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Surface modification of cyclodextrin/lignin biopolymer microparticles with polyethylene for fast and selective removal of anionic dyes

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Abstract

In this research, beta-cyclodextrin was grafted over lignin biopolymer by epichlorohydrin and functionalized with polyethyleneimine to prepare composite microparticles. After that, FTIR spectroscopy was used to characterize microspheres. The best result for removing methyl orange (MO) in the presence of 0.44 g L^{-1} of adsorbent, pH 6.5, pollutant concentration of 20 mg L^{-1}, and temperature of 25 °C after 15 min was approximately 97%. This adsorbent showed fast removal and excellent selectivity towards anionic dyes.

Keywords: Biopolymer, Lignin, Cyclodextrin, Adsorption, Polyethyleneimine

Introduction

Access to clean drinking water is essential for maintaining a healthy life. Factors such as industrialization, uncontrolled urbanization, excessive utilization of natural water resources, and population growth have significantly influenced water quality [1]. Among the various water pollutants, dyes, in addition to creating toxicity for the environment, also change the color of the water. Adsorption is considered a flexible, operational [2], simple, and economical method for wastewater treatment [3]. Cyclodextrin is a cheap, widely available, biocompatible, and biodegradable material [4]. Beta-cyclodextrin (β-CD) has a hydrophobic inner cavity and a hydrophilic outer surface [5]. A hydrophobic cavity is a place where a wide range of organic guest molecules with appropriate size and polarity can form host-guest complexes [4]. Hydrophilic groups of cyclodextrin lead to the dissolution of cyclodextrin in water and prevent its direct use to remove pollutants. Therefore, modification is necessary to produce an insoluble cyclodextrin polymer [6]. After cellulose, lignin (complex aromatic polymer and renewable) is earth's second most abundant biopolymer. Due to its unique physicochemical properties, biocompatibility, renewability, low cost, abundance, and active sites in its molecules, lignin has a great tendency to adsorb various types of organic and inorganic pollutants from water [7]. In the present work, we focused on synthesizing polyethyleneimine functionalized cyclodextrin/lignin composite microparticles. Lignin has been used as a green biopolymer to make beta-cyclodextrin insoluble. This multifunctionalized composite shows fast and selective methyl orange (MO) removal.

Experimental

Polyethyleneimine functionalized β-CD/lignin composite microparticles as an attractive adsorbent was prepared using a modified method proposed by Wei et al. [6]. The inverse suspension polymerization method was used to prepare microspheres. In beaker 1, sodium dodecylbenzene sulfonate, β-CD (4 g), sodium hydroxide (20 wt%), and lignin (1 g) were combined and mixed. In beaker 2, branched polyethyleneimine, sodium alginate solution (5 wt%), and deionized water were added and mixed. The aqueous phase solution was prepared by combining the contents of both beakers. Then, the aqueous phase solution was added to liquid paraffin at 60 °C. After 30 min, 5 ml of epichlorohydrin was added, and the reaction was allowed to proceed for 2 h. Finally, our adsorbent was dried at 60 °C overnight.

Results and discussion

FT-IR spectra of microspheres, β-CD, and lignin samples are shown in Fig. 1. The peak at 1640 cm^{-1} is attributed to C-C stretching vibrations of the β-CD polymer chain. Lignin exhibits a characteristic peak of benzene ring vibration at 1594 cm^{-1}, which overlaps with the 1640 cm^{-1} peak in the microspheres, likely due to the cross-linking between β-CD and lignin. The 1156 and 1030 cm^{-1} peaks correspond to the C-O-C and C-OH vibrations of β-CD and lignin, respectively; these peaks are also present in the microspheres. A new peak at 1460 cm^{-1} in the microspheres is related to the C-N stretching vibration, indicating the successful incorporation of polyethyleneimine into the microspheres. The broad peaks observed at 3430 cm^{-1} and 2920 cm^{-1} are attributed to OH/NH and CH_2 stretching vibrations, respectively [6].

The adsorption process of MO at two different initial concentrations (20 and 40 mg L^{-1}) using microparticles is depicted in Fig. 2. All the curves demonstrated rapid adsorption of MO within the first 15 min, attributed to the abundance of vacant surface sites in the adsorbent. After this initial phase, the curves gradually flattened as they approached equilibrium conditions. The decrease in the MO adsorption rate over time can be attributed to the slow diffusion of MO molecules into the bulk of the adsorbent [8].

When the initial concentration of the pollutant was higher (40 mg L^{-1}), the amount of adsorption increased because a higher initial concentration led to a stronger driving force for mass diffusion [6].

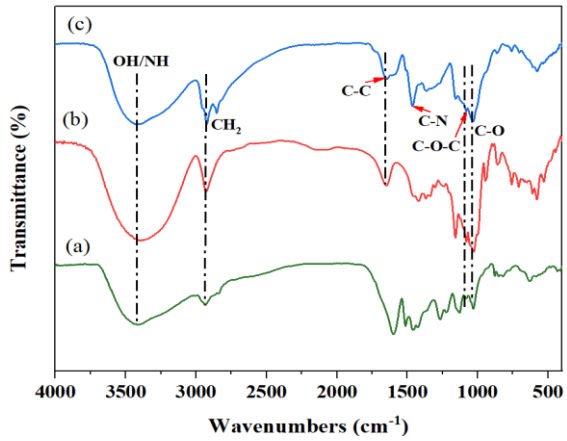

Figure 1. FTIR spectra of (a) lignin, (b) β-CD, and (c) microparticles.

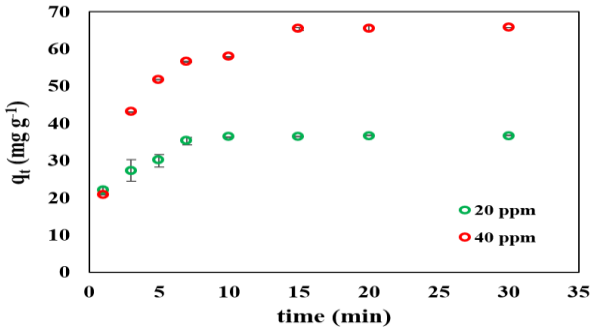

Figure 2. Adsorption kinetics MO on microparticles (C_0: 20 and 40 mg L^1, pH 6.5, dosage: 0.44 g L^{-1}, and time: 1-30 min).

Conclusions

A multifunctional adsorbent was synthesized by grafting β-CD on lignin using an epichlorohydrin crosslinker to remove MO. FTIR analysis exhibited the correctness of the synthesis of microspheres. Based on the adsorption results, the microspheres quickly remove the MO from the aqueous environment. The maximum adsorption capacity for 20 and 40 mg L^{-1} pollutant concentrations were 37 and 68 mg g^{-1}, respectively.

Acknowledgments

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