Adsorption of Cu(II) from aqueous solution on sulfuric acid treated palygorskite

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Abstract. The absorption behavior of Cu$^{2+}$ from aqueous solution on sulfuric acid treated palygorskite were investigated, the results showed that palygorskite had high absorption ability for Cu$^{2+}$ from aqueous solution. Effects of the shaking time, pH and the copper ion concentration on the removal rate were discussed. The absorption behavior of Cu$^{2+}$ could be well imitated by the Langmuir isothermal equation.

1. Introduction
Palygorskite is a common clay mineral in nature. It is a nontoxic layer of chain like clay which is rich in magnesium aluminosilicate.[1] Because of its special structure, palygorskite has relatively higher specific surface area, and a lot of Si-O bonds on the palygorskite to enhance the metal ions adsorb on its surface or in its micro-channe.[2] So, it is widely applied to remove of harmful metal ions by adsorption technology. The properties of the negative charge on the surface of the palygorskite make it a excellent material for enriching and removing harmful metal ions from solution. Recently, adsorption of heavy metals and organic contaminants on palygorskite has been extensively studied. Because palygorskite clay has high surface area, non-toxic and low cost, it has excellent chemical stability and strong adsorption properties.[3-8] Palygorskite was treated by heating, inorganic acid or organic reagents, more hydroxyl groups can be obtained on the surface of palygorskite, which was beneficial to strengthen the adsorption of metal ions.[9] However, in order to further improve the adsorption capacity of palygorskite clay, the development of different treatment approaches remains an active research area.

In recent years, in order to prevent the excessive production of algae in the water, copper sulfate has been used in large quantities, resulting in the accumulation of copper ions in the wastewater.[10] Cu$^{2+}$ can moves through the water, accumulates the soil, and enters to our living environment and cause serious harm to human beings and other organisms. Therefore, it is necessary to study the removal of copper ions from water, during the past few years, many new methods have been used to remove Cu$^{2+}$ from aqueous solutions. For example, ion exchange, solvent extraction, chemical precipitation, adsorption, and so on. Among these, adsorption methods have gradually aroused the interest of researchers because of their low toxicity and low cost. Many different adsorbents have been reported to adsorb copper ions, but the adsorption capacity of these adsorbents is not high.[11] Therefore, it is still a challenge to use different treatment methods to treat adsorbents and to look for adsorbents with high adsorption capacity.

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The purpose and the significance of the present study are 1) to investigate the absorption behavior of Cu$^{2+}$ on sulfuric acid treated palygorskite; 2) evaluation of the effect of shaking time, pH, Cu$^{2+}$ concentration on the removal rate. The research results are helpful to the application of palygorskite clay in wastewater treatment.

2. Experimental

2.1. Materials

The chemical reagents used in this study were all analytical purity. Different concentrations Cu$^{2+}$ solution of concentrations were prepared by dissolving a certain amount of CuSO$_4$·5H$_2$O in deionized water. The powdered palygorskite was purchased from Xuyi, Jiangsu Province, China. It was dipped in 2 M H$_2$SO$_4$ for 24 h, and then repeatedly washed with deionized water until pH reached 6. Then, palygorskite was dried in the baking box for 10 hours at 110°C, and then gradually cooled to 25°C, ground into powder and stored in a dry closed container.

2.2. Adsorption procedures

All of the adsorption test were operated at 25°C in a thermostat bath by mixed 100 mg sulfuric acid treated palygorskite and 20 mL of Cu$^{2+}$ solution in airtight polypropylene tubes. The pH value of the water phase is changed by adding a small amount of 0.1 M HNO$_3$ and 0.1M NaOH solution. The mixtures were shaken for 60 min, the liquid and solid phases were separated by centrifugation.

2.3 Analysis and calculations

The concentration of Cu$^{2+}$ in the solution after adsorption was analyzed by atomic absorption spectroscopy, the Cu$^{2+}$ removal rate was calculated on the basis of the equation (1) and the adsorption capacities of Cu$^{2+}$ were determined according to the equation (2).

\[
y = \left( \frac{C_o - C_e}{C_o} \right) \times 100\% \quad (1)
\]

\[
Q_e = \frac{(C_o - C_e) \times V}{M} \quad (2)
\]

In equation (1), $y$ is the removal rate of Cu$^{2+}$, $Q_e$ (mg/g) is the adsorption quantity, $C_o$ (mg/L) and $C_e$ (mg/L) are the concentration of Cu$^{2+}$ before and after adsorption respectively. $V$(L) is the volume and $M$ (g) is the quality of palygorskite.

3. Results and discussion

3.1 Effect of H$_2$SO$_4$ concentration

The effect of removal rates for Cu$^{2+}$ on sulfuric acid modified palygorskites using different concentrations H$_2$SO$_4$ were investigated. It is apparent in Table 1 that a maximum removal rate of Cu$^{2+}$ was obtained when the H$_2$SO$_4$ concentration was 2 mol/L. At higher sulfuric acid concentration, the more cations in the structure of palygorskites were dissolved and parts of the structure were collapsed, the specific surface area declined, which was not conducive to the removal of Cu$^{2+}$. However, At lower sulfuric acid concentration, acid can effectively remove impurities of attapulgite particles. Protons exchange cation in turn from outside to inside in attapulgite, enlarging the hole channel, the specific surface area of palygorskite has been improved, so the adsorption capacity was increased

Table 1. Adsorption capacities for Cu$^{2+}$ on modified palygorskites using different concentrations H$_2$SO$_4$.

| H$_2$SO$_4$ concentration (M) | 0   | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|------------------------------|-----|-----|-----|-----|-----|-----|
| Removal rate of Cu$^{2+}$, % | 75.2| 85.4| 94.2| 92.2| 87.5| 80.3|

conditions: ($C_o = 20$ mg/L, $m = 0.10$ g, pH = 6.00, contact time 60 min).

3.2. Effect of shaking time

The adsorption kinetics of Cu$^{2+}$ was investigated by 20 mg/L Cu$^{2+}$ in aqueous solution contacting with 100 mg palygorskite. We tested the effect of the shaking time on the removal rate of Cu$^{2+}$ from
aqueous solution and the results were presented in Fig. 1. It demonstrated that the removal rate of Cu\textsuperscript{2+} significantly increased when the shaking time from 0 to 40 min. It was also shown that when the shaking time exceeded 60 min, the removal rate of Cu\textsuperscript{2+} was not obvious increased. So 60 min were selected as the optimum contact time for all further experimental work.

![Effect of shaking time](image1)

Fig. 1. Effect of shaking time (C\textsubscript{o} = 20 mg/L, m = 0.10 g, pH = 6.00).

### 3.3 Effect of pH

Adsorption of Cu\textsuperscript{2+} on palygorskite from different pH solutions were explored, and the outcomes of the experiment were displayed in Fig 2. The pH value changed from 1.0 to 6.0, the Cu\textsuperscript{2+} removal rate notably increased. However, when the pH value was above 6.0, the Cu\textsuperscript{2+} removal rate was not obvious changed. In strong acid environment, a large number of H\textsuperscript{+} in the solution will compete with Cu\textsuperscript{2+} for the adsorption of adsorbents, thus reducing adsorption of Cu\textsuperscript{2+} on the palygorskite. In the lower acid environment, fewer protons are adsorbed on the surface of the palygorskite, the increased of the negative charge site on the surface of palygorskite led to increased adsorption of Cu\textsuperscript{2+}.

![Adsorption of Cu\textsuperscript{2+}](image2)

Fig. 2. Adsorption of Cu\textsuperscript{2+} from different pH solution (C\textsubscript{o} = 20 mg/L, m = 0.10 g)

### 3.4 Effect of Cu\textsuperscript{2+} concentration

Effect of Cu\textsuperscript{2+} concentration on the removal rate were revealed in Fig. 3. The Cu\textsuperscript{2+} concentration changed from 10 to 60 mg/L, the Cu\textsuperscript{2+} removal rate of were sharply decreased from 95% to 79%, it is suggested that the lower concentration was beneficial to the removal of copper ions. So, if the
palygorskite was used to treat wastewater, when Cu\(^{2+}\) concentration is higher, it was necessary to pretreat the wastewater to reduce the Cu\(^{2+}\) concentration, and then further adsorbed Cu\(^{2+}\) with palygorskite.

![Figure 3](image)

**Fig. 3.** Effect of initial Cu\(^{2+}\) concentration \((m = 0.10g, \text{pH} = 6.00)\)

### 3.5 Adsorption isotherms

To study the adsorption isotherm of palygorskite to Cu\(^{2+}\), two equation (Langmuir and Freundlich isotherms equation) were selected. The Freundlich isotherm equations was calculated through the equation (3)

\[
\log Q_e = \log m + n \log C_e \tag{3}
\]

where \(Q_e\) is the adsorption quantity, \(C_e\) is the concentration of Cu\(^{2+}\) after adsorption. The values \(m\) and \(n\) could be obtained from the equation (3) and the data were given in **Table 2**.

The Langmuir isotherm equations was determined through the equation (4) \(^{[12]}\)

\[
\frac{C_e}{Q_e} = \frac{1}{B \times Q_m} + \frac{C_e}{Q_m} \tag{4}
\]

where \(B\) is the constant, \(Q_e\) is the adsorption quantity and the maximum adsorption quantity, respectively. \(C_e\) is the Cu\(^{2+}\) concentration after adsorption. The values of \(Q_m\) and \(B\) could be obtained from the the equation (4) and the results were presented in **Table 2**.

By comparing linear correlation coefficient \((r^2)\) in **Table 2**, it has been found that \(r^2\) was higher in the Langmuir isotherm equation, so the adsorption process was well imitated by the Langmuir equation, and its saturated adsorption quantity for Cu\(^{2+}\) was about 11.5 mg/g.

| Table 2. | Langmuir and Freundlich contents and correlation coefficients |
|------------------|------------------|------------------|------------------|------------------|
|                | \(Q_m\) | \(B\) | \(r^2\) | \(m\) | \(n\) |
| Freundlich equation | - | - | 0.9862 | 3.08 | 0.49 |
| Langmuir equation | 11.5 | 0.36 | 0.9966 | - | - |

### 4. Conclusions

The absorption behavior of Cu\(^{2+}\) on sulfuric acid treated palygorskite were studied. The effects of H\(_2\)SO\(_4\) concentration, shaking time, pH and initial Cu\(^{2+}\) concentrations on adsorption of Cu\(^{2+}\) to palygorskite were investigated. Results showed that the optimal absorption condition was the palygorskite treated in 2 mol/L H\(_2\)SO\(_4\). The absorption balance was established in 60 minutes and the appropriate pH value for adsorption was above 6.0. Under the experimental conditions, the Cu\(^{2+}\)
adsorption behavior on sulfuric acid treated palygorskite accorded with the Langmuir equation, and its saturated adsorption quantity for Cu$^{2+}$ was about 11.5 mg/g.

Acknowledgments
This work was supported by the Undergraduate Training Programs for Innovation and Entrepreneurship Foundation.

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