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HIGHLY EFFECTIVE ELECTRO-FENTON OXIDATION TREATMENT FOR CONCENTRATED BREWERY WASTEWATER

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ABSTRACT

The brewing industry typically produces 3-10 liters of wastewater per liter of beer produced which contains sugars, soluble starch, ethanol, and volatile fatty acids (VFAs) and is typically characterized by 2,000-20,000 mg/L COD, 200-3,000 mg/L total suspended solids (TSS), and 10-124 mg/L phosphorus. In this study, the high strength brewery wastewater was treated with a multi-plated (BDD/Graphite) electrolysis cell configuration with Fenton's reagent in a galvanostatic mode of operation. A novel cell configuration with five electrode plates (BDD/Graphite), which provide a higher current/voltage ratio than the conventional three plate configuration, was used in this study to provide more surface for anodic ·OH production, as well as electrical regeneration of Fe^{2+} at the cathode. The test was performed with cathodically generated in-situ H_2O_2 and externally added H_2O_2 to determine the optimal dose for the overall process. The ·OH formed by Fenton's reaction, as well as anodic oxidation, degraded the organic matter present in the wastewater. This hybrid treatment method enables the brewery to meet the requirements of the wastewater discharged into the municipal system at a shorter time with higher treatment efficiency than the conventional treatment processes. All the experiments in this study were performed in a controlled environment which showed removal efficiency of as much as 90.5% of COD at an H_2O_2 dose of 0.1 mM with a Fe^{2+}/ H_2O_2 ratio (w/w) of 17. Fe^{2+}/ H_2O_2 ratios higher or lower than this value showed lower COD removal efficiency with higher energy consumption, which might be the effect of parasitic reactions of ·OH. The next step of the research will focus on optimization of the overall process including current intensity, Fe^{2+} concentration, and cell configuration, as well as the quantification of ·OH production.

Keywords: Boron-doped diamond (BDD); Brewery; Organics; Oxidation; Mass transfer; Energy consumption.

1. INTRODUCTION

The brewing industry has contributed a significant portion of economic power in human history, including in the formation and growth of Canada (Eberts 2007). Beer is considered as the fifth most consumed beverage in the world after tea, carbonates, milk, and coffee (Fillaudeau, Blanpain-Avet et al. 2006). This alcoholic beverage is made from a malted grain (usually barley), water, and possibly a herb or spice for flavor (e.g. hops), with the whole being fermented with yeast (Eberts 2007). Brewing beer involves two main steps: a) brewing and b) packaging of the finished product. The by-products (e.g., spent grains from mashing, yeast surplus, etc.) generated from these steps are considered pollutants when mixed with effluents. Also, cleaning of tanks, bottles, machines, and floors produce high quantities of polluted water, which contain both chemical (with very high organic content) and microbial contaminants (Doubla, Laminsi et al. 2007, Doubla, Laminsi et al. 2007). It is estimated that in the production of 1 L of beer, 3–10 L of waste effluent is generated, depending on the production technique and specific water usage. In other words, large quantities of water are consumed and polluted during the beer brewing process (Kanagachandran and Jayaratne 2006, Simate, Cluett et al. 2011). Since brewing constitutes an important economic segment of any country, it is necessary to reduce the pollutant concentration before discharge via an effective treatment system.

The conventional method of beer brewery wastewater treatment is based on biological methods, which naturally lead to longer hydraulic retention times and are subject to failures due to shock loading and improper maintenance. These processes also require a lot of space. Moreover, the biodegradation of flavonoids present in the brewery requires specific bacterial strains to achieve higher removal efficiencies (Krishnan Vijayaraghavan 2006, Doubla, Laminsi et al. 2007). Table 1 shows existing treatment methods for brewery wastewater.

Table 1: Summary of Existing treatments of Brewery wastewater (Simate, Cluett et al. 2011)

Process	COD Reduction (%)
Quenched plasma	98
UASB	73-91
Aerobic reactor	90-98
Combined bioreactor	98
Membrane bioreactor	96
Electrochemical method	97
Microbial fuel cells	94
Nanofiltration	96
Reverse osmosis	100

The application of electrochemical advanced oxidation processes (EAOPs) is well-suited for degrading biorefractory organic pollutants because it is possible to achieve partial or complete decomposition of the organic substances. The electrochemical method of treatment is favored, because they are neither subject to failure due to variation in wastewater strength nor due to the presence of toxic substances, and they require less hydraulic retention time (Simate, Cluett et al. 2011). These EAOPs have been shown to be more efficient and cost-effective than some widely used advanced oxidation processes (AOPs) such as the Fenton oxidation or ozonation in the treatment of organic pollutants (Dirany, Sires et al. 2010). For example, the anodic oxidation with a BDD anode has been successfully applied for the treatment of photographic processing wastewater (Bensalah, Bedoui et al. 2013), textile industry wastewater (Ö. 2014), pharmaceutical caffeine removal (Ganzenko, Oturan et al. 2015), and even antibiotics (Dirany, Sires et al. 2010).

Primarily, the in situ generation of hydroxyl radical (·OH) with a very high standard reduction potential (E° (·OH/H2O) = 2.80 V/SHE) provides the oxidative ability of these EAOPs (C. Barrera-Díaz 2014). These ·OH radicals non-selectively react with most organics up to their full/partial mineralization, i.e., convert them into CO_2, water, and inorganic ions. The formation of these radicals are characterized by the continuous supply of hydrogen peroxide to a contaminated acidic solution by the reduction of O_2 as follows (Jiang and Zhang 2007, El-Ghenymy, Rodriguez et al. 2014):

[1] $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Electro-Fenton (EF) process is the most popular EAOP based on Fenton's reaction chemistry. It involves the addition of a small quantity of Fe^{2+} ion as a catalyst to an acidic solution to react with electro-generated H_2O_2 to give homogeneous ·OH and Fe^{3+} ion from Fenton's reaction (2). This reaction becomes optimal at a pH ~3 and is catalytic because it can be propagated from Fe^{3+} reduction to Fe^{2+}, which takes place mainly at the cathode (3) (Jiang and Zhang 2007, Dirany, Sires et al. 2010).

[2] $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$

[3] $Fe^{3+} + e^- \rightarrow Fe^{2+}$

The reaction between an organic pollutant (R) and •OH is expressed as follows (Bensalah, Bedoui et al. 2013, Ganzenko, Oturan et al. 2015) :

[4] $R + \bullet OH \rightarrow Products$

This study is intended to reduce the high organic content of brewery wastewater by optimizing the process parameters using electro-Fenton and electro-oxidation technology, which consumes minimum energy at a specific time period.

2. MATERIALS AND METHODS

2.1 Wastewater

Untreated wastewater samples were supplied by Brasserie Labatt Québec Limitée. Samples for both process and non-process wastewater were collected and then mixed properly in order to get a homogenous sample. Non-process wastewater (condensed water) has low viscosity, low turbidity, and is almost colorless with sharp yeast odor but process wastewater i.e. brew pushing water has high viscosity, high turbidity, a dark color, and a strong yeast odor. The most important operating parameters for the electro-Fenton system are certainly pH, the concentration of catalyst (Fe2+), and current intensity (Ganzenko, Oturan et al. 2015). The optimal range of pH has been studied extensively and shown to exist around the value of 3 (Plgnatello 1993, Jiang and Zhang 2007, Enric Brillas 2009). The optimal catalyst (Fe2+) concentration of 0.2 mM Fe2+ was found by electro-Fenton in different studies (El-Ghenymy, Rodriguez et al. 2014, Ganzenko, Oturan et al. 2015) and hence used in this study with a current intensity of 800 mA.

Table *2* shows the typical brewery wastewater characteristics along with the analyzed values from this study.

2.2 Chemicals

Hydrogen peroxide (CAS 7722-84-1) and Iron (II) sulfate heptahydrate (CAS 7782-63-0) as a catalyst source were obtained from Sigma–Aldrich. The pH of the solutions was set using 1M H_2SO_4 and 1M NaOH. All the solutions were prepared with ultrapure water produced by a Millipore Milli-Q (simplicity 185) system with a resistivity of >18 MX cm.

2.3 Experimental setup

All experiments were carried out in an open, undivided electro-Fenton reactor in a batch mode at a temperature of 40 ± 2 °C to mimic the actual conditions of the processes employed in the brewery industry. The setup consisted of 600 mL glass beaker, which was filled with 500 mL of sample wastewater. A DC power supply with constant voltage and current capacity of 35 V and 0.8 A respectively, was used for E-Fenton experiments. The anode was a BDD thin-film on a niobium substrate with an area of 25 cm^2 (Neocoat), and graphite plates of the same size were used as cathodes placed equidistant (8 mm) from the anode. For the entire experiment, the pH was adjusted with 1M H_2SO_4 or 1M NaOH to 3.5 ± 0.5 and measured with a pH meter. The solution was stirred continuously throughout the process with a magnetic bar on a magnetic stirrer. Certain amounts of Fe (II) was added to the electrolyte solution to initiate the electro-Fenton reactions following a sufficient amount of time to allow the solution to become air saturated.

A novel cell configuration was used in this study which comprised of two anodes and three cathodes and was inserted into the reactor (fully submerged) in such a manner that more electrode area was exposed to the organic matter present in the solution. Monopolar parallel cell connection in a horizontal position was used to conduct all the experiments.

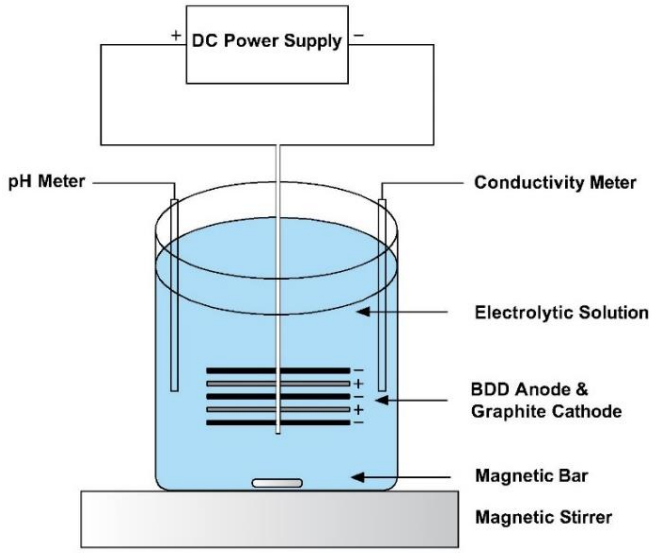

Figure 1: Schematic of Undivided Electrolysis Cell used for EF/EO treatment of Brewery wastewater.

3. RESULTS AND DISCUSSION

The most important operating parameters for the electro-Fenton system are certainly pH, the concentration of catalyst (Fe^{2+}), and current intensity (Ganzenko, Oturan et al. 2015). The optimal range of pH has been studied extensively and shown to exist around the value of 3 (Plgnatello 1993, Jiang and Zhang 2007, Enric Brillas 2009). The optimal catalyst (Fe^{2+}) concentration of 0.2 mM Fe^{2+} was found by electro-Fenton in different studies (El-Ghenymy, Rodriguez et al. 2014, Ganzenko, Oturan et al. 2015) and hence used in this study with a current intensity of 800 mA.

Table 2: Characteristics of brewery wastewater

Parameter	Typical Value (Simate, Cluett et al. 2011)	Labatt Sample
pH	3–12	3.77-6.88
Conductivity (μS)	-	436-597
Temperature (°C)	18–40	40 ± 2
COD (mg/L)	2000–6000	6930-7798
BOD (mg/L)	1200–3600	-
COD:BOD ratio	1.667	-
VFA (mg/L)	1000–2500	-
Phosphates as PO4 (mg/L)	10–50	-
TKN (mg/L)	25–80	-
TS (mg/L)	5100–8750	9200-10000
TSS (mg/L)	2901–3000	1104-1200
TDS (mg/L)	2020–5940	8096-8800

3.1 Change of Conductivity and applied Voltage over time

Brewery wastewater has high conductivity (Table *2*) which eliminates the need for electrolyte addition. With time the conductivity of the sample increases which reduces the applied potential requirement (Figure *2*) and consequently the energy consumption for the overall process. During electrolysis, at BDD anodes, oxidation of water occurs promoting

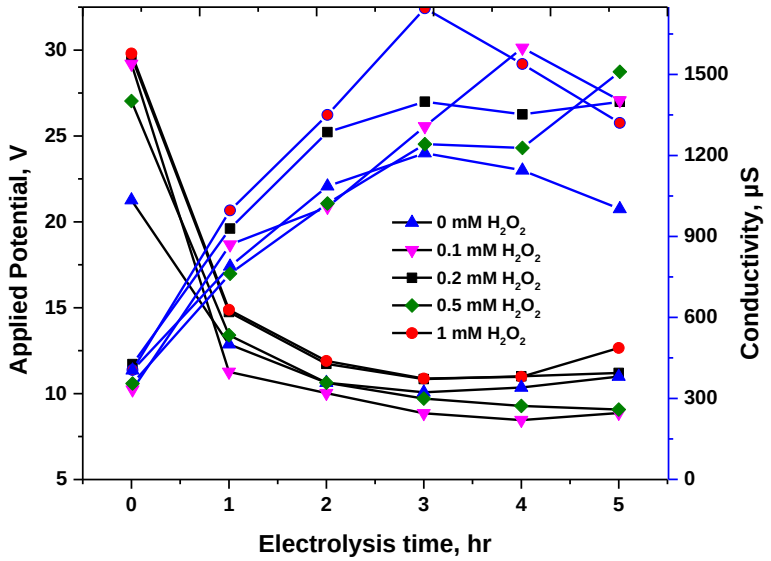

Figure 2: Conductivity (blue) and Voltage (black) as a function of Electrolysis time

the production of weakly adsorbed hydroxyl radicals (Eq. 1), which unselectively and completely mineralize organic pollutants with a high current efficiency (Marco Panizza and Cerisola 2009, Bensalah, Bedoui et al. 2013, El-Ghenymy, Rodriguez et al. 2014, Ganzenko, Oturan et al. 2015). Typically, the voltammetric study of electrolytic processes on BDD electrodes shows a high oxygen evolution overpotential (OEP), explaining the easy mineralization of organics (C. Barrera-Díaz 2014).

[5] $BDD + H_2O = BDD(\bullet OH) + H^+ + e^-$

$= \mathbf{2H^+ + 2e^- + O_2}$

(Oxygen Evolution)

Since water is being oxidized at anode surface, the concentration of electrolytic species present in solution and conductivity will increase with time. It should be mentioned that the addition of 1M H_2SO_4 and 1M NaOH for pH adjustment will also add conductive species into the solution, also increasing overall conductivity over time.

3.2 Removal Efficiency of Chemical Oxygen demand (COD) at different H_2O_2 dose

The combined Electro-Fenton and electrooxidation (EF/EO) treatment method was found to be very effective in reducing the COD value of brewery wastewater. The 5 hr long experiment was able to reduce the COD value by 90.5% in the optimal condition where 0.1 mM H_2O_2 was added externally. Figure 3 shows COD removal as a function of H_2O_2 concentration, where removal efficiency with H_2O_2 dose follows a trend. Lower doses of this oxidation agent were found to be more effective than higher ones. This can be explained through the effect of parasitic reactions of electro-generated hydroxyl radicals: an evolution of H_2 at the cathode inhibiting the in-situ formation of H_2O_2 and •OH self-destruction at the anode (Dirany, Sires et al. 2010, Ganzenko, Oturan et al. 2015).

Since the presence of H_2O_2 and Fe^{2+} is inevitable for Fenton's reaction (Eq. 2), it is the ratio of these two species which controls the optimum amount of •OH radical formation. This ratio has also been reported in the literature for different kinds of pollutant removal (Sansebastianmartinez 2003, Tiwari and Upadhyay 2013). In this study, the effective Fe^{2+}/ H_2O_2 ratio (w/w) was found to be 17.

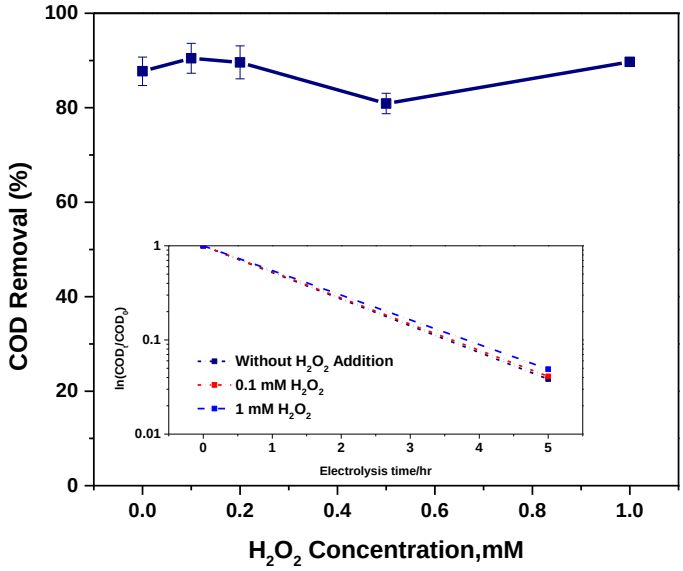

Figure 3: COD Removal from Brewery wastewater as a function of different H_2O_2 Concentration. [Inset COD reduction over time for 0, 0.1 mM & 1 mM H_2O_2 dose]

Figure 3 shows a linear regression for COD removal over time during the electrochemical oxidation of brewery wastewater. It can be observed that $\ln(COD_t/COD_0)$ decreases linearly with time, confirming that electrochemical oxidation of this type of wastewater on the BDD electrodes follows pseudo-first-order reaction. Typically, BDD electrodes with high oxygen evolution potential (OEP) have hydroxyl radical mediated oxidation, and because of the high reactivity and very short average lifetime of these radicals, mass transfer controls the maximum rate and no significant differences can be observed with respect to the kinetics of the electrochemical oxidation (C. Barrera-Díaz 2014). Average mass transfer coefficients for the electrochemical system can be calculated by Eq. 5,

[6] $$COD_t = COD_0 e^{-(k_m A/V)t}$$

Where k_m is the average mass transfer coefficient in the electrochemical cell (m/s), A is electrode area (m^2), and V is the volume of the electrolyte (m^3). k_m could be calculated from the slope value of the plot of $\ln(COD_t/COD_0)$ versus time. The value of k_m at 0.1 mM and 1 mM H_2O_2 is 3.62×10^{-5} and 3.55×10^{-5} respectively, which is approximately 10% higher than without the H_2O_2 addition situation. This indicates that mass transport is slightly enhanced by the addition of H_2O_2 externally at the BDD anode (Chen, Li et al. 2014). This higher mass transfer coefficient could be attributed to the faster reaction coefficient in case of sufficient H_2O_2 concentration.

3.3 Current Efficiency and Energy Consumption for the Overall Process

Current efficiency (CE) and energy consumption (EC) for this study were calculated in order to find the energy effectiveness of this treatment process. The average current efficiency (ACE) during electrolysis has been calculated using the following relation (M. Panizza 2001, Radjenovic and Sedlak 2015):

[7] $$\text{ACE} = \frac{[(COD)_0 - (COD)_t]}{8It} FV$$

Where $(COD)_0$ and $(COD)_t$ are the chemical oxygen demands (g O_2/m^3) at times 0 and t (s), respectively; I is current (A), F is Faraday constant (96 485 C/mol) and V is the volume of the electrolyte (m^3). And the energy consumption (E), has been calculated using the following relation, and expressed as KWh/m^3/kg COD (M. Panizza 2001, Chen, Li et al. 2014, Radjenovic and Sedlak 2015):

[8] $$\text{E} = \frac{UIt}{1000\,V}$$

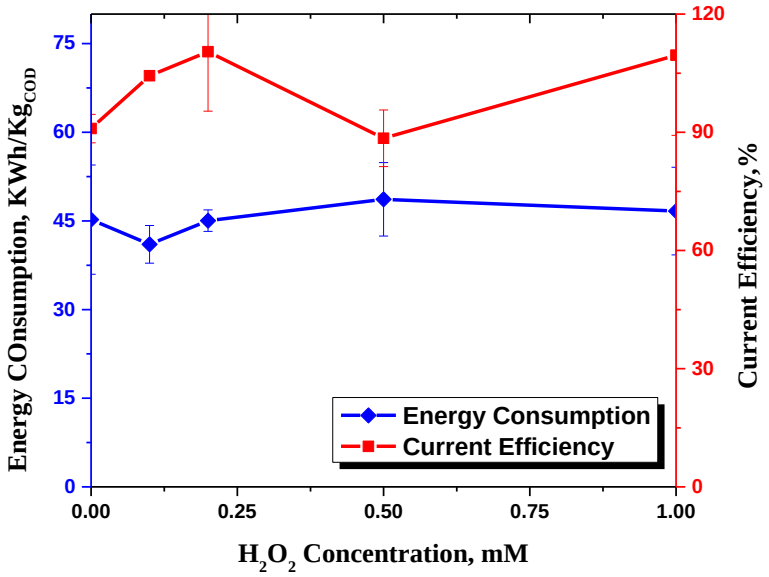

Figure 4: Energy Consumption and Current Efficiency for the EF/EO treatment.

Where *U* and *I* are average cell voltage (V) and electrolysis current (A) respectively; *t* is the time of electrolysis (h); *V* is the volume of the electrolyte (m^3). Figure 4 shows the changes of CE and EC with different H_2O_2 dose. Minimum energy consumption was calculated at 0.1 mM H_2O_2 where the current efficiency was 104%.

4. CONCLUSIONS

1. Degradation of organic matter present in brewery wastewater (BW) by the EF/EO process is successful, depending on the set of operating parameters applied.
2. Optimal H_2O_2 dose for removal of organics from BW was found to be 0.1 mM which gives a catalyst/oxidant i.e. Fe^{2+}/ H_2O_2 ratio (w/w) of 17 at 0.2 mM of Fe^{2+} concentration and 800 mA applied current intensity. Highest COD removal obtained using these conditions is 90.5%.
3. Mass transfer was found to be enhanced by the addition of H_2O_2 externally at the BDD anode.
4. The next step of the research will focus on optimization of the overall process including current intensity, Fe^{2+} concentration, cell configuration, time, and current intensity required to achieve 100% removal.

5. ACKNOWLEDGEMENT

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6. REFERENCES

Bensalah, N., A. Bedoui, S. Chellam and A. Abdel-Wahab (2013). "Electro-Fenton Treatment of Photographic Processing Wastewater." *CLEAN - Soil, Air, Water* **41**(7): 635-644.

C. Barrera-Díaz, P. C., F. J. Fernández, R. Natividad, and M.A. Rodrigob, (2014). "Electrochemical Advanced Oxidation Processes: An Overview of the Current Applications to Actual Industrial Effluents." *J Mex Chem Soc* **58**(3): 256-275.

Chen, Y., H. Li, W. Liu, Y. Tu, Y. Zhang, W. Han and L. Wang (2014). "Electrochemical degradation of nitrobenzene by anodic oxidation on the constructed TiO2-NTs/SnO2-Sb/PbO2 electrode." *Chemosphere* **113**: 48-55.

Dirany, A., I. Sires, N. Oturan and M. A. Oturan (2010). "Electrochemical abatement of the antibiotic sulfamethoxazole from water." *Chemosphere* **81**(5): 594-602.

Doubla, A., S. Laminsi, S. Nzali, E. Njoyim, J. Kamsu-Kom and J. L. Brisset (2007). "Organic pollutants abatement and biodecontamination of brewery effluents by a non-thermal quenched plasma at atmospheric pressure." *Chemosphere* **69**(2): 332-337.

Doubla, A., S. Laminsi, S. Nzali, E. Njoyim, J. Kamsu-Kom and J. L. Brisset (2007). "Organic pollutants abatement and biodecontamination of brewery effluents by a non-thermal quenched plasma at atmospheric pressure." *Chemosphere* **69**(2): 332-337.

Eberts, D. (2007). "To Brew or Not to Brew: A Brief History of Beer in Canada." *Manitoba Historical Society*.

El-Ghenymy, A., R. M. Rodriguez, E. Brillas, N. Oturan and M. A. Oturan (2014). "Electro-Fenton degradation of the antibiotic sulfanilamide with Pt/carbon-felt and BDD/carbon-felt cells. Kinetics, reaction intermediates, and toxicity assessment." *Environ Sci Pollut Res Int* **21**(14): 8368-8378.

Enric Brillas, I. S. s., and Mehmet A. Oturan (2009). "Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry." *Chemical Reviews* **109**(12): 6570–6631.

Fillaudeau, L., P. Blanpain-Avet and G. Daufin (2006). "Water, wastewater and waste management in brewing industries." *Journal of Cleaner Production* **14**(5): 463-471.

Ganzenko, O., N. Oturan, D. Huguenot, E. D. van Hullebusch, G. Esposito and M. A. Oturan (2015). "Removal of psychoactive pharmaceutical caffeine from water by electro-Fenton process using BDD anode: Effects of operating parameters on removal efficiency." *Separation and Purification Technology* **156**: 987-995.

Jiang, C.-c. and J.-f. Zhang (2007). "Progress and prospect in electro-Fenton process for wastewater treatment." *Journal of Zhejiang University SCIENCE A* **8**(7): 1118-1125.

Kanagachandran, K. and R. Jayaratne (2006). "Utilization Potential of Brewery Waste Water Sludge as an Organic Fertilizer." *JOURNAL OF THE INSTITUTE OF BREWING* **112**(2): 92–96.

Krishnan Vijayaraghavan, D. A., and Renny Lesa (2006). "Electrolytic Treatment of Beer Brewery Wastewater." *Ind Eng Chem Res* **45**(20): 6854-6859.

M. Panizza, P. A. M., G. Cersola, Ch Comninellis (2001). "Electrochemical treatment of wastewaters containing organic pollutants on boron-doped diamond electrodes: Prediction of specific energy consumption and required electrode area." *Electrochemistry communications* **3**: 336-339.

Marco Panizza and G. Cerisola (2009). "Direct And Mediated Anodic Oxidation of Organic Pollutants." *Chemical Reviews* **109**(12): 6541–6569.

Ö., A. (2014). "Reduction of COD in wastewater from a textile industry by Electro-fenton process." *Global NEST Journal* **16**(XX): XX-XX.

Plgnatello, Y. S. a. J. J. (1993). "Photochemical Reactions Involved in the Total Mineralization of 2,4-D by Fe^{3+}/H,0,/UV." *Environ Sci Technol* **27**(2): 304-310.

Radjenovic, J. and D. L. Sedlak (2015). "Challenges and Opportunities for Electrochemical Processes as Next-Generation Technologies for the Treatment of Contaminated Water." *Environ Sci Technol* **49**(19): 11292-11302.

Sansebastianmartinez, N. (2003). "Pre-oxidation of an extremely polluted industrial wastewater by the Fenton?s reagent." *Journal of Hazardous Materials* **101**(3): 315-322.

Simate, G. S., J. Cluett, S. E. Iyuke, E. T. Musapatika, S. Ndlovu, L. F. Walubita and A. E. Alvarez (2011). "The treatment of brewery wastewater for reuse: State of the art." *Desalination* **273**(2-3): 235-247.

Tiwari, A. K. and V. K. Upadhyay (2013). "“Fenton’s reagent dose calculation with respect to COD value and the process requirement optimization for effective oxidation of Aqueous Mother Liquor Effluent of an API manufacturing industry” at large scale." *International Journal of Advanced Research* **1**(7): 158-164.