Preparation of Mg/Al Layered Double Hydroxides in Phosphorylated Cellulose Microspheres for Tetracycline Hydrochloride Removal from Water

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Highlights

- Phosphorylated cellulose microspheres were conducted as porous microreactor.
- In situ synthesis method was used to design the Mg/Al LDH@PCM adsorbent.
- The Mg/Al LDH@PCM showed high adsorption capacity of TC from water.

1. Introduction

Tetracycline hydrochloride (TC) is one of tetracycline antibiotics, which has been commonly used in the world to resist disease and prevent humans and animals from microbial infections. Due to the abuse of antibiotic and the lack of supervision, almost all kinds of antibiotics were detected in surface water, groundwater, sea water, and even tap water. The presence of antibiotic in the environment has been associated to chronic toxicity and the prevalence of resistance to antibiotics in bacterial species.[1] Therefore, it is imperative to remove the antibiotics from water for a safe water supply. This will ensure the health and life quality for millions of people under the antibiotic contamination threats.

Adsorption technology is one of the most attractive options because of its convenience, ease of use, and high efficiency.[2] The key of adsorption technology is the design of adsorbents including the choice of adsorbent material and the design of the adsorbent structure. Cellulose stands out due to its low cost, wide availability, renewability, biodegradability, biocompatibility, etc.[3] However native cellulose does not have satisfactory adsorption capacity for antibiotic. It is necessary to combine cellulose with other inorganic materials with high adsorption capacity. Layered double hydroxides are kinds of lamellar inorganic materials, which have been widely applied as adsorbents to remove pharmaceuticals from aqueous solutions in recent years.[4]

In this work, phosphorylated cellulose microspheres (PCM) were conducted as porous microreactor, Mg/Al layered double hydroxides (Mg/Al LDH) were prepared by in situ synthesis method in the internal holes of PCM. Phosphate group could attract cations and provide more sites for them. Thus, more Mg/Al LDH particles could be loaded dispersedly into PCM with better adsorption performance for TC.

2. Methods

PCM was fabricated by solid phase synthesis method as our previous report.[5] Then, Mg/Al LDH@PCM was prepared by in situ synthesis method. Phosphorylated cellulose microspheres (wet weight: 20 g) were dispersed in 300 mL of deionized water with a three-neck round-bottom flask. Magnesium nitrate ($Mg(NO_3)_2 \bullet 6H_2O$), aluminum nitrate ($Al(NO_3)_3 \bullet 9H_2O$), and urea were dissolved in above deionized water in the ratio 2:1:7 to give the final concentrations of 10, 5, and 35 mM, respectively. Then the mixture was refluxed at 100 ^oC under continuous stirring for 12 h. Finally, the microspheres were washed with deionized water to remove the unreacted reactants and to gain Mg/Al LDH@PCM. Their morphological, structural, and physicochemical properties were characterized by SEM, FTIR, XRD, and DSC, etc. Furthermore, EDX and XPS were used to confirm the in-situ synthesis process and to investigate the adsorption mechanism. Batch and dynamic adsorption experiments were conducted to explore the adsorption performance.

3. Results and discussion

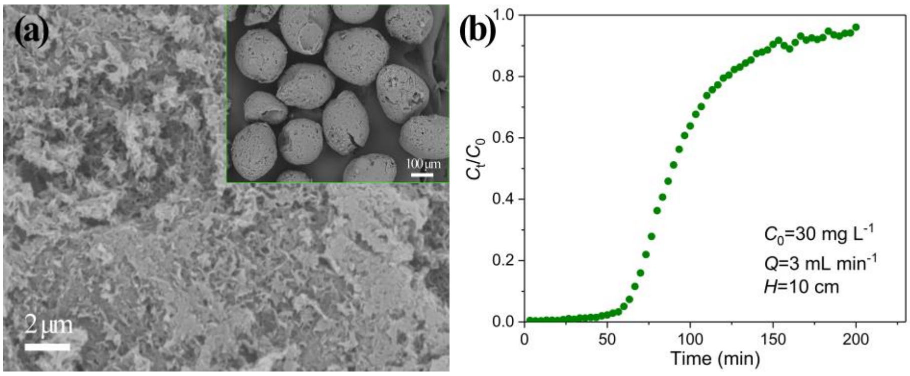

Figure 1. (a): SEM images of Mg/Al LDH@PCM; (b): breakthrough curve of TC by Mg/Al LDH@PCM using fixed bed column at initial concentration (C_0) of 30 mgL^{-1}, flow rate (Q) of 3 mL min $^{-1}$, and column height (H) of 10 cm.

SEM images of Mg/Al LDH@PCM are shown in figure 1a. The microspheres with good spherical shape (Figure 1a inset) have average diameters in the range of 100-300 µm. The diameter distribution of microspheres is in line with Gaussian distribution with the sol-gel transition method. Thus, the Mg/Al LDH@PCM microspheres were loaded in the fixed-bed column with the highest fractionation efficiency, which was favorable for dynamic adsorption. The surface structure of the microspheres is shown in Figure 1a, in which micropore and nanopore structure can be observed. Mg-Al LDH nanosheets are loaded in the micropore and nanopore of PCM. The porous structure not only allowed TC to penetrate into the microspheres but also provided loading sites for Mg/Al LDH to facilitate TC adsorption.

The breakthrough curve of TC by Mg/Al LDH@PCM using fixed bed column are shown in Figure 1b. The breakthrough time, volume of treated solution, adsorption capacity and removal efficiency of the breakthrough point were 67 min, 200 mL, 10.27 mg g^{-1} and 97.73%, respectively. And the saturation time, volume of treated solution, adsorption capacity and removal efficiency of the saturation point were 150 min, 450 mL, 14.82 mg g^{-1} and 62.66%, respectively. The fixed-bed column displayed good capacity for treating water for a continuous time, which is highly desirable in environmental engineering.

4. Conclusions

The Mg/Al LDH@PCM was successfully constructed by in situ synthesis method. The size of Mg/Al LDH synthesized in PCM was controlled by the micropore and nanopore structures of PCM. Batch and fixed-bed column adsorption experiment suggested that the adsorbent had high adsorption capacity for TC. Electrostatic interaction and ion exchange might control the adsorption process.

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Keywords
Mg/Al LDH@PCM, Tetracycline hydrochloride, Batch adsorption, Fixed-bed column