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Cross-linked chitosan thin film coated onto glass plate as an effective adsorbent for adsorption of reactive orange 16

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ABSTRACT

Fabrication of an immobilized cross-linked chitosan-epichlorohydrine thin film (CLCETF) onto glass plate for adsorption of reactive orange 16 (RO16) dye was successfully studied using the direct casting technique. Adsorption experiments were performed as a function of contact time, initial dye concentration (25 mg/L to 350 mg/L), and pH (3–11). The adsorption isotherm followed the Langmuir model. The adsorption capacity of CLECTF for RO16 was 356.50 mg/g at 27 ± 2 °C. The kinetics closely followed the pseudo-second-order model. Results supported the potential use of an immobilized CLECTF as effective adsorbent for the treatment of reactive dye without using filtration process.

1. Introduction

Most of the textile, clothing, leather, cosmetics, paper, printing, and plastic industries use synthetic dyes as part of their production processes. Colored effluents from these industries contain several types of synthetic dyestuffs [1]. These dyes are considered hazardous, toxic, and nonbiodegradable and tend to suppress photosynthetic activity in aquatic systems by preventing the penetration of sunlight and oxygen, thereby posing serious environmental problem and direct destruction to the aquatic system when discharged into water stream [2,3]. Most of these dyes also have direct and indirect toxic effects on humans because they can cause allergies, dermatitis, cancer, jaundice, tumors, skin irritation, and heart defects [4], as well as genetic mutations [5].

Among the various traditional treatment methods of decontamination of effluents that contain dyes, the adsorption method is the best alternative and has been widely used to remove pollutants from effluents [6] because of its high performance, flexibility and simplicity of design, convenience of operation, and selectivity. Adsorption also does not result in formation of harmful by-products [7]. Activated carbon is the most effective adsorbent for dye removal from aqueous effluents because of its organized pore structure and rational surface area that leads to high adsorption capacity. However, its high cost has motivated the search for inexpensive, locally available, and effective biosorbents [1]. Among these biosorbents, chitosan is an abundant cationic biopolymer produced through a deacetylation process of the naturally occurring biopolymer chitin [8]. The presence of active adsorption sites, such as amino ($-NH_2$) and hydroxyl ($-OH$) groups, on the chitosan backbone explains why it is a special biopolymer and benchmark research material in various water treatment technologies. Given that the amino groups can be easily protonated in acidic solution, strong electrostatic attraction combined with higher adsorption affinity, especially toward an unlimited number of anionic dyes, can be achieved [8–11].

Similar to other polysaccharides, natural chitosan has low mechanical properties, has high swelling and shrinkage index, compressible at high operating pressure, and soluble in many organic acids [12]. Thus, chemical modification through a cross-linking process is an important step to enhance the mechanical resistance, reduce hydrophobicity, and stabilize chitosan at drastic pH [13]. To date, the widely used cross-linking agents that preferentially bind to the free amino and hydroxyl groups are glutaraldehyde (1, 5-pentanodial) and epichlorohydrine (1-cloro-2, 3-epoxipropane), respectively [14,15]. However, the irreversible cross-linking reaction between a free amino group and a dialdehyde bifunctional cross-linking agent, such as glutaraldehyde, leads to deceased adsorption performances involving a decrease in the content of free amine groups and a decrease in the accessibility to the internal sites or blockage of a number of adsorption sites [16–18]. Therefore, a cross-linked chitosan-epichlorohydrine in bead form has been

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successfully applied for the adsorption of various types of water pollutants, such as metal ions [15,19] and organic acid [20].

The application of chitosan and its cross-linked derivatives in the form of flakes, powder, and beads is significantly limited in scaling up the adsorption system for industrial applications because particle characteristics, such as size, shape, and density, can cause hydrodynamic pressure drop and column obstruction [8,10,21]. In addition, this method is costly and time consuming, and the separation step during analysis is difficult to perform. An alternative to overcome these obstacles is immobilization of chitosan and its derivatives on an inert solid support, such as a glass material. The immobilization process would result in less amount of chitosan sorbent being used, without requiring the separation step and affecting the overall pollutant adsorption capacity. Fabricating an immobilized biopolymer adsorbent system can also facilitate treatment of relatively large volume of pollutants with superior mass transfer and without requiring a filtration process.

Recently, numerous studies on adsorption of dyes have been conducted using immobilized chitosan onto glass plate [22,23] and glass beads [24]. However, using unmodified chitosan in wastewater treatment applications has several disadvantages, such as relatively high swelling index and considerable leachability that generates more organic intermediates. High chemical oxygen demand values can be obtained in the treated solution [25]. Moreover, separation of the adsorbents from the treated solution is difficult, and the adsorbents in powder, flakes, and beads forms are difficult to apply to continuous flow systems, and also limited to scale-up for industrial applications. Thus, to overcome these above problems, the present study was aimed to fabricate an immobilized cross-linked chitosan-epichlorohydrine thin film (CLCETF) deposited onto a glass plate without using any organic or inorganic binders as a promising immobilized adsorbent film. Furthermore, a new adsorption reactor based on the immobilized thin film concept was designed in this study. The rotation of the immobilized adsorbent film allows us to ensure efficient mixing with water pollutants and maximum mass transfer without using any filtration or separation processes. This paper discusses the results of a study on the evaluation of this new adsorption system with a non-conventional immobilized adsorbent film of CLCETF for reactive dye adsorption. Reactive orange 16 (RO16), as an anionic sulfonated reactive azo and non-biodegradable dye, was chosen as a model pollutant in this study.

2. Materials and methods

2.1. Chemicals and materials

A medium molecular weight of chitosan with a monomer molecular weight of 322 g/mol was purchased from Sigma-Aldrich. The degree of deacetylation calculated by infrared spectroscopy based on the published method was 68.20% [26]. Epichlorohydrine (≥98% [w/v] aqueous solution) was supplied by Fluka. RO16 was purchased from Sigma-Aldrich (CAS no.: 12225-83-1, chemical formula: $C_{20}H_{17}N_3Na_2O_{11}S_3$, MW: 617.54, dye content ≥70%, $\lambda_{max} = 493$). The molecular structure of RO16 is shown in Fig. 1. Analytical grade chemicals (CH_3COOH, HCl, and NaOH) were purchased from R&M Chemicals. All materials were used as received without further purification. Ultra-pure water (18.2 MΩ/cm) was used in this study.

2.2. Preparation and immobilization of CLCETF

The 45 mm × 80 mm glass plate was first rinsed with technical-grade acetone and left to dry inside an oven for 1 h at 60 °C. The cross-linked chitosan-epichlorohydrine viscous solution was prepared based on a previously published method [27]. A fixed weight, 3.65 ± 0.05 gm of the bubble-free, colorless, and transparent cross-linked chitosan- epichlorohydrine gel was directly cast onto the front face of the glass plate and allowed to dry for 4 days at room temperature (RT = 27 ± 2 °C). After complete drying, the weight of the immobilized CLCETF coated on a single face of the glass plate was 0.045 ± 0.05 gm (≈1.25 mg/cm^2). The same coating process was repeated to coat the back side of the glass plate and finally obtain a double-sided glass plate coated with CLCETF. The molecular structure of the CLCETF is shown in Fig. 2.

2.3. Characterization of CLCETF

Scanning electron microscope (Zeiss Supra 35 VP, Germany) was used to determine the thickness and surface morphology of CLECTF. Shimadzu infrared spectrometer was used for the Fourier transform infrared spectroscopy (FTIR) spectral analysis of CLECTF before and after adsorption.

The Brunauer–Emmett–Teller (BET) estimation of CLECTF was determined under N_2 gas at 77 K by using a surface area analyzer (Micromeritics, Model ASAP 2020, USA). The mechanical adhesion strength test of CLECTF to the surface of the glass plate was performed using the sonication method. In this experiment, a double-sided glass plate coated with CLECTF was placed in a 250 mL beaker containing water to completely cover the immobilized CLECTF onto the glass plate. The sonication process was performed for 5 s using an ultrasonic cleaner set, model WUC-D06H (50 Hz to 60 Hz) from Daihan Scientific Co., Ltd. The immobilized CLECTF was then kept inside an oven at 100 °C for 15 min. Thereafter, the sample was cooled to room temperature before weighing. The process was repeated up to a total of 30 s of sonication time.

2.4. Adsorption study

The CLECTF was placed upright inside a cylindrical glass cell with 120 mm height and 50 mm width. A plastic cover provided with a sample holder from the inside direction of the glass cell was connected to a top-mounted vertical motor for stirring process. The stirring rate was controlled using a speed regulator device. The initial volume of the dye solution and stirring rate were fixed at 250 mL and 100 rpm, respectively, throughout this study. All the experiments were performed at room temperature (27 ± 2 °C).

The CLECTF was stirred in the dye solution until equilibrium was achieved. At time $t = 0$ and equilibrium, the changes in RO16 concentrations were measured using a double-beam UV–vis-spectrophotometer (Shimadzu, Model UV 1601, Japan) at maximum wave length of 495 nm. After reaching equilibrium, the CLECTF was completely withdrawn from the dye solution without post-treatment filtration process; the remaining RO16 concentrations were similarly measured. The adsorbed amount at equilibrium, q_e (mg/g), was examined by Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of the dye at initial and equilibrium, respectively; V (L) is the volume of the solution; and W (g) is the mass of the CLCETF coated on both sides of the glass plate.

2.5. Effect of solution pH on RO16 adsorption

The effect of pH on the adsorption experiment was examined as a preliminary study to determine the suitable pH for adsorption of RO16 on CLECTF, which is helpful in understanding the pH dependence of biosorption. In this experiment, a 250 mL of 100 mg/L RO16 initial concentration was used, and the pH was intentionally