SYNTHESIS OF ACRYLIC-BASED β-CYCLODEXTRIN POLYMER: A POTENTIAL ADSORBENT SYSTEM FOR PHARMACEUTICAL RESIDUAL FROM WATER

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In this work, we report the synthesis of acrylic-based β-cyclodextrin (β-CD-Ac) monomers and their free radical polymerization. β-CD-Ac was synthesized by reacting β-CD and acryloyl chloride and subsequently was polymerized using azobisisobutyronitrile (AIBN). Both monomer and polymer products were characterized via ^{1}H-NMR and Solid-State NMR, respectively. The crosslinked polymer was prepared as a potential adsorbent system to tackle the problem of pharmaceutical residuals in the water. Hence, the capacity of the system was tested against the Metoprolol drug and was evaluated as a function of kinetics, the mass of adsorbent, PH, and concentration.

Keywords: β-cyclodextrin derivatives; Adsorption; β-cyclodextrin polymer; Wastewater treatment; Metoprolol

INTRODUCTION

Metoprolol (MTP), a frequently employed sympathetic blocking agent (as depicted in Figure 1), serves as a therapeutic agent for the management of elevated blood pressure and a spectrum of cardiovascular disorders, including myocardial infarction, arrhythmia, and hypertension. The pervasive presence of MTP in aquatic ecosystems can be attributed to its inherent resistance to hydrolysis and extensive utilization, rendering it a recurrent environmental contaminant. As a consequence of its deleterious implications for both ecological well-being and human health, it is imperative to effectuate the removal of this pollutant from wastewater streams prior to their discharge into ecosystems or aquatic bodies [1–4]. Hence, there exists a pressing need for the development of adsorbents characterized by facile separation properties from aqueous matrices and a heightened affinity for MTP, thereby affording enhanced removal efficiency [5–9].

Cyclodextrins (CDs) are a class of cyclic oligosaccharides obtained from the biodegradation of starch using glucanotrasferance enzyme. They can form guest-host inclusion complexes with vast numbers of molecules in their nanocavities. Cyclodextrins have a torus-shaped molecular structure with a relatively hydrophobic inner cavity and a hydrophilic outer surface and are composed of six (α-), seven (β-), and eight (γ-) units of D-glucopyranose. β-CD is the most widely available, least priced, and generally most useful. The CDs are widely used in encapsulation applications, an advantageous property in many industries such as drug delivery, biomedical devices, and water treatment applications. Hence, an adsorption system based on β-cyclodextrin will be prepared as an adsorption system to tackle the problem of MTP water pollution and pharmaceutical in general [10–13].

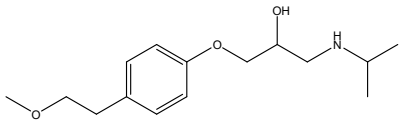

Figure 1. Metoprolol Structure

METHODOLOGY

The objective of this work is to prepare an adsorbent system based on β-CD for the removal of Metoprolol from water. The synthesis consists of two steps; the first is the preparation of a β-CD monomer, ie vinylated β-CD derivative which was approached by the acylation reaction of acryloyl chloride and β-CD to yield acrylate-β-CD with different degrees of substitution. The second step was to proceed with free radical polymerization of the monomer mixture using Azobisisobutyronitrile, which yielded an insoluble polymer. Furthermore, the monomer was prepared following the procedure described in the work by Slavkova et al. [14]. Both products of the monomser and polymer reaction were characterized by Solid-State NMR. Consequently, the adsorbent system was tested against MTP drug and was evaluated as a function of kinetics, the mass of the adsorbent, PH, and concentration. Finally, the data from

adsorbent batches were analyzed and fitted to adsorption models of kinetics and isotherm.

RESULTS AND DISCUSSIONS

The PH studies showed that the adsorbent system has a wide working PH, reaching removal efficiency of about 100% from 6 – 11 PH. The isotherm was fitted best to the Freundlich model, suggesting multilayer adsorption and a heterogeneous adsorption system (Figure 2). The adsorption capacity in kinetics studies reached equilibrium at 20 min with about 23 mg/g, and was fitted to the pseudo-second order adsorption model which indicates that the nature of the adsorption is more of a chemisorption rather than physisorption (Figure 3).

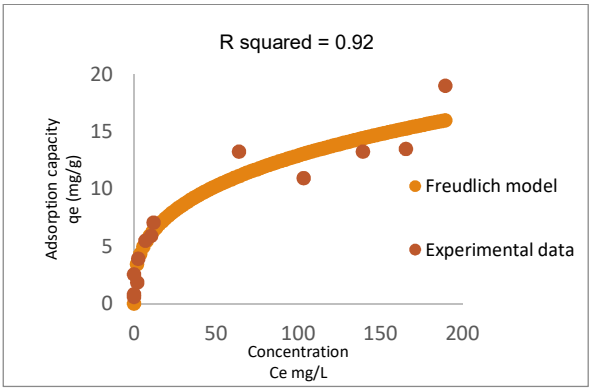

Figure 2. Adsorption isotherm study

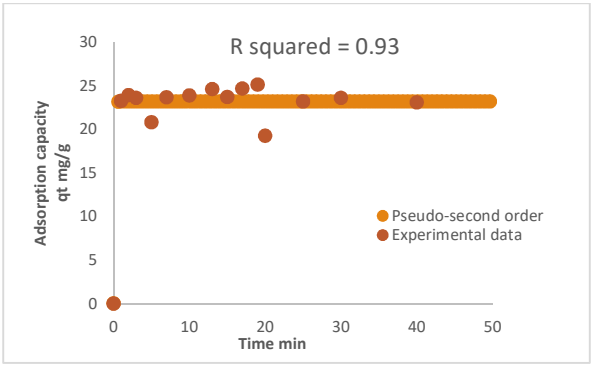

Figure 3. Adsorption kinetic study

CONCLUSION

An adsorption technology based on β-CD was developed in two steps and was characterized using solid-state NMR. The adsorption system achieved the highest adsorption capacity (23 mg/g) at 20 min in a wide range of PH.

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