

# Ion Exchange Resin on Treatment of Copper and Nickel Wastewater

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**Abstract.** On the conditions of static and dynamic ion exchange, the removal effect of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by D001 resin was investigated. Besides, the thermodynamic and kinetic characteristics in the process of adsorption were studied. The results showed that when the initial concentrations of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in the copper and nickel wastewater were 100mg/L, the temperature was 25°C and pH was 5, the removal rate at the state of equilibrium were 99.14% and 99.33% respectively. In the dynamic ion exchange experiment, when the influent flow rate was 10L/h, the exchange capacity of the resin was 13829.79mg/L for  $\text{Cu}^{2+}$  and 22656.70mg/L for  $\text{Ni}^{2+}$  at the time of breakthrough.

## 1. Introduction

Copper and nickel wastewater are common heavy metal wastewater, mainly from metal smelting, processing, mineral mining, printing and dyeing industry[1]. At present, methods for the treatment of copper and nickel wastewater mainly include electrochemical method[2], ion exchange method and biological method[3-4], photocatalytic technology[5] and so on. Among them, the ion exchange method has a wide range of applications in the treatment of copper and nickel wastewater, because it has the advantages of good separation selectivity and good effluent effect, simple operation and reproducible resin[6].

In this experiment, the effects of D001 ion exchange resin on the treatment of copper and nickel wastewater were investigated. On the basis of a series of static experiments, the thermodynamics and kinetics were analyzed, and the ion exchange column was used to study the dynamic ion exchange. The feasibility of ion exchange method for the treatment of copper and nickel wastewater was verified, and it provided the theoretical basis for practical heavy metal wastewater treatment.

## 2. Materials and methods

### 2.1. Materials

The D001 ion exchange resin was used as the material for the treatment of copper and nickel wastewater, it was a strongly acidic styrene cation exchange resin with a brown opaque appearance. The moisture content of the resin is about 50%~55%, the particle size is 0.5mm, the pH range is 0~14, and the temperature does not exceed 100°C.

The experimental reagents mainly include:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{NiSO}_4$ , NaCl, hydrochloric acid, sulfuric acid, the copper reagent and nickel reagent, all the purity levels of the reagents are analytical pure.

The experimental equipment mainly include: UV-759 ultraviolet visible spectrophotometer, PHS-



3C digital pH meter, FA1104 electronic digital balance, DHG-9033BS-III digital thermal oven, TS-100B thermostat oscillator.

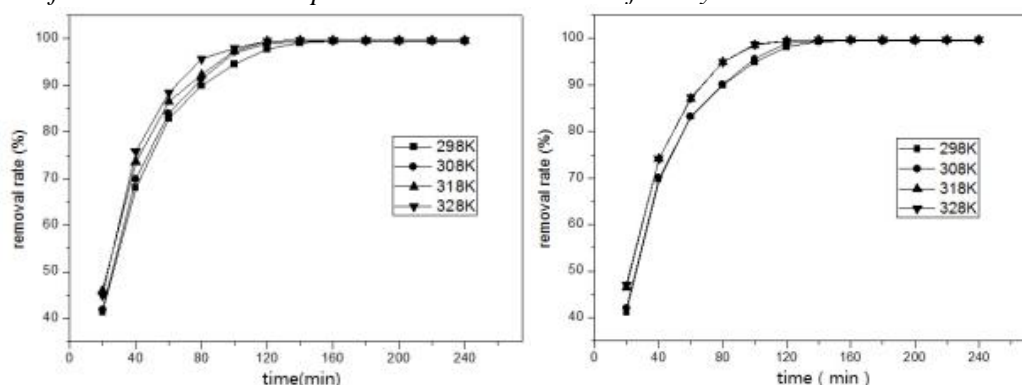
## 2.2. Methods

**2.2.1. Static Ion Exchange Experiment.** Placing the same amount of D001 resin in a number of conical flasks respectively, adding 200mL of simulated wastewater respectively, and putting into the thermostat oscillator for reacting under the same condition in a certain period of time, measuring the concentration of heavy metal ion in the supernatant fraction at regular intervals, stopping oscillations after the reaction balance, exploring effects of contact time and temperature on removal rates two metal ions, and examining the differences of removal rates of two ions when the two kinds of ions existed in the water.

**2.2.2. Dynamic Ion Exchange Experiment.** Adding a certain amount of D001 resin into the ion exchange volume, injecting copper and nickel wastewater in which the concentrations of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  are both 200mg/L into the water storage tank. Opening the pump, and keeping a constant flow for ion exchange reaction. Collecting the water samples from the bottom of exchange column at regular intervals and measuring the concentrations of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , in this way the outflow curve at different flow rates is obtained. Investigating the effects of inflow on the removal of heavy metals.

## 3. Results and discussion

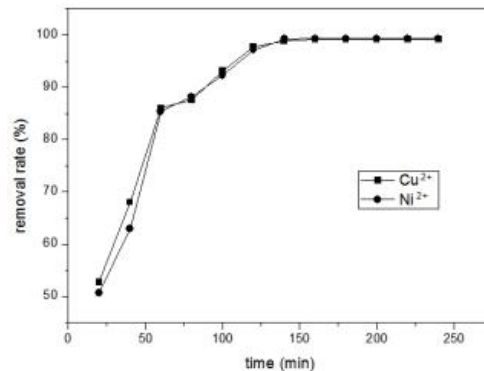
### 3.1. Effect of contact time and temperature on removal rate of heavy metals



**Figure 1.** Effect of contact time and temperature on the removal rate of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . Mixing 200mL  $\text{CuSO}_4$  solution and  $\text{NiSO}_4$  solution with the initial metal concentration of 100 mg/L and 10mL D001 resin respectively, oscillating respectively under different temperature conditions. The removal rates of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by resin are shown in figure 1. The removal effects of two ions by resin are very close, with the increase of ion contact time, the removal rates of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  increase firstly, then basically keep stable up to ion exchange balance. The increase in temperature leads to the increase of the diffusion rate of ions, and the number of active ions, which are beneficial to the ion exchange reaction. However, the differences of the removal rates of heavy metals at the ion exchange equilibrium are not significant at different temperature. The exchange of two ions basically reach balance after oscillating for 150 minutes at 25°C. The removal rates at equilibrium are 99.57% and 99.61% respectively and the concentrations at equilibrium are 0.43 mg/L and 0.39 mg/L respectively. In order to operate easily and save energy, the ion exchange operation can be carried out directly at room temperature.

### 3.2. Effect of resin on treatment of copper and nickel wastewater

Preparing 200mL simulated copper and nickel wastewater with 100mg/L  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , and mixing it with 10mL D001 resin, oscillating at 25°C. The removal rates of two ions are shown in figure 2.



**Figure 2.** Removal rate of copper and nickel ions with resin

The results indicate that the reaction reaches equilibrium after 150 minutes when two exchangeable ions Cu<sup>2+</sup> and Ni<sup>2+</sup> coexisted in wastewater. And the removal rate of Cu<sup>2+</sup> is nearly 99.14%, the removal rate of Ni<sup>2+</sup> is nearly 99.33%. So the exchange degrees of these two heavy metal ions with resin are basically same. The removal rate of Ni<sup>2+</sup> is slightly higher than that of Cu<sup>2+</sup>, which indicates that the selective differences of D001 resin on two kinds of heavy metal ions are not large.

### 3.3. Dynamic model fitting

The adsorption reactions of heavy metal ions generally follow the pseudo first-order kinetic model and second-order kinetic model[7].

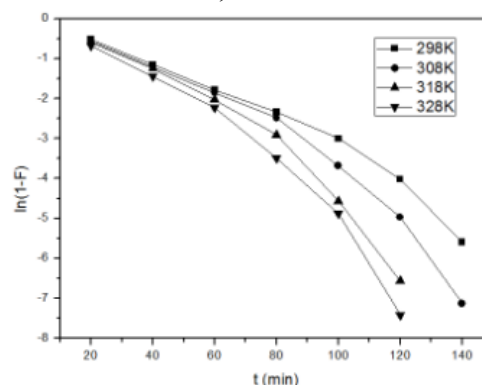
(1) Pseudo first-order kinetic model fitting

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

In the equation,  $q_t$  is the exchange capacity at time  $t$ ;  $q_e$  is the equilibrium exchange capacity;  $k_1$  is the apparent adsorption rate constant.  $q_t/q_e$  is the ion exchange degree, which is presented by  $F$ , replacing (1) with the following form:

$$\ln(1 - F) = -k_1 t \quad (2)$$

Taking  $t$  as the abscissa,  $\ln(1 - F)$  as the ordinate, and the adsorption results of Cu<sup>2+</sup> are fitted according to the pseudo first-order kinetic model, the results are shown in figure 3.



**Figure 3.** Fitting of pseudo-first-order kinetic model in the process of removing Cu<sup>2+</sup>

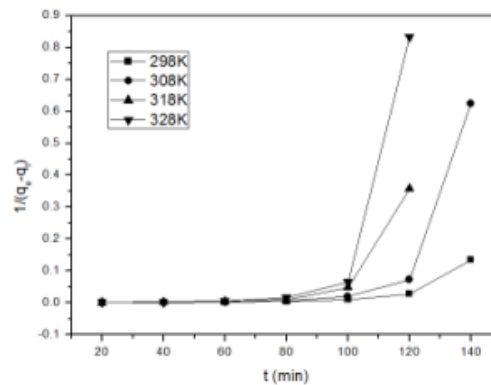
(2) Second-order kinetic model fitting

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

In the equation,  $k_2$  is the second-order reaction constant. Replacing (7) with the following form:

$$\frac{1}{q_e - q_t} = k_2 t + \frac{1}{q_e} \quad (4)$$

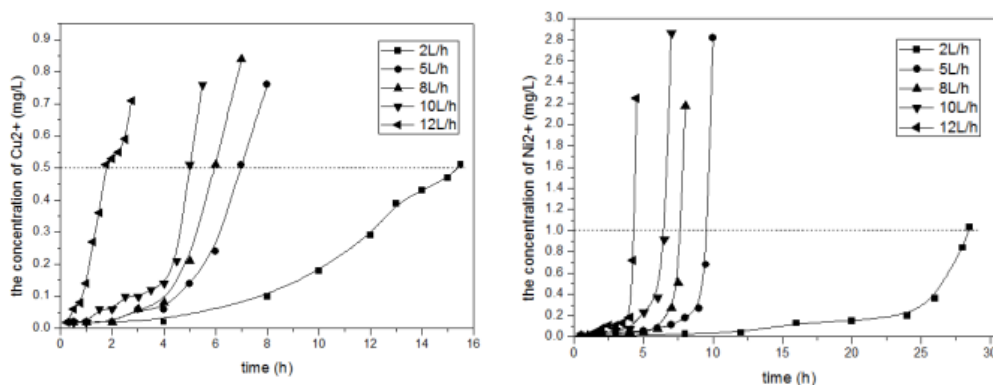
Taking time  $t$  as the abscissa,  $1/(q_e - q_t)$  as the ordinate, and the removal results of  $\text{Cu}^{2+}$  are fitted according to the second-order kinetic model, the results are shown in figure 4.



**Figure 4.** Fitting of second-order kinetic model in the process of removing  $\text{Cu}^{2+}$

### 3.4. Effect of influent flow rate on effluent curve

In the dynamic ion exchange experiments, loading the resin in the column, and at the room temperature, pouring the prepared simulated copper and nickel wastewater (the concentrations of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  are both nearly  $200\text{mg/L}$ ) into the water storage tank. Injecting the wastewater into the resin layer at a constant flow rate, and collecting samples at the outlet at regular periods and measuring the concentrations of the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , then drawing the effluent curves at different flow rates. When drawing the curves, the breakthrough point concentration of  $\text{Cu}^{2+}$  is  $0.5\text{mg/L}$ , and the breakthrough point concentration of  $\text{Ni}^{2+}$  is  $1.0\text{mg/L}$ . Taking the data of concentration of heavy metals and reaction time before breakthrough respectively to draw curves at different flow rates, like the figures 5, and analyzing the effect of influent flow rate on the resin breakthrough.



**Figure 5.** Effect on  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  effluent curve of flow rate

According to the figures, as for the removals of two metal ions, when the influent flow is higher, the exchange layer goes down faster, the breakthrough point appears earlier. Taking the effluent curve for  $\text{Cu}^{2+}$  removal as an example, when the influent flow rate is  $2\text{L/h}$ , at the beginning, the concentration of  $\text{Cu}^{2+}$  in the effluent flow is very low, and after reacting for  $15.5$  hours, the concentration of  $\text{Cu}^{2+}$  in the effluent flow reaches breakthrough concentration, so the breakthrough time of resin is  $15.5$  hours. However, when increasing the influent flow rate, the breakthrough point appears earlier. When the flow rate is  $12\text{L/h}$ , there is a breakthrough phenomenon after reacting for  $1.5$  hours. In the condition of that the influent flow rate is  $10\text{L/h}$ , at the time of breakthrough, the exchange capacity of resin on  $\text{Cu}^{2+}$  reaches  $13829.79\text{mg/L}$ , and that on  $\text{Ni}^{2+}$  reaches  $22656.70\text{mg/L}$ .

Besides that, at the time of breakthrough, the treatment water is maximum under this flow rate.

#### 4. Conclusions

1 ) In the static ion exchange experiments, when the temperature is higher, the removal rates of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  are higher, after treatment of the copper wastewater and nickel wastewater with resins at  $25^{\circ}\text{C}$  for 150 minutes, the removal rates of two ions are 99.57% and 99.61% respectively. For the treatment with copper and nickel wastewater with resins, the removal rate of  $\text{Cu}^{2+}$  is 99.14%, the removal rate of  $\text{Ni}^{2+}$  is 99.33%.

2 ) The ion exchange process of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by resins accords with Langmuir isothermal adsorption model and pseudo second-order dynamic equation.

3 ) In the dynamic ion exchange experiences, greater the influent rate of wastewater, faster the resin breaks through, and the the most suitable influent rate is 10L/h.

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