Experimental study on phosphorus removal of water by Zn/Mg/Al layered double hydroxide

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Abstract. Zn/Mg/Al layered double hydroxide (Zn/Mg/Al-LDH) was prepared by co-precipitation method. The structure of Zn/Mg/Al-LDH was characterized by XRD. The results show that the samples have typical hydrotalcite structure. They were used as adsorbents to remove phosphorus from wastewater. The effects of pH value, phosphorus concentration, adsorbent dosage, oscillation intensity and reaction time on phosphorus adsorption capacity were investigated by single factor control variable method. The results show that the adsorption equilibrium of Zn/Mg/Al-LDH can be reached after 24 h. The optimal experimental conditions are as follows: stirring rate is 180 R/min, pH value is 6, and reaction temperature is 50 ℃. Under above conditions, when the initial phosphorus concentration is 50 mg/L, the adsorption capacity of Zn/Mg/Al-LDH for phosphorus is 54.10 mg/g when the adsorption equilibrium is reached. When the initial phosphorus concentration is 200 mg/L, the adsorption capacity is 69.70 mg/g, and the saturated adsorption capacity is 70.37 mg/g. In the simulated practical engineering application, when the discharged phosphorus meets the standard, the phosphorus adsorption capacity of Zn/Mg/Al-LDH is 37.09 mg/g, and the phosphorus removal rate is as high as 99.76%.

1. Introduction
Phosphorus exists in the form of phosphate in nature, which is an important element of life. However, the total amount of phosphorus has a great impact on the growth and development of organisms and environmental conditions. The sources of phosphorus containing wastewater include domestic sewage, industrial wastewater, fertilizer loss from forest and farmland, and rainfall and snowfall. Phosphorus containing wastewater in industry mainly includes fertilizer, medicine, metal surface treatment, printing and dyeing and food industry [1]. If the untreated or preliminarily treated sewage is directly discharged into the water area, a large amount of phosphorus in the sewage will be discharged into the environmental water. The nutrients in the water will exceed the self-purification capacity of the water, and the input and output of nutrients will be unbalanced. This will lead to the imbalance of species distribution in the aquatic ecosystem. For example, algae in the water grows in large numbers, which reduces the dissolved oxygen in the water. The aquatic organisms will be suffocated due to insufficient oxygen supply. Their death body’s oxidation and decomposition will produce toxic and harmful gases such as hydrogen sulfide, which lead to the deterioration of water quality. And it will play a bad effect on fisheries, industry, agriculture and drinking water. For example, long-term drinking of water containing phosphorus will lead to osteoporosis, mandibular necrosis and other diseases. Therefore, phosphorus removal from wastewater has great practical significance. At present, the most commonly used phosphorus removal methods are chemical precipitation method, biological method and adsorption method [2, 3]. 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, hydrotalcite and so on [4]. Hydrotalcite is mainly through the use of anion exchange properties, as well as adsorption properties to achieve the application in water pollution control. Due to the wide range of sources, low price and large specific surface area, this kind of material has attracted more and more attention of scholars. In this paper, Zn/Mg/Al-LDH was used as adsorbent and its phosphorus removal performance was studied.

2. Experimental

2.1. Preparation and characterization of Zn/Mg/Al-LDH

Zn/Mg/Al-LDH was prepared by co-precipitation method. The mixed salt solution with Zn: Mg: Al molar ratio of 3:1:1 and the mixed base solution of NaOH and Na2CO3 were added into a three port round bottom flask under the same dropping speed. The pH value was adjusted to 11, and the mixture was aged at 75 °C for 10 h under high speed stirring. Finally, the filter cake was dried in an oven at 85 °C for 12 h. After grinding and passing through 80 mesh sieve, the powder sample was obtained. 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.

2.2. Drawing of phosphorus standard curve

According to “Water Quality-Determination of total phosphorus-ammonium molybdate spectrophotometric method (GB 11893-89)”, 0.0, 0.50, 1.00, 3.00, 5.00, 10.00 and 15.00 mL 2 μg/mL phosphate standard solution was added respectively into seven 50mL colorimetric tubes with plugs. Ultrapure water was added to 25mL, 4mL potassium persulfate was then added. They were put into a large beaker, and was heated in a vertical autoclave at 120 °C, 1.1kg/cm3 for 30min. When the pressure drops to zero, it was taken out for cooling, and diluted with water to the scale. 1mL 100g/L ascorbic acid solution to each digestion solution was added and shaken well. After 30s, 2mL prepared molybdate solution was added and mixed well. It was then placed at room temperature for 15min to develop colour. Phosphorus standard curve was drawn by using 30mm cuvette with ultrapure water as reference at 700nm wavelength and measuring the absorbance by deducting reagent blank.

2.3. Adsorption ability test

2000 mL of phosphorus containing wastewater with initial phosphorus concentration of 50 mg/L was prepared. The pH value was adjusted to 6 and it was placed in a constant temperature water bath. 0.5000g Zn/Mg/Al-LDH was added, the speed was adjusted, stirred for a certain time. About 5 mL of sample filtration was taken to determine the content of TP in the filtrate. Similarly, phosphorus containing wastewater with initial phosphorus concentration of 200mg/L was prepared. According to the above method, 2.0000g Zn/Mg/Al-LDH was added to determine the content of TP in the filtrate. The equilibrium adsorption capacity \( q_e \) of phosphorus per gram of hydrotalcite 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. Structure of Zn/Mg/Al-LDH

Figure 1 is the XRD spectrum of Zn/Mg/Al-LDH. It can be seen that Zn/Mg/Al-LDH presents the characteristic diffraction peak of hydrotalcite. The low angle diffraction peaks (20 = 11.7, 23.5, 34.1)
are sharp and narrow, which indicates that the hydrotalcite sample with good structure has been successfully prepared.

Figure 1. XRD spectrum of Zn/Mg/Al-LDH.

3.2. Standard curve of total phosphorus in water
Figure 2 is the standard curve of total phosphorus in water. It can be seen that the standard curve equation of total phosphorus in water is \( y = 0.0291x + 0.0103 \), where \( y \) is the absorbance, \( x \) is the phosphorus content, and \( R^2 = 0.9993 \), which indicates that the linear relationship of the curve is good. The following total phosphorus content can be calculated according to this equation. At the same time, all TP are determined by ammonium molybdate spectrophotometry [5].

Figure 2. The standard curve of total phosphorus in water.

3.3. Adsorption concentration and time
Figure 3 shows the relationship between adsorption concentration and time on adsorption performance. It can be seen that the adsorption curve of Zn/Mg/Al-LDH at the initial phosphorus concentration of 50g/L and 200g/L is basically the same. The adsorption rate is fast at first, and gradually tends to be flat after 200min. It presents a linear state after 600min, which is close to the adsorption equilibrium. At this time, the phosphorus adsorption capacity of Zn/Mg/Al-LDH is 96.49% of the equilibrium adsorption capacity when the initial phosphorus concentration is 50g/L. And it is 97.13% when the initial phosphorus concentration is 200g/L.
3.4. Stirring rate

Figure 4 Influence curve of effect of stirring rate on Adsorption Performance

Figure 4 shows the effect of stirring speed on the adsorption performance. It can be seen that with the increase of stirring speed, the phosphorus adsorption capacity of Zn/Mg/Al-LDH increases gradually at first, reaches the maximum at 180 r/min, and then decreases gradually. This is mainly due to the fact that the adsorbent does not fully contact with the sewage when stirring at low speed, resulting in poor adsorption effect. However, when the stirring speed is too fast, the contact time between the adsorbent and phosphorus ion in anhydrous water is too short to well absorb, resulting in the decrease of adsorption capacity. Therefore, the stirring rate of 180 r/min is chosen.

3.5. pH value

Figure 5 shows the effect of pH value of wastewater on adsorption performance. It can be seen that the adsorption capacity of Zn/Mg/Al-LDH is relatively high in the range of pH = 5 ~ 8. When pH = 6, the
maximum adsorption capacity is 37.22mg/g. This is due to the partial dissolution of Zn/Mg/Al-LDH when the acidity and alkalinity of wastewater is too strong, which reduces the efficiency of phosphorus removal.

![Figure 5 Influence curve of effect of pH value on adsorption performance](image)

**3.6. Reaction temperature**

![Figure 6 Influence curve of effect of pH value on adsorption performance](image)

Fig. 6 is the relationship curve of the effect of reaction temperature on the adsorption performance. It can be seen that the adsorption capacity of Zn/Mg/Al-LDH for phosphorus increases with the increase of temperature between 25 °C and 50 °C. When the temperature is higher than 50 °C, the adsorption capacity decreases with the increase of temperature. Therefore, the saturated adsorption performance of Zn/Mg/Al-LDH is the best at 50 °C.

**3.7. Drawing of adsorption isotherm**

The adsorption isotherm fitted by computer simulation is shown Figure 7. Langmuir adsorption isotherm model was used to fit the data. The isothermal adsorption equation of phosphorus is as follows.

\[
q_e = \frac{45.74 \rho e}{1 + 0.65 \rho e}, \quad R^2=0.9738
\]

According to the equation, the saturated adsorption capacity of Zn/Mg/Al-LDH for phosphate in wastewater is 70.37mg/g.
3.8. Determination of adsorbent dosage

Table 1. Relationship between dosage of Zn/Mg/Al-LDH and equilibrium adsorption capacity as well as phosphorus removal efficiency

| dosage (g) | Equilibrium phosphorus concentration (μg) | Equilibrium adsorption capacity (mg/g) | Phosphorus removal efficiency (%) |
|------------|------------------------------------------|---------------------------------------|----------------------------------|
| Initial phosphorus concentration is 50mg/L |
| 2.4300     | 3.21                                     | 38.51                                 | 93.57                            |
| 0.1737     | 2.22                                     | 36.70                                 | 95.55                            |
| 0.1203     | 1.35                                     | 35.72                                 | 97.31                            |
| 0.0728     | 0.67                                     | 35.28                                 | 98.66                            |
| 0.0404     | 0.49                                     | 34.90                                 | 99.01                            |
| Initial phosphorus concentration is 200mg/L |
| 7.3800     | 42.80                                    | 42.60                                 | 78.60                            |
| 2.0102     | 20.78                                    | 38.17                                 | 89.61                            |
| 1.890      | 5.2                                      | 37.17                                 | 97.39                            |
| 0.6003     | 0.49                                     | 33.90                                 | 99.76                            |

According to the discharge limits of water pollutants in Guangdong Province (DB44/26-2001), the maximum allowable discharge concentration of total phosphorus (based on phosphorus) is 0.5mg/L. Zn/Mg/Al-LDH samples were repeatedly added into water to meet the discharge standard. The relationship between dosage of Zn/Mg/Al-LDH and equilibrium adsorption capacity and phosphorus removal efficiency is shown in Table 1. It can be seen that there is a certain difference between the actual adsorption amount and the adsorption amount measured in the adsorption equilibrium. With the increase of adsorbent dosage, the adsorption capacity decreased. When the initial phosphorus concentration was 50mg/L and 200mg/L, the average adsorption capacity was 36.22mg/g and 37.96mg/g, respectively. The phosphorus adsorption capacity of adsorbent with adsorption time of 1 h is 37.09 mg/g in practical application. It has more practical reference value, and the phosphorus removal rate is as high as 99.76%.

3.9. Safety performance test

In order to ensure that Zn, Mg and Al elements in Zn/Mg/Al-LDH will not be heavily dissolved in the process of wastewater phosphorus removal, which will cause new pollution, the safety performance test is also carried out. The determination of Zn, Mg and Al in water samples adopts the method of
determination of 32 elements in water quality by inductively coupled plasma atomic emission spectrometry (HJ 776-2015), and the results are shown in Table 2 below.

Table 2. ICP results of determination of Zn, Mg and Al in water

| element | Zn (mg/L) | Mg (mg/L) | Al (mg/L) |
|---------|-----------|-----------|-----------|
| Concentration | 0.72 | 4.660 | 0.015 |
| Emission standard | 2.0 | 450 | (Total hardness) 0.2 |

It can be seen that the dissolution concentrations of Zn, Mg and Al in the water samples after reaction equilibrium measured by ICP are 0.017 mg/L, 4.660 mg/L and 0.015 mg/L respectively, which are far lower than the emission limits specified in various standards. Therefore, using Zn/Mg/Al-LDH to remove phosphorus in wastewater will not cause secondary pollution to water.

### 4. Conclusions

The results show that the adsorption equilibrium of Zn/Mg/Al-LDH is reached after 24h. The optimal experimental conditions are as follows: stirring rate is 180r/min, pH value is 6, and reaction temperature is 50 °C. Under the optimal conditions, when the initial phosphorus concentration is 50mg/L, the adsorption capacity of Zn/Mg/Al-LDH for phosphorus is 54.10mg/g when the adsorption equilibrium is reached. When the initial phosphorus concentration is 200mg/L, the adsorption capacity is 69.70mg/g, and the saturated adsorption capacity is 70.37mg/g. In the simulated practical engineering application, when the discharged phosphorus meets the standard, the phosphorus adsorption capacity of Zn/Mg/Al-LDH is 37.09mg/g, and the phosphorus removal rate is as high as 99.76%. With the increase of adsorbent dosage, the adsorption capacity decreased. Using Zn/Mg/Al-LDH to remove phosphorus in wastewater will not cause secondary pollution to water.

### Acknowledgments

Authors wishing to acknowledge financial support from Guangdong Province higher education excellent young teachers training programme.

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