Research on disposal of copper(II)-containing wastewater by secondary strontium residue

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Abstract. Secondary strontium residue (SSR) was used as absorbent to remove Cu²⁺ in solution and the effects of experimental conditions on absorption of Cu²⁺ were investigated. The results showed that the absorption process reached balance in around 40 min. The absorption capacity achieved the maximum when PH value reached 6, and the maximum adsorption of Cu²⁺-containing wastewater by secondary strontium residue was 5.46 mg/g. Removal ratio of Cu²⁺ was in relation to initial concentration of Cu²⁺ in solution. Adsorptive process tallied with Langmuir Isothermal adsorption model.

1. Introduction

Copper, as one of the dominating metal contaminants, is extremely detrimental to aquatic organisms and human beings. In accordance with the provisions of heavy metal concentration in industrial wastewater discharge, the concentration of copper and compounds in the discharge outlet shall not exceed 1.0 mg/L, and the concentration of copper ions discharged into surface water shall be less than 0.1 mg/L [8]. Water for aquaculture requires copper concentration to be less than 0.01 mg/L, when the copper concentration reaches 0.1 ~ 0.2 mg/L, it can lead to fish’s death. As an essential microelement, copper is involved in metabolic processes of body, which is essential to the formation of red blood cells [6], however, excessive intake of copper can lead to liver and kidney damage, mucosal inflammation, invasive capillary damage, depression, gastrointestinal inflammation and necrosis [4]. Therefore, the World Health Organization recommends that the concentration of copper in drinking water shall not exceed 1.5 mg/L [1].

There are many removal methods of copper ions contained in wastewater, among which seven traditional treatment methods of chemical precipitation, electrolysis, ion exchange, reverse osmosis, macromolecule organic chelating agents and polymer flocculants, biochemical, adsorption are included [13,7,2,9]. Secondary strontium residue is the remaining residue after the extraction of strontium (strontium chloride) from strontium residue (waste residue generated from production of strontium carbonate, with Celestine as raw materials), and it imposes adsorption upon hexavalent chromium and phosphorus [12]. Preliminary studies of the project team indicate that secondary manganese residue can be used in the treatment of wastewater containing copper [15]. For this purpose, this thesis conducted influencing factors that secondary strontium residue has on copper(II)
adsorption, as well as kinetic study of the adsorption process, expecting to provide new approaches for resources utilization of strontium residue waste.

2. Experiment

2.1. Materials and Reagents

In the experiment, the test material strontium residue was taken from waste residue of certain strontium carbonate manufacturing enterprise in Tongliang, Chongqing. Secondary strontium residue means residue after extraction of strontium (strontium chloride) from strontium residue, by using 7% wt of sulfuric acid solution to soak (to remove soluble strontium from secondary strontium residue), and with secondary strontium residue as adsorbent, after calcinations under 600 °C for an hour. The components of secondary strontium residue are shown in Table 1.

Simulated wastewater containing Cu²⁺ was prepared, as well as a certain amount of CuCl₂·2H₂O (AR, Chongqing Chuandong Chemical Co., LTD.) and solution with distilled water (100mg Cu²⁺ in one liter).

Table 1. The component of SSR (%)

| Sr  | Ba  | Si   | Fe  | Al  | S   | Ca | Mg |
|-----|-----|------|-----|-----|-----|----|----|
| 4.326 | 0.523 | 30.199 | 1.512 | 1.940 | 1.867 | 0.542 | 1.114 |

2.2. Adsorption Experiment

50 mL Cu²⁺ solution with given mass concentration was taken and put into a 250-mL conical flask, with certain capacity of secondary strontium residue added as absorbent, and absorption experiment was conducted with DF-101S thermal-arrest thermostatic magnetic stirrer.

2.3. Measurement of copper ion concentration

50 mL of Cu²⁺ water sample with given concentration was taken and put into the conical flask, appropriate amount of secondary strontium residue adsorbent was added, and then stirred and absorbed with a magnetic stirrer for a certain amount of time. The supernatant liquid was taken, and hydrogenated-flame combination atomic fluorescence spectrometer method was adopted to measure copper ion content. Adsorption rate and adsorbing capacity of secondary strontium residue to absorb Cu²⁺ can be calculated by the following formula:

\[
\eta = \frac{c_0 - c}{c_0} \times 100\% \quad (1)
\]

\[
q = \frac{(c_0 - c)V}{m} \quad (2)
\]

where, \( \eta \) represents secondary strontium residue’s removal ratio of Cu²⁺; \( c_0 \) represents mass concentration (mg/L) of Cu²⁺ in the solution before absorption; \( c \) represents mass concentration (mg/L) of Cu²⁺ in the solution after absorption; \( q \) represents adsorbing capacity (mg/g) of secondary strontium residue for Cu²⁺; \( V \) represents the volume of solution (L); \( m \) means weight (g) of secondary strontium residue.
3. Results and discussions

3.1. Effect of the strontium residue dosage on the adsorption of Cu\(^{2+}\)

At 25 °C, with removal ratio of copper (II) and absorbing capacity of copper (II) as ordinate, and with dosage of secondary strontium residue as abscissa, we can reach an adsorption isotherm, as shown in Figure 1.

![Figure 1](image)

**Figure 1.** Relationship between SSR amount and the removal ratio as well as adsorbing amount of Cu\(^{2+}\)

Figure 1 shows that with the increase in secondary strontium residue, the removal ratio of Cu\(^{2+}\) in the solution also increased, and they were almost in direct proportion to each other when the secondary strontium residue was less than 0.3g. As the secondary strontium residue exceeded 0.3g, the increase in removal ratio of copper ions slowed down. The secondary strontium residue’s absorption capacity of copper ions maximized when the secondary strontium residue was 0.1 g. With the increase of secondary strontium residue, the absorption capacity decreased. It indicated that the secondary strontium residue’s adsorption efficiency of copper ions dropped when the quantity of SSR exceeded 0.1g. By taking copper ions removal ratio and secondary strontium residue’s absorbing capacity of copper ions into consideration, when initial mass concentration of Cu\(^{2+}\) reached 20 mg/L, dosage of the secondary strontium residue adsorbent should be 0.3g. With the increase of secondary strontium residue, the surface adsorption of secondary strontium residue particle became stronger, which led to less free copper ions in the solution. Therefore, the removal efficiency of copper ions became better. However, when the secondary strontium residue exceeded 0.3 g, the increase in removal ratio of copper ions slowed down, which indicated that desorption was involved in the adsorption process. From this perspective, the electrostatic force between the secondary strontium residue and copper ions also occupies a certain proportion in the adsorption mechanism.

3.2. Effect of Cu\(^{2+}\) concentration on adsorption capacity

At 25 °C, with metal ion removal rate and secondary strontium residue adsorption capacity as ordinate, and with initial mass concentration of Cu\(^{2+}\) as abscissa, we can draw adsorption isotherm shown in Figure 2.
Figure 2 shows that the removal ratio of copper ions decreased with the increase of initial mass concentration of Cu$^{2+}$ in the solution, while the adsorption capacity increased. When solid matter absorbs solute from the solution, the relationship between absorption capacity and solution concentration satisfies the Langmuir equation,

$$ q = \frac{abc}{1 + bc} \quad (3) $$

where, $a$ represents saturation adsorption capacity, mg/g; $b$ represents adsorption constant, L/mg. In equation (3), different equilibrium concentrations are fitted with adsorption capacity, and the results are as follows, $a = 5.62$ mg/g, $b = 0.270$ L/mg, correlation coefficient is 0.996. It indicates that secondary strontium residue’s absorption of copper ions from the solution perfectly conforms to the Langmuir isotherm model.

3.3. Effect of the initial solution pH value on adsorption efficiency

With other conditions remaining unchanged, initial pH value in the solution has great influence on the removal of Cu$^{2+}$, and the results are shown in Figure 3.

Figure 3. Relationship between pH and the removal rate of Cu$^{2+}$ as well as adsorbing amount of Cu$^{2+}$
The experimental results in Figure 3 indicate that the secondary strontium residue’s removal ratio of Cu$^{2+}$ increased with the increase of pH value, and its adsorption capacity was also raised. When pH was less than 3, the secondary strontium residue’s removal ratio of Cu$^{2+}$ in the solution was lower than 80%, and the adsorption capacity also remained to be very low. In this case, large quantity of H$^+$ in the solution occupied adsorption active sites in the surface of secondary strontium residue particle, which influenced secondary strontium residue’s copper ions absorption. Moreover, H$^+$ competed with Cu$^{2+}$ to have ion exchange reaction with unsaturated ions in the surface of secondary strontium residue particles in the solution, decreasing secondary strontium residue’s removal ratio of copper (II).

According to the study, we can speculate that in the interaction of secondary strontium residue and copper ions, the electrostatic force also occupies a certain proportion. In strong acidic conditions, H$^+$ and Cu$^{2+}$ in the solution generate electrostatic force with electronegative groups of secondary strontium residue. As part of electronegative groups of the secondary strontium residue have been consumed by H$^+$, the secondary strontium residue’s removal ratio and adsorption capacity of Cu$^{2+}$ decrease. When pH exceeds 3, the secondary strontium residue’s removal ratio and adsorption capacity of Cu$^{2+}$ in the solution increase significantly. When pH reaches 6, the secondary strontium residue’s removal ratio of Cu$^{2+}$ in the solution reaches optimum value, and its absorption capacity also maximizes. When pH exceeds 6, the copper ions in the solution begin to produce a small quantity of precipitation. The copper hydroxide precipitate not only occupies adsorption activity center of the secondary strontium residue, but also hinders the ion exchange reaction between Cu$^{2+}$ and unsaturated ions in the surface of secondary strontium residue particles.

3.4. Adsorption kinetics of Cu$^{2+}$ in strontium residue

With other conditions fixed in certain circumstances, change the adsorption time, and measure removal ratio of Cu$^{2+}$ and changes in secondary strontium residue adsorption capacity.

![Image](image.png)

Figure 4. Effect of time on the removal rate and adsorbing amount of Cu$^{2+}$

Experimental results are shown in Figure 4. In the initial stage of adsorption, removal ratio of copper ions in solution reached 45.5% in 5 min, and the secondary strontium residue’s adsorption ratio of Cu$^{2+}$ was fast. When the adsorption time reached 40 min, removal ratio of copper ions reached 87%, and the secondary strontium residue’s adsorption capacity of copper ions reached 2.93 mg/g. With the increase of adsorption time, the removal ratio of copper ions in solution increased slowly, and reached balance in general.

According to existing research results and theoretical speculation, the secondary strontium residue’s absorption mechanism of metal ions may due to ion exchange reaction between unsaturated...
ions and copper ions in the surface of secondary strontium residue particles. In the first 5 min of adsorption process, the surface of secondary strontium residue has a large number of adsorption active sites. The absorption at the moment could be mixed absorption transformation of monomolecular layers into monomolecular layers and polymolecular layers, thus leading to increase in removal ratio of copper ions, while with relatively slow increase. As the absorption time increases, the removal ratio of copper ions in the solution no longer increases, and the secondary strontium residue’s adsorption capacity of copper ions reaches balance.

Figure 4 shows that relation curve between the active secondary strontium residue’s adsorption capacity and adsorbing time. The following empirical formula with two constants is used to discuss kinetic parameter of secondary strontium residue adsorption. The two-constant empirical model adopts empirical formula similar to Langmuir absorption isotherm, to quantitatively describe the relationship between q (t) and t, and the formula is as follows,

\[ q(t) = \frac{abt}{1 + bt} \]  

where, a represents saturated adsorption capacity (mg/g); b represents adsorption constant (s\(^{-1}\)); t represents the adsorption time (s).

By refitting data shown in Figure 4 with formula (4), we get a=3.12 mg/g; b=0.374 s\(^{-1}\), and the correlation coefficient is 0.947. Thus, equation (4) is the kinetic equation in adsorption process of copper in secondary strontium residue.

4. Conclusion
In the secondary strontium residue’s adsorption process of Cu\(^{2+}\) involved in aqueous phase, it reached balance in around 40 min. When pH value of the solution reached 6, the secondary strontium residue’s removal ratio and adsorption capacity of Cu\(^{2+}\) reached the optimum value.

With the increase of initial mass concentration of Cu\(^{2+}\) in the solution, removal ratio of copper ions decreased, while the adsorption capacity increased. The secondary strontium residue’s absorption of copper ions from the solution conforms to the Langmuir isotherm absorption model. For water sample with lower copper content (if mass concentration of copper ions reached 10 mg/L), removal rate of Cu\(^{2+}\) exceeded 90%, and the residual mass concentration of Cu\(^{2+}\) in the solution could meet the standards of copper ion in drinking water as the World Health Organization recommends. With the increase of pH value in solution, the removal ratio of Cu\(^{2+}\) increased, and the adsorption capacity was also on the rise.

In the initial stage of adsorption, the secondary strontium residue’s adsorption rate of Cu\(^{2+}\) was faster, and the copper ion removal rate reached 87% in 40 min of adsorption time. After that, with the increase of adsorption time, increase in removal rate of copper ions slowed down. The adsorption of copper ions in secondary strontium residue satisfies the two-constant empirical kinetics model.

Acknowledgments
This work was supported by the program of Chongqing Science and Technology Commission (No. 2010AC7180).

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