Study on preparation and treatment of phosphorus removal performance with M/Mg/Al (M=Zn/Co/Cu) hydrotalcites

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Abstract. A series of M/Mg/Al (M=Zn/Co/Cu) hydrotalcites were synthesized by co-precipitation method. XRD was used to characterize their structure. The results showed that the prepared hydrotalcites samples have typical hydrotalcite structure with high crystalline. The hydrotalcites samples were used as absorbent in the treatment of phosphorus removal of wastewater. Single factor control variable method was used to study the relationship between the conditions such as the type of metal, synthesis condition, preparation method, calcination time, type of absorbent, and the adsorption ability of phosphorus in wastewater. The results showed that Zn/Mg/Al hydrotalcites have better phosphorus removal ability than the Mg/Al, Co/Mg/Al and Cu/Mg/Al hydrotalcites. Zn/Mg/Al hydrotalcites prepared with the metal ratio of Zn/Mg/A=3:1:1, reaction temperature of 75℃, pH of 11 has the best phosphorus removal effect. After calcined at 300℃ for 4h, the Zn/Mg/Al hydrotalcites has the best phosphorus removal efficiency of 76.6%. Zn/Mg/Al hydrotalcites have much better phosphorus removal efficiency than active carbon.

1. Introduction
In recent years, with the rapid development of industry and agriculture, water eutrophication and other water environmental problems have led to the deterioration of lakes, rivers and other water environmental problems. Water eutrophication is not only a problem of water environmental pollution in China, but also a global problem of water environmental pollution. Phosphorus is one of the most influential factors leading to water eutrophication, and it is also the crux to control water eutrophication [1]. Therefore, the control of phosphorus concentration in water plays a key role in solving water eutrophication and other pollution problems. It is urgent to solve the problem of water eutrophication. The development of low-cost, efficient, environment-friendly phosphorus removal agent has great application value and prospect in water pollution control. At present, the most commonly used phosphorus removal methods are chemical precipitation, biological method and adsorption method. At present, the main metal salts used for phosphorus removal by chemical precipitation method are calcium lime, aluminum sulfate, ferric chloride and ferric sulfate [2, 3]. However this method usually needs to add a large amount of metal salts, and will also produce a large amount of sludge, which is not conducive to the operation of sewage structures in the next step. And some metal salts will pollute the water body for the second time. Biological phosphorus removal technology is widely used because of its high efficiency, low cost and no sludge. However, biological phosphorus removal technology has high requirements for removal instrument, and phosphorus removal efficiency is greatly affected by water quality. It is also not conducive to the recovery and utilization of phosphorus resources. Phosphorus removal by adsorption is mainly through the use of adsorbent's huge specific surface area and ion
exchange to adsorb phosphate in water onto adsorbent, so as to remove phosphorus from sewage, which has both physical and chemical processes. At present, the commonly used adsorption materials are fly ash, activated alumina, activated carbon, hydrotalcites and so on.

Phosphorus removal by hydrotalcites is mainly based on the anion exchange and adsorption properties of hydrotalcites. Hydrotalcites have high treatment efficiency for printing and dyeing wastewater, and the removal efficiency is more than 99%. The treatment efficiency of acid violet dye by Mg/Al hydrotalcites studied by Xue Jilong is as high as 99.7%, and the adsorption capacity is about 1000mg/g [4]. The removal rate of acid red dye wastewater by binary Mg/Al hydrotalcites studied by Ni Zheming and Zhang Feng is as high as 99.95%, and the adsorption capacity is about 2000 mg/g. After repeated recycling, the treatment efficiency of acid red dye is still as high as 90% [5]. In addition, hydrotalcites are also used in heavy metal industry, showing high adsorption efficiency for Cu, Cd, Pb, Cr and other heavy metals. In this paper, the phosphorus removal performance of M/Mg/Al (M = Zn/Co/Cu) hydrotalcites in water was studied in order to provide an effective experimental basis for wastewater phosphorus removal technology.

2. Experimental

2.1. Preparation of phosphorus stock solution
Potassium dihydrogen phosphate solution was used to simulate the phosphorus containing wastewater. Potassium dihydrogen phosphate was dried in a blast drying oven to constant weight. 0.0878 g, 2.197 g and 4.3940 g samples were weighed respectively, dissolved with deionized water, transferred to a 1000 mL volumetric flask, and mixed into solution. Finally, Phosphorus stock solution A with phosphorus concentration of 20 mg/L, phosphorus stock solution B with phosphorus concentration of 500 mg/L and phosphorus stock solution C with phosphorus concentration of 1000 mg/L were obtained. Phosphorus stock solution is prepared when used right now.

2.2. Preparation of hydrotalcites

2.2.1. Co-precipitation method. Co-precipitation method was used to prepare hydrotalcites. 150 mL deionized water was added into a three port round bottom flask and placed in a constant temperature water bath with temperature of 75 ℃. The mixed salt solution with a certain molar ratio of M/Mg/Al (M = Zn/Co/Cu) and the mixed alkali solution of NaOH and sodium carbonate were added into the three port round bottom flask at the same dropping speed. The pH value was adjusted. The mixed solution aged for 10 h under high speed stirring. The obtained slurry was filtered and washed with deionized water until no sulfate ion was detected (no precipitation by barium nitrate titration). Finally, the filter cake was dried in an oven at 85 ℃ for 12 h. After grinding and passing through 80 mesh sieve, the powder hydrotalcites samples were obtained. The synthesis schedule is shown in figure 1.

![Synthesis schedule of hydrotalcites](image)

**Figure 1. Synthesis schedule of hydrotalcites**

2.2.2. Ultrasonic wave assisted co-precipitation method. According to the above method 2.2.1, the three port flask containing the mixed liquid was put in the ultrasonic reactor, reacted for 0.5h and aged for 9.5h. The following steps are the same as the above method 2.2.1.
2.2.3. Calcination treatment. The obtained hydrotalcites were calcined at 300 °C for 4 h in muffle furnace to obtain the calcined product.

2.3. Characterization of hydrotalcites
X-ray diffraction (XRD) patterns were determined using a Shimadzu 6100X diffractometer equipped with Cu Kα radiation (λ=1.5406 Å) operating with 40 kV and 30 mA.

2.4. Adsorption ability test
2 L of phosphorus containing wastewater with initial phosphorus concentration of 50 mg/L was prepared by using phosphorus stock solution B. The pH value was adjusted to 6, and was then placed in a constant temperature water bath. 0.5000 g hydrotalcites were added into the wastewater, stirred for a certain time (5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, 10 h, 12 h, 14 h, 16 h, 20 h, 24 h, 28 h) under a rotation speed of 180 R/min. About 5 ml sample was taken respectively for filtration. The content of TP in the filtrate was determined. In the same way, phosphorus containing wastewater with initial phosphorus concentration of 200 mg/L was prepared by using phosphorus stock solution C. according to the above method, 2.0000g hydrotalcite was added to determine the content of TP in the filtrate. The equilibrium adsorption capacity \( q_e \) of phosphorus per gram of hydrotalcites is calculated according to the following formula,

\[
q_e = \frac{(\rho_0 - \rho_e) \times V}{m}
\]

Where: \( \rho_0 \) is the initial phosphorus concentration (mg/L), \( \rho_e \) is the equilibrium phosphorus concentration (mg/L), \( V \) is the volume of Phosphorus Solution (L), \( m \) is the mass of adsorbent (g).

3. Results and discussion

3.1. Type of metal
Figure 2 shows the XRD spectra of hydrotalcites prepared with different types of metals. It can be seen that hydrotalcites prepared by different types of metals show diffraction peaks near 11.6 °, 23.4 °, 34.5 °, 38.8 °, 46.9 °, 61.6 ° and 63.8 °. The narrow and sharp peaks as well as stable baseline, indicating that Zn/Mg/Al, Cu/Mg/Al, Mg/Al and Co/Mg/Al hydrotalcites with good structures have been successfully synthesized.

![Figure 2. XRD spectra of hydrotalcites prepared with different types of metals](image)

The above prepared Mg/Al, Zn/Mg/Al, Cu/Mg/Al and Co/Mg/Al hydrotalcites were used in wastewater phosphorus removal treatment. The relationship between phosphorus concentration in wastewater and time was shown in Figure 3.
It can be seen from Fig. 3 that under the condition of initial phosphorus concentration of 20mg/L, the phosphorus removal efficiency of hydrotalcites prepared with different types of metals presents a similar curve. The adsorption rates are fast at first, and gradually goes slowly, and tend to be flat after 4h. The order of phosphorus removal efficiency of different types of hydrotalcites is: Zn/Mg/Al > Cu/Mg/Al > Mg/Al > Co/Mg/Al hydrotalcites. Zn/Mg/Al hydrotalcites are the best, which have the phosphorus removal efficiency of 47.10% and adsorption capacity of 18.82 mg/g. This is mainly due to the single crystal phase of Zn/Mg/Al hydrotalcites, which forms more ion exchange sites, making it easier for phosphate ions to enter the structure of Zn/Mg/Al hydrotalcites, resulting in better phosphorus removal effect.

3.2. Synthesis conditions

Figure 4 shows the XRD spectra of Zn/Mg/Al hydrotalcites prepared with different metal molar ratios. It can be seen that the samples show typical diffraction peaks of hydrotalcite. The sharp peaks and stable baseline indicate that the samples have a good layered structure. In addition, the characteristic peak of ZnO appears in sample a, which indicates that Zn is not easy to enter the laminate to form hydrotalcite when the content is too high.
Figure 4 shows the XRD spectra of Zn/Mg/Al hydrotalcites prepared with different metal ratios. It can be seen that the samples show typical diffraction peaks of hydrotalcite. The sharp peaks and stable baseline indicate that the samples have a good layered structure. In addition, the characteristic peak of ZnO appears in sample a, which indicates that Zn is not easy to enter the laminate to form hydrotalcite when the content is too high.

Zn/Mg/Al hydrotalcites were prepared according to the above co-precipitation method and orthogonal test reaction conditions. The results of phosphorus adsorption experiment (initial phosphorus concentration is 20 mg/L) are shown in Table 1.

| Test number | Molar ratio (A) | pH value (B) | Temperature (°C) | Phosphorus Adsorption efficiency (%) |
|-------------|-----------------|--------------|------------------|--------------------------------------|
| 1           | 1:1:1           | 9            | 65               | 34.0%                                |
| 2           | 1:1:1           | 10           | 75               | 39.6%                                |
| 3           | 1:1:1           | 11           | 85               | 37.9%                                |
| 4           | 2:1:1           | 9            | 65               | 41.6%                                |
| 5           | 2:1:1           | 10           | 85               | 39.2%                                |
| 6           | 2:1:1           | 11           | 75               | 39.7%                                |
| 7           | 3:1:1           | 9            | 85               | 44.4%                                |
| 8           | 3:1:1           | 10           | 65               | 45.0%                                |
| 9           | 3:1:1           | 11           | 75               | 48.9%                                |
| k1          | 111.5%          | 120.0%       | 120.6%           |                                      |
| k2          | 120.5%          | 123.8%       | 128.2%           |                                      |
| k3          | 123.3%          | 126.5%       | 121.5%           |                                      |
| k1          | 37.2%           | 40.0%        | 40.2%            |                                      |
| k2          | 40.2%           | 41.3%        | 42.7%            |                                      |
| k3          | 41.1%           | 42.2%        | 40.5%            |                                      |
| R           | 3.9%            | 2.2%         | 2.5%             |                                      |

Order: A>C>B
Excellent level: A>B>C

It can be seen that based on the order that R_R > R_T > R_Phi, the metal molar ratio has the greatest influence on the experiment, followed by temperature, and pH has little influence on the experiment can be concluded. Thus, the adsorption efficiency of phosphorus is the best, when the preparation conditions of Zn/Mg/Al hydrotalcites are Zn: Mg: Al = 3:1:1, temperature is 75 °C, pH = 11.

3.3 Preparation method

Zn/Mg/Al hydrotalcites prepared by the above co-precipitation method and ultrasonic assisted co-precipitation method as well as calcined samples were used for phosphorus adsorption experiment (initial phosphorus concentration was 20mg / L) to explore the influence of preparation methods on phosphorus adsorption performance. Figure 5 shows the phosphorus adsorption performance curve of hydrotalcites samples prepared by different methods. It can be seen that the samples prepared by different methods present similar adsorption performance curves. The adsorption rate is fast when the adsorption time is less than 1 h. With the increase of adsorption time, the adsorption rate gradually slows down. After 2 h, the adsorption curve becomes a straight line, and the adsorption efficiency is basically unchanged. The order of phosphorus removal efficiency of different samples is as follows: calcined samples > ultrasonic assisted co-precipitation samples > co-precipitation samples. This might be the
interlayer water of Zn/Mg/Al hydrotalcites is removed after calcination at high temperature. And the CO3²⁻ in the interlayer is decomposed into CO₂ and H₂O, which provides more adsorption sites for phosphate ions. Thus the adsorption performance is improved.

3.4. Calcination time

Fig. 6 shows the effect of calcination time on the adsorption performance of the sample. It can be seen from the figure that the adsorption capacity increases at first and then decreases. The phosphorus removal efficiency of the sample is the highest of 75.8% when the calcination time reaches 4h. This is due to the continuous separation of OH⁻ and CO₃²⁻ ions between the hydrotalcites laminates in the form of H₂O and CO₂ with the increase of calcination time. This leads to the collapse of the laminates, the destruction of some layered structures and the reduction of adsorption sites, which results in the decline of adsorption efficiency.

3.5. Type of absorbent

The adsorption properties of Zn/Mg/Al hydrotalcites and two kinds of activated carbon (a and b) for phosphorus were also studied. The results are shown in Table 2. It can be seen that the adsorption performance of Zn/Mg/Al hydrotalcites for phosphorus is much higher than that of activated carbon.
After adsorption for 1 h, the treatment efficiency reaches 54.8%, which is 1.8 times of that of activated carbon. The phosphorus removal efficiency of activated carbon a and b is similar.

Table 2. The phosphorus adsorption performance of Zn/Mg/Al hydrotalcites and activated carbon

| Absorbent               | Adsorption time |          |          |
|-------------------------|-----------------|----------|----------|
|                         | Absorbance      | Removal efficiency | Absorbance | Removal efficiency |
| Zn/Mg/Al hydrotalcites  | 0.566           | 54.8%    | 0.435    | 64.8%   |
| Activated carbon a      | 0.862           | 29.8%    | 0.743    | 39.8%   |
| Activated carbon b      | 0.876           | 28.6%    | 0.795    | 35.4%   |

4. Conclusion

The results show that Zn/Mg/Al hydrotalcites have better phosphorus removal performance than Mg/Al, Co/Mg/Al and Cu/Mg/Al hydrotalcites. The hydrotalcites show the best phosphorus removal effect when the ratio of Zn/Mg/Al is 3:1:1, the temperature is 75 ℃, and the pH is 11. The removal efficiency of Zn/Mg/Al hydrotalcites can reach 76.6% after calcination for 4 h at 300 ℃. In addition, the adsorption capacity of Zn/Mg/Al hydrotalcites for phosphorus is much higher than that of activated carbon.

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