_e} \quad (5)$$

where q_{m1} and q_{m2} are the maximum adsorption capacities of two different adsorption sites while K_1 and K_2 are the energies of adsorption for these adsorption sites. The Sips model is a combination of Langmuir and Freundlich models:

$$q_e = \frac{q_m(K_S C_e)^{n_S}}{1 + (K_S C_e)^{n_S}} \quad (6)$$

where K_S (L mmol⁻¹) is the Langmuir equilibrium constant and n_S is the Freundlich heterogeneity factor.

As presented earlier, the BiLangmuir model fit rather well to the equilibrium curves obtained for DTPA-silica gel (Figs. 4a and 5a and Table 4). Even though the adsorption system was relatively complex, the K_L parameters presented in Table 4 can give some insight into the adsorption mechanism by which Co(II) ions are bound by surface DTPA-groups. At pH 3 and $4K_{L1}$ values were clearly higher than K_{L2} values. At pH 3 these values were also related to the binding sites with higher adsorption capacity (q_{m1}). This indicates that these adsorption sites were surface DTPA-groups, which were able to capture Co(II) from its EDTA chelate. However, the results at pH 4 indicated that lower affinity binding sites had higher adsorption capacity in the solution without EDTA. This cannot be explained by the suggestion that the high affinity groups were DTPA-moieties and the low-affinity groups amino-moieties [24]. Instead, it is most likely that high- and low-affinity groups denoted different speciations of the surface-bound DTPA. At pH 4, 74.9% of DTPA is found as R-NH-H₂DTPA²⁻ and 18.5% as R-NH-HDTPA³⁻ (MINEQL, ver. 2.53, R = silica gel). The group with the higher negative charge should clearly have higher affinity for the positive Co(II) ions. However, the surface concentration of this group was also lower, giving lower adsorption capacity. Similarly, at pH 3 high-affinity surface groups could be assigned to R-NH-H₂DTPA²⁻ (50.3%) and low-affinity groups to R-NH-H₃DTPA⁻ (42.7%).

Table 5 and Figs. 4b and 5b show that the Sips model fit better with the experimental data obtained for DTPA-chitosan than the BiLangmuir model. Only at pH 2 did the BiLangmuir model fit well, but the parameters obtained indicated that there was only one kind of binding site on the surface, thus the BiLangmuir equation became a simple Langmuir equation. Moreover, the model overestimated the q_m values. The poor fit of the BiLangmuir/Langmuir model to the data obtained for DTPA-chitosan could be attributed to system heterogeneity. It can be seen from Figs. 4b and 5b that the shape of the isotherm curve was highly affected by both pH and EDTA content, unlike the isotherm of DTPA-silica gel. This indicates that DTPA-chitosan has a much more complex structure than DTPA-silica gel.

Table 5 shows that the heterogeneity factor n_S of the Sips model was greater than one when solution pH was 3 or the Co(II):EDTA ratio was 1:2. Thus, these systems were highly heterogeneous, which was also seen from the S-shape isotherm curves. This type of curve is typically formed when there is a weak interaction between the surface and adsorbate at low adsorbate concentrations, but once some adsorption takes place, adsorbent-adsorbate interactions increase [38]. In the case of DTPA-chitosan, weak surface affinities at low Co(II)EDTA concentrations could be attributed to crosslink formation [25]. Due to the more rigid structure of the

Table 4
Isotherm parameters for DTPA-silica gel.

Co:EDTA ratio		$q_{m,exp}$ (mmol/g)	q_{m1} (mmol/g)	K_{L1} (L/mmol)	q_{m2} (mmol/g)	K_{L2} (L/mmol)	R^2
Two-site Langmuir model							
pH 2	1:0	0.23	0.09	31.82	0.16	2.77	0.997
	1:1	0.12	0.06	22.10	0.15	0.65	0.991
	1:2	0.06	0.02	58.70	0.04	7.19	0.977
pH 3	1:0	0.27	0.16	193.36	0.13	3.83	0.998
	1:1	0.16	0.10	270.92	0.08	7.31	0.999
	1:2	0.07	0.06	330.26	0.03	0.65	0.991
pH 4	1:0	0.25	0.07	540.89	0.21	5.19	0.992
	1:2	0.03	0.01	78.56	0.04	1.18	0.952
Co:EDTA ratio		$q_{m,exp}$ (mmol/g)	q_m (mmol/g)	K_S (L/mmol)	n_S	R^2	
Sips model							
pH 2	1:0	0.23	0.26	10.78	0.73	0.998	
	1:1	0.12	0.27	1.59	0.53	0.991	
	1:2	0.06	0.07	18.03	0.73	0.992	
pH 3	1:0	0.27	0.30	37.30	0.27	0.993	
	1:1	0.16	0.19	48.27	0.16	0.995	
	1:2	0.07	0.08	85.16	0.07	0.976	
pH 4	1:0	0.25	0.32	18.80	0.56	0.984	
	1:2	0.03	0.08	3.18	0.56	0.962	

oxide substrate, a similar effect was not seen in the case of DTPA-silica gel.

3.4. Reaction mechanism

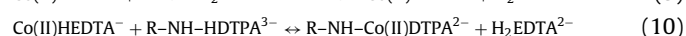
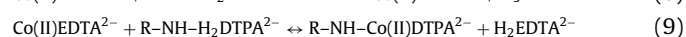
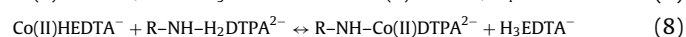
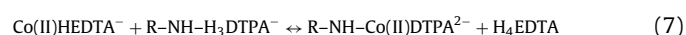
In order to understand the reaction mechanism it was important to find out whether EDTA is released during Co(II) adsorption. The speciation of free EDTA and Co(II)EDTA was accomplished using CE. The calibration curves (Supplementary information, Figure S3) of EDTA were not affected by pH unlike those of Co(II)EDTA. This can be explained by Co(II)EDTA speciation, which was seen as split peaks in electropherograms (Fig. 6). However, the total amount of Co(II)EDTA-species could be determined by CE as well as ICP.

It is evident from Fig. 6 that the EDTA content in the solution increased as Co(II) was adsorbed on the DTPA-modified surface. Furthermore, the amount of EDTA released correlated well with the amount of Co(II) adsorbed (Fig. 7), indicating that surface DTPA-groups were able to capture Co(II) from its dissolved EDTA chelates.

The speciation of Co(II)EDTA at different pH values is presented in the supplementary information (Tables S1 and S2). At pH 2 there were some free Co^{2+} ions in the Co(II):EDTA 1:1 solution, but in the other systems the amount of free Co^{2+} was insignif-

icant compared to the amount of chelated Co(II). This further confirmed that Co(II)EDTA-chelates were dissociated due to the high-affinity DTPA-groups. The adsorption efficiency varied from 38% to 96% at pH 2 and 3 depending on the total Co(II) concentration. DTPA-chitosan could remove over 50% of Co(II) from the 1.7 mM Co(II)EDTA 1:2 solution, whereas DTPA-silica gel had a better adsorption performance in the lower concentration range, reaching 96% removal from 85 μ M Co(II)EDTA solution.

Determination of the reaction mechanism of the system presented here is complicated due to the fact that DTPA and EDTA as well as their Co(II) chelates have different speciations at different pH values. Mechanisms can be suggested based on the speciation calculations. The most abundant surface group after Co(II) chelation in the studied pH range was $R-NH-Co(II)DTPA^{2-}$ and the solution chelate, which donated Co(II), was expected to be the one with the lowest stability constant (Table S2). Based on this, the reaction mechanisms can be written as

**Table 5**
Isotherm parameters for DTPA-chitosan.

Co:EDTA ratio		$q_{m,exp}$ (mmol/g)	q_{m1} (mmol/g)	K_{L1} (L/mmol)	q_{m2} (mmol/g)	K_{L2} (L/mmol)	R^2
Two-site Langmuir model							
pH 2	1:0	0.83	0.90	13.08	–	–	0.998
	1:1	0.43	0.51	2.18	0.11	50.86	0.999
	1:2	0.30	0.37	1.06	0.02	42.96	0.999
pH 3	1:0	0.84	0.92	31.82	–	–	0.881
	1:1	0.45	1.04	1.24	–	–	0.919
	1:2	0.30	0.45	2.12	–	–	0.899
pH 4	1:0	0.86	0.92	19.92	–	–	0.440
	1:2	0.18	–	–	–	–	–
Co:EDTA ratio		$q_{m,exp}$ (mmol/g)	q_m (mmol/g)	K_S (L/mmol)	n_S	R^2	
Sips model							
pH 2	1:0	0.83	0.88	12.43	1.08	0.999	
	1:1	0.43	0.81	5.60	0.66	0.999	
	1:2	0.30	0.31	0.18	2.18	0.982	
pH 3	1:0	0.84	0.84	35.18	1.79	0.950	
	1:1	0.45	0.49	0.18	2.26	0.981	
	1:2	0.30	0.31	0.18	2.18	0.982	
pH 4	1:0	0.86	0.92	19.92	1.01	0.502	
	1:2	0.18	–	–	–	–	

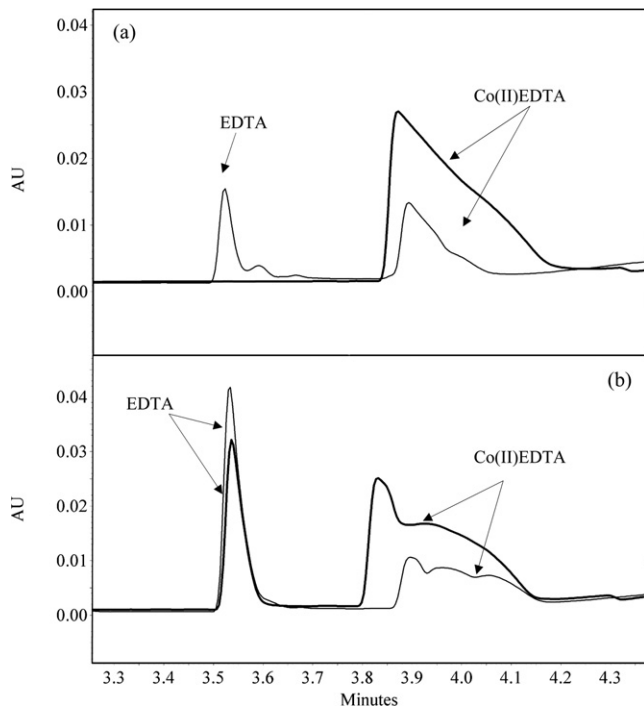


Fig. 6. Comparison of electropherograms before (bold line) and after (thin line) adsorption of Co(II) in (a) Co(II)EDTA 1:1 and (b) Co(II)EDTA 1:2 systems, pH 3. Co(II) concentration: 0.85 mM.



of which Eq. (7) is suggested to be the main mechanism at pH 2 and (9) at pH 3. At pH 4 all the reactions except (7) may occur. The idea behind the mechanisms presented here was that the most unstable solution chelate reacted with the surface group with the highest affinity towards positive metal ions. It was also assumed that DTPA surface groups formed rather similar coordination compounds with Co(II) ions as they would have formed in the solution phase [39], and the above equations are simplified presentations of coordination. If the stability constant of surface DTPA-groups was assumed to be near that of the solution species ($pK: 26.53$ [32]) the previous mechanisms would also be favorable since the stability constants of Co(II)EDTA-chelates varied from 18 to 23.5 [32], [Table S2]. However, it should be emphasized that the system under investigation was very complex and, besides binding free Co(II) released from EDTA chelates, whole Co(II)EDTA-chelates or free EDTA could have been bound by the surface amino groups [19,20]. On the other hand, in this study, both results with CE and fittings to the BiLangmuir model indicated that most of the Co(II) was bound to the DTPA-modified surfaces in the ionic form.

Table 6
Regeneration of DTPA-silica gel and -chitosan by 2 M HNO₃. Adsorption from 1 mM Co(II)EDTA (1:2)-solution, pH 3.

Type of adsorbent	No. of cycles	Adsorption capacity of Co(II)EDTA		
		Before regeneration (mg/g)	After regeneration (mg/g)	Regeneration efficiency (%)
DTPA-silica gel	1	8.56	8.01	136.5
	2	8.56	8.16	132.5
	3	8.56	8.09	138.2
	4	8.56	8.38	114.2
DTPA-chitosan	1	2.35	2.18	102.3
	2	2.35	2.18	102.3
	3	2.35	2.25	101.3
	4	2.35	2.26	101.2

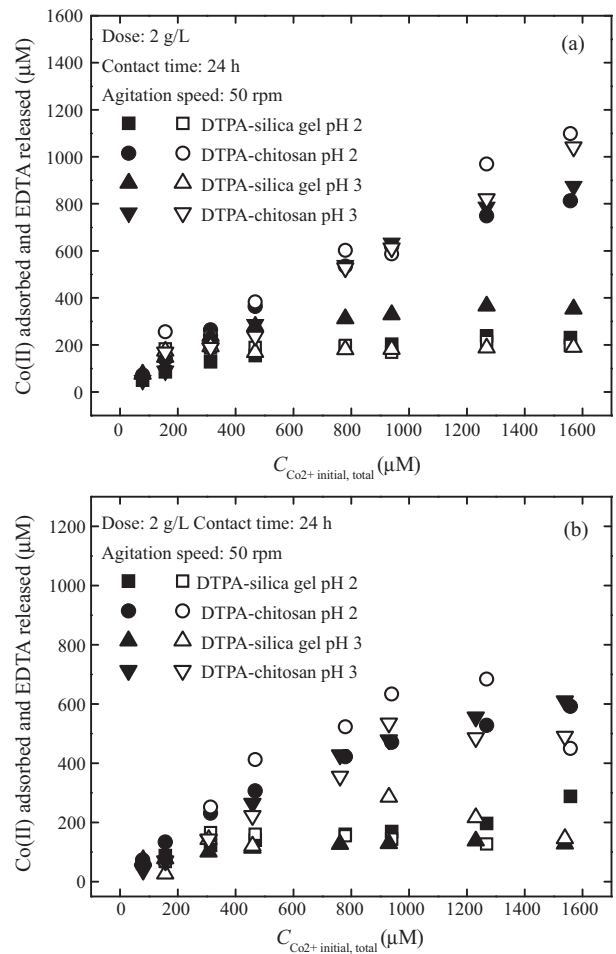


Fig. 7. The relationship between the amount of Co(II) adsorbed and EDTA released as a function of total initial concentration of Co(II). (a) Co(II):EDTA 1:1 and (b) Co(II):EDTA 1:2. Filled symbols: Co(II) adsorbed; open symbols: EDTA released.

3.5. Regeneration and stability of the adsorbents

Earlier studies showed that DTPA-modified silica gel and chitosan were regenerable using 1–2 M HNO₃ when adsorption tests were done in pure metal solutions [24,25]. The regeneration results after adsorption tests in 1 mM Co(II)EDTA solutions are presented in Table 6. For DTPA-chitosan, adsorption efficiency was not affected by regeneration. However, for DTPA-silica gel, adsorption capacity increased after the first regeneration cycle, indicating that some EDTA groups became attached to the surface and increased the ligand loading. Overall, regeneration studies confirmed the stability of the DTPA-groups in the Co(II)EDTA solutions.

DTPA leaching at different pH values was further examined by CE-measurements. A small peak assigned to dissolved Co(II)DTPA chelate was observed in the case of DTPA-chitosan after adsorption experiments at pH 3 and 4 (Figure S4). When the peak was calibrated for Co(II)DTPA, the leached amount was found to be around 10 μM , i.e. 0.5 mol% of the total amount of functional groups. A Co(II)DTPA peak was not observed for DTPA-silica gel, demonstrating its stability, which has also been seen with analysis of leached silicon [24].

4. Conclusions

The DTPA-modified silica gel and chitosan were found to be promising materials for Co(II) adsorption in the presence of organic complexants such as EDTA and oxalate or inorganic species such as Ca(II) and Fe(II). The two adsorbents performed differently depending on the solution pH and the concentration of Co(II). Both modified adsorbents could remove Co(II) even if it was totally chelated by EDTA. DTPA-silica gel was more effective when the EDTA was present in less than two-fold excess, after which the modified chitosan showed better adsorption performance. An excess of oxalate ions or Fe(II) did not influence the Co(II) adsorption by DTPA-chitosan due to its high ligand loading. However, adsorption of Co(II) was enhanced by oxalate in the case of DTPA-silica gel, which was attributed to the oxalate binding on the surface creating more adsorption sites for Co(II). Furthermore, DTPA-chitosan was an efficient adsorbent in simulated decontamination solutions and both adsorbents showed good adsorption properties in solutions traced with radiocobalt ^{57}Co .

The effect of EDTA on Co(II) adsorption was studied by both kinetic and equilibrium experiments. Kinetic experiments showed that the adsorption of free Co(II) on DTPA-silica gel was controlled by intraparticle diffusion, but adsorption of Co(II)EDTA by surface chelation reaction. This was attributed to the large size of Co(II)EDTA and electrochemical repulsion between negatively charged DTPA-groups and Co(II)EDTA. In the case of DTPA-chitosan, a similar effect was not seen due to its macroporous structure, which enabled both Co(II) and Co(II)EDTA diffusion into the adsorbent pores.

The equilibrium studies showed that the BiLangmuir model was most accurate in the case of DTPA-silica gel and the Sips model in the case of DTPA-chitosan. The latter was due to the high heterogeneity of the DTPA-chitosan surface, which was also apparent from the S-shaped isotherm plots. The BiLangmuir model suggested that there were two kinds of active sites on the DTPA-silica gel surface. Based on the K_L/q_m values these sites were attributed to the different speciation of surface DTPA-groups.

Finally, the measurements with CE showed that DTPA-modified adsorbents were able to capture Co(II) from its EDTA chelate, as demonstrated by the increase in dissolved EDTA as Co(II) was adsorbed on the surface. This demonstrated the applicability of the studied adsorbents to treatment of effluent streams containing both Co(II) and EDTA.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.12.113.

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