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Preparation of cationic softwood kraft lignin and its application in dye removal

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ABSTRACT

The cationization of polymers was regarded as an effective method to improve their performance for various applications. In this work, the cationization of kraft lignin was investigated using glycidyl-trimethylammonium chloride (GTMAC) with kraft lignin in an aqueous solution under altered conditions. The conditions investigated were temperature, time, pH, GTMAC to lignin molar ratio, and lignin concentration. The optimized conditions based on charge density and solubility of cationic lignin were found to be 70 °C, 1 h, 12.5 pH, 2/1 GTMAC/lignin molar ratio, and 1.0 wt.% lignin concentration. The solubility of the resulting cationic lignin reached 90% in 1 wt.% lignin concentration and the charge density reached 1.10 meq/g under the optimized conditions. The cationic lignin was characterized and compared with unmodified kraft lignin using elemental analysis, Fourier Transform Infrared (FTIR) spectrophotometer, proton nuclear magnetic resonance (^{1}H NMR) and thermogravimetry (TGA) analysis in order to confirm the success of the grafting reaction. The cationic lignin was used as a flocculant for dye removal (Remazol Brilliant Violet, Reactive Black, and Direct Yellow) from model wastewater.

1. Introduction

Lignin is the second most abundant terrestrial biopolymer in the world after cellulose and its content in wood ranges from 20% to 30% on a dry basis. In most pulp mills, it is considered a byproduct of the chemical pulping processes [1]. Kraft process is currently the leading chemical pulping technique used worldwide. Black liquor (i.e. spent liquor of kraft pulping) is currently combusted to recover the pulping chemicals, and its lignin is utilized as fuel at the mill [2]. However, kraft lignin has the potential to be used in the production of value-added products [3]. In recent years, kraft lignin has attracted much attention for its potential use because of its renewability, nontoxicity and biodegradability. The utilization of kraft lignin has been limited due to its physicochemical properties such as water insolubility and limited charged groups on its structure (i.e. a low charge density) [4,5]. Therefore, to widen its application, it is essential to improve its water solubility and charge density.

Wastewater from dyeing and finishing processes in the textile industry has strong color, a high level of toxicity and is generally non-biodegradable. The removal of dyes from the wastewater becomes necessary in order to protect environment. Usually, the cationic flocculants are extensively used in dye-containing wastewater treatment to coagulate and flocculate the negative charged dye molecules. Inorganic coagulants such as ferric chloride, aluminum sulfate and poly aluminum salts are widely used due to their low costs. These inorganic coagulants, however, have to be used in high concentrations, which result in a large volume of sludge. The high concentration of aluminum or ferric ions remaining in the treated wastewater

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may have an adverse effect on human health [6]. For this reason, cationic polymeric flocculants, especially natural cationic polymers, such as cationic starch derivatives and chitosan derivatives, have been studied in the past [7,8].

For cationization of natural polymer, amination is one of the various methods that can improve the water solubility and charge density of natural polymers [9]. As presented in the literature, polymers, including starch or chitosan, were used as flocculants for wastewater after cationization [7,8]. Glycidyl trimethylammonium chloride (GTMAC) has previously been used to produce cationic chitosan in the absence of any catalyst [10], or in the presence of acid or base as a catalyst [8,9,11]. The same cationic reagent was also used for preparing cationic starch in an alkaline aqueous solution for removing anionic dyes from aqueous solutions [7,12,13]. In other reports, it was found that the increase in the degree of substitution (DS) improved the water solubility of starch and chitosan, and increased their flocculation capability significantly (by 80%) [9,14]. In addition, cationic hemicelluloses with the DS in the range of 0.1–0.3 [15,16], cationic cellulosic fibers with the DS of 0.19–0.92 [17], cationic cotton with the grafting yield of 30% [18] and cationic nanocrystalline cellulose with the charge density of 2.75 meq/g [19] were synthesized using GTMAC under alkaline environment.

In the past, a lignin-based cationic polyelectrolyte was produced by grafting dimethylamine, acetone and formaldehyde onto enzymatically hydrolyzed and hydroxymethylated cornstalk lignin and used as a flocculant for dye removal [20]. It was observed that, by adding 70 mg/L of cationic lignin-based polymer with 2.55 meq/g charge density, 95% of acid black dye was removed from the dye solution with the concentration of 100 mg/L [20]. The Laszlo group used kraft lignin with 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHMAC), which was followed by a peroxidase polymerization to synthesize insoluble cationic lignin, and the product was used for the decolorization of orange dye from wastewater. The results showed that the peroxidase-treated aminated kraft lignin was capable of removing 92% of dyes from the solution containing 0.2 mmol/L orange II. [4]. In addition, lignin rich fibrous materials were grafted with GTMAC in order to produce products with cationic charge densities [21,22]. Although there have been some developments in this area, the cationization of kraft lignin with GTMAC has not yet been studied fundamentally, and is the first objective of this work. In this method, the GTMAC treatment was conducted in an aqueous solution. Compared to the organic solvent used in the past, the method used to cationize lignin in this study is (1) simpler, as it is a one-step reaction, and (2) more industrially attractive, as the reaction was conducted in an aqueous solution, thus there is no need for solvent recovery in the present method. The produced lignin is water soluble and its dye removal efficiency is very high.

Softwood kraft lignin was modified using GTMAC as a cationic reagent under alkaline aqueous environment. The effects of the amination conditions on the solubility and charge density of products were discussed in details. The structure, elemental and thermal properties of cationic lignin was assessed by FTIR, TGA, NMR and GPC. The modified cationic lignin was then used as a flocculant for removing dye from a model wastewater solution. The purpose of this work was to (a) present a novel method to produce water soluble cationic kraft lignin by grafting GTMAC onto kraft lignin backbone, (b) investigate how the modification conditions affect the solubility and charge density of kraft lignin, and (c) to evaluate the performance of this cationic lignin as a flocculant for removing anionic dyes from aqueous solutions. The main novelty of this work was to introduce a simple method to improve the water solubility and charge density of kraft lignin, and to develop a new biodegradable flocculant for removing anionic dyes from wastewater.

2. Experimental

2.1. Materials

Softwood kraft lignin was supplied by FPInnovations from its pilot plant facilities in Thunder Bay, ON. The kraft lignin was produced via LignoForce™ technology [23]. Glycidyl-trimethylammonium chloride (GTMAC), 75 wt.% in water, polydiallyldimethyl-ammounium chloride (PDADMAC, 100–200 kg/mol), 20 wt.% in water, sodium hydroxide (reagent grade), trimethylsilyl propanoic acid (99.7%, TMSP), Remazol Brilliant Violet 5R (V5), Reactive Black 5 (B5), and Direct Yellow 50 (Y50) were obtained from Sigma–Aldrich company. Potassium polyvinyl sulfate (PVSK, 100–200 kg/mol, 97.7 wt.% esterified) was provided by Wako Pure Chem. Ltd., Osaka, Japan. All chemicals were applied without further purification. Dialysis membrane (Cut off of 1000 g/mol) was obtained from SpectrumLabs. Table 1 provides the properties of dyes used in this study. In this Table, the molecular weight, UV absorption wavelength and standard curves used for determining concentration of dyes are listed.

2.2. Cationic modification of kraft lignin

Water was mixed with 1 g of kraft lignin in a 250 mL three-neck round-bottom glass flask, while stirring at 100 rpm. A 0.2 M NaOH solution was then gradually added into the solution to adjust the initial pH to 12.5. The concentration of lignin in the aqueous solution was controlled to match a desired percentage. The temperature of the system was then increased to the desired temperature, and subsequently various amounts of GTMAC were added to the system while stirring at 100 rpm. Upon completion, the solution was submerged in cold water for 20 min and neutralized using sulfuric acid to pH 7. The mixture was then poured into membrane dialysis tubes in deionized water, and maintained for 48 h in order to remove any unreacted GTMAC and other impurities. In the first 24 h of dialysis, water was changed every 4 h, and in the second 24 h, water was changed every 6 h. After dialysis, the solution containing cationic lignin (i.e. product) was dried in an oven at 105 °C for 12 h. The dried samples were considered as the main product and kept for analysis.