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ARTICLE

EFFECTS OF NaCl AND H2O2 CONCENTRATIONS ON LIGNIN REMOVAL USING ELECTROCOAGULATION METHOD

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ABSTRAK
Metode elektrokoagulasi telah banyak digunakan untuk berbagai proses pengolahan air limbah. Pada penelitian ini, set alat elektrokoagulasi sederhana dirancang menggunakan tiga pelat elektrode yang disusun secara paralel. Sel elektrokoagulasi ini kemudian digunakan untuk pengolahan larutan model lignin yang merupakan simulasi dari limbah industri pulp dan kertas. Pengaruh dari jenis elektrode, waktu elektrolisis, densitas arus, pengaruh penambahan NaCl dan H2O2, pH dan jarak antar elektrode terhadap penghilangan lignin dalam larutan dipelajari. Hasil penelitian menunjukkan bahwa penambahan NaCl meningkatkan efisisiensi elektrokoagulasi dari 75% ke 98%. Namun, penambahan H2O2 dan interval pemberian dosis tidak mempengaruhi efisiensi elektrokoagulasi.

Kata Kunci: elektrokoagulasi; penghilangan lignin; limbah industri pulp; Natrium klorida..

ABSTRACT
The electrocoagulation (EC) method has been widely investigated for various water treatment processes. In this research, a simple EC apparatus has been constructed using three plates of electrodes arranged in parallel mode. The EC was then applied for the treatment of synthetic lignin solution as a simulated pulp mill wastewater. The effects of types of electrodes, electrolysis time, current density, pH and inner electrodes distance on the removal of lignin from the aqueous solution were investigated. It was found that the addition of NaCl significantly improved the EC efficiency from 75% to 98%. In contrast, the addition of H_2O_2 and the dose interval did not seem to improve the EC efficiency.

Keywords: electrocoagulation, lignin removal, pulp mill wastewater, sodium chloride

INTRODUCTION

The pulp mill wastewater has been characterized for its complexity and high load of organic and inorganic contaminants [1]. One of the concerns associated with pulp and paper mill wastewater is the persistent colour of the treated wastewater. Components in pulp and paper mill wastewater that can cause the colour include cellulose, hemicelluloses, lignin, pulping process additives and microorganisms developing in the wastewater stream. Oxidative reactions of these components may result in coloured degradation products, usually containing carbonyl (C=O) groups and carbon-carbon double bonds (C=C) [2]. Among these components, lignin and depolymerized lignin derivatives may be responsible for most of the colour that develops in pulp and paper mills wastewater, even long after treatment [3].

Currently lignin, which is largely produced at pulp and paper mills, is used without isolation as a source of process energy [4]. Lignin is the second most abundant biopolymer on earth comprising up to 25% of the dry weight of hardwoods and over 30% of softwoods [4, 5]. Lignin in wood, giving a pale yellow colour, is a high molecular weight polymer. During chemical pulping, fibers are liberated by dissolving enough lignin from the middle lamella of wood such that the fibers are freed in an undamaged form from the wood matrix. The reactive chemicals travel in aqueous solution via the cell lumens, through the cell walls and into the middle lamella, progressively dissolving lignin [6].

In the pulping processes, lignin is converted into thio-lignin and alkali-lignin in the Kraft process and into lignosulfonates in the sulphite process. Colour in the Kraft mill effluents is typically from chlorolignin compounds generated from the bleaching stage of the manufacturing process. Their persistence in the treated effluent is particularly due to the presence of carbon-to-carbon linkage of a biphenyl type and to phenylpropane β-aryl ether linkages, from amongst the prominent structures which are known to exist [3].

Electrocoagulation (EC) involves the destabilization of suspensions, emulsions, or dissolved contaminants in the aqueous media by the utilization of electricity. The EC technique is considered to be one promising technique to be applied in water treatment processes due to its simple operating procedure and minimal quantity of precipitates produced. A simple EC cell contains an electrolyte cell with one anode and one cathode [7, 8]. The applications of EC technique in various water treatment processes have been widely reported. Ugurlu et.al reported the removal of 70% of lignin from pulp and paper mill effluent using electrocoagulation technique [9]. Vepsäläinen described the effect of pH, electrolysis time, electrodes distances, material of the electrodes, and temperature on the efficiency of the electrocoagulation processes [10, 11].

Electrocoagulation method is often coupled with other methods, such as oxidation process. This so-called electro-Fenton process is based on the formation of hydroxyl radicals that facilitates the degradation of organic contaminants. The success of this degradation process depends on both the rate of hydroxyl radical formation and the effective contact between the hydroxyl radicals and the organic compounds. The hydroxyl radical is responsible for the degradation of organic pollutants into CO_2 and H_2O [12]. In this research, a simple EC apparatus has been constructed using aluminum and iron plates as sacrificial electrodes. To test its efficiency, the EC cell was then applied for the treatment of lignin solution as simulated pulp mill wastewaters. Various operating conditions, such as pH, applied voltage, and electrodes distance were investigated. The effects of NaCl and H_2O_2 dose intervals on lignin removal efficiencies was also reviewed.

METHODS

2.1 Preparation of EC cell

Metal plate with the thickness of 1.5 mm was cut into three parts as shown in Fig. 1. These tree plates were then arranged in parallel with electrodes distance varying from 1 - 2 cm. This EC design has been reported elsewhere [13, 14].

2.2 Electrocoagulation method

One liter of lignin solution having concentrations of 300 ppm was placed in the EC cell. Upon constant stirring speed (200 rpm), the cell was then turned on for the desired electrolysis time. The resulting solution was let to set, filtered and analyzed for lignin removal using a UV-VIS Shimadzu 1240 spectrophotometer and a calibration curve (not shown). Variations of electrolysis time, current density, pH and electrodes distance were investigated. The lignin removal parameter was calculated using Equation 1.

$$Removal\ (\%) = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Where C_0 is concentration before coagulation and C is concentration after coagulation, both in ppm.

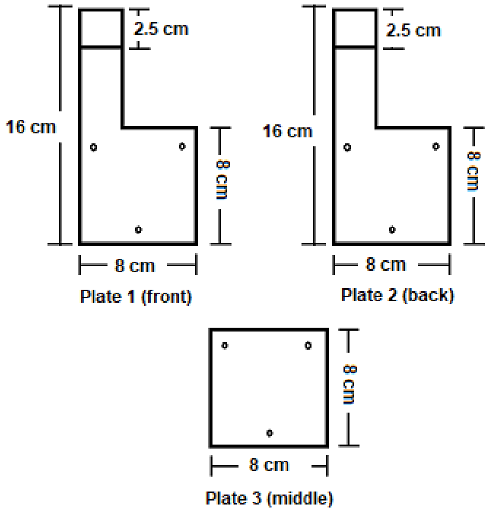


Figure 1. EC electrodes and EC cell

RESULTS AND DISCUSSIONS

3.1. The effects of pH

From Fig. 2(a-b), it is indicated that at pH equal to 7 and 8, the removals of lignin from the aqueous solution were optimized. The pH lower than 7 was not investigated due to the instability of lignin solution.

Upon the application of current, sacrificial electrodes dissolved generating active coagulant species. For aluminum, at pH 7, insoluble aluminum hydroxide ($Al(OH)_3$) was optimally formed enabling the removals of lignin molecules via the adsorption mechanism onto its surface [15]. The formation of insoluble aluminum hydroxide took place via following mechanism.

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \quad (2)$$

$$Al^{3+}(aq) + H_2O(l) \rightarrow Al(OH)^{2+}(aq) + H^+(aq) \quad (3)$$

$$Al(OH)^{2+}(aq) + H_2O(l) \rightarrow Al(OH)_2^+(aq) + H^+(aq) \quad (4)$$

$$Al(OH)_2^+(aq) + H_2O(l) \rightarrow Al(OH)_3(aq) + H^+(aq) \quad (5)$$

At higher pH, the formation of $Al(OH)_4^-$ ions that did not contribute to the coagulation process predominated [8, 9]. Following mechanism occurred.

$$3H_2O(aq) + 3e^- \rightarrow \frac{3}{2}H_2(g) + 3OH^-(aq) \quad (6)$$

$$2Al(s) + 6H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g) \quad (7)$$

The dissolution of iron was more complex due to the two possible oxidation states of iron species: Fe^{2+} and Fe^{3+} [16]. Depending on the pH and dissolved oxygen content available, Fe^{2+} may be oxidized to Fe^{3+}, and may potentially undergo further hydrolysis reaction to form $Fe(OH)_3$.

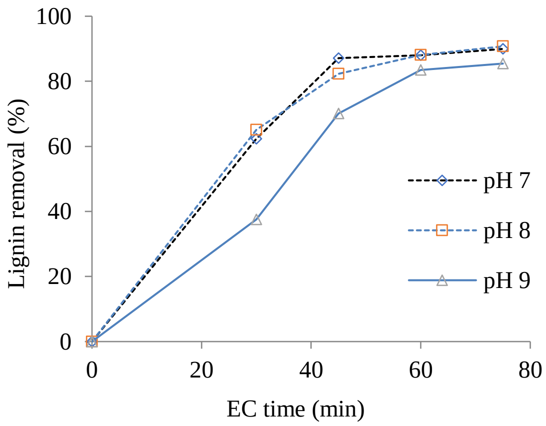
$$Fe(aq) \rightarrow Fe^{2+}(aq) + 2e^- \quad (8)$$

$$Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) \quad (9)$$

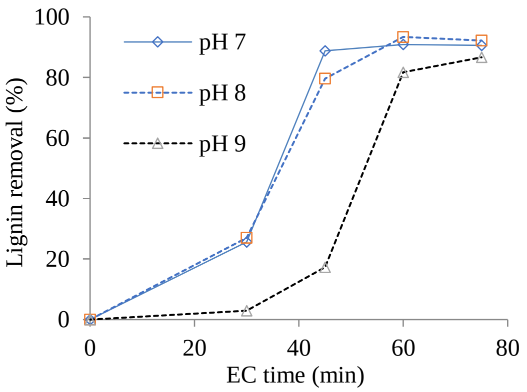
$$Fe^{3+}(aq) + 3H_2O(l) \rightarrow Fe(OH)_2(s) + 3H^+(aq) \quad (10)$$

Meanwhile, the reaction at the cathode was as follow.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad (11)$$



(a)

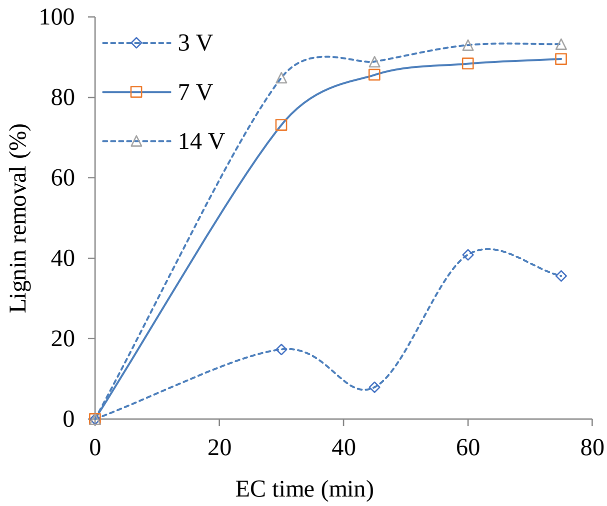


(b)

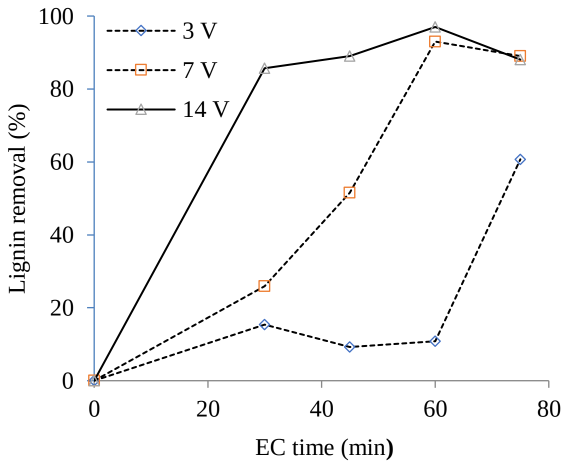
Figure 2. Effect of solution pH on EC efficiency: (a) iron and (b) aluminum

3.2. Effect of applied voltage

The high voltage applied to the electrocoagulation system resulted in a more efficient removal of lignin (Fig. 3). The higher the voltage resulted in more ions released to the solution [17]. The metal ions underwent a sequential hydrolysis reaction producing active species for coagulation and/or adsorption. Furthermore, another mechanism-via flotation- may increase the removal of lignin from solution [18]. The removal of lignin via flotation mechanism was due to the upward flux of some gases resulted from reactions in cathodes and anodes [19].



(a)

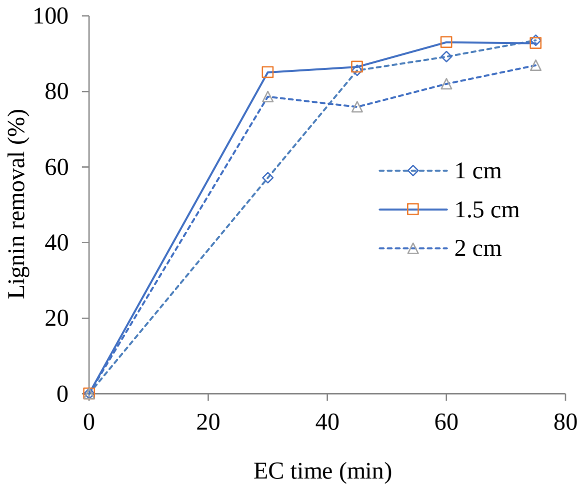


(b)

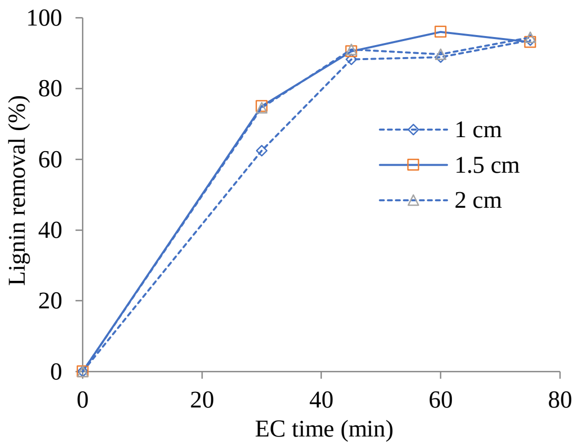
Figure 3. Effect of applied voltage on EC efficiency: (a) iron and (b) aluminum.

3.3. Effect of electrode distance

To investigate the effect of electrode distance on the lignin removal efficiency, tests were carried out for 1, 1.5 and 2 cm of electrode distances. It was suggested that the increase in electrode distance may increase the resistance to mass transfer and may slow down the kinetics of both charge transfer and metal oxidation (Fig.4). However, for both iron and aluminum, the optimum electrode distance was at 1.5 cm. The lower rate of lignin removal for electrode distance of 1 cm was unexplained. Compared to pH and applied voltage, the effect of the electrode distance on the treatment efficiency was considered to be insignificant. Similar result was also reported elsewhere [20].



(a)



(b)

Figure 4. Effect of electrode distance on EC efficiency: (a) iron and (b) aluminum.

3.4. Effect of NaCl concentrations

The effect of NaCl concetrations on the lignin removal efficiency was evaluated by the addition of three variations of concentration, ie 0.5, 1, and 1.5 g/L. The constant parameters of electrocoagulation were EC time of 75 min, initial pH of solution = 7, and applied voltage of 10 V. Fig.5 shows the effect of NaCl concentration variation on lignin removal efficiency. It can be seen that the lignin removal efficiency without the addition of NaCl was only 74.65%. Upon addition of 0.5 g/L and 1 g/L of NaCl solutions, the efficiencies increased to 98.17% and 98.43%, respectively. However, the efficiency decreased to 96.31% upon addition of NaCl 1.5 g/L.

The Na^+ and Cl^- ions in the solution increased the conductivity of the solution, which was proportional to the current produced, hence improved the active coagulant produced. However, at higher concentrations of NaCl the efficiency started to decrease, this was probably due to the increase of OH^- ions at this point that initiated the formation $Fe(OH)_4^-$ which is non-active species for coagulation.

Additionally, the presence of Cl^- ions may also help to degrade lignin and to reduce the passive layer formation on the surface electrode. The Cl^- ions can be oxidized to form Cl_2 and OCl^- ions. The OCl^- ion was reported to be a powerful oxidation agent that can oxidize lignin.

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \quad (12)$$

$$Cl_2(g) + H_2O(aq) \rightarrow HOCl(aq) + H^+(aq) + Cl^-(aq) \quad (13)$$

$$HOCl(aq) \rightleftharpoons OCl^-(aq) + H^+(aq) \quad (14)$$

$$Fe(OH)_2(s) + HOCl(aq) \rightarrow Fe(OH)_3(s) + Cl^-(aq) \quad (15)$$

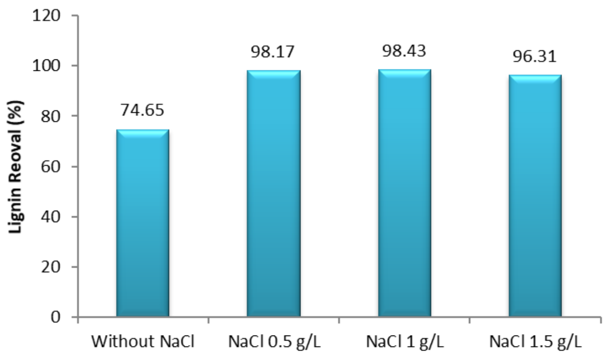


Figure 4. Graph CNPV/TIC with tax variation against year

Thus, NaCl is useful both to increase the conductivity and also to act as an oxidation agent that helps to remove pollutants in solution [12, 21, 22]. The effect of higher concentration of NaCl seems to be insignificant, indicating that small addition of NaCl in solution is sufficient to facilitate better lignin removal.

3.5. Effect of H_2O_2 Dose Intervals

H_2O_2 in the solution may initiate the Fe oxidation process, hence facilitates the coagulation of Fe ions [23]. Therefore, the effect of the H_2O_2 dose intervals to assist better lignin removal was studied. In this study, the dose of H_2O_2 used was 0.66 g/L. The electro-Fenton process involves the formation of free radicals that generated from the reaction between Fe^{2+} ions (at the anode) with H_2O_2 (added to the reactor) by Eq. 16-19. The hydroxyl radical is a reactive oxidant with E° = 2.8 V that is able to degrade lignin macromolecules in solution [24]. Additionally, the formation of $Fe\text{-}OOH_2^+$ and Fe^{3+} will assist the coagulation process during electrocoagulation. However, the result indicated that the addition of H_2O_2 does not have much effect on the removal efficiency (Fig.6). This may be due to the concentration of lignin in a solution was already small. Additionally, the Fenton process was reported to be optimum at pH 3. At pH < 3, the efficiency decreases due to the formation $[Fe(H2O)_6]^{2+}$ complex that slowly reacts with peroxide. While at a high pH, hydrogen peroxide forms a stable $[H_3O_2]^+$ ion which reduces the reaction between peroxide and Fe^{2+} ions [25, 26].

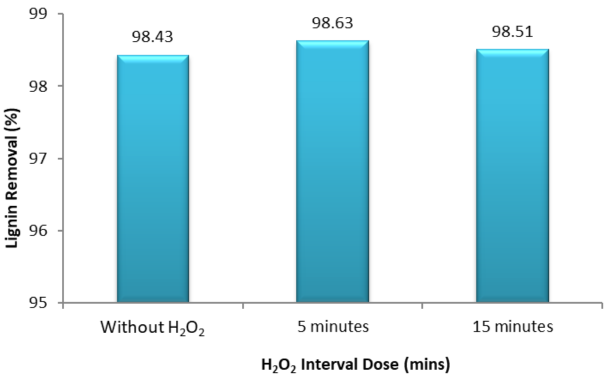


Figure 5. Effect of H_2O_2 Dose Intervals on EC efficiency

CONCLUSIONS

A simple electrocoagulation apparatus was successfully constructed using iron and aluminum as sacrificial electrodes. The performance of the apparatus was tested for lignin removal in aqueous solution. It was found that lignin removal of over 90% was achieved upon following optimum operating conditions: 60 minutes of electrolysis time, pH 7, applied voltage of 7 V, and electrode distance of 1.5 cm. Increasing solution pH to above 7 was not beneficial for lignin removal due to the formation of inactive species for coagulation and/or adsorption. Increasing the applied voltage to 14 V only increase the lignin removal slightly, hence the more economical option was to choose 7 V as the optimum voltage. Compared to pH and applied voltage, the electrode distance was regarded as the most insignificant factors that contributed to the lignin removal efficiency. Furthermore, the addition of NaCl was significantly improved the EC efficiency from 75% to 98%. In contrast, the addition of H2O2 and the dose interval did not seem to improve the EC efficiency.

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