Two Chelating Polymeric Beads And Their Adsorption Properties Toward Trace CO(II) From Waters

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***Abstract*—Efficient removal of trace heavy metal ions from wastewater is highly demanded from industry, to which ion adsorption by using chelating resins combined with intensified mechanical separation technology provides a promising continued operation approach. Whereas many chelating resins have been synthesized, most of them are not targeted for industry applications. Here we reported two chelating resins compatible with the mechanical separation technology. The two chelating resins functionalized with dithiocarbamate were particularly prepared for the removal of Co(II) from aqueous solutions, and the maximum Co(II) adsorption capacity of the dithiocarbamated chloromethyl polystyrene resin and dithiocarbamated animo resin in waters was found to be 39.65 mg and 24.89 mg per gram of the corresponding dry polymer, respectively, at pH 5. The adsorption kinetic of Co(II) was well represented by pseudo-second-order kinetic model, and temperature effect and the reusability were also investigated. This fundamental study provides two optional chelating resins for the treatment of industrial wastewater.**

Keywords—Cobalt ion; Chelating resin; Adsorption; Wastewater

I. Introduction

The increasing level of heavy metal ions in water results in serious risk for people's lives and industrial production [1, 2]. For example, due to the use of cobalt catalysts, the wastewater during the production process of purified terephthalic acid (PTA) contains a trace amount of cobalt ions (80~320 mg·L^{-1}), not only causing metal equipment corrosion and bioreactor pollution, but also depressing the microbial activity in biochemistry pools and significantly slows down the degradation speed of organic matters. Apparently, the efficient removal of Co(II) ions from these industrial wastewaters is of vital significance. However, because of the unstable treatment effect at low concentration of Co(II) ions, the traditional methods such as physical adsorption [3-5], chemical precipitation [6, 7], ion exchange [8-10] and membrane separation [11-13] could not meet the wastewater discharge standard. The efficient and low-cost removal of trace amounts of heavy metal ions from aqueous solution has been a challenging problem in the field of wastewater treatment [14], toward which developing high-performance chelating polymeric beads combined with intensified mechanical separation technology provides a promising solution.[15] The whole process is composed of two procedures: First, the chelating beads are introduced into the wastewaters for the adsorption of heavy-metal ions. Second, the adsorbed chelating beads are removed from wastewaters by using, e.g., hydrocyclone technology [16-18] so as to remove the Co(II) ions in wastewaters.

The success of this technique relies on the development of excellent chelating polymeric beads, which are expected to not only capture the heavy-metal ions in complicated solutions with a high capacity but also satisfy the requirements of the hydrocyclone separation technology: First, the chelating beads should present a slightly larger mass density than water so as to suspend in solution for efficient ion adsorption; Second, the particle size of those beads should be uniform and within of the range of 0.05 mm to 1.0 mm for the efficient removal from solution by using intensified hydrocyclone technology; Third, those chelating beads must present high mechanical strengths so that they are not broken during the involved transport and separation processes. Because of those requirements, most conventional chelating resins [19-22] toward the adsorption of Co(II) reported before are not directly applicable.

Polystyrene bead is an ideal kind of matrix, which is widely used in the preparation of functional chelating beads. Myasoedova et al.[23] modified the polystyrene beads by aminating chloromethylated styrenedivinyl benzene copolymers with 3(5)-methylpyrazole, with which the selective adsorption of noble metal ions from acid solutions has been studied. The maximum adsorption capacities of Au^{3+}, Pd^{2+} and Pt^{4+} were identified to be 660 $mg\cdot g^{-1}$, 100 $mg\cdot g^{-1}$ and 100 $mg\cdot g^{-1}$, respectively. Denizli et al.[24] synthesized dithiocarbamate-incorporated mono-size polystyrene based microspheres (2 μm in diameter), and those functional microspheres were used for selective removal of Hg(II) from aqueous solutions containing different amounts of Hg(II) (10-100 $mg\cdot L^{-1}$). The reported maximum Hg(II) adsorption capacity was 33.2 $mg\cdot g^{-1}$ at pH 7.0. While non-specific Hg(II) adsorption onto the plain microspheres was 0.85 $mg\cdot g^{-1}$.

The ion adsorption capability of chelating beads is closely related to the nature of functional groups which contain one or more coordination atoms, such as hydroxyl,[25] crown ether,[26, 27] carboxyl,[28] alkali azo Schiff base,[29] nitrogen heterocyclic,[30] dithiocarbamate group (DTC group),[31, 32] Sulphur,[33] sulfonic group [34] etc. The DTC group contains Sulphur and nitrogen ligands which can react with many heavy metal ions and form chelate with high stable constant [35-37]. Liu et al.[38] prepared chitosan Sr(II)-imprinted polymer (i.e., Sr(II)-IIP) with dithiocarbamate groups, and investigated its adsorption properties toward Sr(II). They reported that the maximum static adsorption capacity of Sr(II)-IIP for Sr(II) was 86.66 $mg\cdot g^{-1}$ at 45 °C, The experimental data were in good agreement with pseudo-second-order and Langmuir isotherm model. Li [39] developed a carbamide-based dithiocarbamate (CDTC) chelator for the removal of heavy metal ions from wastewater. The adsorption isotherms showed CDTC had a high adsorption capability for Cu (63.1 $mg\cdot g^{-1}$). It exhibited a distinctive selectivity for the removal of metal ions (Cu(II) > Zn(II) > Cr(III) > Pb(II) > Cd(II)) when they coexisted.

DTC chelating resins were usually prepared by dealing the polyamine resins with CS_2 at alkali condition. Herein, we report two chelating beads functionalized with dithiocarbamate for the removal of Co(II) from synthetic wastewater compatible with the industrial separation process. Their adsorption capacity and adsorption kinetics for Co(II) were investigated and compared with those of three commercial resins. The effects of adsorbent dosage, pH, contact time, and temperature were systematically examined. Furthermore, the reusability of the DTC resins for cobalt was explored and discussed.

II. Experimental

A. Materials and instruments

Chloromethylated polystyrene beads (CPS), amino resin (D380), D151 resin, D301R resin were purchased from the Chemical Plant of Nan Kai University (Tianjin, China). Activated carbon was purchased from J&K Scientific Ltd. (Beijing, China), and CH90 resin was purchased from (Wuhan, China), and polyethyleneimine was purchased from Sigma Aldrich Co. (USA). Carbon disulfide, sodium hydroxide, chloroform, and alcohol were purchased from General Chemical (Shanghai, China). All other reagents were of analytical grade and used as received. All solutions were prepared with ultrapure water.

In the experiments of Co(II) ion adsorption, the pH values of the aqueous solutions were measured using a Hanna HI221 model pH meter, and the temperature dependent experiments were carried out in a Nickel Electro Clifton NE1-22 model thermostatic bath. The mimic wastewaters of different Co(II) concentration were prepared by dissolving cobalt chloride hexahydrate in distilled water. The concentration of Co(II) ions was measured using a 200Agilent 725ES inductively coupled plasma optical emission spectroscopy (ICP-OES).

B. Synthesis of DTC resins

1) Pretreatment of the resins

The resins should be pretreated before used. Chloromethylated polystyrene resin, amino resin, D151 resin, D301R resin and CH90 resin were extracted in an absolute ethyl alcohol for 12 h, then washed in sequence by using deionized water, 0.1 $mol\cdot L^{-1}$ HCl solution and 0.1 $mol\cdot L^{-1}$ NaOH solution, and then washed to neutral using deionized water, finally dried in a vacuum oven at 50 ℃.

2) Synthesis of DTC-CPS

As illustrated in Fig. 1, the synthesis procedure of the DTC-CPS chelating beads involved three steps:

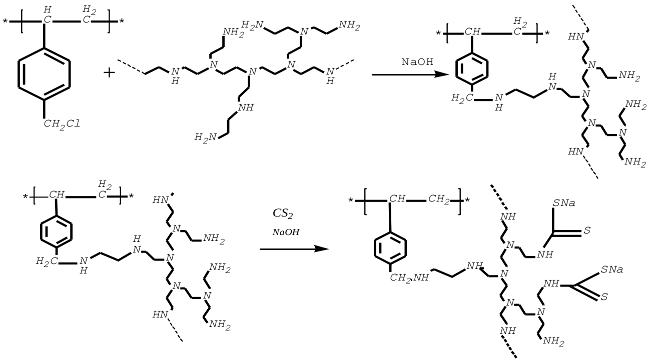

Fig.1. *A typical synthesis flow chart of DTC chelating resin.*

a) First, the CPS beads (10.0 g) were added into chloroform (50 ml) in a round-bottom flask, and then the obtained suspension was stirred for 12 h at 600 rpm at 25 °C. The swollen CPS beads were afterward washed by using both alcohol and ultrapure water for three times and then filtrated from the supernatant;

b) Second, the sodium hydroxide (4.0 g) was dissolved in ultrawater (100 ml), followed by the addition of the PEI (10.0 g) into this solution. Afterward, the pretreated CPS beads were added into the solution, and the mixture was stirred for 15 h at 600 rpm at 50 °C;

c) Third, the pretreated CPS beads grafted with the PEI were added into a mixture composed of ultrawater (100 ml), carbon disulfide (10 ml) and sodium hydroxide (4.0 g). The resulting mixture was stirred for 12 h at 600 rpm at 20 °C, and then continuously for another 12 h at 50 °C. The obtained product was washed separately with water and ethanol; afterward, it was dried in a vacuum oven at room temperature, milled, and sieved for utilization in the adsorption experiments.

3) Synthesis of DTC-D380

The synthesis procedure of the DTC-D380 beads is similar to that of the DTC-CPS. The main steps include: 10.0 g of the D380 resins were added into 50 ml of chloroform in a round-bottom flask, and the resulting suspension was stirred at 600 rpm at 25 °C for 12 h, then the D380 resins were dissolved in 100 ml of NaOH solution and 50 ml CS2 was dropped in. The resulting mixture was stirred at 600 rpm at 10 °C for 12 h, and then continuously at 50 °C for another 12 h. The obtained DTC-D380 beads were washed separately with water and ethanol; then, it was dried in a vacuum oven at room temperature, milled, and sieved for utilization in the adsorption experiments.

The physical characteristics of the chelating beads with DTC resins (abbreviated as DTC resins in the followings) were listed in table I. As can be seen, their density and particle size meet the requirement from the separation technology. During the adsorption-desorption measurements, we also found these two DTC resins remain their physical form after long-time stirring which suggests that the DTC resins present sufficient mechanical strength.

Table I. Physical characteristics of two prepared DTC resins

Physical characteristicss	**DTC -CPS**	**DTC-D380**
physical form	spherical beads	spherical beads
particle size	0.6~0.9mm (>90%)	0.7~1.1mm(>90%)
matrix	Crosslinked-Polystyrene	Styrene-DVB
functional groups	DTC group	DTC group
dry density	1.06~1.11g/cm^3	1.04~1.05 g/cm^3

C. Adsorption studies

All of the adsorption experiments including maximum capacities, effects of adsorbent dosage and pH value, adsorption kinetics and isotherms were conducted batch-wise.

Equilibrium adsorption isotherm studies were conducted with Co(II) solutions of various initial concentrations ranging from 80.0 to 320.0 mg·L^{-1} at different temperatures (20, 30 and 40 °C, respectively) in 150 ml erlenmeyer flasks, followed by shaking at 210 rpm to achieve adsorption equilibrium. The amounts of both DTC-CPS and DTC-D380 beads used were 0.2 g, and the solution volume was maintained at 100 ml. To ensure the adsorption equilibrium, the adsorption time was extended up to 24 h in these experiments. The residual Co(II) concentration in solution was measured by inductively coupled plasma atomic emission spectroscopy. The adsorption capacity at equilibrium of the adsorbents for Co(II) was calculated with the following equation,

$$q_e = \frac{(C_0 - C_e)V}{m}. \qquad (1)$$

Here and are the initial and final concentrations of Co(II) ions in the solution (unit: mg·L^{-1}) , respectively. V is the volume of the solution (L) and is the weight of the adsorbent (g). All assays were carried out in triplicate and only the average values were reported. The removal efficiency (Re%) of the resins was calculated by.

$$\mathrm{Re}\% = (C_0 - C_e)/C_0 \times 100\% \qquad (2)$$

In order to estimate the equilibrium adsorption rates for the uptakes of Co(II) on different DTC chelating beads, time-dependent adsorption studies were carried. The adsorption kinetics were investigated in the synthetic water, in which the initial metal ion concentration, adsorbent dosage and the pH were chosen to be 80.0 mg·L^{-1}, 2.0 g·L^{-1}, and 5, respectively.

The effect of dosage on the adsorptions of Co(II) was evaluated at an initial Co(II) concentration of 80.0 mg·L^{-1} with an increase of adsorbent dosage from 0.1 g·L^{-1} to 1.0 g·L^{-1} at pH 5.0. The same evaluations were conducted at different pH adjusted from 1 to 6 by adding dilute NaOH or HCl solutions, and the adsorbent is fixed at 2.0 g·L^{-1} with the total suspension volume of 100 ml.

The adsorption kinetics experiments were performed at 25 °C, wherein the initial metal ion concentration, adsorbent dosage and the pH of the adsorption solutions were chosen to be 80.0 mg·L^{-1}, 0.2 g/100 ml, and 5, respectively.

Finally, Regeneration of cobalt saturated adsorbents was performed by the agitated mixing of 0.2 g of Co(II) loaded-resins and 20 mL of 0.1 mol·L^{-1} HCl solution at room temperature for 2 h. The DTC resins were collected after the desorption process, and washed thoroughly for three times by using ultrapure water and then dried in a vacuum. By using the same affinity adsorbent four times adsorption-desorption cycles were performed to evaluate the reusability of the DTC resins.

III. Result and discussions

A. Effect of the adsorbent dosage

The influence of adsorbent dosage on the removal of Co(II) in water with an initial concentration of 80.0 mg·L^{-1} at neutral pH condition is shown in Fig. 1. It is

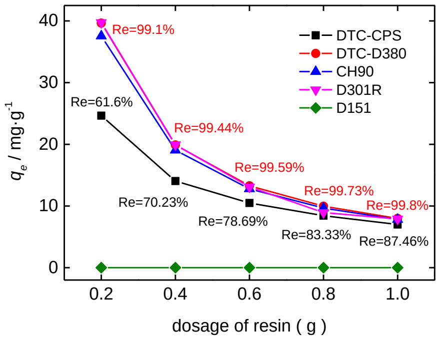

Fig.1. *Effects of adsorbent dosage on the adsorptions of Co(II) on different resins. The Co(II) concentration is 80.0 mg·L^{-1}, and solution volume is 100.0 mL, and temperature is 25 °C and the stirring speed is 210 rpm, and for each measurement the adsorption time is 12 h.*

noticed that the removal percentage of Co(II) for DTC-D380 resin increased from 99.1% to 99.8% with an increase of adsorbent dosage from 0.1 g/100 ml to 10 g/100 ml. Under the same experimental condition the removal percentage of Co(II) for DTC-CPS resin increased from 61.6% to 87.46%, which was attributed to the increasing active sites/Co ratio with the increase of adsorbent dosage. Because the maximum q_e was achieved at 2.0 g·L^{-1} adsorbent dosage, it was concluded that the sufficient dosage is 2.0 g·L^{-1}, and thus all other adsorption experiments were carried out with this adsorbent dosage. In addition, the adsorptions of DTC-CPS and DTC-380 were compared to those of the commercial pure resins including the CH90, D301R and D151 resins. Figure 1 shows that D151 resin cannot adsorb Co(II) ions at the experiment condition. DTC-D380 presents almost the same excellent adsorption performance as both D301R and CH90, and noticeably better performance than DTC-CPS.

B. Effect of pH

The pH value of the solution plays a significant role in adsorption-based water treatment processes, because the speciation of Co(II) and the surface charge of the adsorbents are strongly influenced by the water pH value [40, 41]. The pH effect on the adsorption of Co(II) by the DTC resins and other adsorbents is shown in Fig. 2. It was noticed that the adsorption capacities increased for DTC resins when the pH increases over a range of pH 1-5. This is probably because of the competition of H^+ ions with Co(II) for being adsorbed on the same active site. At pH greater than 5, the adsorption capacities of DTC resins decreased gradually with the increase of pH, the reason is that the Co(II) take a hydrolysis reaction and form the Co(OH) 2 precipitate. Because the pH of industrial wastewater is approximately 5, we keep the pH=5 in the following studies (unless otherwise specified).

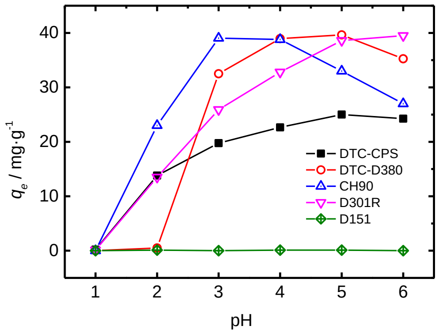

Fig. 2. *Effects of pH on the adsorptions of Co(II) on different adsorbents. The Co(II) concentration is 80.0 mg·L^{-1}, and adsorbent dosage is 2.0 g·L^{-1}, and temperature is 25 °C and the stirring speed is 210 rpm, and for each measurement the adsorption time is 12 h.*

C. Kinetics of adsorption

The adsorption kinetics of Co(II) on the different adsorption resins was investigated. Fig. 3 plots the change of adsorbed Co(II) as a function of contact time.

Fig. 3 shows the adsorption capacity of Co(II) as a function of contact time onto the different resins. For DTC-380 resins, during the initial 30min adsorption period, the adsorption capacity, qe, presented a sharp increase with increasing contact time, reaching a plateau after almost 120min. Specifically, within the 30min, qe reached 36.45mg·g-1 (92.44% of the total adsorption); at 120min, more than 99.7% of the total adsorption was completed, and q_e was found to be 39.535 mg·g^{-1}. After 120 min, the adsorption rate slowed down and, after 180 min, reached equilibrium, while the maximum of q_e was found to be 39.645 mg·g^{-1}. The adsorption capacities of Co(II) as a function of contact time onto DTC-CPS, CH90 and D301R resins are similar to that of DTC-D380 resin. In addition, as can be seen from Fig.3, the sequence of rate of adsorption from high to low is: DTC-D380, CH90, D301R, and DTC-CPS.

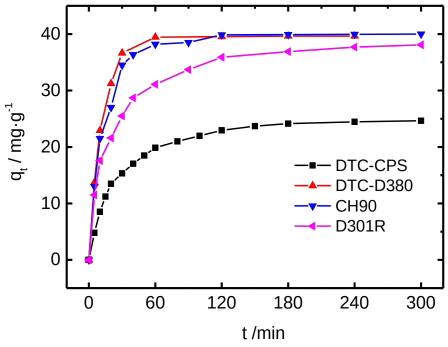

Fig.3. *Effect of contact time on the adsorptions of Co(II) on different adsorbents. The Co(II) concentration is 80.0 mg·L^{-1}, and adsorbent dosage is 2.0 g·L^{-1}, and pH is 5, and temperature is 25 °C and the stirring speed is 210 rpm.*

To further quantify the reaction order of adsorption on the DTC resins, the pseudo-first-order and pseudo-second-order kinetic models were used to simulate the kinetics.

The pseudo-first-order kinetic model of Lagergren can be linearized as:

$$\log q_e - q_t = \log q_e - \frac{K_f}{2.303}t \qquad (3)$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t (mol·g^{-1}), and k_1 (min^{-1}) is the rate constant of first-order adsorption. By using linear plot of ln(q_e–q_t) versus t (figure not shown), k_1 and the correlation coefficient (R^2) were calculated and given in table II.

TABLE II. Pseudo-first-order kinetic parameters for the adsorptions of Cu (II) onto the DTC resins

resin	time range	$q_{e.exp}$ (mg·g^{-1})	K_f (min^{-1})	q_e (mg·g^{-1})	R^2
DTC-CPS	0-720min	24.89	0.0013	13.48	0.9741
	0~60min	24.89	0.025	21.60	0.9716
DTC-D380	0-180min	39.645	0.0519	22.26	0.8478
	0~50min	39.645	0.0875	41.88	0.9976

As suggested in many similar studies, the first-order equation of Lagergren does not fit well to the whole range of contact time and is applicable over the initial stage of the adsorption processes [42, 43]. Similarly, in this study, the correlation coefficient for the pseudo-first-order kinetic model is found low and a clear difference of calculated theoretical q_e and experimental $q_{e.exp}$ was observed. These findings indicated a poor pseudo-first-order fit to the experimental data.

The kinetic data were further analyzed by pseudo second-order kinetic model, which can be expressed as [44, 45]

$$\frac{t}{q_t} = \frac{1}{K_s q_e^{\,2}} + \frac{t}{q_e} \qquad (4)$$

where K_s (g·mol^{-1}·min^{-1}) is the rate constant of second order adsorption. The fitted q_e and R^2 values for pseudo-second-order kinetic model are given in table III.

Table III. Pseudo-second-order kinetic parameters for the adsorptions of Co(II) onto two DTC resins.

resin	$q_{e.exp.}$ (mg·g^{-1})	K_s (mg/g·min)	q_e (mg·g^{-1})	R^2
DTC-CPS	24.89	0.00268	25.3	0.9998
DTC-D380	39.645	0.00041	40.95	0.9990

As can be seen, a high correlation coefficient (0.9998) was obtained and moreover the q_e value was highly in agreement with $q_{e,exp}$. These findings indicated that the adsorption kinetics of Co(II) on the chelating resins can be defined by the second-order kinetics model, and the chemical adsorptions are the rate-controlling step which may involve valence forces through sharing or exchange of electrons between metal ions and adsorbents [44, 45].

D. Adsorption isotherms

The adsorption isotherms at different temperatures are determined, and the saturated adsorption amounts as a function of temperature are displayed in Fig. 4. It is obvious that the adsorption capacities of the DTC resins increases with raising temperatures. In particular, this trend is noticeable for DTC-CPS, and for DTC-D380 the dependence on temperature is relatively weak. In generally, the adsorption action originating from the chelating interaction is a chemisorption action, and the adsorption process is an endothermic process. Thus, the increase of temperature is in favor of the adsorption.

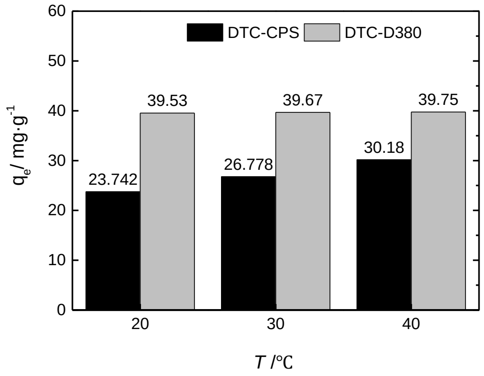

Fig.4 *Adsorption capacities of two DTC resins at three different temperatures. The Co(II) concentration is 80.0 mg·L^{-1}; adsorbent dosage is 2.0 g·L^{-1}; pH is 5; the stirring speed is 210 rpm. For each measurement the adsorption time 12 h.*

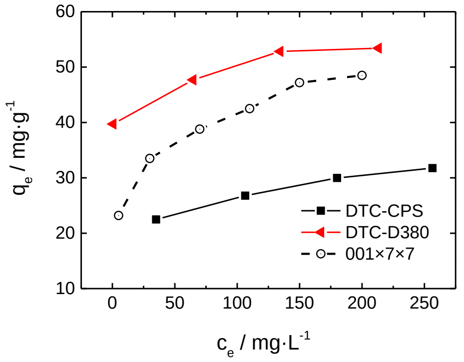

Fig.5 *Adsorption isotherms (solid lines) of the DTC resins to Co(II) versus the Co(II) final concentrations. The adsorbent dosage: 2.0 g·L^{-1}; pH=5; temperature: 25 °C; the stirring speed: 210 rpm. For each measurement the adsorption time is 12 h.The dashed line is from Qiu et al.[20] for comparison.*

The Adsorption capacities of two DTC resins also depend on the Co(II) concentration in the solution. Fig. 5 plots the adsorption isotherms of the DTC resins versus the Co(II) final concentration in the solution. Because of the balance between adsorption and desorption, the adsorption capacities of two DTC resins increased with the increase in the final Co(II) concentration. While at the extremely low Co(II) concentration condition (1.0 mg·L^{-1}), the adsorption capacity of DTC-D380 was around 40.0 mg·g^{-1}, and that of DTC-CPS was around 20.0 mg·g^{-1}. For comparison, we also extracted the data from Qiu et al. [20] wherein the 001×7×7 ions exchanges chelating beads were examined for the adsorption of Co(II) from 250 mL wastewater with Co(II) concentration 100.0 mg·L^{-1} at 35 °C and stirring speed 240 rpm. Although operation conditions in the present work and in Qiu's work are different, our DTC-D380 presents overall better adsorption performance than the 001×7×7 ions exchanges chelating beads, and even better performance than DTC-CPS.

E. Reusability of DTC resins

It is desirable that an adsorbent could be regenerated and reused so that it can be put into cyclic use in a cost effective manner. To investigate the regeneration, the DTC resins were first saturated with Co(II) by shaking the resins with initial cobalt concentration of 80.0 mg·L^{-1} and adsorbent dosage of 2.0 g·L^{-1} at pH 5 for 24 h. Regeneration of cobalt saturated adsorbents was achieved by using 0.1 mol·L^{-1} HCl solution. As a result, the desorption process reached equilibrium after 60 mins. Fig. 6A shows the adsorption efficiency of the regenerated DTC resins for Co(II) with initial cobalt concentration of 80.0 mg·L^{-1} and adsorbent dosage of 2.0 g·L^{-1} at pH 5 for 4 times. The DTC-CPS and DTC-D380 retained 99.6% and 98.6% for Co(II), respectively, of original adsorption capacity after one adsorption–desorption cycle. After 4 cycles of reuse, the regenerated DTC-CPS and DTC-D380 still maintained about 98.8% and 95.6%, respectively, of the original adsorption capacity for Co(II), indicating the good reusability of the adsorbent for cobalt removal. Simultaneously, the regeneration study was shown in Fig. 6B. The desorption efficiency of cobalt on the DTC-CPS and DTC-D380 decreased slowly with increasing cycle numbers, and the desorption efficiency remained more than 97% and 96% after 4 regeneration cycles, indicating the cobalt adsorbed DTC-CPS and DTC-D380 could be regenerated efficiently with 0.1 mol·L^{-1} HCl solution.

IV. Conclusion

In this study, we developed two kinds of chelating beads aiming to recover the Co(II) from wastewater by combining the intensified separation technology. We showed that the two chelating beads could be synthesized with the matrix functionalized with two different dithiocarbamated resins, and their physical characteristics meet the multiple requirements from the separation technology.

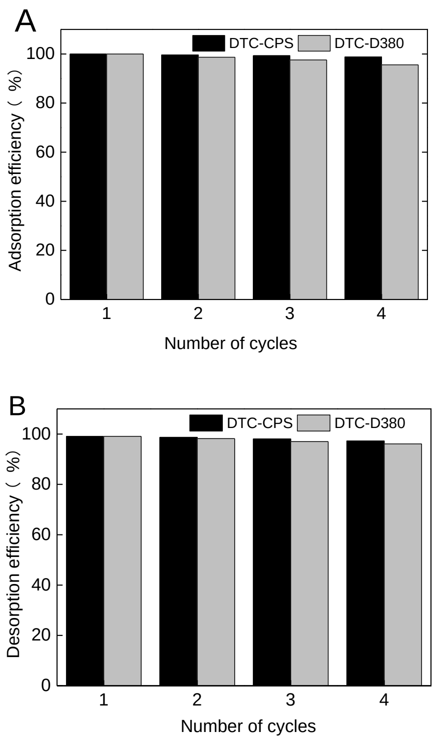

Fig.6 *(A) Adsorption efficiency of the regenerated DTC-CPS and DTC-D380 for Co(II) with initial cobalt concentration of 80.0 mg/L and adsorbent dosage of 2.0 g·L^{-1} at pH 5 for 4 times. (B) Desorption cycles for Co(II) adsorbed on the DTC-CPS and DTC-D380 using 0.1 mol·L^{-1} HCl solutions.*

The prepared DTC-D380 and DTC-CPS were evaluated for the removal of trace amount of Co(II) from synthetic wastewater. At the initial Co(II) concentration of 80.0 mg·L^{-1}, the maximum Co(II) adsorption capacities of the DTC-D380 and DTC-CPS were identified, respectively, as 39.645 mg and 24.89 mg per gram of dry polymer at pH 5 and temperature 25 °C. In particular, we compared the adsorption capabilities of those two chelating beads to those of the other resins and the available data, and found that DTC-D380 presents excellent adsorption performance. In addition, the adsorption kinetics of Co(II) was well represented by the pseudo-second-order kinetics model. The temperature effect on the Co(II) adsorption was not significant for DTC-D380 and significant for DTC-CPS. Finally we also found that the two developed DTC resins could be used at least four times without losing their original activities. The present study showed that the DTC-D380 can be used as an efficient adsorbent combining the separation technology for the recovery of Co(II) from wastewater.

Acknowledgement

This work is supported by the National Basic Research Program of China (2014CB748500), the National Natural Science Foundation of China (21206036, 51322805), and Shanghai Science Technology Committee Rising-Star Program (14QA1401300), and Innovation Program of Shanghai Municipal Education Commission (15ZZ029).

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