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EVALUATION OF ELECTROCOAGULATION AS A METHOD OF PRE-TREATMENT FOR HIGHLY CONCENTRATED BREWERY WASTEWATER

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Abstract: This study investigated the effectiveness of electrocoagulation as a pre-treatment for brewery wastewater. The performance of a batch electrocoagulation system with four electrode plates was explored with respect to turbidity and chemical oxygen demand (COD) removal, electrical energy and electrode consumption, and sludge production. A parallel connection mode was used to connect the electrodes of the sacrificial materials, Fe and Al. All experiments were conducted at a current density of 150 A/m^2 and initial pH of 5 and 7 for the Fe and Al electrodes, respectively. Different combinations of the two electrode materials (Fe/Fe, Al/Al, Fe/Al and Al/Fe (anode/cathode configuration)) were investigated with regards to the electrode materials and operating time. At the current density applied and initial pH used for the respective electrode materials, the optimum operating time for electrocoagulation was found to be 10 minutes and the corresponding turbidity removal was 99%, 98.5%, 97%, and 99% for Fe/Fe, Al/Al, Fe/Al and Al/Fe (anode/cathode configuration) electrodes, respectively. Both electrode materials exhibited somewhat similar characteristics in turbidity removal and, therefore, other parameters were considered to base the selection of an optimum electrode configuration. Aluminum electrodes consumed lower electrode materials yet required higher electrical potential. Experiments with the Fe/Al configuration produced the lowest sludge volume and required the lowest potential as compared to others, and therefore were chosen as the optimum electrode configuration. The COD removal efficiency was examined using this optimum configuration and showed an around 60% removal rate. The effluent from the optimized electrocoagulation reactor would substantially reduce the wastewater load for a post-treatment setup such as anodic oxidation or electro-Fenton.

1 Introduction

The rapid growth of industrialization and urbanization have stimulated the need for water resources and reclamation, along with the increment in the levels of environmental pollution, simultaneously from urban and industrial waste while industrial effluent is mainly responsible to increase the environmental disproportion due to its physical and chemical composition (Hilario Garcia, Matzenbacher et al. 2017). Brewing industry has high economic value and beer is considered as one of the most consumed beverage globally (Sultana 2016, Maintinguer, Lazaro et al. 2017)**.** Around the globe, the production of beer has increased about 37.26 million kiloliters from 2004 to 2014 and among all countries China ranked top in beer production volume, followed by Brazil (about 5.42 million kiloliters) and Vietnam (Maintinguer, Lazaro et al. 2017). To produce this alcoholic beverage, the brewery consumes large volume of water and generates highly polluted effluent, which accounts 70% of consumed water. Generally, it produces 3-10 L of waste effluent for per liter of beer production (Subramaniyam, Subashchandrabose et al. 2016, Maintinguer, Lazaro et al. 2017). Primarily, two factors control the amount of wastewater generation: (i) production, (ii) specific water usage. Typically, this type of wastewater has a high organic matter concentration such as sugars, soluble starch, ethanol, volatile fatty acids, and very low concentrations of heavy metals. Therefore,

if not treated properly before discharge it may cause the potential threat to the environment, aquatic life and human beings (Choi 2015, Subramaniyam, Subashchandrabose et al. 2016). In addition, regulations regarding the management of environmental issues has become more stringent than before and therefore, it is mandatory for the brewing industry to comply with environmental laws and ensure the treatment and safe disposal of brewery wastewater (Simate, Cluett et al. 2011, Choi 2015).

As a treatment method of treating brewery wastewater, conventionally physical, chemical and biological processes are used (Maintinguer, Lazaro et al. 2017). Although various treatment methods have been reported in the literature for treating brewery wastewater (Choi 2015, Eyvaz 2016), the application of electrocoagulation (EC) has the potential for pre-and post treatment of wastewater due to it's simple, reliable and cost effective process. However, there is limited information on the treatment of brewery wastewater using electrocoagulation. To the best of our knowledge, only one research study reported the use of electrocoagulation for treating brewery wastewater. Therefore, the objective of this study is to investigate the potential of electrocoagulation process as a method of pre-treatment for highly concentrated brewery wastewater.

1.1 Overview of Electrocoagulation

Electrocoagulation (EC) is an electrochemical treatment method which is associated with the anodic dissolution of a sacrificial metal electrode (typically aluminum, iron, or stainless steel (SS), because these metals are cheap, readily available, proven effective, and non-toxic). In this electrolytic system, hydroxy ions and hydrogen gas forms simultaneously, the hydroxy ions remove the suspended solids and colloidal particles from the electrochemical system by coagulation and flocculation (Terrazas, Vazquez et al. 2010, Butler, Hung et al. 2011, Kuokkanen, Kuokkanen et al. 2013). A summary of some chemical reactions which occur on electrodes and in the bulk wastewater in EC process, is shown in Table 1 (Inan, Dimoglo et al. 2004).

Table 1: Reactions at the electrodes and in the bulk wastewater

Anode	Cathode (Simate et al. 2011)
$4OH^- = 2H_2O + O_2(g) + 4e^-$	$2H_3O^+ + 2e^- = H_2(g) + 2H_2O$
$2H_2O = O_2(g) + 4H^+ + 4e^-$	(in acid solutions)
$2Cl^- = Cl_2(g) + 2e^-$	$2H_2O + 2e^- = H_2(g) + 2OH^-$
$Cl_2(g) + H_2O = HOCl + H^+ + Cl^-$	(in alkaline solutions)
	$O_2 + 2H_2O + 4e^- = 4OH^-$
Al-anode,	$Al(s) + 4OH^- = [Al(OH)_4]^- + 3e^-$
$Al(s) = Al(aq)^{3+} + 3e^-$	(at very high pH)
$Al(aq)^{3+} + 3H_2O = Al(OH)_3 + 3H^+$	
Fe-anode,	$Fe(OH)_3 + OH^- = [Fe(OH)_4]^-$
$Fe(s) = Fe(aq)^{2+} + 2e^-$	$[Fe(OH)_4]^- + 2OH^- = [Fe(OH)_6]^{3-}$
$Fe(aq)^{2+} + 2H_2O = Fe(OH)_2 + 2H_2O$	(at very high pH)
$Fe(OH)_2 + HOCl = Fe(OH)_3 + Cl^-$	
$Fe^{2+} = Fe^{3+} + e^-$	
$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$	

2 Materials and Methods

2.1 Physical-chemical Characteristics of Brewery Wastewater

Brewery wastewater was collected after fermentation from the Brewhouse, Labatt Brasserie, LaSalle, Quebec every two months and send directly to us. The sample was stored at 2-8°C and before running each experiment the required amount allowed to reach room temperature. Analyses were performed to characterize the Labatt brewery wastewater by measuring some parameters which are listed in the Table 2:

Table 2 Labatt brewery wastewater characteristics

Parameters	Labatt Brewery Sample
pH	6.91±0.38
Conductivity, µS	552 ± 59
TS, mg/L	913 ± 5
TSS, mg/L	148 ± 15
TDS, mg/L	765 ± 20
VTSS, mg/L	135 ± 9
FTSS, mg/L	13 ± 7
COD, mg/L	1860 ± 70
TOC, mg/L	574 ± 32
TN, mg/L	74 ± 10
TP, mg/L	6.71 ± 3.5
TFe, ppb	66 ± 12

2.2 Experimental Procedure

A glass cylindrical EC cell with 850 ml of homogenously brewery wastewater sample was employed in this study. Iron and Aluminum was used as electrode material with an inter electrode gap of 2 cm and a monopolar arrangement with four electrode plates (two anodes and two cathodes) in parallel connection mode (Figure 1). The EC cell used electrodes with 38.7 cm^2 of effective area with a current density of 150 A/m^2. A DC power supply (Agilent Technologies) was used to provide the electrical connection. To provide mixing in the system, a magnetic bar with 250 rpm was employed at the bottom of the cell reactor. For all experiments with Fe electrode an initial pH of 7 and for Al an initial pH of 5 was employed. All experiments were carried out at room temperature. The effluent from EC cell was filtered through a filter paper (Whatman 42 ashless-NJ, USA) after each run and then analyzed the filtrate for turbidity. In the study of sludge production, the sludge was filtered through a filter paper (Whatman 110 mm diameter) and then the dry weight of the solid residue on the paper was taken to calculate the sludge generation rate. Before each run, electrolytic cell (including the electrodes) was cleaned with 1M hydrochloric acid (HCl) solution for at least 15 min and then rubbed with a sponge and rinsed with tap water and at the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and re-weighted (Kobya, Can et al. 2003, Kobya, Demirbas et al. 2010).

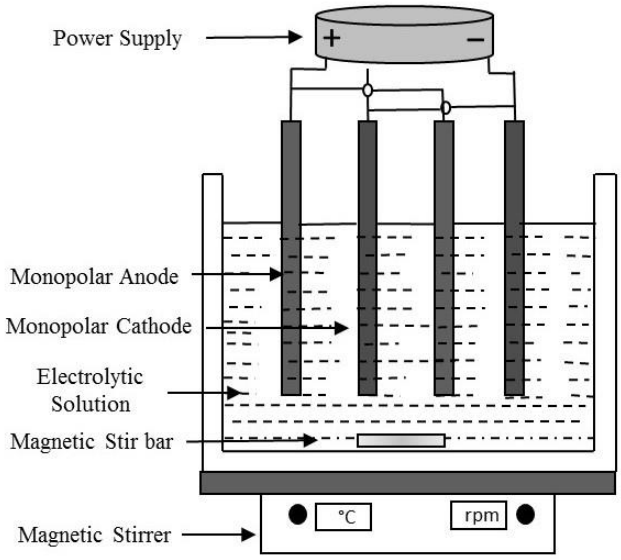

Figure 1: Electrocoagulation Experimental Setup

2.3 Evaluation techniques

For pH, turbidity and conductivity measurement, a calibrated pH meter (Oakton Instruments, 310 series, Vernon Hills, IL, USA), turbidity meter (Orion, Thermo scientific) and conductivity meter (Oakton Instruments, Vernon Hills, IL, USA) were respectively used. COD, TN, and TP were measured by reactor digestion method using Hach kits. In brief, the measurement of parameters by Hach kits involves the addition of sample solution into a reagent containing vial, which is heated for a specified period of time, then cooled to room temperature. The concentration of the parameter sought is then measured using a spectrophotometer (DR2800, Hach). The range of the COD vials was 20-1500 mg/L and a proper dilution factor was used to measure concentrations higher than this range.

The removal efficiencies (R%) with respect to turbidity and COD have been calculated using the following equation (Kuokkanen, Kuokkanen et al. 2013):

[1] $$R\ (\%) = \frac{[C_0 - C_t]}{C_0} \times 100$$

Where, C_0 and C_t are pollutant concentration before and after EC treatment, respectively.

Theoretically, the dissolution of the anode material can be determined based on Faraday's law as Kg/m^3 (Kobya, Ulu et al. 2011, Fajardo, Rodrigues et al. 2015),

[2] $$m_{metal} = \frac{M_w I t}{F z V}$$

Where I is the current intensity (A), t corresponds to time of electrocoagulation process, M to the molar mas of the metal (g/mol), z to the valence electrons of the metal (2 for Fe and 3 for Al) and F to the Faraday's constant (96485 C/mol).

3 Results and Discussion

The performance of the electrocoagulation system was systematically evaluated in this study with four different electrode combinations as Fe/Fe, Al/Al, Fe/Al and Al/Fe (anode/cathode) configuration. At a current density of 150 A/m^2 and initial pH used for the respective electrode materials, the system performed well for the first 10 minutes and then starts to deteriorate and therefore, 10 minutes was selected as the optimum operating time for further analysis. To determine the effective electrode configuration for the pre-treatment of brewery wastewater following parameters were considered,

3.1 Turbidity removal

All four combinations used in this study showed satisfactory results in terms of turbidity removal. For Fe/Fe, Al/Al, Fe/Al and Al/Fe removal was 99%, 98.5%, 97%, and 99%, respectively (Figure 2). The possible mechanism of removing suspended and colloidal particles from the wastewater can be stated as (Kobya, Demirbas et al. 2010, Kobya, Ulu et al. 2011, Eyvaz 2016),

(i) Chemical precipitation: the formation of the insoluble compounds, with iron electrodes precipitates such as $Fe(OH)_2$, $Fe(OH)_3$ or $FePO_4$ and with aluminum electrodes insoluble compounds such as $Al(OH)_3$, $AlPO_4$,
(ii) Co-precipitation
(iii) Adsorption – charge neutralization.

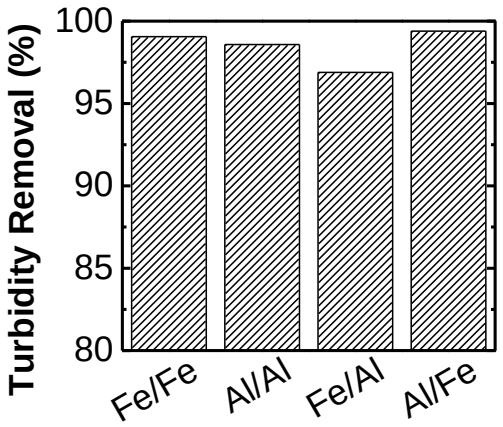

Figure 2: Turbidity removal in different electrode configurated electrocoagulation cell [Experimental condition: reaction time = 10 minutes, initial pH 7 (for Fe) and 5 (for Al)]

3.2 Electric potential requirement and electrode consumption

The requirement of electric potential and theoretical electrode consumption were investigated to determine the most effective electrode configuration to treat brewery wastewater. Figure 3 displays the results of this study, Aluminum electrode as anode dissociates lower electrode materials yet requires higher electrical potential as well as higher electrical energy consumption which increases the system cost significantly (Enric Brillas 2009).

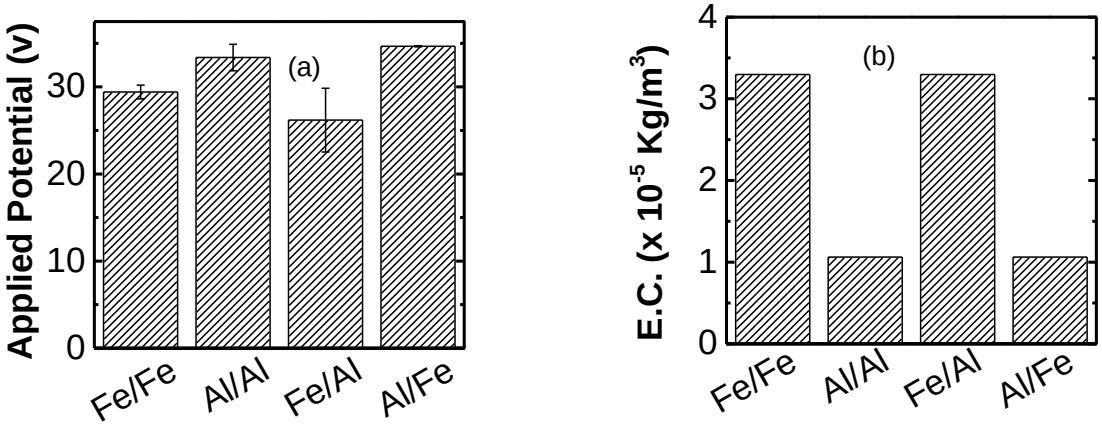

Figure 3: Electrical potential requirement and theoretical electrode consumption for different electrode configurated electrocoagulation cell [Experimental condition: reaction time = 10 minutes, initial pH 7 (for Fe) and 5 (for Al)]

3.3 Sludge production

The study of sludge production is an important parameter in electrocoagulation process as it is associated with the problems of solid waste generation and disposal. Most of the contaminants in the electrocoagulation process are present in the form of sludge either by isolation or flotation on the surface of the wastewater (Kobya, Ulu et al. 2011). The study of sludge generation showed lower quantity of sludge production with Fe/Al electrode configuration as seen in Figure 4, therefore, this combination was selected as the optimum electrode configuration.

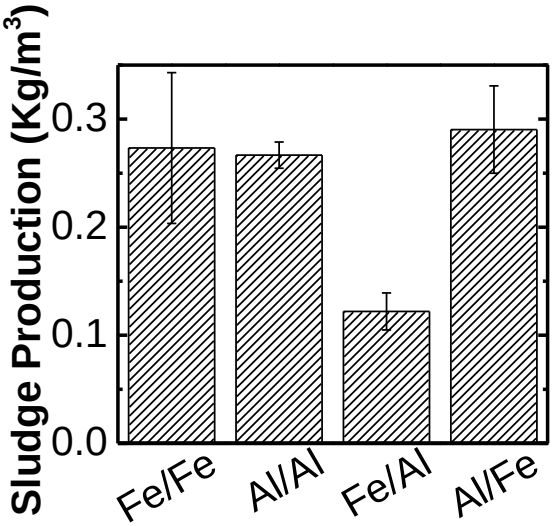

Figure 4: Sludge generation in electrocoagulation process [Experimental condition: reaction time = 10 minutes, initial pH 7 (for Fe) and 5 (for Al)]

3.4 COD removal Efficiency

To observe the COD removal efficiency using Fe/Al configuration a set of experiments was employed and it showed 60% of COD removal. The major limitation associated with electrocoagulation is electrode

passivation which affects the process performance in long run. Deposition of calcium carbonate and magnesium hydroxide at cathode and formation of an oxide layer at anode surface was reported in previous studies (Kabdaşlı, Arslan-Alaton et al. 2012). The chemical cleaning procedure mentioned in section 2.2 plays a vital role in removing the passivation layer from the electrode surface and regenerate the performance of the system (Eyvaz, Gürbulak et al. 2014).

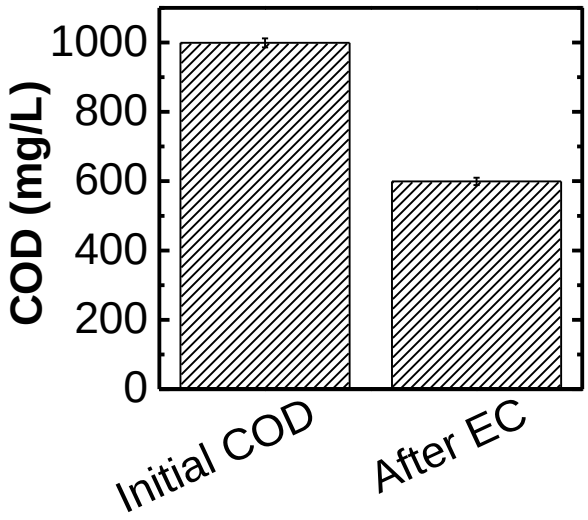

Figure 5: COD removal in electrocoagulation cell using Fe/Al configuration [Experimental condition: reaction time = 10 minutes, initial pH 7]

4 Conclusion

Electrocoagulation seemed to be an effective pre-treatment method for removal of turbidity and a significant portion of COD from brewery wastewater. A turbidity removal of 97% and COD removal of 60% was achieved using Fe/Al electrode configuration. Passivation of electrodes can be removed by chemical cleaning. For a post treatment method, the incoming wastewater load could be significantly minimized by using electrocoagulation as a pre-treatment which in turn increase the operating life span of the overall system.

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