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Study on Adsorption of Cu^{2+} in WasteWater by Residual Sludge as Adsorbent

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Abstract. Utilizing residual sludge as adsorbent to treat Cu^{2+} in wastewater, The effects of pH, concentration, sludge dosage, temperature and adsorption time on Cu^{2+} adsorption were studied. The results was showed that removal rate of Cu^{2+} was better using residual sludge adsorbent to adsorb wastewater containing 20 mg/L Cu^{2+} when adsorption time was 3h, pH was 6~7, temperature was 20 ℃ and sludge dosage was 2.0 g/L.

1. Introduction

Various methods can be used to treat heavy metal in wastewater. Traditional methods such as Chemical Precipitation, Activated Carbon Adsorption, Ion-exchange, Oxidation-reduction, Electrolysis and Reverse Osmosis are likely to produce serious secondary pollutants and have high cost on raw material and related operation. The result of the study shows that heavy metal wastewater can be treated and specially high removal rate can be achieved on common metal such as Zn^{2+}, Cu^{2+}, Cd^{2+}, Cr^{2+} and Pb^{2+} by utilizing the altering current residual sludge [1-3].

This experiment uses pre-treated residual sludge as adsorbent to absorb Cu^{2+} ions from wastewater. It further studies the impact of pH, concentration, and sludge dosage, temperature and adsorption time on the adsorption effect.

2. Experiment

2.1. Equipment and Reagent

AL104 Electronic Balance (Shanghai Mettler Toledo Instrument Ltd.); LHS-150SC Constant Temperature and Humidity Incubator (Shanghai Yiheng Technology Ltd.); SHA-B Constant Temperature Oscillator (Changzhou Guohua Electronic Equipment Ltd.); KQ-C Glass Instrument Air Blast Dryer (Gongyi Yuhua Instrument Factory); DZF-6020 Vacuum Drying Ovens (Shanghia Huitai Instrument Manufacturing Ltd.); LD5-2A Centrifuge (Beijing Lab Centrifuge Ltd.); PHS-3C Acid Meter (Shanghai Jinmai Instrument Ltd.); WFX-100B Atomic Absorption Spectrophotometer (Beijing Ruili Analytical Instrument Ltd.); V70 Fourier-transform Chromatographic Infrared Analyzer (Germany Bruker Instrument).

Copper ions standard reserving solution (200 mg/L); Copper ions standard solution (10 mg/L); Experiment reagent such as sodium hydroxide, nitric acid, hydrochloric acid, Copper sulphate and hydrogen peroxide are all analytical reagent grade, water is bi-distilled water.

2.2. Standard Work Curve

Based on aspects of test condition, extract 0.00mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL, 10.00 mL, 12.00 mL and 14.00 mL Copper ions standard solution at concentration of 10.0 mg/L respectively, diluted with water to 100mL. The concentration will be 0.00 μg/mL, 0.20 μg/mL, 0.40 μg/mL, 0.60 μg/mL, 0.80 μg/mL, 1.00 μg/mL, 1.20 μg/mL and 1.40 μg/mL respectively. Measure absorbance and draw standard work curve. Based on the standard work curve, the regression equation is expressed as A=0.0534C-0.0074, and correlation is R^2=0.9992.

2.3. Sludge Performance Parameters

Water content radio of residual sludge (81.52%), pH 6.8, volatile content (43.47%).

3. Results and discussion

3.1. Effect of adsorption time on adsorption amount

Weight certain amount of 2.0 g/L sludge and add to Erlenmeyer flask. Add precisely 25.00 mL Copper ions solution (this also applies to the rest of the test conditions) and use 0.1mol/L HCl and NaOH to adjust solution pH to 6.5±0.1. Then place the flask in Constant Temperature Incubator, oscillating under 180 rmp. Filter with 0.45 μm filter film and take supernatant to measure Copper ions content.

Adsorption of Cu^{2+} using sludge is a rapid process and the adsorption increases with prolongation of time. Fig.1 shows that removal rate of Cu^{2+}can reach 89.30%, 84.73%, 73.53% of the total adsorption amount from 20mg/L~40mg/L. Adsorption effect will be stable after 3 hours.

3.2. Effect of Solution pH on Adsorption

Fig. 2 shows the effect of solution pH on the adsorption. When pH is within the range of 4 to 6.5, the removal rate of Cu^{2+} using residual sludge rapidly increases with the increase of pH. However, when pH further increases, the removal rate decreases instead of increase. Therefore the best pH range of absorption effect of Cu^{2+} using residual sludge is 6 to 7.

3.3. Effect of Solution Concentration on Adsorption

The concentration of metal solution has a huge impact on adsorption effect. Removal rate of Cu^{2+} increases with the increase of concentration. It is suitable for removal of copper ions on relatively high concentration solution. The result is illustrated in Fig. 3

3.4. Effect of Temperature on Adsorption

Change of temperature can impact adsorption of metal to certain extent [4]. The result of Fig.4 shows that removal rate of Cu^{2+} rarely changes when temperature rises from 10 ℃ to 50℃. However, within a certain range, the temperature has little impact on the adsorption of the same concentration Cu^{2+}.The experiment selection temperatures was 20℃.

3.5. Effect of Dosage on Adsorption

Dosage of adsorbent has certain impact on adsorption. Higher dosage results in higher removal rate on solution with concentration of 20, 30 and 40mg/L, Results illustrated in Fig. 5

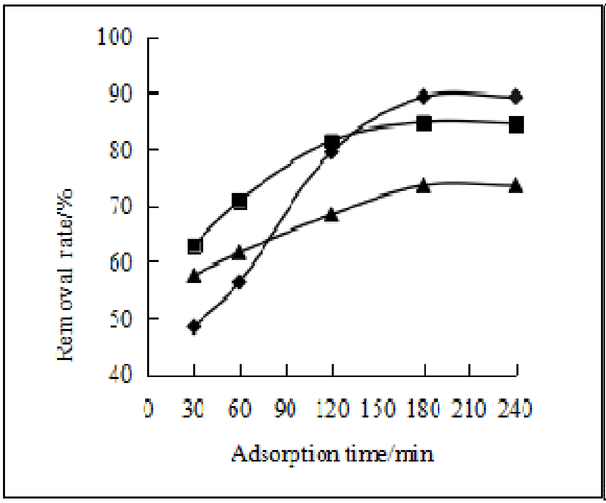

Fig. 1 Adsorption time Curve

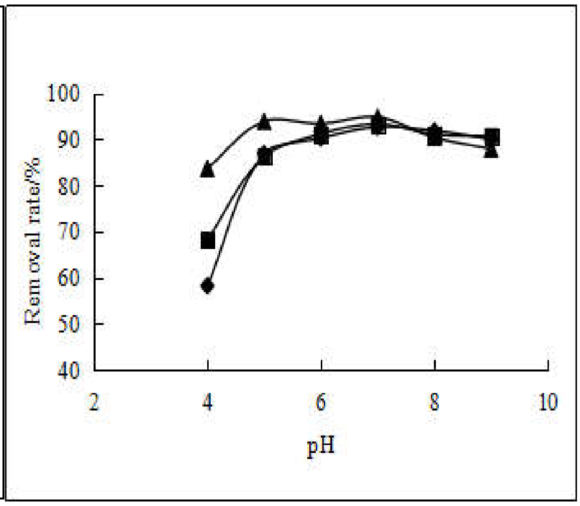

Fig. 2 Effect of pH on removal rate

◆C_0=20mg/L ■C_0=30mg/L ▲C_0=40mg/L

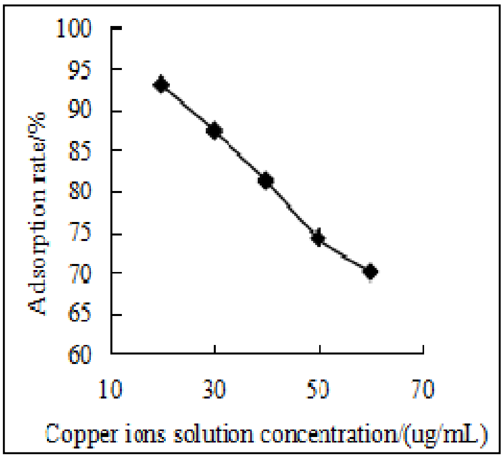

Fig. 3 Effect of copper ions solution concentration on removal rate

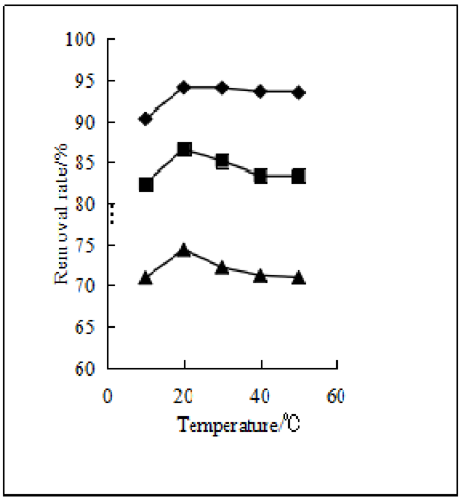

Fig. 4 Effect of temperature on removal rate

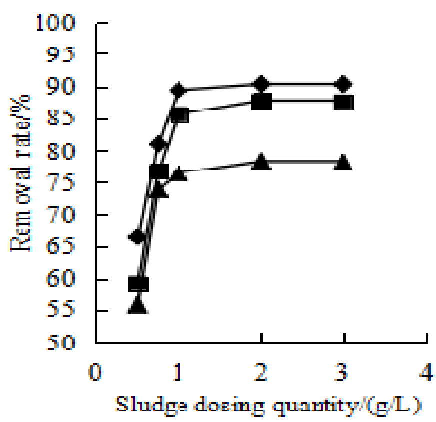

Fig. 5 Effect of dosage on removal rate

3.6. Absorption Isotherm

The basic form of Langmuir absorption equation is expressed as follow.

$$Q_e = \frac{Q_m K_l C_e}{1 + K_l C_e}$$

Where Q_e is equilibrium adsorption capacity of the adsorbent. C_e is the concentration of the adsorbent in the water when reached equilibrium adsorption (mg/L). Q_m is saturated adsorption capacity (mg/g). K_l is the absorbability constant of the Langmuir equation[5].

Freundlich equation is typical isotherm adsorption model, whose logarithmic equation is stated as follow.

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e$$

Where Q_e is quantity of the metal ion being absorbed by unit mass of adsorbent when reached equilibrium adsorption; C_e is concentration of metal ion in the solution when reached equilibrium adsorption; K_F and n are absorption capacity and absorbability constant respectively. Freundlich adsorption isotherm is the oldest empirical formula of adsorption which describes the equilibrium of the sorption of a material at a surface. It fits exponential distribution therefore does not have limit for maximum adsorption capacity. K_F is the indicator of absorption capacity while n is the indictor of absorbability. Those two indicators is best suited for describing adsorption capacity of metal ion in dilute solution.

The series of experiments which carried out under 20 ℃, study the regularity of adsorption of Cu^{2+} 20 mg/L using residual sludge 2 g/L, fitting Langmuir absorption equation and Freundlich adsorption isotherm. Fig. 6, 7 and table 1.The results suggest that correlation R^2 of Freundlich adsorption isotherm is closed to 1 than the one of Langmuir absorption equation, therefore having better fitting effect. Adsorption data can be described using the Freundlich equation. When $0.1<1/n<1.0$ ($1<n<10$), adsorbent has relatively high adsorption capacity on metal ion. From table 1, fitting parameter of Freundlich equation of adsorption of Cu^{2+} using residual sludge is n=1.3165 (more than one), suggesting that residual sludge has related high adsorption capacity therefore can be used as material to adsorb Cu^{2+}.

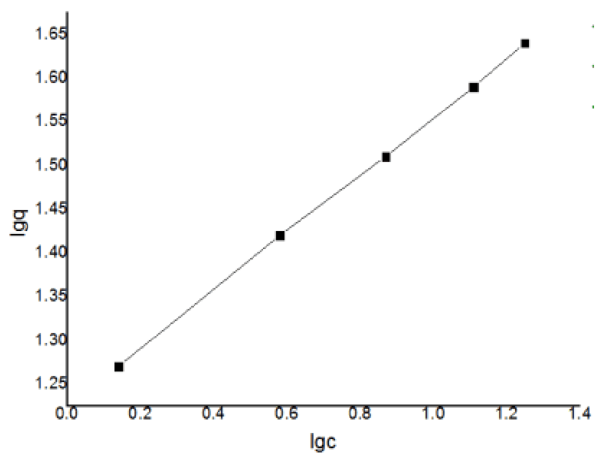

Fig. 6 Adsorption of Cu^{2+} using residual sludge on solution with different concentration using Langmuir absorption equation

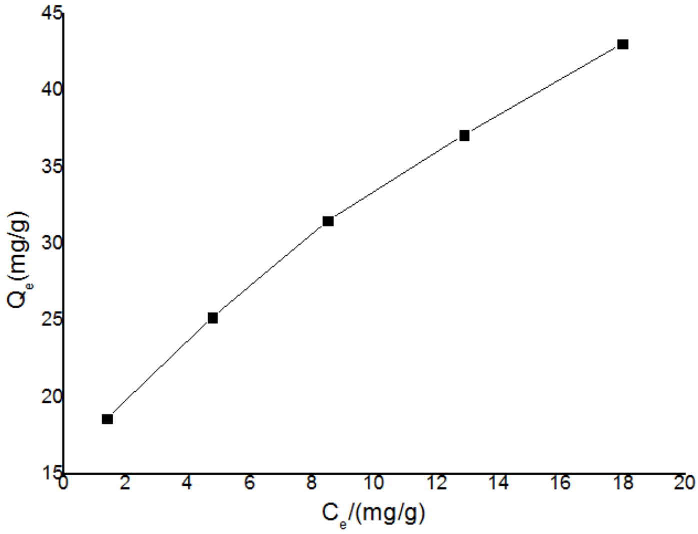

Fig. 7 Adsorption of Cu^{2+} using residual sludge on solution with different concentration using Freundlich adsorption isotherm

Table 1. Freundlich and Langmuir equation of excess sludge absorbing Cu^{2+}

C_o/(mg/L)	20	30	40	50	60
C_e/(mg/L)	1.39	3.79	7.50	12.89	17.97
Absorption Capacity q (%)	93.03	87.37	81.25	74.22	70.06
Q_e/(mg/L)	18.61	26.21	32.50	37.11	42.03
Freundlich equation	lgq=0.3109lgC+1.2324 (R^2=0.9974)		Langmuir equation	$C_e/Q_e=0.0212C_e+0.0601$ (R^2=0.9810)	

3.7. Analysis of Characteristic Change of Infrared Spectra of Residual Sludge before and after Absorption of Cu^{2+}

From the infrared spectra in Fig. 8, we can conclude that the correspondent large absorption band-width at position 3406 cm^{-1} is absorption region of hydroxyl and amino. The absorption peak at position 2918cm^{-1} is the symmetric stretching vibration of fatty chain CH_2.Position 2751cm^{-1} is the asymmetric stretching vibration of fatty chain CH_2. Position 1652cm^{-1} is the C=O stretching vibration of Amide I. Position 1352cm^{-1} is the C-N stretching and flexural vibration of Amide II.The Absorption peak at position 1036cm^{-1} is the C-O-C stretching vibration of Polysaccharide or Polysaccharide like substance and the C-OH stretching vibration of primary alcohol and carboxyl. Based on the above analysis, the main functional groups of residual sludge are hydroxyl, amino and amide.Comparing Fig. 8 with Fig. 9, the wave number and peak shape of Infrared Spectrum absorption peak are similar. However, the differ lies on the peak wave number of the correspondent functional groups, thus stating that chemical composition and substance composition has changed.

Based on the comparison of the Infrared Spectrum, the peak wave number of $-NH_2$ and carbon fatty chain γ(C-H) deflected. So did vibration peak wave number of the functional group of band,such as Amid I and Amid II although the deflection was minimal. The analysis shows that main groups of adsorption of Cu^{2+} using Residual sludge are carbon fatty chain γ(C-H), $-NH_2$ and so on.

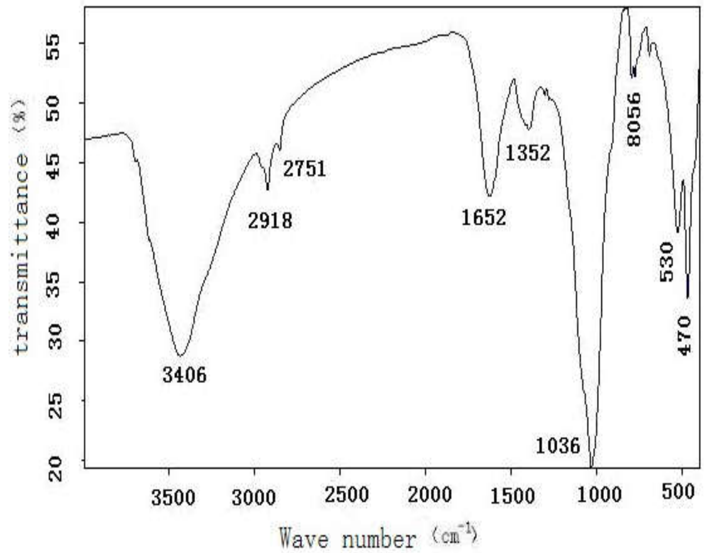

Fig. 8 Infrared spectrum of residual sludge before absorption of Cu^{2+}

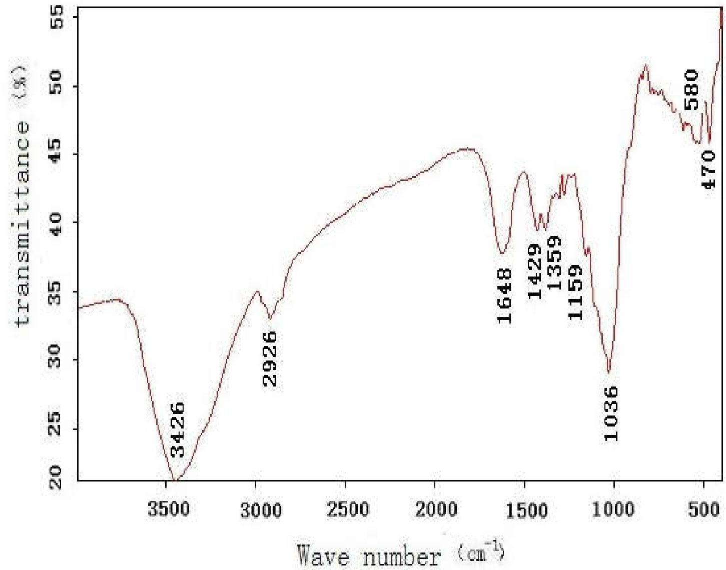

Fig. 9 Infrared spectrum of residual sludge after absorption of Cu^{2+}

4. Conclusion

This article studies the adsorption of Cu^{2+} using residual sludge and the factor which impact the adsorption effect, such as pH, concentration and sludge dosage, temperature and adsorption time. The results show that adsorption time has a huge impact on the adsorption effect while solution pH has a relatively high impact. Concentration of Copper ions solution can affect the adsorption at a certain level. Therefore, residual sludge 2 g/L is very suitable for processing wastewater containing Cu^{2+} 20 mg/L. Main groups of adsorption of Cu^{2+} using Residual sludge are carbon fatty chain γ(C-H), $-NH_2$.

Acknowledgments

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