Study on the adsorption of phosphate in water by La-modified cellulose

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Abstract. In this experiment, cellulose microspheres were prepared by hydration at high temperature and impregnation with lanthanum chloride solution. The surface morphology and structural characteristics of the modified biomass were analyzed by SEM, XRD and IR. In addition, the adsorption capacity of La-modified cellulose to phosphate in water at different pH and initial concentration had been studied, and the acid condition was more favourable for phosphate removal.

1. Introduction
Phosphorus is an important resource, but excessive phosphorus content in the water environment will lead to eutrophication of water body, rapid propagation of algae and plankton, and deterioration of water quality[1]. At present, the main dephosphorization technologies are chemical precipitation, biological, adsorption, combined treatment methods and so on[2-4]. Adsorption method has attracted the attention of scholars at home and abroad due to its advantages of low cost, simple operation, reliable operation, high treatment efficiency and small secondary pollution[5]. Biomass adsorbent[6] has the advantage of wide source, low production cost, high porosity and large surface area, etc. Cellulose is found in cotton, hemp, straw, wood and other substances, which has the advantages of renewable, degradable, non-toxic and harmless, good biocompatibility, etc[7]. In this paper, lanthanum chloride modified cellulose was used to prepare high-efficiency adsorption materials, which could not only solve the problem of eutrophication of water body, but also recover and utilize important phosphorus resources. In the process of dephosphorization, no new pollutants were produced, which could turn waste into treasure.

2. Materials and methods

2.1. Adsorbent and adsorbate
Cellulose powder (5g) was stirring with 100mL distilled water in a beaker to fully dissolve, then it was poured into a reaction kettle and put into an oven for 24h at 200 °C. After cooling, pour the liquid in the reaction kettle into the beaker and then put it into the oven for drying at 90 °C for 24 hours. After cooling, the modified cellulose was washed once with anhydrous ethanol, twice with 1mol/L hydrochloric acid solution and three times with distilled water, respectively. The modified cellulose and lanthanum chloride (2:1) were mixed in 200mL distilled water stirring for 24h. pH value of the La-modified cellulose was adjusted to 10 by 6M NaOH, and then the solution was transferred to a
crucible and heated in the muffle furnace at 500 ℃ for 2 h. The La-modified cellulose was put in the sealed bag for standby after cooling. The La-modified cellulose was characterized by a scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR) analysis and X-ray diffraction (XRD).

Sodium dihydrogen phosphate was purchased from Shenyang Xinxing reagent factory. 1g/L phosphorus standard stock solution was dissolving sodium dihydrogen phosphate in the distilled water. The diluted phosphate solution was prepared by the stock solution. Phosphate concentration was calculated by the standard curve.

2.2. Experiments of adsorption
The adsorbent (0.01g) was mixed with a certain concentration of sodium dihydrogen phosphate solution and vibrated in the oscillator (25℃, 200r/min) for 24h. After centrifugation, a certain amount of supernatant was taken to dilute and then coloration to determine the absorbance value. After adsorption, the concentration of phosphate was determined, and the adsorption rate was calculated according to formula (1).

\[ P = \frac{C_0 - C}{C_0} \times 100\% \quad (1) \]

\( C_0 \) was the initial concentration of phosphate solution (mg/L); \( C \) was the concentration of phosphate after adsorption (mg/L); \( P \) was the adsorption rate(%).

3. Results and Discussion

3.1. Surface morphology analysis

![Surface morphology of La-modified cellulose](image)

Figure 1. Surface morphology of La-modified cellulose

The surface morphology of La-modified cellulose is shown in Figure 1. It could be seen that the cellulose lanthanum chloride composite prepared by hydrothermal modification had small particle size and belonged to nanometer level. The adsorbents were spherical, most of them were stacked together, and a few scattered. The distribution was not very dense, the particle size and the surface were uneven. It could be clearly seen that there were dense small protrusions on the particle surface when it was magnified. These small protrusions made its relative specific surface area increase, so it was suitable to be an adsorbent.
3.2. FTIR analysis

![Infrared spectra of La-modified cellulose](image)

The infrared spectrum is highly characteristic, which can be used for qualitative analysis of molecular structure and chemical bond. It showed that there was an obvious stretching vibration peak at 3343.25 cm\(^{-1}\), which was the C-OH stretching vibration peak and there were more hydroxyl groups in La-modified cellulose molecule. There was a stretching vibration peak at 2902.60 cm\(^{-1}\), which was CH\(_3\)-CO vibration peak. There was an absorption peak at 1427.16 cm\(^{-1}\), which was the bending vibration of -COOH in the O-H plane bending vibration. There were dense absorption peaks at 1370.27 cm\(^{-1}\)-1033.10 cm\(^{-1}\), indicating the presence of methyl, aldehyde and ether groups in the La-modified cellulose molecule.

3.3. XRD

![XRD of La-modified cellulose](image)

The La-modified cellulose appeared the characteristic peaks of La-O compound at 2\(\theta\) of 32°, 34°, 36° and 54°, which confirmed the loading of lanthanum on the modified cellulose.
3.4. Effect of pH

![Figure 4: Effect of pH on phosphate removal rate](image)

The adsorption effect of La-modified cellulose on sodium dihydrogen phosphate (100mg/L) in the range of pH 3~11 is shown in Figure 4. It can be seen that the adsorption effect under acid condition was significantly better than that under alkaline condition. When the pH was equal to 3, the phosphorus removal rate of La-modified cellulose adsorbent reached 98%. The phosphate removal rate decreased with pH increasing. The reason was that the ion form of phosphate in solution and the static charge on the surface of adsorbent affected the removal rate of phosphate. When the pH value of adsorbent was low, it combined with positive charge and was easy to adsorb phosphate ion with negative charge. The concentration of OH⁻ in the solution increased with pH increasing, which competed with phosphate ions for similar adsorption potential and affected the phosphate removal effect.

3.5. Effect of phosphate concentration

![Figure 5: Effect of phosphate concentration on its removal rate](image)

The effect of phosphate concentration on its removal rate was shown in Figure 5. It could be seen that the overall removal rate decreased with the increase of the initial phosphate concentration. The reason was that the concentration gradient of phosphorus in the liquid membrane on the outer surface of the adsorbent became larger and larger with the increase of the initial phosphate concentration, which was conducive to the migration of phosphate to the outer surface of the adsorbent. When the initial phosphate concentration was low, the competition of phosphate ion for adsorption sites was small and the removal rate was good.
4. Conclusion
The results of SEM and FTIR analysis showed that after the modification, the particle distribution of cellulose was more dispersed, the surface roughness was increased. The surface of the particles was uneven and increased, and the adsorption performance of the La-modified cellulose was improved. Acidic conditions were more favourable for the adsorption. When the pH of the solution was low, the adsorbent surface was easy to carry positive charge, which made it easier to combine the acid ions with negative charges. The lower the initial concentration of phosphate solution was, the higher the phosphorus removal rate of La-modified cellulose was.

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