Study on Phosphate Removal from Water Using Adsorbent Synthesized from Spent Zn-Mn Battery

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Abstract. The adsorbent synthesized from spent Zn-Mn battery was used to purify phosphate from aqueous solution. From the results it could be seen that pH value affected phosphate removal significantly, optimum pH in the purification process was 8.0. The removal rate of phosphate increased when the adsorbent dosage improved. The reaction process was fast and the purification ratio could reach 96.2% for 10 minutes. The adsorption isotherm of phosphate purification fitted Langmuir equation and Freundlich equation. The Q₀ value in Langmuir equation was 56.82 mg/g and the n value in Freundlich equation was 3.61. From spent Zn-Mn battery effective adsorbent for phosphate removal could be synthesized.

1. Introduction
Eutrophication of water bodies may cause cyanobacteria blooms in rivers and lakes and threaten ecological balance and human health [1]. The main reason is that the nitrogen and phosphate content in the water is too high, especially when the mass concentration of phosphate exceeds 0.02 mg/L [2]. Phosphate in the water mainly comes from wastewater discharged by industry, life and agriculture. Therefore, the removal of phosphate from wastewater is one of the environmental problems that need to be solved urgently[3]. The adsorption method is a typical method which is currently used more frequently in the treatment of phosphate-containing wastewater due to its simple operation, high efficiency, low pollution, and renewable adsorbent. The development and preparation of materials with high efficiency, low cost and fast adsorption rate are the hotspots of this technology research[4-6]. In this study we used adsorbent synthesized from spent battery to remove phosphate from aqueous solution.

2. Materials and Methods

2.1. Materials and Reagents
A spent zinc-manganese battery was disassembled and placed in a 500 mL beaker, then added 450 mL of 0.5 mol/L sulfuric acid into the beaker. The beaker was put in an ultrasonic vibrator, the water bath was heated to 60°C and the mixture was continuously stirred until the soluble component completely dissolved. The slurry in the beaker was filtered, and sodium hydroxide solution was added into the filtrate to adjust the pH of the filtrate to 10 to make precipitate, and then the slurry was aerated with the air pump for 30 minutes. The aerated slurry was placed in a centrifuge, and the supernatant was decanted after centrifugation. The precipitate was placed in an oven and dried at 60°C and then the dried precipitate was ground to obtain the adsorbent in this study. A stock solution with a phosphate
content of 1g/L was prepare with potassium dihydrogen phosphate, and then diluted it to prepare simulated phosphate-containing wastewater.

2.2. Sorption Studies
A certain amount of adsorbent was added into a 250 mL Erlenmeyer flask, then added a phosphate-containing solution, adjusted the pH to a certain value, oscillated on a shaker for a certain period of time, then filtered, and took the filtrate to determine the content of phosphate of the purified water.

3. Results and Discussion

3.1. Effect of pH on the Phosphate Removal.
The amount of adsorbent was 0.0900 g, the amount of phosphate-containing wastewater was 120 mL, and the initial concentration of phosphate-containing wastewater was 10 mg/L, the pH was adjusted to 3,4,5,6,7,8,9,10 and the mixture was shaken at 25 °C for 2 hours. The experimental data were depicted in Figure 1. Figure 1 showed that the pH value significantly affected the removal rate of phosphate by the adsorbent. In the adsorption process, when the pH value of the solution enhanced from 3 to 6, the purification rate of phosphate in the water by the adsorbent improved obviously. In the range of pH 6~8, as the pH value increased, the purification rate of phosphate in water by the adsorbent increased by a small margin. When the pH was 8.0, the purification rate of phosphate in the water reached the maximum purification rate of 98.0%, and the content of phosphate in the purified water was 0.2 mg/L. When the pH value of the solution was greater than 8, as the pH value of the solution increased, the purification rate of the phosphate in the water by the adsorbent decreased. This was mainly because under the condition of higher pH the hydroxide radicals in the water competed with the phosphate in the water for the active sites on the adsorbent. From the experimental results, it could be seen that the pH value of 8.0 was a suitable pH value for the purification of phosphate, and this pH value also coincided with the wastewater discharge standard, which is between 6 and 9.

3.2. Effect of Adsorbent Dosage on the Phosphate Removal.
The amount of phosphate-containing wastewater was 120 mL, and the initial concentration of phosphate-containing wastewater was 10 mg/L. The adsorbent dosage was 0.0300 g, 0.0600 g, 0.0900 g, 0.1200 g and 0.1500 g, the pH was adjusted to 8, the mixture was shaken at 25 °C for 2 hours. The experimental data were depicted in Figure 2. Figure 2 showed that with the increase of the adsorbent dosage, the removal rate of phosphate by the adsorbent was continuously increasing. When the dosage increased from 0.03g/120mL to 0.09g/120mL, the removal rate increased significantly. This was mainly due to the increase in dosage led to increase of the active sites of the adsorbent and increased the solid-liquid contact area, which in turn increased the removal rate. When the dosage of adsorbent was 0.09g/120mL, the removal rate reached 98.0%. After purification, the phosphate concentration dropped to 0.2mg/L. Then the subsequent increase in dosage had little effect on the improvement of the removal rate, when the dosage reached 0.15g/120mL, the removal rate only increased by 0.9% compared with 0.09g/120mL.
3.3. Effect of Contact Time on the Phosphate Removal
The amount of adsorbent was 0.0900 g, the amount of phosphate-containing wastewater was 120 mL, the initial concentration of phosphate-containing wastewater was 10 mg/L, the pH was adjusted to 8, and the mixture was shaken at 25 °C for 10 min, 30 min, 60 min, 90 min, 120 min, 150 min and 180 min, the experimental data was described in Figure 3. Figure 3 showed that the phosphate removal efficiency of the adsorbent changed with the adsorption time. It could also be seen that when the adsorption time was between 0 and 10 min, the removal rate of phosphate by the adsorbent increased rapidly with time. At 10 min, the phosphate removal rate reached 96.2%, and the phosphate concentration after purification dropped to 0.38 mg/L. This was mainly due to the microporous structure on the surface of the adsorbent, the phosphate radicals could relatively fastly occupy surface active sites on the adsorbent. When the adsorption time was between 10 to 120 min, the removal rate of phosphate by the adsorbent continued to increase, but the increasing rate gradually decreased,
because the surface active sites decreased and the adsorption reaction gradually slowed down. When the adsorption time was 150 min, the removal rate reached 98.1%, and the adsorption reached equilibrium.

Figure 3. Effect of time on phosphate removal

3.4. Sorption Isotherm.

Figure 4 showed the adsorption isotherm of phosphate.

Figure 4. Effect of time on phosphate removal

It can be seen from Figure 4 that as the concentration of phosphate in the solution increased, the amount of phosphate adsorbed by the adsorbent improved significantly, indicating that the adsorbent used can effectively purify phosphate in the water. The adsorption isotherm of phosphate removal was regressed according to Langmuir and Freundlich models.

Langmuir equation:
Freundlich equation:

\[ \frac{C_e}{q_e} = \frac{1}{Q_0C_e} + \frac{1}{Q_0K_F} \]  

Equation (1)

The regression results were shown in Equation 3 and 4 and Figure 5.

Langmuir equation, \( r^2 = 0.9872 \):

\[ \frac{C_e}{q_e} = 0.0666 + 0.0176C_e \]  

Equation (3)

Freundlich equation, \( r^2 = 0.9921 \):

\[ \ln q_e = 2.907 + 0.2764 \ln C_e \]  

Equation (4)

**Figure 5.** Linearized forms of Langmuir and Freundlich isotherms

It could be seen that the adsorption data of phosphate using the adsorbent was very close to the Langmuir equation and Freundlich equation. \( Q_0 \) was 56.82 mg/g and \( n \) value was 3.61, indicating that the adsorbent synthesized from the waste zinc-manganese battery was relatively effective in the purification of phosphate.

4. Conclusion

The adsorbent synthesized from spent Zn-Mn battery was used to purify phosphate from aqueous solution. From the results it could be seen that pH value affected phosphate removal significantly, optimum pH in the purification process was 8.0. The removal rate of phosphate increased when the adsorbent dosage improved. The reaction process was fast and the purification ratio attained 96.2% for 10 minutes. The adsorption isotherm of phosphate purification fitted Langmuir equation and Freundlich equation, The \( Q_0 \) value in Langmuir equation was 56.82 mg/g and the \( n \) value in
Freundlich equation was 3.61. From spent Zn-Mn battery effective adsorbent for phosphate removal could be synthesized.

5. References

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