



# Efficient extraction of lignin from black liquor via a novel membrane-assisted electrochemical approach



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## ABSTRACT

A novel membrane-assisted electrochemical approach for the precipitation of lignin from black liquor has been developed. Without the addition of acid or CO<sub>2</sub>, the pH in the black liquor solution was lowered to 4.7 due to water electrolysis, leading to pH-dependent lignin precipitation. Simultaneously, Na<sup>+</sup> ions traversed the membrane to the cathode compartment to balance the OH<sup>-</sup> that was generated in the cathodic reaction, facilitating caustic recovery. Owing to lignin precipitation and oxidation, greater than 70% of the chemical oxygen demand (COD) was removed, which surpasses the efficacy of COD reduction via conventional acidic precipitation. In addition, it has been demonstrated that the pH change was significantly influenced by the electrolyte condition in the system. With decreasing cation concentration in the cathode compartment, Na<sup>+</sup> transport through the membrane was facilitated, which inhibited competitive H<sup>+</sup> transport and improved the performance of the electrochemical cell. This novel approach may serve as a promising alternative for the cost-effective extraction of lignin and recovery of NaOH from the black liquor with modulation feasibility.

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## 1. Introduction

Black liquor is a highly viscous aqueous waste that is generated by the alkaline Kraft process in wood pulping, consisting of inorganic pulping chemicals as well as organics from extracted wood constituents [1]. The solid content of black liquor varies between 15% and 40% by weight, whereas lignin makes up 30–45% of the total solid composition [2,3]. Lignin is an amorphous complex polyphenolic plant constituent that is the second most abundant plant derived polymer (after cellulose) [4]. Although million tons of lignin is produced every year in black liquor, only a minimal amount is separated through direct extraction from plants [5]. In the Kraft process, over 90% of lignin is simply burned to recover the chemicals from black liquor. Extract some lignin from black liquor would reduce the load of the Kraft recovery system, and it thus to increase pulping capacity. On the other hand, the presence of lignin in wastewater streams significantly increases the chemical oxygen demand (COD) and biological oxygen demand (BOD), which are responsible for serious damage to the environment and human health [6]. Conversely, there is strong potential for deriving great economic value from the lignin in black liquor, which

may be employed as raw material for the production of vanillin, phenols, activated carbons, etc., or be converted to combustible fuel gases such as hydrogen, methane and CO via gasification [7].

Due to the great importance of lignin in environmental and economical consideration, substantial efforts have been made for its extraction from black liquor using various biological, chemical and electrochemical techniques [8–10]. Biological technologies involve the use of fungi and bacteria through aerobic and anaerobic schemes [10], although the efficiency of the microorganisms is limited by the presence of toxic compounds within the black liquor. Supercritical fluid extraction and solvent extraction have also been attempted in the removal of low molecular weight lignin from black liquor; however, these techniques suffer from high operating costs [11]. Recently, economically attractive methods have been achieved by acid precipitation (particularly sulfuric acid) and CO<sub>2</sub> precipitation owing to their capacities for color and COD reduction as well as cost effectiveness [12]. These processes have developed due to the fact that pH is the dominating parameter that controls the solubility of Kraft lignin, where lignin proceeds to precipitate when the pH of the black liquor solution is below 10.5 [13–15]. However, the highly acidic filtrate and the associated operation problems limit the wide application of acid precipitation [16]. Meanwhile, although it has been identified that lignin precipitation from black liquor via CO<sub>2</sub> acidification is superior to acid precipitation as it has lower operating costs and provides a precipitate that is more

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easily filtered, its chief drawback is that the pH cannot be reduced any lower than 8 [17]. In this regard, acid precipitation can produce higher lignin yields than its CO<sub>2</sub> counterpart, as it may attain a much lower pH.

Electrochemical techniques have been employed for organics separation from black liquor, due to the fact that it can generate sufficient flocculant in situ to reduce the chemicals that are employed and subsequently disposed of [18,19]. Electrolysis treatment was carried out on black liquor at different electrode potentials. Complete COD removal was achieved at a higher potential treatment with the oxidation of lignin at the anode and hydrogen production at the cathode; however, it required significantly higher energies spanning from 17,700 J at 1.5 V to 149,000 J at 12 V/g of COD removal [20]. Furthermore, membrane-assisted electrolysis (also called electrodialysis) was employed as a pretreatment of black liquor [21]. However, the majority of these investigations focused on the removal of COD and caustic recovery, rather than lignin extraction [21,22].

As mentioned above, the solubility of lignin in black liquor can be determined to a significant degree via its pH, providing a potential solution for improving membrane-assisted electrochemical processes. It has been suggested that the pH might be modulated by electrochemical reactions in conjunction with a cationic exchange membrane, leading to the caustic recovery and lignin precipitation from black liquor. In this regard, the aim of this study is to develop a membrane-assisted electrochemical method for the treatment of black liquor, wherein a Nafion membrane was employed due to its excellent operation stability [23]. This approach may serve as a promising alternative for overcoming the disadvantages of existing conventional black liquor treatments.

## 2. Experimental

### 2.1. Chemicals

The chemicals utilized in this study included iridium chloride hydrate IrCl<sub>3</sub>·3H<sub>2</sub>O (Pressure Co.), tetrabutyl orthotitanate (Fluka), isopropyl alcohol (Sigma-Aldrich), tantalum pentachloride Ta<sub>2</sub>Cl<sub>5</sub> (NOAH Technologies Corporation), sodium hydroxide (Anachemia), sodium sulfate (Fisher Scientific), sulfuric acid (Aldrich), and diethyl ether (Aldrich), all of which were analytical grade chemicals. Acetonitrile (Caledon Laboratory, Ltd.) was HPLC grade. Pure water (18 MΩ cm) was obtained from a NANO pure<sup>®</sup> Diamond<sup>™</sup> UV ultrapure water purification system. The lignin sample used for comparison was prepared from black liquor by passing carbon dioxide (CO<sub>2</sub>) through a black liquor solution that was provided by a local pulp and paper mill. The precipitated

lignin was subsequently purified by rinsing with a dilute sulphuric acid solution. The solutions used in this research were prepared by dissolving the corresponding chemicals in ultrapure water.

### 2.2. Fabrication and characterization of Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> electrodes

The Ti/TiO<sub>2</sub>-IrO<sub>2</sub> electrode was prepared by a thermal decomposition technique [24]. The Ti substrate strips were cleaned in an ultrasonic bath of acetone for 10 min followed by 10 min in distilled water, and then etched in 18% HCl at approximately 85 °C for 30 min. Meanwhile, the coating solution was prepared by mixing the tantalum precursor (0.14 g Ta<sub>2</sub>Cl<sub>5</sub> dissolved in 7.5 ml isopropanol) and the iridium precursor (0.30 g IrCl<sub>3</sub>·3H<sub>2</sub>O dissolved in 2.5 ml of ethanol). Subsequently, the coating solution was painted onto the Ti substrates using the brush technique, and was repeated until a 30 g/m<sup>2</sup> oxide coating load was obtained. Finally, the electrodes were annealed at 450 °C for 1 h. The surface morphology and composition of the coatings were characterized by a JEOL 5900LV scanning electron microscope (SEM), which was equipped with X-ray energy dispersive spectrometry (EDS).

### 2.3. Electrochemical investigations of lignin solution and black liquor

A VoltaLab (PGZ-301 Dynamic-EIS Radiometer) potentiostat was employed for the present electrochemical investigation. A U-shaped electrochemical cell as shown in Fig. 1 was segmented into the anode and cathode compartments, which were separated by a Nafion<sup>®</sup> N117 membrane (4.5 cm in diameter × 183 μm thick, DuPont Company). The fabricated Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> electrode (2.0 cm<sup>2</sup>) was employed as the working electrode, and the reference electrode was Hg/HgO electrode. A Pt mesh (10 cm<sup>2</sup>) counter electrode was cleaned prior to each experiment via flame annealing and quenched with pure water. The electrolytes for electrochemical study were deaerated with ultrapure argon gas prior to measurements. Cyclic voltammograms (CVs) for the different electrolyte systems were recorded out in the electrode potential region between -0.80 and 1.45 V at a scan rate of 50 mV/s. Electrochemical impedance spectra of mass transport effect were measured from 100 kHz to 7.5 mHz with an a.c. voltage amplitude of 10 mV. For a comparison to the electrochemical treatment, the acidification of the 10% 50 ml black liquor solution was carried out by the dropwise addition of a 4 M sulfuric acid solution with rapid stirring. The pH was monitored until a pH of 4.7 was attained.

The durability and permeability properties of the Nafion membrane were measured by monitoring its proton conductivity after several cycles of the consecutive electrochemical treatment

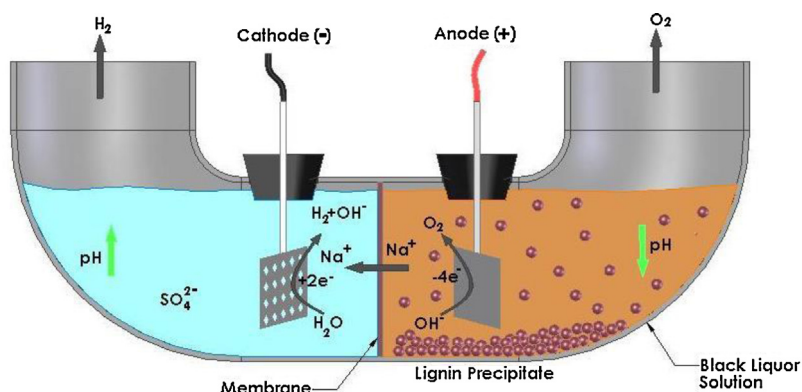


Fig. 1. Schematic diagram of the experimental setup designed for the membrane-assisted electrochemical treatment of black liquor.

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