

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

Qingxu Yao^a, Peng Xu^b, Yonggang Huo^c, Aiguo Shang^d, Fengmei Yu^e

Rocket Force of the Engineering University, Xi'an, China

^aahyao8755@163.com, ^bxupeng76345@163.com, ^chuoarmy@163.com,

^dshangaiguo1962@163.com, ^efengmeiyu1220@163.com

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. γ -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, acetone and methanol in sequence and air-dried at room temperature. The obtained 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-SiO₂.

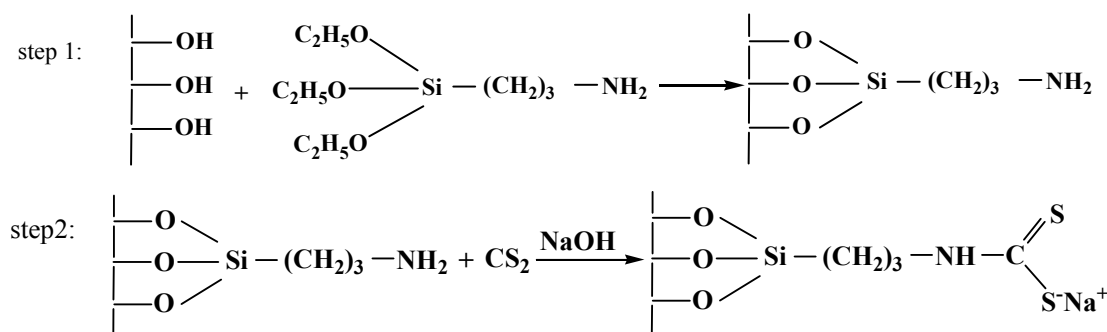


Figure 1. Schematic illustration of adsorbent DTC-SiO₂

2.3. Adsorption experiments

The solution was prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (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-SiO₂ 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):

$$q = \frac{(C_0 - C_1)V}{m \cdot M} \quad (1)$$

Where C_0 ($\text{mg}\cdot\text{L}^{-1}$) and C_1 ($\text{mg}\cdot\text{L}^{-1}$) 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-SiO₂, M ($\text{g}\cdot\text{mmol}^{-1}$) is the molecular mass of Co which is 58.5, and q ($\text{mmol}\cdot\text{g}^{-1}$) is the adsorption capacity of the sorbent.

3. Results and Discussion

3.1. Characteristic of the Adsorbent

FTIR spectrum of DTC-SiO₂ 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-SiO₂ contains 7.993% C, 3.040% N and 2.032% S. The density of anchored dithiocarbamate ligands is about 0.312mmol/g by calculation.

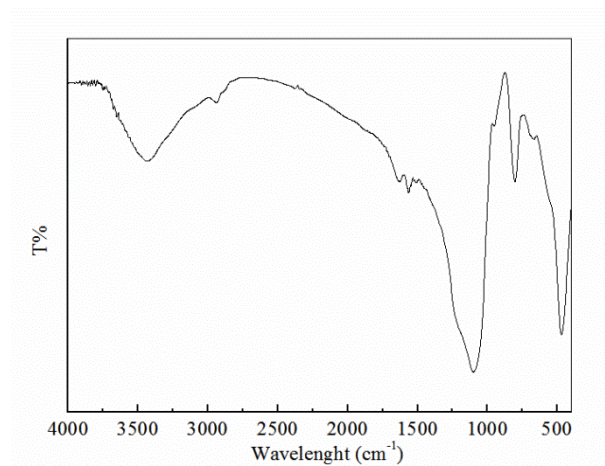


Figure 2. FT-IR spectrum of DTC-SiO₂

Table 1. Elemental analysis results of DTC-SiO₂

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-SiO₂ (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 $\text{Co}(\text{OH})^+$ and $\text{Co}_2(\text{OH})_3^+$ become numerous gradually.

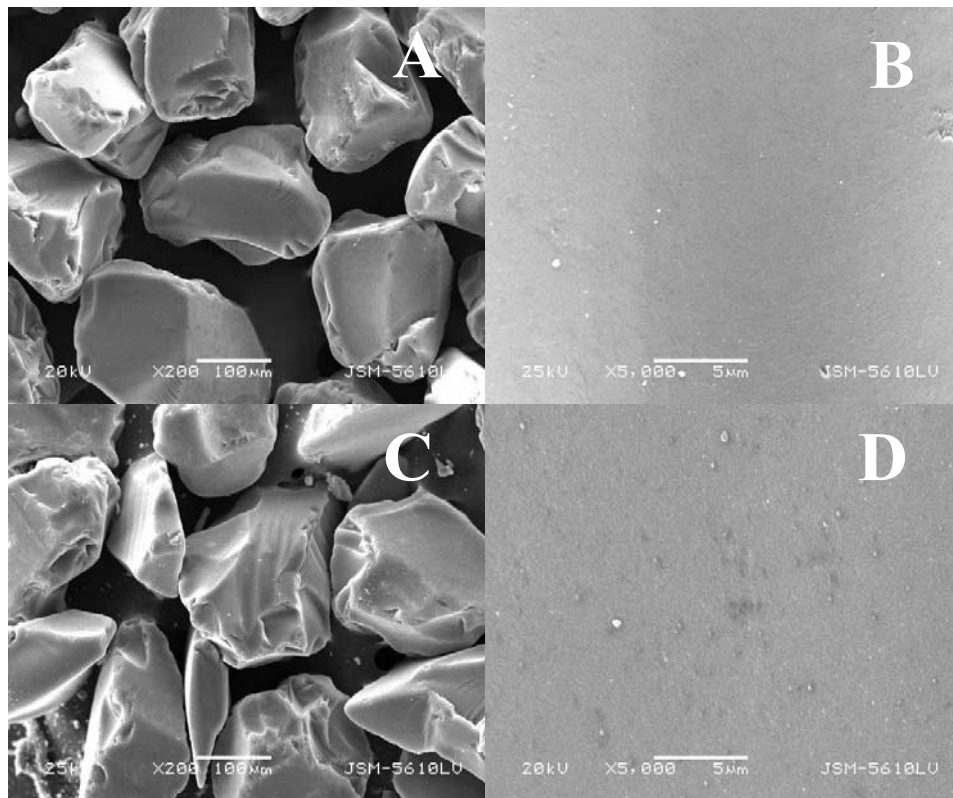


Figure 3. Images of silica gel and DTC-SiO₂ by SEM

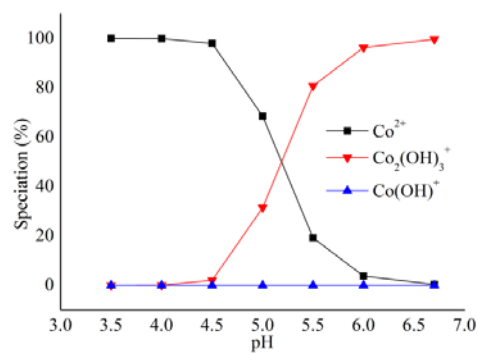


Figure 4. Speciation of Co²⁺ in solution with different pH values

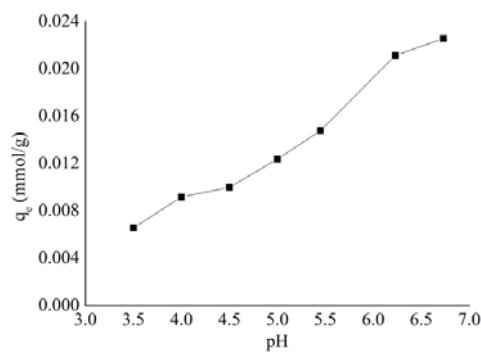


Figure 5. Effect of pH on the adsorption of Co²⁺

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_3O^+ 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_3O^+ 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 smooths 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.

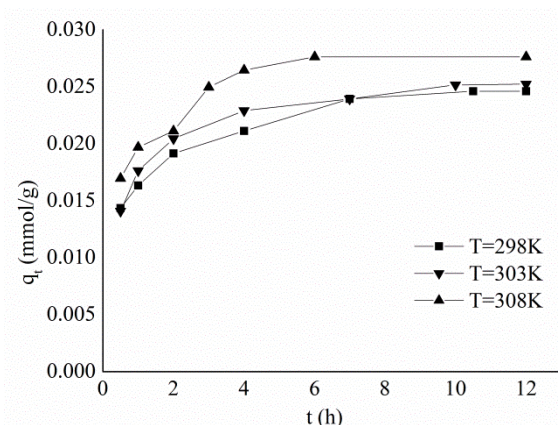


Figure 6. Effect of contact time on the adsorption of Co^{2+}

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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Pseudo-second-order model:

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

Where k_1 (h^{-1}) and $k_2(\text{g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1})$ are the adsorption rate constants of pseudo-first-order and pseudo-second-order models respectively, q_e ($\text{mmol}\cdot\text{g}^{-1}$) and q_t ($\text{mmol}\cdot\text{g}^{-1}$) are the amount of Co^{2+} adsorbed per gram of DTC-SiO₂ 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-SiO₂ 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.

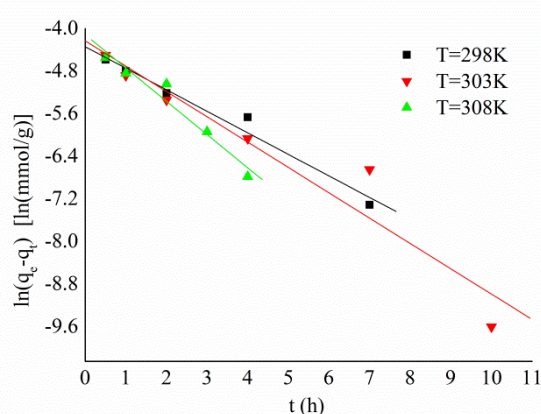


Figure 7. Linear fitting with Pseudo-first-order model for Co^{2+} adsorption

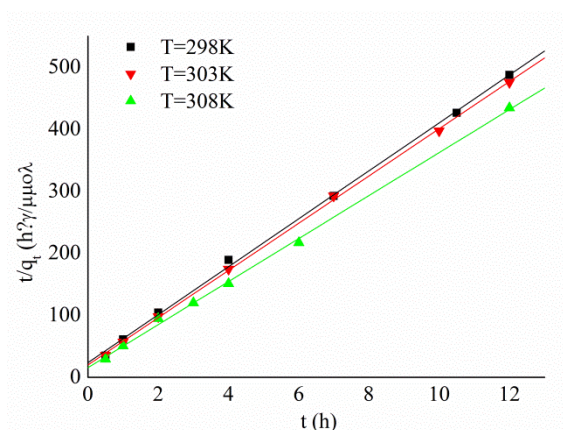


Figure 8. Linear fitting with Pseudo-second-order model for Co^{2+} adsorption

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

T	Psuedo-first-order Model			Psuedo-second-order Model		
	k_1 (h^{-1})	$q_e(\text{Cal})$ ($\text{mmol}\cdot\text{g}^{-1}$)	R^2	k_2 ($\text{g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}$)	$q_e(\text{Cal})$ ($\text{mmol}\cdot\text{g}^{-1}$)	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 Co^{2+} on the adsorption capacity. The equations can be written as follows:

Langmuir isotherm equation:

$$q_e = q_{\max} \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad (4)$$

Freundlich isotherm equation:

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

D-R isotherm equation:

$$\ln q_e = \ln q_m - K_{DR} \cdot \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \cdot \ln(1 + 1/C_e) \quad (7)$$

$$E = (2K_{DR})^{-0.5} \quad (8)$$

Where C_e ($\text{mmol} \cdot \text{L}^{-1}$) is the equilibrium concentration of Co^{2+} in solution, K_L ($\text{L} \cdot \text{mmol}^{-1}$) is the equilibrium constant of Langmuir isotherm related to the affinity of binding sites, $q_{\max}$ ($\text{mmol} \cdot \text{g}^{-1}$) is the maximum amount of Co^{2+} per unit weight of DTC-SiO₂ for complete monolayer coverage. K_F ($\text{mmol}^{(1-1/n)} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$) 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} ($\text{mol}^2 \cdot \text{KJ}^{-2}$) is a constant relate to the adsorption energy, ε ($\text{J} \cdot \text{mol}^{-1}$) is the Polanyi potential, E ($\text{KJ} \cdot \text{mol}^{-1}$) is the mean free energy of adsorption represent the energy required to transfer one mole of an adsorbate to the surface from infinity in solution.

The experimental adsorption isotherms of Co^{2+} 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 $q_{\max}$ is 0.0598mmol/g calculated by Langmuir isotherm equation at 298K. The Freundlich and D-R isotherm models fit the plots more appropriately than Langmuir model with the high correlation coefficients (R^2) 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 Co^{2+} 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 $8 \text{KJ} \cdot \text{mol}^{-1}$ representing that the adsorption of Co^{2+} onto DTC-SiO₂ follows chemical mechanism which have been proved by pseudo-second-order kinetic model.

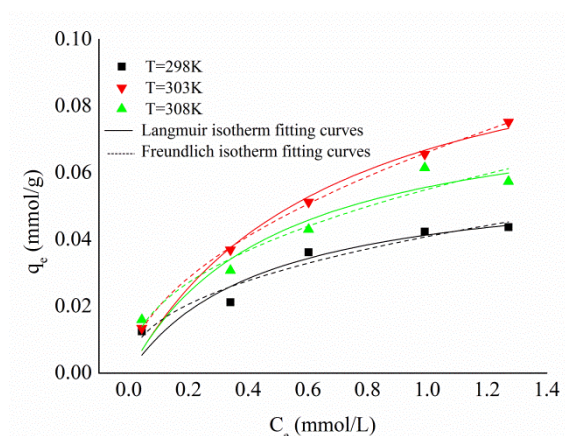


Figure 9. Langmuir and Freundlich isotherm fitting curves for Co^{2+} adsorption

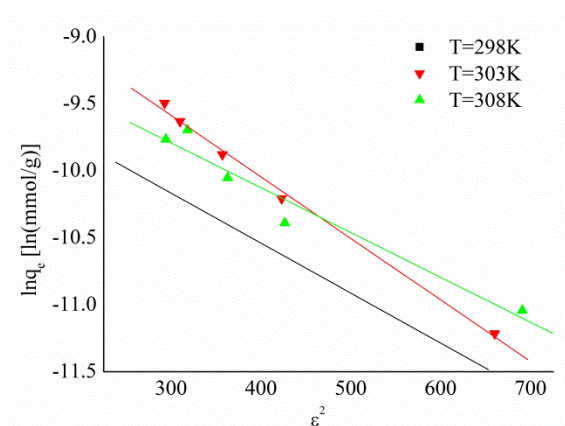


Figure 10. Dubbin-Radushkevich (D-R) isotherm fitting curves for Co^{2+} adsorption

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-SiO₂ 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⁺.

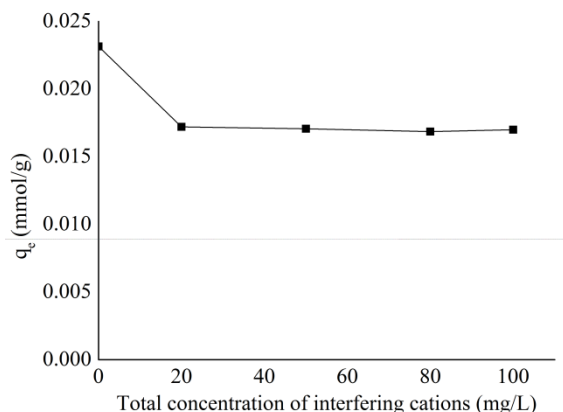


Figure 11. Effect of interfering ions on adsorption capacity of Co²⁺ (the weight ratio of Na⁺, K⁺, Ca²⁺ and Mg²⁺ is 1:1:1:1)

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 Dubbin-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.

References

- [1] E. Repo, L. Malinen, R. Koivula, et.al., Capture of Co(II) from its aqueous EDTA-chelate by DTPA-modified silica gel and chitosan, *J. Hazard. Mater.* 187 (2011) 122-132.
- [2] S.S. Metwally, R.R. Ayoub, Modification of natural bentonite using a chelating agent for sorption of 60Co radionuclide from aqueous solution, *Appl. Clay Sci.* 126 (2016) 33-40.
- [3] M.M. Hamed, M.M.S. Ali, M. Holiel, Preparation of activated carbon from doum stone and its application on adsorption of 60Co and 152+154Eu: Equilibrium, kinetic and thermodynamic studies, *J. Environ. Radioact.* 164 (2016) 113-124.
- [4] H. Omar, H. Arida, A. Daifullah, Adsorption of 60Co radionuclides from aqueous solution by raw and modified bentonite, *Appl. Clay Sci.* 44 (2009) 21-26.
- [5] F. Granados, V. Bertin, S. Bulbuliana, M. Solache-Ríos, 60Co aqueous speciation and pH effect on the adsorption behavior on inorganic materials, *Appl. Radiat. Isot.* 64 (2006) 291-297.
- [6] A. Asthana, R. Verma, A.K. Singh, M.A.B.H. Susan, Glycine functionalized magnetic nanoparticle entrapped calcium alginate beads: A promising adsorbent for removal of Cu(II) ions, *J. Environ. Chem.* 4 (2016) 1985-1995.
- [7] E. Bringas, J. Saiz, I. Ortiz, Removal of As(V) from groundwater using functionalized magnetic adsorbent materials: Effects of competing ions, *Sep. Purif. Technol.* 156 (2015) 699-707.
- [8] Y. Pan, P. Cai, M. Farmahini-Farahani, Y. Li, X. Hou, H. Xiao, Amino-functionalized alkaline clay with cationic star-shaped polymer as adsorbents for removal of Cr(VI) in aqueous solution, *Appl. Surf. Sci.* 385 (2016) 333-340.

- [9] T. Yokoi, Y. Kubota, T. Tatsumi, Amino-functionalized mesoporous silica as base catalyst and adsorbent, *Appl. Catal., A*. 421-422 (2012) 14-37.
- [10] J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu, D. Zhu, Amino-functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal, *J. Colloid Interface Sci.* 348 (2010) 293-299.
- [11] J.F. Dingman, K.M. Gloss, E.A. Milano, S. Siggia, Concentration of heavy metals by complexation on dithiocarbamate resins, *Anal. Chem.* 46 (1974) 774-777.
- [12] Q. Li, J. Yu, F. Zhou, X. Jiang, Synthesis and characterization of dithiocarbamate carbon nanotubes for the removal of heavy metal ions from aqueous solutions, *Colloids Surf., A*. 482 (2015) 306-314.
- [13] S. Kanchi, P. Singh, K. Bisetty, Dithiocarbamates as hazardous remediation agent: A critical review on progress in environmental chemistry for inorganic species studies of 20th century, *Arab. J. Chem.* 7 (2014) 11-25.
- [14] J.G.P. Espínola, J.M.P. de Freitas, S.F. de Oliveira, C. Airolidi, Immobilized dithiocarbamate groups on silica: Chemisorption of some cations from ethanolic solution, *Colloids Surf., A*. 87 (1994) 33-38.
- [15] K.A. Venkatesan, T.G. Srinivasan, P.R.V. Rao, Cobalt-extraction studies on dithiocarbamate grafted on silica gel surface, *Colloids Surf., A*. 180 (2001) 277-284.
- [16] L. Bai, H. Hu, W. Fu et. al., Synthesis of a novel silica-supported dithiocarbamate adsorbent and its properties for the removal of heavy metal ions, *J. Hazard. Mater.* 195 (2011) 261-275.
- [17] L. Guo, C. Niu, X. Wang, X. Wen, G. Zeng, DTC-GO as effective adsorbent for the removal of Cu^{2+} and Cd^{2+} from aqueous solution, *Water Air Soil Pollut.* 227 (2016) 169.
- [18] W. Guo, W. Hu, J. Pan, H. Zhou, W. Guan, X. Wang, J. Dai, L. Xu, Selective adsorption and separation of BPA from aqueous solution using novel molecularly imprinted polymers based on kaolinite/ Fe_3O_4 composites. *Chem. Eng. J.* 171 (2011) 603-611.
- [19] S. Wang, L. Tan, J. Jiang, J. Chen, L. Feng, Preparation and characterization of nanosized TiO_2 powder as an inorganic adsorbent for aqueous radionuclide Co(II) ions, *J. Radioanal. Nucl. Chem.* 295 (2013) 1305-1312.
- [20] E. Tertre, G. Berger, E. Simoni, S. Castet, E. Giffaut, M. Loubet, H. Catalette, Europium retention onto clay minerals from 25 to 150 °C: experimental measurements, spectroscopic features and sorption modeling. *J. Geochim. Cosmochim. Acta.* 70 (2006) 4563-4578.
- [21] G.M. Rashad, M.R. Mahmoud, A.M. Elewa, E. Metwally, E.A. Saad, Removal of radiocobalt from aqueous solutions by adsorption onto low-cost adsorbents, *J. Radioanal. Nucl. Chem.* 309 (2016) 1065-1076.
- [22] D.D. Do, Adsorption Analysis: Equilibria and Kinetics, in: Imperial College Press, London, 1998, pp.54.