# Recovery of Co(II) and Mn(II) from Pure Terephthalic Acid Wastewater

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The adsorption of Co(II) and Mn(II) onto the 001 × 7 × 7 ion-exchange resin has been studied. Batch experiments were performed to study the effects of various parameters such as stirring speed, temperature, dosage of resin, and pH on the adsorption process. The adsorption capacity ($K_F$) for cobalt and manganese were calculated from the Freundlich adsorption isotherm. The adsorption of cobalt and manganese on the 001 × 7 × 7 ion-exchange resin followed the pseudosecond-order equation. The adsorption and desorption of Co(II) and Mn(II) onto the 001 × 7 × 7 ion-exchange resin were investigated by using a dynamic method. The effects of flow rate, temperature, and desorbant concentration were studied. The studies showed that this cation-exchange resin can be used as an efficient adsorbent material for the removal of cobalt and manganese from pure terephthalic acid (PTA) wastewater.

## Introduction

Pure terephthalic acid (PTA) is the main material in the polyester industry and is widely applied in chemical fiber, containers, packing, film-producing, and so on. *p*-Xylene is oxidized to form PTA in the presence of acetic acid solvent and Co, Mn, and Br complex catalyzers. There is a large amount of wastewater in the refining unit of PTA. The main components in the wastewater after organic acids are removed via the method of ultrafiltration and reverse osmosis which are metal ions like cobalt and manganese. Owing to the high price of cobalt and manganese, it is important to recycle these metal ions to protect the environment and decrease production costs.

A number of technologies have been developed over the years to remove metal ions from water, including chemical precipitation, electroflotation, ion exchange, reverse osmosis, and adsorption on activated carbon. The removal of heavy metal pollutants at high concentrations from water can be readily accomplished by chemical precipitation or electrochemical methods. At low concentrations, the removal of such pollutants is more effectively implemented by ion exchange or adsorption on solid sorbents such as activated carbon[1] or coal fly ash.[2] Some investigators have studied the removal of inorganic metal ions, namely, cadmium, cobalt, copper, mercury, and lead.[3−8] Rengaraj et al.[9] studied the adsorptive removal process of Co(II), Cr(III), and Ni(II) using the IRN77 cation-exchange resin. Results showed that the adsorption of cobalt, chromium, and nickel on this cation-exchange resin followed the Lagergren kinetic model. The adsorption equilibrium was described well by the Freundlich isotherm model. The film diffusion of Co(II) in IRN77 and SKN1 ion-exchange resins was the main rate-limiting step in the research results.[10] Sharma et al.[11] studied the removal of manganese from aqueous solutions and wastewaters. The process of Mn(II) removal is exothermic in nature. However, improved sorption capacity of ion-exchange resins may have advantages over nonspecific adsorbents. This work aims to use the 001 × 7 × 7 ion-exchange resin to recover cobalt and manganese from PTA wastewater. Through batch and column experiments, the optimum parameters that influence adsorption and desorption were determined.

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## Experimental Procedure

***Materials.*** The 001 × 7 × 7 resin was purchased from the Nankai Chemicals Factory. The as-received resin was rinsed with acidic or basic solutions and rinsed with distilled water several times to remove any leached materials. The physical properties and specifications of the resin as reported by the suppliers are shown in Table 1. The conditioning followed the recommendations provided by the manufacturers, and it was carried out to remove all impurities from the resin and to obtain a free base form.

Analytical grade chemicals were used throughout the study. The pH of the solutions was adjusted using various concentrations of HCl. Stock solutions of the test reagents (100 $mg \cdot L^{-1}$) were prepared by dissolving cobalt acetate and manganese acetate in distilled water.

***Instrument.*** Atomic absorption spectrophotometric measurements were made with an atomic absorption spectrophotometer TAS-986 using an air−acetylene flame. The pH values of the solutions were measured with a Aolilong-868 pH meter using the full range of 0 to 14. A mechanical shaker of controlled speed was used for batch equilibration. The column experiments were performed by using a 10 mm i.d. Pyrex glass column partly filled with 4 g of 001 × 7 × 7 resin. The height of the resin was 55 mm.

***Batch Equilibrium Adsorption.*** Adsorption tests were carried out by batch way at (25, 35, and 45) °C in a 250 mL tank reactor. The general method of adsorption involved adding and equilibrating 0.4 g of wet resin with 200 mL of metal ion complex solution for 2 h at 210 rpm. The metal concentrations in solution were measured by atomic absorption spectrophotometry. The amount of metal adsorbed per unit mass was calculated as follows:

$$Q_i = \sum_{i=1}^{n} \frac{(C_{i-1} - C_i)V_i}{m} \quad (1)$$

where $Q_i$ is the amount of Co(II) or Mn(II) adsorbed onto a unit amount of the adsorbent ($mg \cdot g^{-1}$); $C_i$ and $C_{i-1}$ are the

10.1021/je900827e 
Published on Web 03/03/2010

**Table 1. Characteristics of 001 × 7 × 7 Cation-Exchange Resin[a]**

| characteristics | | values |
|---|---|---|
| physical characteristics | | |
| | physical form | uniform particle size spherical beads |
| | particle size | < 0.315 mm, 2 % maximum; > 1.25 mm, 2 % maximum |
| | whole beads | 90 % minimum |
| chemical characteristics | | |
| | matrix | styrene-DVB gel |
| | functional groups | sulfonic acid |
| | ionic form as shipped | $Na^+$ |
| | total exchange capacity | (a) ≥ 4.5 mmol (dry)/g; (b) ≥ 2.0 mmol (wet)/mL |
| | moisture holding capacity | (35 to 40) % ($Na^+$ form) |

[a] Information provided by the manufacturer.

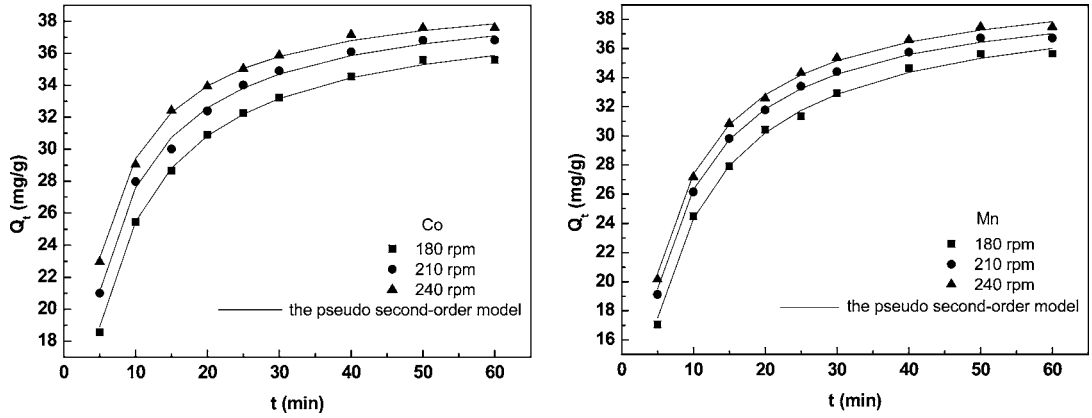



**Figure 1.** Effect of stirring speed on the adsorption of metal ions ($C_{Co2+}$ = 100 mg·L$^{-1}$, $C_{Mn2+}$ = 100 mg·L$^{-1}$, resin quantity = 0.4 g, temperature = 35 °C).

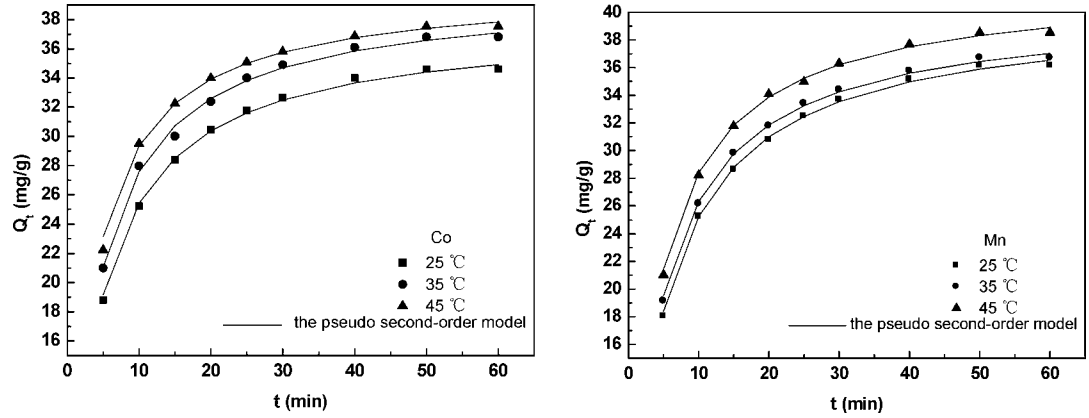



**Figure 2.** Effect of temperature on the adsorption of metal ions ($C_{Co2+}$ = 100 mg·L$^{-1}$, $C_{Mn2+}$ =100 mg·L$^{-1}$, resin quantity = 0.4 g, stirring speed = 210 rpm).

concentrations of Co(II) or Mn(II) (mg·L$^{-1}$) in the aqueous phase, before and after adsorption, respectively; *m* is the mass of resin (g); *V* is the volume of the metal ion complex solution (L); and *n* is the sampling number.

***Dynamic Adsorption.*** The aqueous solution containing Co(II) and Mn(II) passed through the resin bed at a certain flow rate to preconcentrate Co(II) and Mn(II). Then, the retained Co(II) and Mn(II) are eluted with $H_2SO_4$ at a certain flow rate.

## Results and Discussion

***Metal Ion Uptake Study by Batch Technique. Effect of Stirring Speed.*** Figure 1 shows the effect of stirring speed on adsorption of Co(II) and Mn(II). The reaction rate increased with the increasing stirring speed. The equilibrium amount adsorbed of Co(II) and Mn(II) increased with stirring speed.

***Effect of Temperature.*** Figure 2 shows the effect of temperature on the adsorption of Co(II) and Mn(II). The equilibrium amount adsorbed of Co(II) is (34.84, 36.41, and 36.68) mg·g$^{-1}$ at (25, 35, and 45) °C, and Mn(II) is (36.37, 36.41, and 38.39) mg·g$^{-1}$. The results indicated the process of adsorption is endothermic.

***Effect of Resin Dosage.*** Figure 3 presents the removal of Co(II) and Mn(II) as a function of 001 × 7 × 7 resin dosage. The resin dosage varied from (0.5 to 4.5) g·L$^{-1}$. Increasing the resin dosage increased the percent removal of Co(II) and Mn(II). Results showed that a minimum resin dosage of 0.8 g was required for the quantitative removal of Co(II) and Mn(II) from 200 mL of solution containing 100 mg·L$^{-1}$ of Co(II) and Mn(II). The results also clearly indicated that the removal efficiency increases up to the optimum dosage beyond which the increase in removal efficiency is negligible.[12] It is apparent that the equilibrium metal ion concentration decreases with increasing resin dosage for a given initial metal concentration. This is to be expected because, for a fixed initial solute concentration,

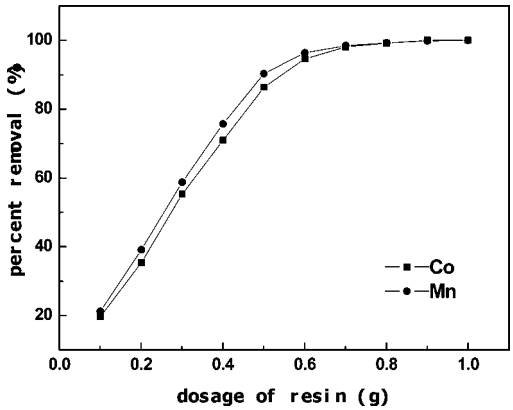



**Figure 3.** Effect of resin dosage on the adsorption of metal ions ($C_{Co2+}$ = 100 mg·L$^{-1}$, $C_{Mn2+}$ =100 mg·L$^{-1}$, temperature = 35 °C, stirring speed = 210 rpm).

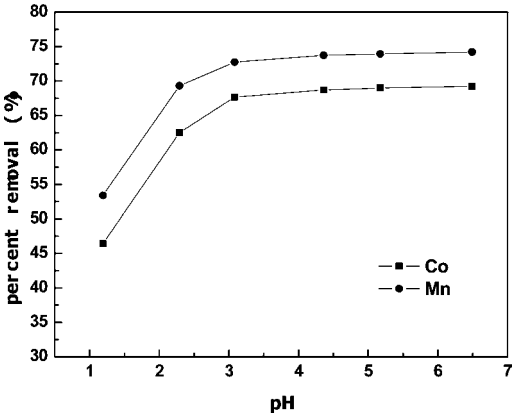



**Figure 4.** Effect of pH on the adsorption of metal ions ($C_{Co2+}$ = 100 mg·L$^{-1}$, $C_{Mn2+}$ =100 mg·L$^{-1}$, resin quantity = 0.4 g, temperature = 35 °C, stirring speed = 210 rpm).

increasing adsorbent doses provides greater surface area or adsorption sites.[13]

***Effect of pH.*** To optimize the pH for maximum removal efficiency, experiments were conducted with 200 mL of 100 mg·L$^{-1}$ of metal solution containing 0.4 g of 001 × 7 × 7 cation-exchange resin in the pH range 1 to 7, and the results are depicted in Figure 4. The result represents the effect of initial pH on the removal of Co(II) and Mn(II) by the 001 × 7 × 7 resin. Maximum adsorption was observed in the pH range of 3 to 7. The percent removal of Co(II) and Mn(II) is 68 % and 73 %, respectively. When pH > 7, the Co(II) and Mn(II) will form hydroxide precipitates.[14] The pH of PTA wastewater is equal to 4, so pH = 4 was selected for subsequent studies.

***Adsorption Isotherm.*** In this study, the general adsorption isotherm models, Langmuir and Freundlich, were used in establishing the mechanism for cobalt and manganese complex adsorption onto the 001 × 7 × 7 resin. The experimental results obtained for the adsorption of cobalt and manganese on the 001 × 7 × 7 ion-exchange resin at 35 °C under optimum conditions of stirring speed and the dose of adsorbent were fitted with the Langmuir and Freundlich adsorption isotherms (Figure 5).

Table 2 shows the $R^2$ values of the Freundlich adsorption isotherms for cobalt and manganese, which are larger than the values for the Langmuir adsorption isotherms. Hence, the equilibrium data of Co(II) and Mn(II) both fit the Freundlich adsorption isotherm well. The Freundlich isotherm is given by:

$$Q_e = K_F C_e^{1/n} \tag{2}$$

where $Q_e$ is the equilibrium amount of Co(II) or Mn(II) adsorbed

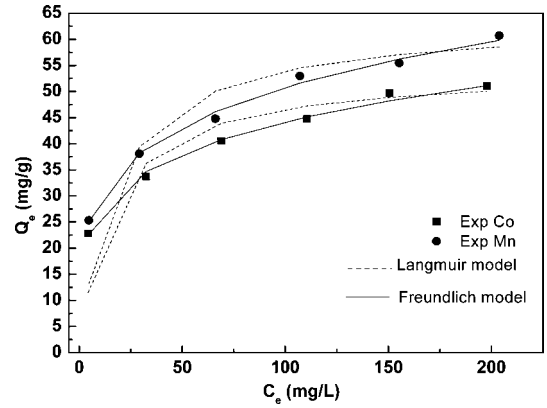



**Figure 5.** Model fit of adsorption isotherm of Co(II) and Mn(II) on 001 × 7 × 7.

onto a unit amount of the adsorbent (mg·g$^{-1}$); $C_e$ is the equilibrium concentration (mg·L$^{-1}$); and $K_F$ and $n$ are the Freundlich constants, where $K_F$ and $n$ are the constants representing the adsorption capacity and intensity of adsorption, respectively. The logarithmic form of the equation becomes:

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent ($Q_e$) and the concentration of the metal in solution at equilibrium ($C_e$).

The values of $Q_0$ for Co(II) and Mn(II) are (54.05 and 63.69) mg·g$^{-1}$, respectively. The values of $Q_0$ for the 001 × 7 × 7 resin for cobalt and manganese are much higher than the adsorbents already reported in the literature (14.4 and 27.2) mg(Co)·g$^{-1}$, (1.65 and 6.5) mg(Mn)·g$^{-1}$.[15−18]

The adsorption capacities ($K_F$) and adsorption intensities ($n$) are presented in Table 2. Values of $1 < n < 10$ show favorable adsorption of metals on the 001 × 7 × 7 cation-exchange resin. Higher values for $K_F$ indicate higher affinity for cobalt and manganese.

***Adsorption Kinetics.*** The kinetics of Co(II) and Mn(II) adsorption on the 001 × 7 × 7 resin followed the pseudosecond-order rate expression:

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2 \tag{4}$$

where $Q_t$ is the amount of Co(II) or Mn(II) adsorbed onto the adsorbent at time $t$ (mg·g$^{-1}$). Integration of eq 4 leads to eq 5.

$$\frac{1}{Q_e - Q_t} - \frac{1}{Q_e} = kt \tag{5}$$

Then

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t \tag{6}$$

The theoretical curves calculated are compared with experimental points in Figures 1 and 2. The pseudosecond-order kinetic model parameters are shown in Table 3.

To assess the nature of the diffusion process responsible for adsorption of Co(II) and Mn(II) on the 001 × 7 × 7 resin, the experimental data were calculated by a different model. If film diffusion is the rate-determining step in the adsorption of Co(II) and Mn(II) on the 001 × 7 × 7 resin surface, the values of $F$ ($F = Q_t/Q_e$) have a linear relationship with $t$ (Figure 6). If particle diffusion is rate-limiting, then the values of [1 − 3(1

**Table 2. Parameters of Adsorption Isotherm Models**

| models | adsorbate | regression equation | parameters | | |
|---|---|---|---|---|---|
| | | | $Q_0$ (mg·g$^{-1}$) | $b$ (L·mg$^{-1}$) | $R^2$ |
| Langmuir | Co | $C_e/Q_e = 0.0185C_e + 0.2953$ | 54.05 | 0.06 | 0.991 |
| | Mn | $C_e/Q_e = 0.0157C_e + 0.2828$ | 63.69 | 0.06 | 0.989 |
| | | | $K_F$ | $n$ | $R^2$ |
| Freundlich | Co | $Q_e = 16.47C_e^{0.2142}$ | 16.47 | 4.67 | 0.995 |
| | Mn | $Q_e = 17.59C_e^{0.2302}$ | 17.59 | 4.34 | 0.996 |

**Table 3. Pseudosecond-Order Kinetic Model Parameters**

| experiment conditions | Co | | Mn | |
|---|---|---|---|---|
| | $Q_e$ (mg·g$^{-1}$) | $k$ (min$^{-1}$) | $Q_e$ (mg·g$^{-1}$) | $k$ (min$^{-1}$) |
| 180 rpm | 39.063 | 4.801 | 39.841 | 3.938 |
| 210 rpm | 39.841 | 5.650 | 40.323 | 4.659 |
| 240 rpm | 40.161 | 6.821 | 40.984 | 4.912 |
| 25 °C | 37.736 | 5.469 | 40.161 | 4.203 |
| 35 °C | 39.841 | 5.650 | 40.323 | 4.659 |
| 45 °C | 40.161 | 6.776 | 42.017 | 4.956 |

**Table 4. Pore Diffusion Coefficient for the Removal of Co(II) and Mn(II) onto the 001 × 7 × 7**

| Sl. no. | experiment conditions | pore diffusion coefficient/cm$^2$·s$^{-1}$ | |
|---|---|---|---|
| | | Co(II) | Mn(II) |
| 1 | 180 rpm | $9.535 \cdot 10^{-7}$ | $8.869 \cdot 10^{-7}$ |
| 2 | 210 rpm | $9.827 \cdot 10^{-7}$ | $9.931 \cdot 10^{-7}$ |
| 3 | 240 rpm | $1.030 \cdot 10^{-6}$ | $1.019 \cdot 10^{-6}$ |
| 4 | 25 °C | $9.570 \cdot 10^{-7}$ | $9.430 \cdot 10^{-7}$ |
| 5 | 35 °C | $9.827 \cdot 10^{-7}$ | $9.931 \cdot 10^{-7}$ |
| 6 | 45 °C | $1.056 \cdot 10^{-6}$ | $1.019 \cdot 10^{-6}$ |

$- F)^{(2/3)} + 2(1 - F)]$ ($F = Q_t/Q_e$) have a linear relationship with $t$ (Figure 7).

Figure 7 shows the values of $[1 - 3(1 - F)^{(2/3)} + 2(1 - F)]$ have a linear relationship with $t$. It is evident that the particle diffusion of Co(II) and Mn(II) onto the 001 × 7 × 7 ion-exchange resin is shown to be the main rate-limiting step. The pore diffusion coefficients are presented in Table 4, and the pore diffusion theoretical curves calculated compared with experimental points are presented in Figure 8.

***Metal Ion Uptake Study Using Column Technique. Effect of the Feed Flow Rate.*** The flow rate of the feed solution through the column is an important parameter, since it not only affects the recovery of Co(II) and Mn(II) but also controls the time of analysis. To evaluate the effect of flow rate, a set of solutions containing 200 mg·L$^{-1}$ of Co(II) and Mn(II) were passed through the column at a flow rate that varied from (4 to 8) mL·min$^{-1}$. Table 5 shows that both the equilibrium amount adsorbed and the percent removal decreased with the increasing flow rate. However, the production cycle increased with a decreasing flow rate as to the same yield. Therefore, the flow rate of 5.56 mL·min$^{-1}$ was found to be suitable for optimum loading of the analyte and was used for further studies.

***Effect of Temperature.*** Figure 9 shows the breakthrough curves of the Co(II) and Mn(II) ions at different temperatures.

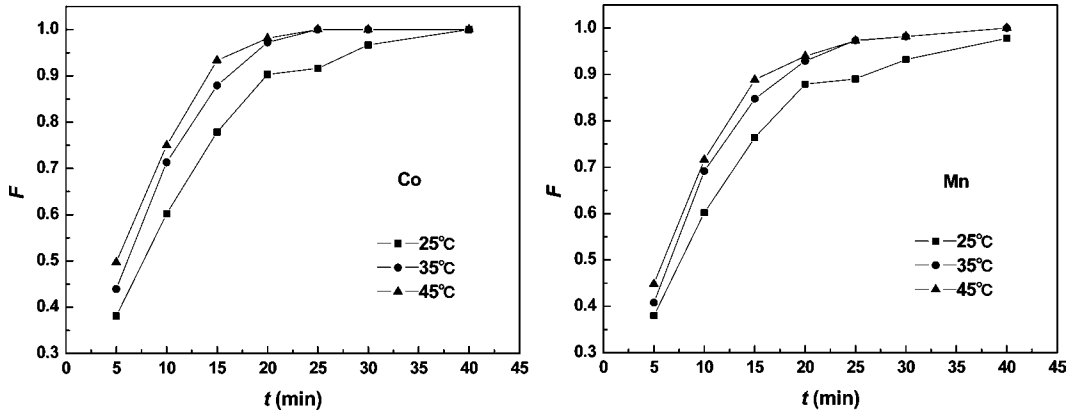



**Figure 6.** $F \sim t$.

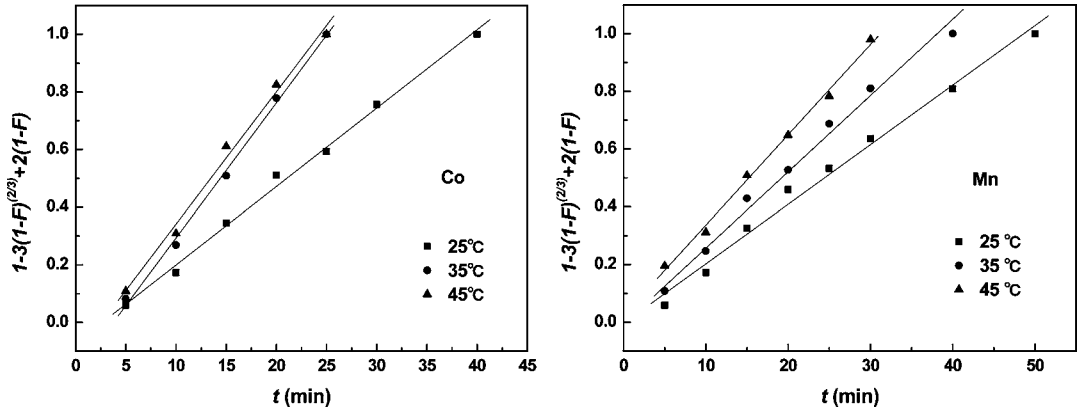
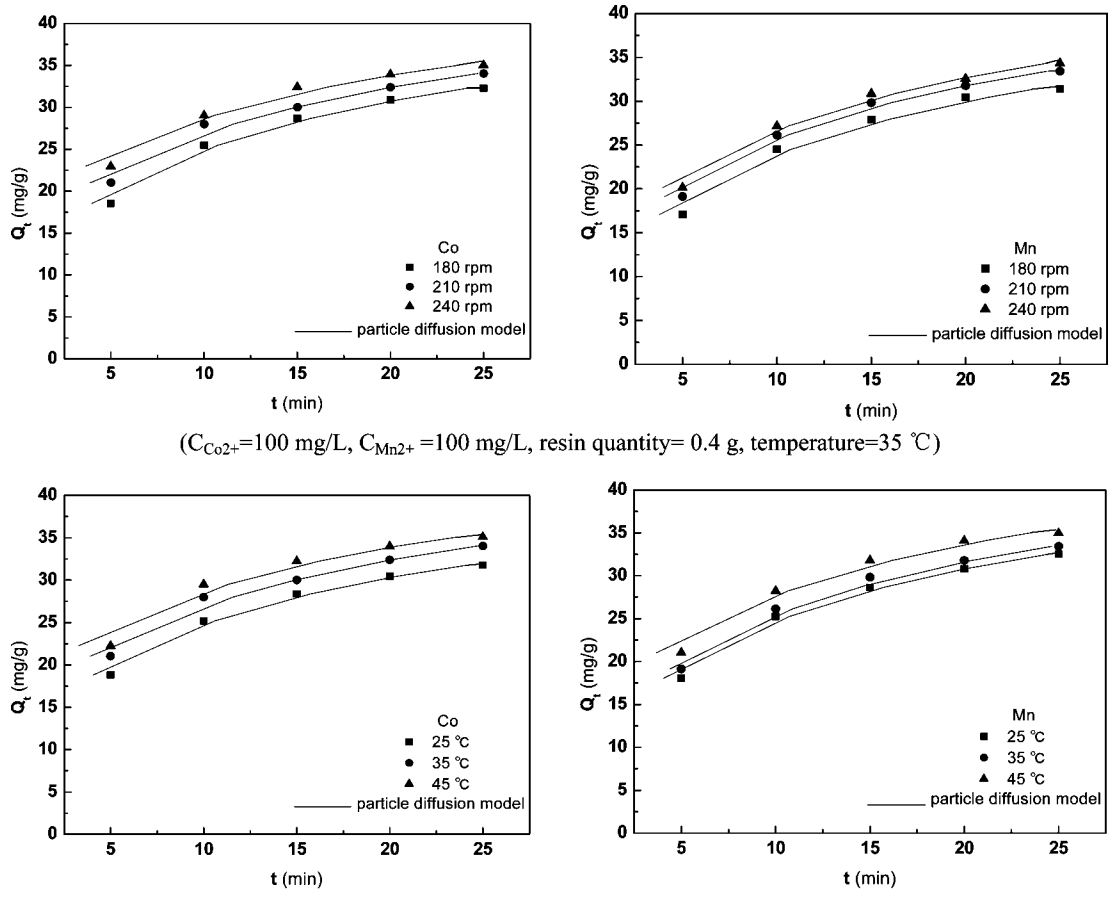



**Figure 7.** $[1 - 3(1 - F)^{(2/3)} + 2(1 - F)] \sim t$.




($C_{Co2+}$=100 mg/L, $C_{Mn2+}$ =100 mg/L, resin quantity= 0.4 g, temperature=35 ℃)

($C_{Co2+}$=100 mg/L, $C_{Mn2+}$ =100 mg/L, resin quantity= 0.4 g, stirring speed=210 rpm)

**Figure 8.** Model fit of kinetic data of Co(II) and Mn(II) on 001 × 7 × 7.

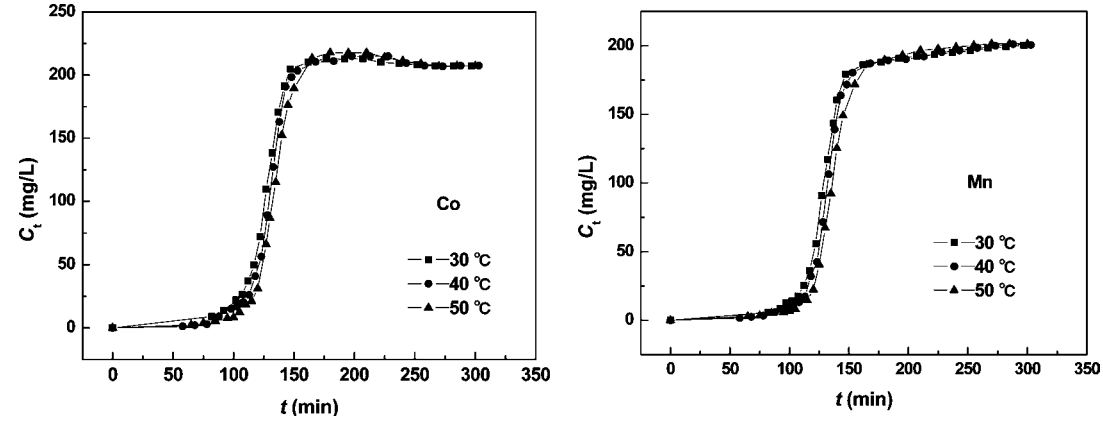



**Figure 9.** Effect of temperature on the adsorption.

**Table 5. Effect of Flow Rate on the Adsorption**

| | Co | | Mn | |
|---|---|---|---|---|
| flow rate | equilibrium amount adsorbed | percent removal | equilibrium amount adsorbed | percent removal |
| mL·min$^{-1}$ | mg·g$^{-1}$ | % | mg·g$^{-1}$ | % |
| 3.79 | 37.94 | 90.81 | 39.47 | 92.36 |
| 5.56 | 35.59 | 86.35 | 37.58 | 89.19 |
| 7.76 | 34.43 | 85.73 | 37.52 | 88.82 |

**Table 6. Effect of Temperature on the Adsorption**

| | Co | | Mn | |
|---|---|---|---|---|
| temperature | equilibrium amount adsorbed | percent removal | equilibrium amount adsorbed | percent removal |
| °C | mg·g$^{-1}$ | % | mg·g$^{-1}$ | % |
| 30 | 35.59 | 86.35 | 37.58 | 89.19 |
| 40 | 35.89 | 89.16 | 38.10 | 90.69 |
| 50 | 38.02 | 91.10 | 39.30 | 91.34 |

The trends of the breakthrough curves are similar. Table 6 shows that increasing temperature increased the equilibrium amount adsorbed and percent removal of Co(II) and Mn(II). The results indicated that the process of adsorption is endothermic. The temperature of PTA wastewater in the plant was 40 °C; therefore, 40 °C was chosen for further studies.

***Elution of Co(II) and Mn(II) from the Resin Column.*** An attempt was made to elute the adsorbed Co(II) and Mn(II) from the resin using dilute sulfuric acid solution. When the flow rate

of 1.0 mol·L$^{-1}$ $H_2SO_4$ eluting solution was (1, 2, and 3) mL·min$^{-1}$, the desorption rate of Co(II) was (99.30, 98.75, and 86.90) %, respectively, whereas Mn(II) was (99.13, 98.64, and 86.07) % at 30 °C. Increasing the temperature, however, decreased the desorption rate of Co(II) and Mn(II).

## Conclusions

In the batch experiments, the equilibrium amount adsorbed increased with stirring speed. Other parameters such as temperature, resin dosage, and pH have some influence on cobalt and manganese adsorption, and the best values for maximizing cobalt and manganese recovery could be defined. The equilibrium isotherm data of Co(II) and Mn(II) both fit the Freundlich isotherm well. The experimental data shows that the adsorption process obeys the pseudosecond-order equation. The particle diffusion of Co(II) and Mn(II) onto the 001 × 7 × 7 ion-exchange resin was shown to be the main rate-limiting step.

In column experiments, the effects of flow rate, temperature, and desorbant concentration were studied. The optimized operation conditions were obtained. When the temperature is 40 °C and the feed flow rate is 5.56 mL·min$^{-1}$, the adsorption rate of Co(II) and Mn(II) reached 89.16 % and 90.69 %, respectively. A desorption study with $H_2SO_4$ (1 mol·L$^{-1}$) resulted in removal of nearly 99 % of loaded Co(II) and Mn(II) from the resin column at 30 °C. The results showed that the 001 × 7 × 7 cation-exchange resin can be used as an efficient adsorbent material for the recovery of Co(II) and Mn(II) from PTA wastewater.

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Received for review October 12, 2009. Accepted February 12, 2010.

JE900827E