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Development of a polyaniline-lignocellulose composite for optimal adsorption of Congo red

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ABSTRACT

A polyaniline lignocellulose composite (PLC) was synthesized and used in the removal of Congo red (CR) from aqueous solution. The adsorption process showed good fits to both the pseudo-second-order and pseudo-first-order models and the Redlich Peterson isotherm. Boundary layer diffusion was the rate-limiting step. The adsorption was spontaneous and endothermic. The combined effect of pH and initial dye concentration was antagonistic; the combined effect of initial dye concentration and temperature was synergistic, while the combined effect of pH and temperature was reciprocal. The maximum CR adsorption capacity of PLC was evaluated as 1672.5 mg g^{-1}. The optimal removal was calculated as 99.85% at pH 4.29, initial dye concentration of 28.5 mg L^{-1} and adsorbent dosage of 0.69 g L^{-1}. The predicted removal capacity showed a good correlation to the experimental results. PLC has demonstrated a superior adsorption capacity to many other adsorbents reported and could be used as an efficient adsorbent for CR removal from industrial wastewater.

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1. Introduction

Several synthetic dyestuffs are used by different industries like food processing, rubber, paper, leather, plastics, cosmetic, printing, etc. as visual enhancer and to increase the attractiveness of the product [1]. About 10,000 types of dyes are commercially used worldwide and 5–10% of them remain unused and lost in industrial effluents [2,3]. These dyes are non-biodegradable and highly soluble in water. Hence they easily penetrate into the ecological chain [4–6]. These dyes also cause visual contamination to the landmass and the water which it comes into contact with.

Congo red (CR) is the most frequently studied dye with respect to removal from dye-containing aqueous solution as well as simulated wastewater [1,7–13]. Congo red is an anionic diazo dye formed by coupling tetrazotized benzidine with two molecules of napthionic acid [14]. Congo red easily couples with fibers and vastly used in textile industries [14]. Congo red is also found in effluents of rubber, paint and pigments, paper and plastics industries. Due to its structural stability, this dye is non-biodegradable.

Adsorption is the most attractive technology available for treatment of dye-containing wastewater. Researchers working on remediation of dye-containing wastewater reported different kind of adsorbents including metal oxides [11,15–18], graphene-based adsorbents [12,19–21], zeolites [22–25] and other adsorbents [8,10,13,26–28].

Researchers have used lignins and ligno cellulose (LC) materials derived from various forestry and agricultural sources in removing different pollutants from water and wastewater [29–34]. The benefit of choosing lignins as an adsorbent lies in their easy availability and versatility with respect to the available functional groups, which make it a broad-range biosorbent for different classes of water pollutants [35]. Lignin-based adsorbents are superior by far because of their oxygen binding sites, which can bind several pollutants. Modifying lignin-based adsorbents with polyaniline (PANI) offers further advantages such as lower cost, enhanced conductivity, mechanical flexibility and stability, which enhance the adsorption capabilities of these adsorbents [36]. Thus, the distinct advantage offered by PANI-LC composite (PLC) over other low-cost adsorbents is their enhanced adsorption capabilities.

Most of the studies reporting adsorption have not examined the interdependent relationship of the operating parameters of the adsorption process. The individual parameters and their interrelationships are important in optimizing the adsorption process

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according to the operating parameters and for understanding the mechanism of removal. Response surface methodology (RSM) is a statistical tool that correlates the inter-dependent relationship within the individual parameters associated with the adsorption process variables utilized in some adsorption studies [37,38].

In this present communication, we have extracted the LC from pinecones, coated it with PANI and exploited its anion-exchanging nature for the removal of the anionic dye CR from aqueous solution. The analysis of the adsorption process using isotherm and thermodynamic models evaluated the adsorption constants and the adsorption parameters. Furthermore, a three-factor central composite design (CCD) combined with RSM is applied to optimize the response as the removal percentage of CR using PLC (temperature, pH and the initial dye concentration are varied during the adsorption). Finally, the adsorption capacity of the different adsorbent reported by other researchers also compared with the present adsorbent for its adsorption capacity.

2. Materials and methods

Mature pine cones from Monterey Pine (*Pinus radiata*) collected from a local park in Pretoria, South Africa. Alkaline hydrolysis of the scales of the cones, followed by acidification derived the lignin. The dye CR (chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, CI = 22,120, FW = 696.7 and λ_{max} = 488 nm) was obtained from Sigma Aldrich, South Africa (analytical grade). Aniline (ANI) and ammonium persulfate (APS) required for polymeric coating of lignin particles was also bought from Sigma Aldrich South Africa (analytical grade). The acid and base (HCl and NaOH) used for pH adjustment were of reagent grade. All other reagents used in this study were of analytical grade.

A stock solution of CR (1000 mg L^{-1}) was prepared by dissolving 1000 mg of the dye in distilled water and making up the volume up to 1000 mL. The working CR solutions used in the experiments were prepared by diluting the stock solution to the required concentration using deionized water.

2.1. Preparation of LC

The LC was extracted by alkaline extraction from mature pinecones and the method is described in detail in our previous work [39]. The method adopted here involves a slight modification of the method of lignin isolation reported by Brdar et al. [31].

2.2. Preparation of PLC

The detailed method for preparation of PLC is described in our previous work [39]. In brief, the required amount ANI was dissolved in water acidified with HCl. The required amount of LC was dispersed in and the polymerization was initiated by adding APS. Finally, the dark green mass was isolated and washed with acetone to remove oligomers and unreacted ANI. The solid PLC was used for further experiments.

2.3. Characterization of the PLC

Point of zero charge (pH_{zpc}) of the material was determined by varying the zeta potential as a function of pH. The IR spectra of the PANI, LC and PLC were recorded with an attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectrometer (Perkin-Elmer Spectrum 100 spectrometer), equipped with an ATR accessory and a germanium crystal. Field emission scanning electron microscope (FE-SEM; LEO Zeiss SEM) was used to check the morphologies of PLC composite. Before taking the images, the samples were coated with carbon. The X-ray diffraction (XRD) spectra of LC and PLC were recorded at room temperature using a powder diffractometer (Rigaku, Japan) by employing the Cu Kα radiation (λ = 0.154 nm). The scans were conducted at a 2θ = 10–80° at a scan rate of 1° per minute. The Brunauer–Emmett–Teller (BET) surface area analyses of the LC and PLC were performed using a low-temperature N_2 adsorption–desorption technique with a Micromeritics ASAP 2020 gas adsorption apparatus, USA. The degassing was conducted at 120 °C for 5 h and the analysis was performed at −197.4 °C in a liquid nitrogen bath. The point of zero charge (pH_{zpc}) of the PLC was measured using Malvern zetasizer. UV–vis spectrophotometer (Shimadzu 1800) was used for colorimetric analysis of the dyes. The response surface methodology (RSM) was conducted using Design Expert 7 software.

2.4. Adsorption experiments

In order to study the effect of pH, the solution pH was varied from 2.0 to 10.0 using either HCl or NaOH. Here, 0.05 g PLC was added to 50 mL of CR solution (100 mg L^{-1}) in 200 mL glass bottles and thereafter placed into a thermostatic shaker water bath at 35 °C. The agitation speed and the time used were 200 ± 5 rpm and 24 h, respectively. As a control, a similar experiment was also performed at same pH conditions without adding the adsorbent. After 24 h of contact time, the samples were centrifuged and analyzed for residual CR concentration using a visible spectrophotometer at λ_{max} = 488 nm.

The kinetic experiments for the CR adsorption were conducted at pH 4.0 ± 0.1. Further details of how these experiments were conducted are provided in the supplementary section (Supplementary materials: M1).

For equilibrium isotherm studies, 0.05 g of PLC was added to 100 mL glass bottles containing 50 mL of CR solution with varying concentration of 50.0–1800.0 mg L^{-1}. Further details are available in the supplementary section (Supplementary materials: M2).

The amount of CR adsorbed per unit mass of the adsorbent was calculated using

$$q_e = \frac{q_i - q_r}{m} \quad (1)$$

where q_e is the adsorbed amount of CR per unit mass of the adsorbent (mg g^{-1}) and q_i and q_r are initial and residual amount (mg) of CR, respectively, added and remaining in solution. m is the mass (g) of the adsorbent added for the experiments.

2.5. Response surface methodology (RSM) and data analysis

The RSM is a statistical analysis tool that predicts and develops a regression model from the quantitative data obtained from some experiments. These model equations are to predict and optimize the operating conditions of some processes [40–43]. This optimization is thus useful in achieving an understanding of the mutual dependency of the variables, which actually governs the experimental system. In this study, RSM is used to understand how operating variables such as initial concentrations of the dye, pH of the solution and mass of the adsorbent (PLC) are inter-dependent on each other in adsorption process.

This study was performed by employing the widely utilized standard RSM design central composite experimental design (CCD). CCD study minimizes the total number of experimental runs in determining the response effect. The CCD of this study is related to three numerical factors (center points) and one α value of 1.682. In this case, the CCD of three independent variables, namely mass of the adsorbent (m, g), concentration of the influent dye solution (C, mg L^{-1}) and pH of the system is considered. The observed response is indicated as the removal percentage (R, %). Three levels were assigned for all the independent variables. Table 1 shows the coded variables (C, pH and m) with the actual values and the response (R).

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