Research of Co(II) Adsorption on Silica Gel Grafted with Dithiocarbamate (DTC-SiO₂) in Aqueous Solution

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Abstract. Dithiocarbamate grafted silica gel (DTC-SiO₂) was prepared following two simple reaction steps. The properties of the composite were characterized by FTIR, SEM and element analysis. Its ability to remove Co²⁺ ions in aqueous solution with low concentration was also studied by static adsorption experiments. The effects of pH value in solution, contact time and temperature were investigated. The results show that the DTC-SiO₂ exhibits excellent adsorption property for Co²⁺. The adsorption kinetics could be well described by pseudo-second-order model and the adsorption isotherms could be depicted by both Freundlich and Dubinin-Radushkevich models. The adsorption process belongs to chemisorption. The slightly influence of common interfering metal ions (Na⁺, K⁺, Ca²⁺ and Mg²⁺) on the adsorption capacity revealing the synthesized DTC-SiO₂ performs excellent selective adsorption to Co²⁺.

1. Introduction
Low-level radioactive wastes (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 [1]. However, these wastes are still hazardous and need to be treated and stored properly due to the existence of some radioactive metal ions such as ⁶⁰Co. As a long-lived γ emitter, ⁶⁰Co is high toxic and harmful to human beings and environments. Therefore, the study of eliminating ⁶⁰Co from aqueous solution has been the focus about LLRW disposal [2-5]. Using effective adsorbents to capture these nuclides seemed to be a popular method, and various chelating resins grafted with functional ligands have been synthesized [6-10]. The composites grafted with dithiocarbamate (DTC) agent which behaved strongly binding ability to heavy metals while not complexing alkali and alkaline earth metals [11] have been the focus of attention [12,13]. Espinola et. al. [14] prepared a silica gel anchored bis-DTC ligand and found its high selectivity of attaching Co(II). Venkatesan et. al. [15] discussed the difference between extracting Co(II) and Co(III) by DTC-functionalized silica sorbents. Bai [16] synthesized a kind of macromolecular dithio-carbamate through the reaction of polyethyleneimine with carbon disulfide (CS₂) and then immobilized it onto the silica gel and studied its adsorbing abilities of Pb(II), Cd(II), Cu(II) and Hg(II).

In this research, the dithiocarbamate was anchored onto the commercial silica gel through the procedure reported by DenBelyker et.al. [15]. To discuss the adsorption property as well as the mechanism, static experiments of the compound adsorbing non-radioactive cation Co²⁺ with low...
concentration in solution were carried out. The selective ability to Co\(^{2+}\) was also examined in this paper.

2. Synthesis and Experiments

2.1. Reagents and Apparatus
Silica gels of 80-100 mesh size, were purchased from Qingdao Haiyang Chemical Corporation, China. \(\gamma\)-Aminopropyltriethoxysilane (APTES) was obtained from Nanjing Up-chemical Corporation, China. Carbon disulfide (AR), isopropanol (AR), toluene (AR), methanol (AR) and acetone (AR) were procured from Damao Chemical Reagent Factory in Tianjin, China.

Various apparatuses were used to characterize the synthesized adsorbent. Scanning electron microscopy (SEM) was performed using a Kyocera Corporation JSM-5610LV instrument. FT-IR spectra were recorded using a PerkinElmer Spectrum BX II spectrometer.

2.2. Synthesis of adsorbent
The preparation of the adsorbent was following the procedure reported in reference [15]. The process is shown in Figure 1. In the first step, silica gels were purified by immersing in 50% (v/v) nitric acid solution for 24h and dried at 373K under vacuum for 24h. The active gels were then allowed to react with APTES in toluene for 6h. The mixtures were washed with toluene, isopropanol, acetonemethonal and acetone in sequence and air-dried at room temperature. The abtained white-colored products grafted with amino ligand were then mixed with 100ml 0.1M NaOH solution, 20ml isopropanol and 16ml CS\(_2\) and refluxed for 4h under N\(_2\) atmosphere. After filtering, washed and air-dried, the final yellow-colored adsorbents combining with dithiocarbamate on the surface were acquired and named DTC-SiO\(_2\).

2.3. Adsorption experiments
The solution was prepared by dissolving CoCl\(_2\)-6H\(_2\)O (AR) in distilled water. The Co\(^{2+}\) concentration was adopted 5mg/L in most experiments except for adsorption isotherms. Batch experiments were conducted by mixing 20 mg of DTC-SiO\(_2\) within 50 ml of solution (dose: 2.5g/L), and the mixture was agitated on a rotary shaker with the constant speed for a fixed time. The pH of the solution was adjusted with 0.1M NaOH and 0.1M HCl solutions. The amount of Co\(^{2+}\) in solution was determined by AAS and the adsorption capacity was calculated by formula (1):

\[
q = \frac{(C_0 - C_f)V}{m \cdot M}
\]
Where \( C_0 \) (mg·L\(^{-1}\)) and \( C_1 \) (mg·L\(^{-1}\)) are the concentration of Co\(^{2+}\) before and after the adsorption, \( V \) (mL) is the volume of the solution, \( m \) (mg) is the weight of DTC-SiO\(_2\), \( M \) (g·mmol\(^{-1}\)) is the molecular mass of Co which is 58.5, and \( q \) (mmol·g\(^{-1}\)) is the adsorption capacity of the sorbent.

3. Results and Discussion

3.1. Characteristic of the Adsorbent

FTIR spectrum of DTC-SiO\(_2\) is given in Figure 2. A broad band is observed at 3400 cm\(^{-1}\) due to the O-H stretching frequencies of the absorbed water. The shoulder at 2933 cm\(^{-1}\) can be attributed to C-H stretching. The peaks at 1640, 1525 cm\(^{-1}\) are for N-H bending vibration [15] and the weak peak at 1500 cm\(^{-1}\) is for N-CSS' stretching vibration. The shoulder at 970 cm\(^{-1}\) is assigned as vibration of C-S [17]. These peaks indicate the presence of the anchored dithiocarbamate ligand.

The grafted amount of dithiocarbamate was determined by elemental analysis technique and the results are listed in TABLE 1. As is shown, the synthesis DTC-SiO\(_2\) contains 7.993% C, 3.040% N and 2.032% S. The density of anchored dithiocarbamate ligands is about 0.312 mmol/g by calculation.

![FT-IR spectrum of DTC-SiO\(_2\)](image)

**Figure 2.** FT-IR spectrum of DTC-SiO\(_2\)

**Table 1.** Elemental analysis results of DTC-SiO\(_2\)

| Element | C     | S     | Si     | Na    | N     |
|---------|-------|-------|--------|-------|-------|
| Weight% | 7.993 | 2.032 | 37.47  | 0.178 | 3.040 |
| Molar density (mmol/g) | 6.661 | 0.625 | 13.38  | 0.077 | 2.172 |

The SEM images of the silica gel (A and B) and DTC-SiO\(_2\) (C and D) are shown in Figure 3. Although the surface of composite becomes rougher and a few fine pits appear due to the microcorrosion of silica by the solution of 0.1M NaOH [16], it is still obviously the morphology is retained after modification indicating the excellent mechanic stability of silica gel.

3.2. Behavior of Adsorption

3.2.1. Effect of pH. The pH value in solution is considered to have influence on the surface charge of the adsorbent, the ionization and speciation of adsorbate in solution [17,18]. Figure 4 shows the aqueous species of Co(II) as a function of pH value calculated by the EQ3/6 software. Co(II) exists in water with different speciation. The species of Co\(^{2+}\) is predominant at pH lower than 5.5 while the hydroxy complexes of Co(OH)\(^+\) and Co\(_2\)(OH)\(_3\)\(^+\) become numerous gradually.
Figure 3. Images of silica gel and DTC-SiO$_2$ by SEM

Figure 4. Speciation of Co$^{2+}$ in solution with different pH values

Figure 5. Effect of pH on the adsorption of Co$^{2+}$
Generally, the precipitation of Co\(^{2+}\) ion becomes serious when the pH value rises above 8 [19]. Meanwhile, the dithiocarbamate compound is unstable in acidic media and decomposes with the pH value less than 4. Therefore, the range of media pH value was chosen from 3.5 to 7 to discuss its effects on the adsorption. The results are shown in Figure 5. It can be seen clearly that the adsorption depends on pH value strongly. A general increase in adsorption capacities with increasing pH is observed. At low pH value, the abundant H\(^3\)O\(^+\) groups compete with metal ions to seize adsorption sites [16], and thus, low adsorption capacity of Co\(^{2+}\) is obtained. With the pH increasing, the number of H\(^3\)O\(^+\) becomes fewer and the adsorption capacity increases. According to the literature [20, 21], the adsorption of metal ions at lower pH value usually belongs to outer-sphere surface complexation. Hence, the removal of Co\(^{2+}\) increases obviously with the hydroxy complexes forming at 4.5 of pH as observed. At higher pH value (above 6.5), the adsorption is considered to be inner-sphere surface complexation and the maximum uptake of Co\(^{2+}\) seems to be available. Therefore, the media pH value is fixed to 7 during batch adsorption experiments.

3.2.2. Effect of Contact Time. In order to determine the influence of contact time on adsorption, the adsorption capacities of Co\(^{2+}\) versus time at different temperatures of 298K, 303K and 308K respectively were plotted. The results shown in Figure 6. Indicated that the adsorption increases sharply at initial stage and gradually smoothens to equilibrium. All the adsorption processes reach equilibrium after 12h, and therefore, the contact time for the further work in this paper is fixed to 12h. It is also pointed out that the adsorption increase with temperature.

![Figure 6. Effect of contact time on the adsorption of Co\(^{2+}\)](image)

3.3. Mechanic of Adsorption

3.3.1. Adsorption Kinetic. The pseudo-first-order and pseudo-second-order models are suggested to investigate the adsorption kinetic of Co\(^{2+}\). The linear forms of the two models are described as below:

Pseudo-first-order model:
\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  
(2)

Pseudo-second-order model:
\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]  
(3)
Where $k_1$ (h$^{-1}$) and $k_2$ (g·mmol$^{-1}$·h$^{-1}$) are the adsorption rate constants of pseudo-first-order and pseudo-second-order models respectively, $q_e$ (mmol·g$^{-1}$) and $q_t$ (mmol·g$^{-1}$) are the amount of Co$^{2+}$ adsorbed per gram of DTC-SiO$_2$ at equilibrium and at any time $t$, respectively.

The linear fitting curves are shown in Figure 7 and Figure 8 while the calculated values of kinetic parameters are listed in TABLE 2. By compared with the correlation coefficient ($R^2$), the pseudo-second-order model depicts the adsorption process better than the pseudo-second-order model indicating that the adsorption is chemisorption. The value of $k_2$ increases with temperature meaning that the rate of catching Co$^{2+}$ ions by DTC-SiO$_2$ is faster at higher temperature. It could be also proved by the theoretical adsorption capacities at equilibrium as shown in TABLE 2. The equilibrium adsorption capacity $q_e$ is about 0.0259mmol/g (1.52mg/g) calculated by pseudo-second-order equation.

![Figure 7. Linear fitting with Pseudo-first-order model for Co$^{2+}$ adsorption](image)

![Figure 8. Linear fitting with Pseudo-second-order model for Co$^{2+}$ adsorption](image)

**Table 2.** Kinetic parameters of Pseudo-first-order and Pseudo-second-order models by calculation

| T     | $k_1$ (h$^{-1}$) | $q_e$(Cal) (mmol·g$^{-1}$) | $R^2$ | $k_2$ (g·mmol$^{-1}$·h$^{-1}$) | $q_e$(Cal) (mmol·g$^{-1}$) | $R^2$ |
|-------|------------------|----------------------------|-------|--------------------------|--------------------------|-------|
| 298K  | 0.4044           | 0.0130                     | 0.9878| 62.79                    | 0.0259                    | 0.9995|
| 303K  | 0.4757           | 0.0146                     | 0.9622| 72.32                    | 0.0263                    | 0.9998|
| 308K  | 0.6249           | 0.0163                     | 0.9762| 76.56                    | 0.0289                    | 0.9993|
3.3.2. Adsorption Isotherms. The Langmuir, Freundlich and Dubbin-Radushkevich(D-R) isotherm models are used to describe the effect of initial concentrations of Co²⁺ on the adsorption capacity. The equations can be written as follows:

Langmuir isotherm equation:

\[ q_e = \frac{q_{\text{max}} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \]  \hspace{1cm} (4)

Freundlich isotherm equation:

\[ q_e = K_F \cdot C_e^{1/n} \]  \hspace{1cm} (5)

D-R isotherm equation:

\[ \ln q_e = \ln q_m - K_{DR} \cdot \varepsilon^2 \]  \hspace{1cm} (6)

\[ \varepsilon = R \cdot T \cdot \ln(1 + 1/ C_e) \]  \hspace{1cm} (7)

\[ E = (2K_{DR})^{0.5} \]  \hspace{1cm} (8)

Where \( C_e \) (mmol·L⁻¹) is the equilibrium concentration of Co²⁺ in solution, \( K_L \) (L·mmol⁻¹) is the equilibrium constant of Langmuir isotherm related to the affinity of binding sites, \( q_{\text{max}} \) (mmol·g⁻¹) is the maximum amount of Co²⁺ per unit weight of DTC-SiO₂ for complete monolayer coverage. \( K_F \) (mmol⁰·(1⁻/n)·L¹⁻/n·g⁻¹) is roughly an indicator of the adsorption capacity and n is the heterogeneity factor which has a lower value for more heterogeneous surfaces. \( K_{DR} \) (mol²·KJ⁻²) is a constant relate to the adsorption energy, \( \varepsilon \) (J·mol⁻¹) is the Polanyi potential, \( E \) (KJ·mol⁻¹) is the mean free energy of adsorption represnt the energy required to transfer one mole of an adsorbate to the surface from infinity in solution.

The experimental adsorption isotherms of Co²⁺ onto DTC-SiO₂ are plotted in Figure 9 and Figure 10. The parameters of the three isotherm models are summarized in TABLE 3. As is shown, the maximum adsorption capacity \( q_{\text{max}} \) is 0.0598mmol/g calculated by Langmuir isotherm equation at 298K. The Freundlich and D-R isotherm models fit the plots more appropriatly than Lannmuir model with the high correlation coefficients (R²) obtained (0.9463-0.9995 for Freundlich model and 0.9643-0.9979 for D-R model). The results revealed that the surface of DTC-SiO₂ is heterogeneous and the adsorption energy of Co²⁺ onto DTC-SiO₂ is distributed [22]. Otherwise, micropores and gaps on surface could be seen in the SEM images (Figure 3 D), and therefore, D-R isotherm model which based on the pore filling mechanism could also describe the adsorption well. The obtained values of free energy E are all above 8KJ·mol⁻¹ representing that the adsorption of Co²⁺ onto DTC-SiO₂ follows chemical mechaisim which have been proved by pseudo-second-order kinetic model.
Figure 9. Langmuir and Freundlich isotherm fitting curves for Co^{2+} adsorption

Figure 10. Dubinin-Radushkevich (D-R) isotherm fitting curves for Co^{2+} adsorption

Table 3. Isotherm adsorption parameters of the three models

| Models       | Parameters                      | Temperature |
|--------------|---------------------------------|-------------|
|              |                                 | 298K  | 303K  | 308K  |
| Langmuir isotherm | $K_L$ (L/mmol)               | 2.254 | 1.4703| 2.0627|
|               | $q_{max}$ (mmol/g)            | 0.0598 | 0.1126| 0.0828|
|               | $R^2$                         | 0.8966 | 0.9783| 0.8987|
| Freundlich isotherm | $K_F$ (mmol/g·(L/mmol)\(^{-1/n}\)) | 0.0409 | 0.0662| 0.0551|
|               | $n$                            | 2.350  | 1.916 | 2.271 |
|               | $R^2$                         | 0.9466 | 0.9995| 0.9463|
| D-R isotherm  | $K_{DR}$ (kJ^2/mol^2)        | 0.00373 | 0.00459 | 0.00335 |
|               | $q_{max}$ (mmol/g)            | 0.1178 | 0.2719 | 0.1524 |
|               | $E$ (KJ/mol)                  | 11.58  | 10.44  | 12.22 |
|               | $R^2$                         | 0.9643 | 0.9979 | 0.9746 |

3.4. Effect of interfering ions
The influence of interfering cations (Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\)) on the adsorption of Co\(^{2+}\) by DTC-SiO\(_2\) is also studied by introducing those foreign ions simultaneously in solution at 298K with fixed concentration ratio (1:1:1:1). The amount of each foreign cation ranges from 0~100 mg·L\(^{-1}\). As was shown in Figure 11, the adsorption capacity decreases from 0.023 mmol·g\(^{-1}\) to 0.016 mmol·g\(^{-1}\) when the interfering cations are added. However, the value of $q_e$ is likely to keep constant despite the
increase of interfering cations proving that the synthesized DTC-SiO₂ exhibited excellent selective adsorption of Co²⁺.

**Figure 11.** Effect of interfering ions on adsorption capacity of Co²⁺ (the weight ratio of Na⁺, K⁺, Ca²⁺ and Mg²⁺ is 1:1:1:1)

### 4. Summary

In the present work, the adsorbent of DTC-SiO₂ was prepared by anchoring dithiocarbamate onto silica gel and its structure properties were characterized by FTIR, SEM and element analysis. The results indicated the surface morphology as well as mechanic stability was well retained, the coverage of dithiocarbamate group was about 0.312mmol/g. Through batch experiments, DTC-SiO₂ was believed to be effective in adsorbing trace Co²⁺ ions in solution. The adsorption followed pseudo-second-order model, and the equilibrium adsorption capacity at room temperature was theoretical 0.0259mmol/g (1.52mg/g). Freundlich and Dubinin-Radushkevich(D-R) models fit the isotherm adsorption well and the capture of Co²⁺ by DTC-SiO₂ belongs to chemisorption process. The influence of interfering metal ions was also studied and the results proved that the synthesized composite could selectively adsorb Co²⁺ ions from liquid.

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