Decolorization of melanoidins by electrocoagulation process using aluminium electrodes

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Decolorization of melanoidins by electrocoagulation process using aluminum electrodes

The decolorization of melanoidin was studied with a batch electrocoagulation (EC) process using aluminum electrodes. The effects of conductivity (500-3000 µS/cm), initial pH (4.2-8.2), current density (2.5-7.5 A/m²), initial melanoidin concentration (100-800 mg/L), and operating time (0-60 min) were investigated. The results obtained from the EC process were extremely efficient and we were able to achieve a decolorization efficiency of >98% at pH 4.2, 5 A/m², 2500 µS/cm, 100 mg/L in the 10th min. The decolorization performance was dependent on initial pH values since the lower pH values led to faster reactions and higher decolorization efficiency. Melanoidin in the EC process was removed by precipitation and charge neutralization at pH<6.5, and both adsorption and sweep coagulation by amorphous Al(OH)₃(s) occurred at pH>6.5. The operating cost was calculated as 0.0096 €/m³.

Keywords: Melanoidins; Decolorization; Electrocoagulation; Operating Cost

1. Introduction

Melanoidins are found in some wastewaters such as distilleries and fermentation plants that use molasses [1]. There is knowledge about melanoidins structural composition in literature [2]. Melanoidins are high molecular weight nitrogenous brown polymers and formed during the non-enzymatic browning reaction (Millard reaction) between amino compounds and carbohydrates [3]. The existence of melanoidins in water causes a dark brown color. When untreated, melanoidins prevent the penetration of sunlight when discharged into a water resource, thus it affects dissolved oxygen concentration and photosynthetic activity of marine plants, and creates an anaerobic condition thereby killing most of the aerobic marine plants and animals. Hence, melanoidins in wastewater require treatment before its safe disposal into the environment [4].
Removals of wastewaters containing melanoidin have been studied by several methods such as oxidation of ozonation, UV/H₂O₂ and electrochemical process [5-8], adsorption [10] and coagulation-flocculation [3,11]. Conventional biological processes are effective in removing biochemical oxygen demand from wastewaters containing melanoidin. However, the brown color remains or even darkens in the biologically treated effluent due to repolymerization of pigments [12]. Moreover, the biological processes have drawbacks such as longer treatment time, requirements of additional nutrient and pure cultures. Some of the above methods are not successful due to lower efficiencies of color removal. These methods also require high reagent dosages, high operating costs and generate a large amount of sludge [3]. Therefore, the electrochemical treatment methods like electrocoagulation (EC) may be used effectively for the removal of organic pollutants in terms of lower operating time and costs.

In the past decades, the EC process has been widely and successfully introduced to treat numerous wastewaters including tannery [14,15], textile and dying [16,17], distillery and fermentation [18,20], olive mill [21], dairy processing [22], potato chip manufacturing [23], pasta and cookie processing [24], poultry slaughterhouse [25], and so on.

Recently, the EC process has also been used for the removal of residual color and COD from wastewaters containing natural melanoidins such as molasses, alcohol distillery and yeast process [18-20] but no studies have focused on removal mechanism associated with EC from synthetic melanoidin. The purpose of this study was to conduct experimental investigations on the decolorization of synthetic melanoidin in the EC process. The effects of several operating parameters such as initial pH, current density, conductivity, initial melanoidin concentration and operating time on the decolorization
efficiency were investigated, and removal mechanisms were discussed based on experimental results. The operating costs in the EC process were also calculated.

2. Description of EC process

The EC process is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. Three main processes occur during EC: (i) electrolytic reactions at electrode surfaces, (ii) formation of coagulants in the aqueous phase, and (iii) adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation or flotation. Therefore, the mechanisms of EC are highly dependent on the chemistry of the aqueous medium [26,27]. When aluminum is used as an electrode material, the reactions are as follows:

At the anode:

$$\text{Al}_{(s)} \rightarrow \text{Al}^{3+}_{(aq)} + 3e^- \quad (1)$$

$\text{Al}^{3+}$ and hydroxyl ions are generated by electrode reactions: Eqns. 1 and 3 to form various monomeric species such as $\text{Al(OH)}^{2+}$, $\text{Al(OH)}^{+}$, $\text{Al(OH)}^-_{(aq)}$ at low pH values and polymeric species such as $\text{Al}_2(\text{OH})^{4+}_{(aq)}$, $\text{Al}_6(\text{OH})^{15+}_{(aq)}$, $\text{Al}_7(\text{OH})^{17+}_{(aq)}$, $\text{Al}_8(\text{OH})^{20+}_{(aq)}$, $\text{Al}_{12}(\text{OH})^{24+}_{(aq)}$, and $\text{Al}_{13}(\text{OH})^{34+}_{(aq)}$ are transformed initially into $\text{Al(OH)}_{3(aq)}$ and finally polymerized to $\text{Al}_n(\text{OH})_{3n}$ (Eqns. 2 and 3) in the solution [17,26]:

$$n\text{Al(OH)}_3 \rightarrow \text{Al}_n(\text{OH})_{3n} \quad (2)$$

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_{3(s)} + 3\text{H}^+ \quad (3)$$

At the cathode:
\[ 3\text{H}_2\text{O} + 3\text{e}^- \rightarrow \frac{3}{2}\text{H}_2 + 3\text{OH}^- \]  \hspace{1cm} (4)

On the other hand, the cathode may be chemically attacked by hydroxyl ions generated during \( \text{H}_2(\text{g}) \) evolution at high pH values [27]:

\[ 2\text{Al} + 6\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{Al(OH)}_2^- + 3\text{H}_2 \]  \hspace{1cm} (5)

The formation rates of the different species in the EC process also play an important role in the decolorization process. Several interaction mechanisms are possible between organic molecules such as humic substances or melanoidins and hydrolysis by-products and the rates of these depend on the pH of the aqueous medium and types of ions present. There are four removal mechanisms of humic substances in literature, which are, precipitation, charge neutralization of negatively charged colloids by cationic polymeric hydrolysis products, adsorption on amorphous \( \text{Al(OH)}_3(\text{s}) \) and sweep coagulation [3,11,28,29].

3. Materials and methods

3.1. Preparation of synthesis melanoidin

Synthetic melanoidin was prepared with the method as given in the literature [30]. 1 M glucose (99% purity, Merck), 1 M glycine (99% purity, Merck) and 0.5 M \( \text{Na}_2\text{CO}_3 \) (99% purity, Merck) were dissolved in a liter of distilled water. Then the solution was autoclaved at 121 °C for 3 h and following this the resulting brown solution was dialyzed against distilled and deionized water for 2 weeks by a membrane (Cellu Sep H1, Membrane Filtration Products, Inc, USA) having 10 kDa MWCO. The nondialyzable fraction was dried at 60 °C for 24 h. The synthesis of melanoidin was performed and yield was around 10%. Low molecular substances from the powder
product were removed with ether in a Soxhlet extractor. Solutions of known concentrations were prepared by dissolving the powdered melanoidin in distilled water.

3.2. Experimental set-up and procedure

The EC studies were carried out in a batch electrolytic reactor made from plexiglass material with dimensions of 100 mm × 100 mm × 130 mm. Four aluminum electrodes having a 240 cm² total effective electrode area in the reactor were used as cathodes and anodes with effective dimensions of 80 mm × 50 mm × 3 mm. The electrodes were situated 0.5 cm apart and connected to monopolar parallel mode. The electrodes were placed in the reactor and solutions were mixed at 300 rpm in the EC reactor.

The synthetic melanoidin solutions were prepared using distilled water. The pH and conductivity were adjusted to a desired value. In each run, a 0.85 L melanoidin solution was placed into the EC reactor and then the current density was adjusted to a desired value by a digital DC power supply (TDK-Lambda Genesys model; 50 V-30A) operated at galvanostatic mode and the experimental operation was started. In order to determine the decolorization efficiencies, samples were taken periodically from the reactor during the EC process. After each experimental run, the electrodes were dipped into solutions of HCl (35%) and hexamethylenetetramine (2.8%) to remove the oxide and/or passivation layers from the electrodes [26]. The electrode surfaces were rinsed several times with deionized water, dried and weighed before and after each experiment. All experiments were performed at 25 °C.
3.3. Instruments and analysis procedures

Decolorization of melanoidin was measured using a UV-Vis spectrophotometer (Perkin-Elmer 550 SE) at 475 nm that characterized brown colour [7]. The decolorization efficiency ($R_m$) in experiments was calculated from the following equation:

$$R_m(\%) = \frac{(C_i - C_f)}{C_i} \times 100$$  \hspace{1cm} (6)

where $C_i$ and $C_f$ were the initial and present concentrations of the melanoidin in the solution (mg/L), respectively.

The samples were analyzed for chemical oxygen demand (COD) and total organic carbon (TOC) according to Standard Methods [31]. COD was measured by the closed reflux titrimetric method, TOC levels were determined through combustion of the samples at 680 °C using a non-dispersive IR source (Tekmar Dohrmann Apollo 9000).

The CHN elemental composition of nondialyzable melanoidin was determined using a model Thermo Finnigan Flash EA 1112 Series. The compositions of synthetic melanoidin were given as: 42.7±1.6% C, 5.6±0.3% H, 6.6±0.3%N and 6.47±0.2 %C/N.

The infrared spectra of the samples were recorded in the range 4000–650 cm$^{-1}$ on a PerkinElmer Spectro 100 T spectrophotometer using a pellet technique. Fifty scans were collected for each sample at a resolution of ±3 cm$^{-1}$.

A Malvern zeta potential and size analyzer (Malvern Instruments, Zetasizer Nano Series, UK) was used to determine the zeta potential of the solution during the EC process.
The conductivity measurement was carried out using a conductivity meter (Elmetron CX-401 model). The conductivity of the solutions was adjusted by adding NaCl (99.5%, Merck). The pH of the solutions was measured by a pH meter (WTW inolab pH 720 model) and adjusted by adding 0.1 M NaOH or 0.1 M H₂SO₄ (Merck).

4. Results and discussion

The effects of the parameters on the decolorization efficiency of melanoidin by the EC process were studied to determine for the optimum operating conditions. The decolorization mechanism of melanoidin in the EC process was discussed with the experimental results. The operating costs for the optimum operating conditions were also calculated.

4.1. Effect of initial pH on decolorization

pH is an important parameter influencing the removal of melanoidin in the EC process. Water solubility of melanoids can be increased by altering the pH of the solution and colour intensity of melanoidin changes. In general, the brown color intensifies at a high pH, and the bleaching of melanoidin can be observed at low pH values [3]. Thus, melanoidin solutions with pHᵢ 2.0-12.0 without the EC process were adjusted to examine colour (absorbance) changes. Absorbances of the solutions were measured at 475 nm. Polymerization degree of melanoidin solution changed with pHᵢ. The decolorization efficiency at pH 2.0-4.2 decreased from 72.0% to 5.0% (Figure not depicted) due to the precipitation of the melanoidin (depolymerization or decolorization). The studies in the literature revealed that the isoelectric point of melanoidin was 2.5. At pH 2.5, melanoidin has a net zero charge [3]. However, as the pH was increased; the net electrical charge of melanoidin became more negative. At such pHᵢ, melanoidin may acquire a net zero charge consequently leading to its
precipitation from the solution. These results may be attributed to be the predominance of an undissociated form of melanoidin at pH,$i<pK_a$ of the melanoidin, which is 3.5 [3]. The $pK_a$ generally serves as the starting point of the melanoidin precipitation from the solution. Decolorization efficiency at pH, 8-12 decreased from 0.0 to -5.0% (polymerization or colorization). Increasing solution pH,$i$ enhanced the degree of polymerization. There was a stable region between pH,$i$ 4.2 and 8.0 for the decolorization.

The EC experiments were performed in the pH,$i$ range of 4.2-8.2 at 5 A/m$^2$, 2500 µS/cm and 100 mg/L. As seen in Fig. 1a, the decolorization efficiency depended on both operating time and pH,$i$. The pH,$i$ values affected the removal of melanoidin. For example, over 98% of the decolorization efficiency was realized at 10, 21, 25 and 30 minutes with pH,$i$ 4.2, 5.2, 6.2, and 8.2, respectively. The results indicated that the decolorization performance was dependent on pH,$i$ values, because the lower pH values led to faster reactions and higher decolorization efficiency. Almost complete removal of melanoidin was observed after 10 min of the operating time. The final pH,$f$ of the solution was around 6.5, close enough to neutral for discharge to the environment. The decolorization efficiency at pH,$i$ 4.2 was faster than that of the rest of pH,$i$ (Fig.1a). When pH,$i$ was arranged at 4.2, 5.2, 6.2 and 8.2 for the decolorization of melanoidin, final effluent pH,$f$ was observed as 6.5 at 10 min, 7.9 at 21 min, 8.3 at 25 min and 8.9 at 30 min, respectively (Fig.1b). On the other hand, the amounts of aluminium ions generated within the EC reactor according to Faraday’s law at these optimum operating times were 3.95x10$^{-3}$ kg m$^{-3}$ for pH,$i$ 4.2, 8.29x10$^{-3}$ kg/m$^3$ for pH,$i$ 5.2, 9.87x10$^{-3}$ kg/m$^3$ for pH,$i$ 6.2 and 11.84x10$^{-3}$ kg/m$^3$ for pH,$i$ 8.2, respectively. As seen in Fig.3b for pH,$i$ 4.2, the final pH,$f$ of the decolorized solution varied in between 4.2 and 7.5. As an example, pH,$f$ was 6.4 at 10 min.

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Figure 1. (a) Effect of pH$_i$ on decolorization and (b) change of final pH$_f$ during the EC process (Conditions: 5 A/m$^2$, 100 mg/L, 2500 µS/cm).

4.1.1. Decolorization mechanism of melanoidin molecules

Melanoidin molecules (MMs) resemble humic substances, being acidic, polymeric and highly dispersed colloids, which are negatively charged due to the dissociation of carboxylic, hydroxyl and phenolic groups. Melanoidin consists of both hydrophobic (neutral and acidic) and hydrophilic components such as -OH, -NH$_2$, >C=O, -COOH and –NH-CH=O [32-34]. MMs are connected with hydrogen bonds between functional groups. The most active functional groups are carboxyl and phenolic hydroxyl groups, and dissociation of H$^+$ relates to the pH of the solution. When pH is acidic, carboxyl and hydroxyl ions exist in –COOH and –OH forms respectively. When pH is alkaline, they can exist in –COOH$^-$ and –O$^-$ forms [11,34]. When pH is alkaline, MMs take more negative charge and they consequently need more positive charge to neutralize the negative charge. Melanoidins are soluble in dilute alkaline solution but precipitate from an acidified solution (pH<2.5). The acidic nature of melanoidins is usually attributed to the ionization behaviour of –COOH and phenolic –OH groups. Hydrophobic groups of MMs were primarily adsorbed on Al-hydroxydes flocs in the EC process. Thus, it was anticipated that formation of less polar and more hydrophobic molecules would lead to enhanced adsorption on Al-hydroxydes. Adsorption at interfaces, depending on the adsorbate and the interface, was influenced by hydrophilic, electrostatic, hydration and hydrophobic interactions [8,12].

Table 1. The possible mechanism of EC with Al electrode at various pHs

<table>
<thead>
<tr>
<th>pH</th>
<th>Possible Mechanism</th>
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<td>1</td>
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On the other hand, formation rates of the different species played an important role in the decolorization process of melanoidin in the EC process. Several interaction
mechanisms, which discussed in detail by Migo et al. [3], were possible between MMs and hydrolysis product as and the rates of these depend on pH of the medium and types of ions present (Table 1). Monomeric/polymeric-Al-species and Al(OH)$_3(s)$ between pH 4-9 and Al(OH)$_4^−$ in pH >9 were formed during the EC process. Formed amorphous Al(OH)$_3(s)$ (sweep flocs) flocs had a large specific surface area that can absorb some soluble organic compounds such as MMs onto its surface [12,13,35]. Amorphous Al(OH)$_3(s)$ has the minimum solubility within the pH range of 6.5-7.8 [27]. The monomeric and polymeric-Al species were explained in equations 7-11 with respect to change in pH values:

**Charge-neutralization and precipitation:**

\[
\text{MMs} + \text{Monomeric – Al} \rightarrow (\text{MMs} – \text{Monomeric – Al})_{(s)} \quad (\text{pH 4-5})
\]

\[
\text{MMs} + \text{Polymeric – Al} \rightarrow (\text{MMs} – \text{Polymeric – Al})_{(s)} \quad (\text{pH 5-6.5})
\]

**Adsorption and sweep coagulation (pH >6.5):**

\[
\text{MMs} + \text{Al(OH)}_{3(s)} \rightarrow (\text{MMs} – \text{Al(OH)}_{3(s)}) + \text{Al(OH)}_{3(s)}
\]

\[
\text{MMs} + \text{Al(OH)}_{3(s)} \rightarrow (\text{MMs} – \text{Polymeric – Al})_{(s)} + \text{Al(OH)}_{3(s)}
\]

\[
\text{MMs} + \text{Al(OH)}_{3(s)} \rightarrow \text{MMs} – \text{Polymeric – Al} – \text{Al(OH)}_{3(s)} + \text{Al(OH)}_{3(s)}
\]

The decolorization of MMs and the final pH$_f$ of the solution within 10 min of operating time rose to 98.4% and 6.4 when initial pH$_i$ was 4.2. The decolorization results (Figs. 1) showed that the MMs with the species were effectively removed by mechanisms of precipitation and charge neutralization between pH$_i$ 4.2-6.5. Charge
neutralization was achieved when the net negative charge of MMs was neutralized by the positively charged Al\textsuperscript{3+} ions, thus allowing their agglomeration and settling to take effect. The removal mechanism was controlled by adsorption and sweep coagulation due to formed amorphous Al(OH)\textsubscript{3(s)} flocs, which occurred after effluent pH, 6.4 and >10 min of operating time (Fig. 1). The decolorization efficiencies were lower at pH values (5.2-8.2) until the 15th min of operating time since functional groups in MMs became more negative and there were not enough positive polymeric species present for charge neutralization and precipitation. Therefore no precipitation was observed at these pH ranges. After 20 min of operating time, the decolorization efficiency values were increased to >98% which enhanced floc formations and the effluent pH was increased to over 7.70. The removal mechanism was controlled at these pH ranges by adsorption and sweep coagulation.

4.1.2. Zeta potential measurements

Colloids are maintained in suspension by electrostatic repulsion between particles. Zeta potential provides an effective measurement of the charge on a particle. The addition of aluminum coagulant can suppress the electric double layer around the colloidal particle, thus encouraging the pollutant [13]. The relationship between zeta potential and colloidal stability also proves to knowledge regarding the decolorization mechanism of melanoidins.

As seen in Fig.2a, the values of zeta potential firstly decreased sharply until the 4th min of the operating time. The polymeric Al species and amorphous Al(OH)\textsubscript{3(s)} (theoretical amount of Al at 12 min; 4.74 mg/L) were formed by OH\textsuperscript{-} ions after the 4th min of the operating time. This was probably due to an increase in negatively charged ions formed at cathode. For this reason zeta potential started to increase, then MMs
were governed by precipitation and charge neutralization from polymeric Al-species and finally were adsorbed on Al(OH)$_3$ (s). Moreover, carboxyl or amino groups of MMs interacted with hydroxyl ions generated at cathode during the EC process and negatively charge –COO$^-$ was formed and caused the lowering zeta potential especially at the first stage of the EC process. When enough amounts of coagulant were produced at anode, coagulant was interacted with negatively charge fragments of MMs which led to an increase in zeta potential. After EC, zeta potential of treated wastewater decreased with an increase in the final pH$_f$ (Fig.2b). This pH dependent phenomenon was probably due to the deprotonation (-COO$^-$) of acidic organic functional groups such as carboxylic acid (-COOH) in MMs and formation of Al(OH)$_4^-$ . The results of zeta potential measurements also supported the proposed mechanisms.

Figure 2. Zeta potential measurements (a) melanoidin solutions during the EC process and (b) melanoidin solutions at different pH values after the EC process (Conditions: pH$_i$, 4.2, 2500 $\mu$S/cm, 2.5 A/ m$^2$).

4.1.3. FTIR spectrum analysis

The infrared spectra of sludge from the melanoidin were recorded in the 4000-650 cm$^{-1}$ range (Fig.3a). The changed and shifted functional groups were extremely important to understand the changing of melanoidin structure before and after the EC process.

Figure 3. (a) FTIR of sludge and (b) ratios of absorbance before and after the EC process.

For the structural characterization, the samples were analyzed. The stretching frequencies at 3426, 2940, 1721, 1658, 1641, 1566 and 1408 cm$^{-1}$ were corresponding to the presence of an alcoholic (-OH), -C-H stretching, ketonic (=C=O), aldehydic (-
COH), carboxylic (-COOH), carbon carbon double bound (-C=C-) and asymmetric –NO₂ group, respectively (Table 2). As seen in Fig.3b, ratios of absorbances before and after the EC process versus wavenumber, the peak at 1739 cm⁻¹ was conjugated C-C double bonds corresponding to deep brown color during the EC process.

**Table 2.** FTIR of melanoidin and sludge produced during EC process

### 4.2. Effect of current density

Current density and operating time are important operational parameters for the decolorization and cost of the removal processes [20,36]. The decolorization efficiency as a function of the operating time was studied at current density values in the range of 2.5-7.5 A/m² (Fig.4). As seen in Fig.4, a steep increase in melanoidin removal at only >2.5 A/m² was observed and then became gradual. The maximum decolorization efficiencies for the 14th min of operating time in the current density range 2.5-7.5 A/m² were 96.9%, 99.1% and 99.2%, respectively. However, as the current density was increased from 2.5 to 7.5 A/m², the optimum operating time was decreased from 10 to 4 min.

Figure 4. Effect of current density on decolorization efficiency of melanoidin

(Conditions: pH 4.2, 100 mg L⁻¹, 2500 µS cm⁻¹).

This can be attributed to high current densities; the extent of anodic dissolution (Faraday’s law, Eqn. 12) increased positively charged polymeric Al-species resulting in increased melanoidin removal.

\[
E_{LC} = \frac{i t M_w}{z F v}
\]  

\text{(12)}
Where $ELC$ is electrode consumption (kg/m$^3$), $t_{EC}$ (s) is operating time, $z$ is the number of electrons involved in oxidation/reduction reaction for Al, $z = 3$. $M_w$ is the atomic weight of anode material ($M_w = 26.98$ g/mol), $F$ is the Faraday’s constant (96485 C/mol) and $v$ is the volume (m$^3$) of the solution in the EC reactor.

According to Faraday’s law, the charge passed to the solution was directly proportional to the amount of electrode dissolved. Energy consumptions ($ENC$) given in Eqn. 13 are also an extremely important parameter in the EC process like all other electrolytic processes. $ENC$s (kWh/m$^3$) were calculated using the following equation:

$$ENC = \frac{U \cdot i \cdot t_{EC}}{v}$$  \hspace{1cm} (13)

where $U$ is cell voltage (V).

Values of $ENC$ and $ELC$, charge loading ($Q$), current efficiency and removal efficiency ($R_m$) with respect to different current density and operating time were illustrated in Table 2. 97% of the decolorization efficiencies were obtained at 2.5, 5.0 and 7.5 A/m$^2$ for 10, 5 and 4 mins, respectively (Table 3). The values of $ELC$ and $ENC$ were increased as the current density was increased.

Table 3. Decolorization efficiency of melanoidin with different current density

In the EC process, the amount of the aluminum ion produced was proportional to the charge loading. The increase in the decolorization efficiency of melanoidin was expected when charge loading ($F/m^3$) increased since it affected the decolorization efficiency.

$$Q = \frac{i \cdot t_{EC}}{F \cdot v}$$  \hspace{1cm} (14)
It was expected that experiments on the EC process may provide the optimal conditions to generate the amounts of Al\(^{3+}\) ions and Al hydroxides needed for the decolorization of melanoidin. Table 3 showed the effect of charge loading on the decolorization efficiency and on the loss of aluminum mass via dissolution in the EC process. The increase of charge loading increased the amount of Al electrode dissolved in the EC process and improved the decolorization efficiency. >98% of decolorization efficiency at 2.5, 5.0 and 7.5 A/m\(^2\) was achieved at the 10th, 5th, and 4th min of operating times. Charge loading at the optimum operating conditions was found to be ≥ 0.439 F/m\(^3\). The decolorization efficiency and loss of Al electrode mass were ≥98% and 0.0044 kg/m\(^3\).

The Faradic yield or current efficiency (\(C_E\)) is defined as the ratio of the actual electrode consumption to the theoretical value. The \(C_E\) calculation was based on the comparison of experimental weight loss of aluminum electrodes (\(C_e\)) and theoretical amounts of aluminum dissolution (\(C_t\)) according to Eqn.12 by the electrode consumption difference before and after the EC process. \(C_E\) at different current densities was calculated using the following equation:

\[
C_E(\%) = \frac{C_e}{C_t} \times 100
\]  

\(C_E\) at different current densities and operating times were changed in the range 103-115% (Table 3). This difference in mass may be explained by the “corrosion pitting” phenomenon which caused holes and practically led to a metallic Al loss on the electrode surface [37].
4.3. Effect of conductivity

The conductivity of melanoidin solutions affects voltage between electrodes, energy and electrode consumptions due to potential caused by solution resistance reduces by decreasing the distance between the electrodes [16,26]. Sodium chloride (NaCl) was used to obtain the desired conductivity in the EC process. Increasing solution conductivity using NaCl could significantly reduce the adverse effects of bicarbonate and sulphate anions. Fig.5 showed the effect of conductivity on decolorization efficiency of melanoidin between 500-3000 S/cm. From Fig.5a, the decolorization efficiency was increased from 95.4% to 98.2% with an increase in conductivity of the melanoidin for operating time of the 5th min. In addition, the energy consumption was decreased from 0.0377 to 0.0261 kWh/m³ with increasing conductivity (Fig.5b). Voltages were decreased from 3.2 to 2.9, 2.5, 2.3, 2.2 with increasing conductivity. Energy consumption was considerably reduced to almost a third with changes in the conductivity. The electrode consumption was varied from 0.0127 to 0.0038 kg/m³ in the conductivity range of 500-3000 µS/cm. The higher decolorization efficiency with lower energy and electrode consumptions was obtained for melanoidin solutions at about 2500 µS/cm. Our results showed a good agreement with literature studies [16,26,36]. 2500 µS/cm was selected as the optimum conductivity value and used in the all experiments.

Figure 5. Effect of conductivity on decolorization efficiency (Conditions: 100 mg/L, pH 4.2, 5 min; 5 A/m²).

4.4. Effect of initial melanoidin concentration

The melanoidin solutions with different initial melanoidin concentrations (C₀, 100-800 mg/L) were treated in the EC process. The decolorization efficiency was decreased from 98.9% to 94.8% with an increase in concentration of melanoidin from 100 to 800 mg/L.
at the 55th min. When initial melanoidin concentrations were 100, 400 and 800 mg/L, values of COD for melanoidins were 128, 464 and 924 mg/L which had some relation with \( C_0 \) as \( C_{\text{COD}} \) equal to approximately \( 1.20 \times C_0 \) (Fig. 6). The removal efficiencies of color and COD for different initial concentrations and minimum operating times were 98.4% and 97% for 100 mg/L at 10 min, 98.1% and 91% for 400 mg/L at 40 min and 94.8% and 90% for 800 mg/L at 60 min, respectively. Moreover, the electrode consumptions were increased from 0.0096 to 0.0742 kg/m\(^3\) in the concentration range of 100-800 mg/L at optimum operating times.

Figure 6. Effect of initial melanoidin concentration on decolorization and COD efficiencies (Conditions: 2500 \( \mu \)S/cm, pH \( i \) 4.2, 5 A/m\(^2\)).

It is quite clear that under the optimum experimental conditions, lower melanoidin concentrations and the lower operating times resulted in a higher percentage of the decolorization efficiency. This was likely due to the formation of insufficient polymeric Al-species produced by the electrode to coagulate the greater number of MMs at higher concentrations, which led to a decrease in the decolorization and COD efficiencies. In addition, at higher initial melanoidin concentrations, Al(OH)\(_3\)(s) formed near the surface, fouls the electrodes and intermediate products formed in the solution, which blocked the electrode active sites. Both of these factors gave rise to a decrease in the decolorization and COD efficiencies. Briefly, increasing concentration of melanoidin resulted in the increase of anionic charges and coagulant demand in the EC process to maintain effective removal of MMs.

4.5. Operating cost of melanoidin decolorization

Operating cost (\( OC \)) is quite important economical parameter in the EC process. The \( OC \) includes material cost (mainly electrodes), utility cost (mainly electrical energy), as
well as labor, maintenance and other fixed costs. In this study, energy, electrode material and chemicals costs for the decolorization of the melanoidin were taken into account as major cost items in the calculation of the $OC$ as €/m$^3$ [25]:

$$\text{Operating Cost (OC)} = aENC + bELC + cCC \quad (16)$$

Costs for $ELC$ (kg/m$^3$) in Eqn. 12 and $ENC$ (kWh/m$^3$) in Eqn. 13 were calculated. $a$, $b$ and $c$ given for the Turkish market in June 2011 were electrical energy price (0.072 € per kWh), electrode material price (1.65 € per kg Al) and chemical costs ($CC$, 0.73 €/kg for NaOH, 0.29 €/kg for $H_2SO_4$ and 0.15 €/kg for NaCl), respectively.

Table 4 showed operating cost values at optimum operating conditions for the decolorization efficiency of melanoidin. In the EC process, total $OC$ increased with increasing current density and operating time since energy and electrode consumptions were related to these parameters. $OC$s at 2.5-7.5 A/m$^2$ were changed from 0.0084 to 0.0115 €/m$^3$. $OC$s at 500-3000 µS/cm were decreased from 0.0238 to 0.0083 €/m$^3$ since energy and electrode consumptions decreased at constant current density. $OC$s were also increased from 0.0096 to 0.0742 €/m$^3$ with increasing initial concentration (100-800 mg/L) due to an increasing operating time for higher decolorization efficiency and electrode dissolution in the EC process. As a result, the $OC$ for the decolorization efficiency of melanoidin at the optimum conditions (pH 4.2, 5 A/m$^2$, 2500 µS/cm and 10 min for 100 mg/L) was 0.0096 €/m$^3$.

Table 4. Operating cost values for decolorization efficiency of melanoidin at optimum conditions
5. Conclusions

The optimum operating conditions for the decolorization of melaniodin were pH 4.2, 5 A/m², 2500 μS/cm, 100 mg/L and 10 min. The decolorization efficiencies were lower at initial pH values until 10 min of operating time since functional groups in MMs became more negative and there was not enough positive polymeric Al-species present for charge neutralization and precipitation. After 20 min of operating time, the values of the decolorization efficiency were increased to >98% which enhanced floc formations and the removal mechanism was controlled at these pH ranges by adsorption and sweep coagulation. OC at the optimum conditions was 0.0096 €/m³.

Acknowledgements

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REFERENCES


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Table 1. The possible mechanism of EC with Al electrode at various pHs

<table>
<thead>
<tr>
<th>pH range</th>
<th>Net electrical charge of MMs</th>
<th>Coagulation species</th>
<th>Decolorization mechanism of MMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH ≤ 2.5</td>
<td>(+, 0)</td>
<td>Monomeric Al-species: Al(^{+3}), AlOH(^{2+}), Al(OH)(_2^+)</td>
<td>Precipitation of MMs at its isoelectric and pH decreasing degree of MMs polymerization</td>
</tr>
<tr>
<td>4.0 ≤ pH ≤ 5</td>
<td>(-)</td>
<td>Monomeric Al-species: Al(^{+3}), AlOH(^{2+}), Al(OH)(_2^+), Al(_2^+)(OH)(_4^+), Al(OH)(_4^-)</td>
<td>Charge neutralization with monomeric Al-species and precipitation</td>
</tr>
<tr>
<td>5 ≤ pH &lt; 6.5</td>
<td>(-)</td>
<td>Polymeric Al-species: Al(_3^+)(OH)(<em>4^+), Al(<em>6^+)(OH)(</em>{15}^+), Al(<em>7^+)(OH)(</em>{17}^+), Al(<em>8^+)(OH)(</em>{20}^+), Al(</em>{13}^+)O(<em>4^-)(OH)(</em>{34}^-)</td>
<td>Charge neutralization with polymeric Al-species and precipitation</td>
</tr>
<tr>
<td>6.5 &gt; pH &gt; 9</td>
<td>(- -)</td>
<td>Al(OH)(_{3(3)}^+)</td>
<td>Adsorption on Al-hydroxide flocs and sweep coagulation</td>
</tr>
<tr>
<td>pH &gt; 9</td>
<td>(- -)</td>
<td>Al(OH)(_4^-)</td>
<td>Sweep coagulation</td>
</tr>
</tbody>
</table>
### Table 2. FTIR of melanoidin and sludge produced during EC process

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400-3200</td>
<td>OH stretch form –COOH and –COH</td>
</tr>
<tr>
<td>2800-3100</td>
<td>C-H stretch from –CH₂, -CH₃, and –CH₃</td>
</tr>
<tr>
<td>1739</td>
<td>C=C stretching</td>
</tr>
<tr>
<td>1641</td>
<td>H-O-H</td>
</tr>
<tr>
<td>1595</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1375, 1301</td>
<td>O-H stretching</td>
</tr>
<tr>
<td>1217</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>1063</td>
<td>Al-O</td>
</tr>
<tr>
<td>972</td>
<td>Al-O-HO</td>
</tr>
<tr>
<td>1870</td>
<td>C-O-C asymmetric stretching</td>
</tr>
</tbody>
</table>
Table 3. Decolorization efficiency of melanoidin with different current density

<table>
<thead>
<tr>
<th>$j$</th>
<th>$i$</th>
<th>$U$</th>
<th>$t_{EC}$</th>
<th>ENC</th>
<th>ELC</th>
<th>$Q$</th>
<th>$C_E$</th>
<th>$R_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A/m$^2$)</td>
<td>(Amper)</td>
<td>(volt)</td>
<td>(min)</td>
<td>(kWh/m$^3$)</td>
<td>(kg/m$^3$)</td>
<td>(F/m$^3$)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>2.5</td>
<td>0.06</td>
<td>1.44</td>
<td>10</td>
<td>0.0169</td>
<td>0.0043</td>
<td>0.439</td>
<td>108</td>
<td>96.5*</td>
</tr>
<tr>
<td>5.0</td>
<td>0.12</td>
<td>2.26</td>
<td>10</td>
<td>0.0532</td>
<td>0.0086</td>
<td>0.878</td>
<td>109</td>
<td>98.6</td>
</tr>
<tr>
<td>7.5</td>
<td>0.18</td>
<td>2.95</td>
<td>10</td>
<td>0.1041</td>
<td>0.0124</td>
<td>1.317</td>
<td>104</td>
<td>98.8</td>
</tr>
<tr>
<td>2.5</td>
<td>0.06</td>
<td>1.40</td>
<td>5</td>
<td>0.0082</td>
<td>0.0021</td>
<td>0.219</td>
<td>106</td>
<td>6.5</td>
</tr>
<tr>
<td>5.0</td>
<td>0.12</td>
<td>2.30</td>
<td>5</td>
<td>0.0271</td>
<td>0.0046</td>
<td>0.439</td>
<td>115</td>
<td>96.8*</td>
</tr>
<tr>
<td>7.5</td>
<td>0.18</td>
<td>2.95</td>
<td>5</td>
<td>0.0521</td>
<td>0.0062</td>
<td>0.658</td>
<td>103</td>
<td>97.9</td>
</tr>
<tr>
<td>2.5</td>
<td>0.06</td>
<td>1.40</td>
<td>4</td>
<td>0.0066</td>
<td>0.0017</td>
<td>0.176</td>
<td>106</td>
<td>5.8</td>
</tr>
<tr>
<td>5.0</td>
<td>0.12</td>
<td>2.30</td>
<td>4</td>
<td>0.0216</td>
<td>0.0033</td>
<td>0.351</td>
<td>103</td>
<td>74.4</td>
</tr>
<tr>
<td>7.5</td>
<td>0.18</td>
<td>2.95</td>
<td>4</td>
<td>0.0416</td>
<td>0.0051</td>
<td>0.527</td>
<td>106</td>
<td>97.5*</td>
</tr>
</tbody>
</table>

*Optimum decolorization conditions
Table 4. Operating cost values for decolorization efficiency of melanoidin at optimum conditions

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENC</td>
</tr>
<tr>
<td>$C_0$ (mg/L)</td>
<td></td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>ENC</td>
</tr>
<tr>
<td>pH_i (°C)</td>
<td>Rm (%)</td>
</tr>
<tr>
<td>j (A/m²)</td>
<td>t_EC (min)</td>
</tr>
<tr>
<td>t (EC (min))</td>
<td></td>
</tr>
<tr>
<td>$R_m$ (%)</td>
<td></td>
</tr>
<tr>
<td>ENC (kWh/m³)</td>
<td></td>
</tr>
<tr>
<td>ELC (kg/m³)</td>
<td></td>
</tr>
<tr>
<td>OC (€/m³)</td>
<td></td>
</tr>
</tbody>
</table>

| 100 2500 4.2 2.5 10 | 96.5 | 0.0169 | 0.0043 | 0.0084 |
| 100 2500 4.2 5.0 5  | 96.8 | 0.0266 | 0.0046 | 0.0096 |
| 100 2500 4.2 7.5 4  | 97.5 | 0.0417 | 0.0051 | 0.0115 |
| 100 500 4.2 5.0 5   | 95.2 | 0.0377 | 0.0127 | 0.0238 |
| 100 1000 4.2 5.0 5  | 95.8 | 0.0341 | 0.0114 | 0.0214 |
| 100 1500 4.2 5.0 5  | 96.2 | 0.0283 | 0.0078 | 0.0150 |
| 100 2500 4.2 5.0 5  | 96.8 | 0.0266 | 0.0046 | 0.0096 |
| 100 3000 4.2 5.0 5  | 96.8 | 0.0261 | 0.0038 | 0.0083 |
| 100 2500 4.2 5.0 5  | 96.8 | 0.0266 | 0.0046 | 0.0096 |
| 400 2500 4.2 5.0 30 | 95.6 | 0.0268 | 0.0239 | 0.0415 |
| 800 2500 4.2 5.0 55 | 94.2 | 0.0271 | 0.0437 | 0.0742 |
Figure 1. (a) Effect of pH on decolorization (Conditions: 5 A/m², 100 mg/L, 2500µS/cm).

47x32mm (300 x 300 DPI)
Figure 1. (b) change of final pH<sub>f</sub> during the EC process (Conditions: 5 A/m<sup>2</sup>, 100 mg/ L, 2500µS/cm). 46x32mm (300 x 300 DPI)
Figure 2. (a) Zeta potential measurements melanoidin solutions during the EC process (Conditions: pH 4.2, 2500µS/cm, 2.5 A/m²). 52x32mm (300 x 300 DPI)
Figure 2. (b) Zeta potential measurements melanoidin solutions at different pH values after the EC process (Conditions: pH 4.2, 2500µS/cm, 2.5 A/m²).

52x32mm (300 x 300 DPI)
Figure 3. (a) FTIR of Melanoidin

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Figure 3. (b) ratios of absorbance before and after the EC process.
53x32mm (300 x 300 DPI)
Figure 4. Effect of current density on decolorization efficiency of melanoidin (Conditions: pH 4.2, 100 mg/L, 2500 µS/cm)

46x31mm (300 x 300 DPI)
Figure 5. (a) Effect of conductivity on decolorization efficiency (Conditions: 100 mg/L, pH 4.2, 5 min; 5 A/m²).
47x32mm (300 x 300 DPI)
Figure 5. Effect of conductivity on ENC and ELC (Conditions: 100 mg/L, pH 4.2, 5 min; 5 A/m²).
59x32mm (300 x 300 DPI)
Figure 6. Effect of initial melanoidin concentration on decolorization and COD efficiencies (Conditions: 2500µS/cm, pH 4.2, 5 A/m²). 49x40mm (300 x 300 DPI)