

Wet air oxidation vs electro-oxidation: comparison between two clean processes for treatment of highly concentrated aqueous waste

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ABSTRACT

In Quebec, Canada, several industrial activities generate highly concentrated aqueous wastes that are currently incinerated outside of the province, which incurs in high transportation, treatment and environmental costs. These wastes contain 60-90% water and 80–300 g/L chemical oxygen demand, with variable amounts of carboxylic acids, alcohols, aromatics, etc. Former studies on similar products showed they can be effectively treated by wet air oxidation (WAO) using subcritical water ($\approx 200\text{--}325^\circ\text{C}$, 5-25 MPa), achieving up to 95% COD removal in less than 60 min [1-3]. On the other hand, clean and affordable hydroelectricity is available in Québec, which also makes electro-oxidation (EO) an interesting option for wastewater treatment. This process uses high performance electrodes (e.g. boron doped diamond, BDD) under direct current to generate oxidative species (e.g. $\text{OH}\cdot$ radicals, persulfates, perchlorates), performing efficient mineralization of organic compounds to CO_2 and H_2O . EO is conducted under atmospheric pressure and low temperature ($25\text{--}50^\circ\text{C}$) [4,5].

In this work, performances of both WAO and EO were evaluated on concentrated industrial aqueous waste (≈ 200 g/L COD) at different dilution ratios. Results showed that both technologies can achieve $\approx 90\%$ COD removal under optimal conditions. WAO showed a first-order reaction rate, while EO showed a zero-order reaction rate for concentrations above 22 g/L COD. Combined with techno-economic data, these results can help industries select the most beneficial technology for a given wastewater.

INTRODUCTION

Economic activities in Quebec rely on various industrial fields: mining, metallurgy, chemical industry, aeronautic, etc. These activities all generate highly concentrated aqueous wastes (CAW), with chemical oxygen demand (COD) $\approx 80\text{--}300$ g/L and variable amounts of carboxylic acids, alcohols, aromatics compounds, etc. These streams would be too concentrated or toxic to be treated by usual physicochemical or biological treatment plants. Local environmental regulations also prevent incinerating such wastes in Québec. Hence, thousands of m^3/y of CAW are collected by waste management firms to be incinerated outside of Québec, which incurs in high transportation, treatment and environmental costs. There is a clear need for a local treatment solution that would be efficient, affordable and environmentally viable for this category of aqueous waste.

Former studies on similar products showed that CAW can be effectively treated by wet air oxidation (WAO) using subcritical water ($\approx 200\text{--}325^\circ\text{C}$, 5-25 MPa), with or without catalyst (i.e. transition or noble metals), achieving up to 95% COD removal in less than 60 min [1-3]. In this subcritical water media

enriched with air or pure O₂, fast oxidation is performed through generation of OH• radicals, leading to mineralization of organic compounds to CO₂, H₂O, NH₄⁺, SO₄²⁻, PO₄³⁻ and refractory compounds such as acetic acid and other organic acids. Many full-scale WAO plants are in operation around the world, mostly for municipal sludge and spent caustic wastes treatment. However, very few examples concerning industrial CAW treatment have been reported and no such industrial process is in place in the province of Québec. Due to the high complexity and variability of these waste streams, lab-scale experiments on real samples combined with techno-economic data are necessary to further assess industrial potential of WAO in this context.

On the other hand, clean and affordable hydroelectricity is available in Québec, which also makes electro-oxidation (EO) an interesting option for wastewater treatment. This technology uses high performance electrodes under direct current to generate oxidative species (e.g. OH• radicals, persulfates, perchlorates), performing efficient mineralization of organic compounds to CO₂ and H₂O. This process is conducted under atmospheric pressure and low temperature (25–50°C) [4,5]. Recent developments of high performance Boron doped diamond (BDD) electrodes [6], able to sustain higher current densities with longer service life, makes EO an interesting option for CAW treatment. While EO treatment is known to require longer treatment time than WAO, its low investment and maintenance costs compared to other technologies could be very appealing to industries.

CTTÉI has conducted lab-scale experiments with both WAO and EO on several CAW streams generated in Quebec. Kinetic data obtained for a given set of experimental conditions were also compared for both processes.

MATERIALS AND METHODS

Waste samples

Seven different CAW samples were obtained from an industrial waste management firm located near Montréal, Canada, and analysed for several parameters (table 1).

Table 1: CAW samples chemical composition

	CAW #0	CAW #1	CAW #2	CAW #3	CAW #4	CAW #5	CAW #6
COD (mg/L)	194,425	306,750	88,950	107,550	258,125	165,000	156,700
Dissolved solids (mg/L)	n.d.	36,300	26,600	119,100	70,820	63,140	38,490
pH	1.5	6.9	9.8	6.2	5.8	6.4	8.3
Chlorides (mg/L)	1,205	1,436	517	16,674	1,650	1,210	4,650
Total carbon (mg/L)	n.d.	58,425	31,540	37,760	45,470	39,195	43,775
Inorganic carbon (mg/L)	n.d.	7,575	6,650	12,170	3,930	520	<500
Kjeldahl total nitrogen (mg/L)	100	1,240	1,740	6,560	2,400	6,100	1,735
Superior heat value (kJ/kg)	1,301	5,966	1,026	2,568	4,497	2,680	3,147

Identification of main organic compounds in CAW sample #0 was also performed by gas chromatography coupled with mass spectrometry (GC-MS) in a private laboratory, as shown on table 2.

Table 2: Main organic compounds of CAW sample #0 by GC-MS

Compound	Chemical formula	Compound	Chemical formula
Hydrazine	H ₄ N ₂	Benzene-methyl	C ₇ H ₈
Ethanol	C ₂ H ₆ O	Cyclohexanone	C ₆ H ₁₀ O
2-butanone	C ₄ H ₈ O	2(3H)-furanone, dihydro	C ₄ H ₆ O ₂
Acetic acid ethyl ester	C ₄ H ₈ O ₂	Phenol	C ₆ H ₆ O
Propane-2-etoxy-2-methyl	C ₅ H ₁₂ O	Benzaldehyde, 2-hydroxy	C ₇ H ₆ O ₂
Tetrahydrofuran	C ₄ H ₈ O	Phenol, 4-methyl	C ₇ H ₈ O
Benzene	C ₆ H ₆	Phenol, 2,4-dimethyl	C ₈ H ₁₀ O
2-propanol-1-methoxy	C ₄ H ₁₀ O ₂	Phenol,3,5-dimethyl	C ₈ H ₁₀ O

Table 1 and 2 show a complex composition for CAW #0 as well as important variability between different CAW samples. Among organic compounds identified by GC-MS, some are known to be refractory to low temperature WAO (ethanol, acetic acid compounds), which mean aggressive WAO conditions could be necessary to achieve a high oxidation yield ($\geq 300^{\circ}\text{C}$).

Upon reception, CAW samples were centrifuged (8,000 rpm – 5 min) to remove suspended solids. After centrifugation, if an oily film was observed on a sample's surface, it was also removed and only the aqueous phase was kept (which always represented $> 95\%$ of sample's volume). To prevent corrosion of the WAO reactor, chlorides were precipitated and removed as $\text{AgCl}_{(s)}$ by adding $\approx 30\%$ excess of AgNO_3 . Next, AgNO_3 was also precipitated as $\text{AgOH}_{(s)}$ by raising pH > 10 with NaOH, to ensure Ag^+ ions did not interfere or catalyse oxidation reactions.

Wet air oxidation

CTTEI's WAO laboratory equipment was custom-made by *TOP Industrie* (150 ml batch reactor, passivated inox 316 Ti alloy, operating range up to 300 bar/350°C, with a high pressure syringe pump) (Figure 1).



Figure 1: Wet air oxidation laboratory unit

In order to perform each WAO test, the following procedure was applied. First, a volume of the original CAW mixture was measured by taking into account the COD of the original sample and the desired initial COD for each particular test (10 to 40 g/L), in order to obtain a final liquid volume of 70 mL ($\approx 40\%$ of reactor's volume). CAW sample was injected directly to the autoclave and remaining liquid volume was filled with deionized water by using the syringe pump. Second, inert nitrogen gas was

injected to purge the system and thus expel all the air inside the autoclave; during these two steps, agitation was set at 250 rpm to gently homogenize the solution. Once the liquid solution is in place and the autoclave is purged, temperature was raised to a fixed value (ex.: 325°C) and agitation was set to 1,000 rpm. Upon reaching the set temperature, air was added up to a 50% excess factor to ensure the oxidation rate was not limited by oxidant supply. Finally, the reaction was monitored over time by sampling aliquots of 1 mL after 5, 15, 30 and 60 min; each sample was subjected to COD analysis in duplicate (*Hach 435 High Range method*, absorbance measurement at 320 nm on *DR1900* spectrophotometer). Some WAO assays were made in triplicate to evaluate method repeatability.

Electro-oxidation

Electro-oxidation was performed with a *Diapod* lab equipment from *Element Six* (Figure 2). The EO reactor consisted of 7 BDD electrodes in bipolar configuration (72 cm² total anodic surface). A 15 L recirculation tank was connected to the reactor, with a recirculation pump (\approx 34 L/min) and a dosing pump to maintain pH in range 7-8 with NaOH 10%. A power supply (25A DC) provided a current density up to 24,300 A/m² to the electrodes. Polarity was inverted every 20 s to reduce clogging of electrodes.

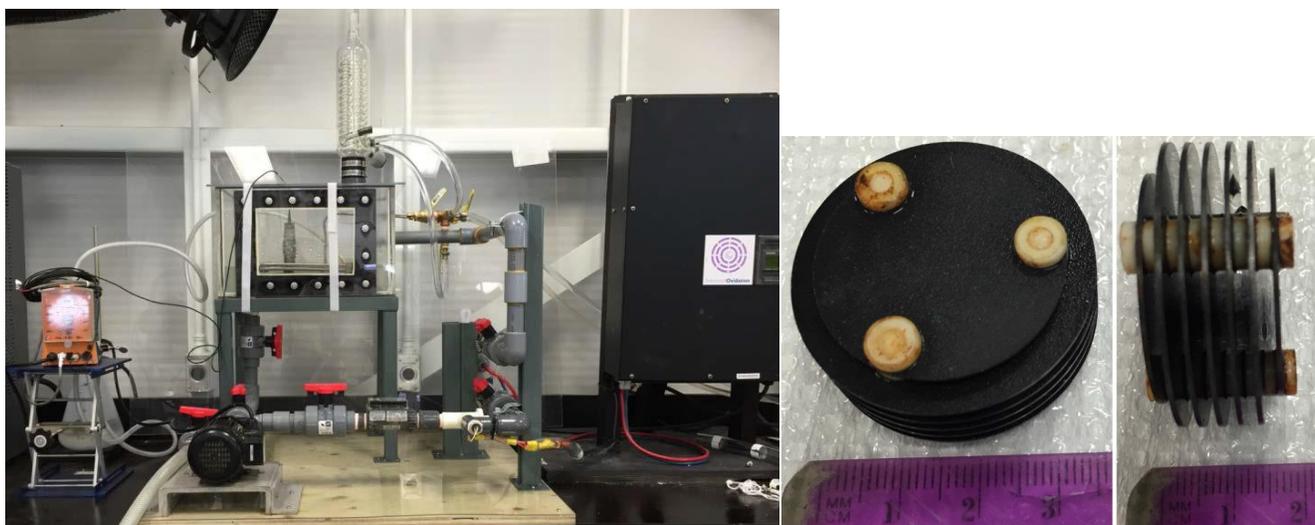


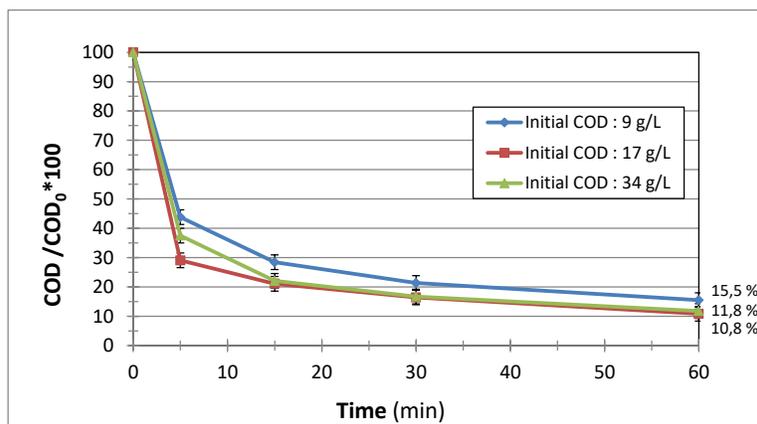
Figure 2 : Electro-oxidation laboratory unit with BDD electrodes

During a typical EO test, a CAW sample was first filled in the tank and the volume was adjusted to 10 L with deionised water to reach desired initial COD (\approx 4–86 g/L). Up to 50 g/L of Na₂SO₄ was added as an electrolyte to ensure the maximum current density could be reached. The recirculation pump was then started, pumping the sample back and forth to the EO reactor and the recirculation tank. A constant reaction temperature (27 ± 1 °C) was maintained by a freshwater cooling system. A reflux column, also cooled by freshwater, prevented evaporation. Power supply was turned on and oxidation reactions started. Several data were collected at different reaction times: current intensity (A), tension (V), pH, temperature, conductivity and volume. A 10 mL aliquot was also sampled for COD analysis in duplicate. Test durations varied from 6 to 12 hours, depending on initial COD concentration. Results were expressed as COD reduction rate over time. A control test was also conducted using the same setup without applying any current on the electrodes.

RESULTS

Wet air oxidation

In previous work (internal report), effects of WAO operating temperature, initial pH and reaction time were studied with an experimental design, and optimised operating conditions were defined using CAW sample #0: **325°C, initial pH 7-8, 15 min, 50% air excess, pressure \approx 150-250 bar** (depending on initial COD and temperature). These experimental conditions were applied on three different dilution ratios of CAW #0, as shown in Figure 3.

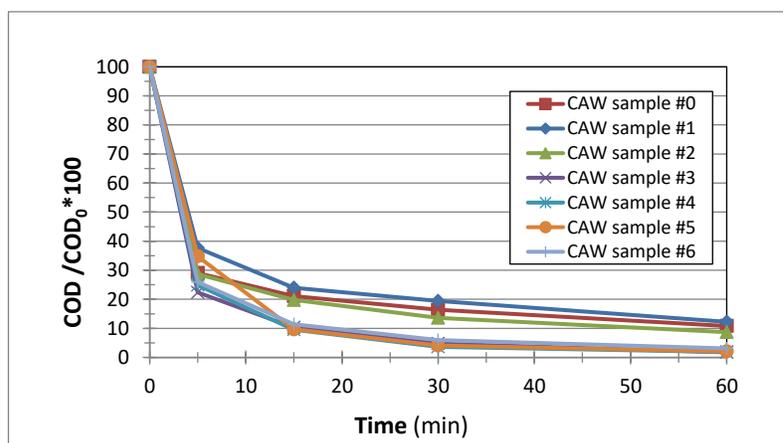


WAO conditions :325°C, 220 – 225 bar, 50% air excess, initial pH 7-8.

Figure 3: WAO of CAW #0: initial concentration effect on COD removal rate

Figure 3 shows that relative oxidation rates ($COD/COD_0 \cdot 100$) are very similar for each concentration tested, especially at 17 and 34 g/L COD. These results confirm the kinetic data from literature: WAO reaction can be seen as a first order reaction with respect to COD concentration [7].

To assess the impact of sample variability on WAO reaction rates, the same operating conditions were applied for CAW samples #1-6 and results are presented on Figure 4.



* 15-20 g/L initial COD, 325°C, 220–225 bar, 50% air excess, initial pH 7-8. Error bars not shown for visibility purpose ($\pm 2,5\%$ standard deviation).

Figure 4: WAO of CAW Samples #0 to 6: effect of samples variability on COD removal rate

Results show an efficient oxidation of all CAW samples at 325°C. COD removal varied from **76 to 89%** after only 15 min treatment and from **88% to 98% after 60 min**. Initial color of CAW samples was

ranging from yellow to dark red before treatment and quickly faded to translucent during treatment (Figure 5).



From left to right : CAW #4 sample before WAO and after 5, 15, 30, 60 min, and final purge

Figure 5: Color changes during WAO of CAW sample #4

In a full-scale industrial process, oxidation duration ≈ 15 min would probably be favored due to economic purposes, and COD removal could be completed by a biological process (or other post-treatment).

Electro-oxidation

According to literature, current density is a major factor influencing oxidation rate in EO processes [4,5], for a fixed anodic surface/sample volume ratio. In order to assess maximum potential of this particular EO equipment, only the highest current density was tested ($\approx 24,000$ A/m²). Fixed surface/volume ratio of 0,72 m⁻¹ was used for each test. COD removal patterns were observed for four different CAW concentrations (Figure 6).

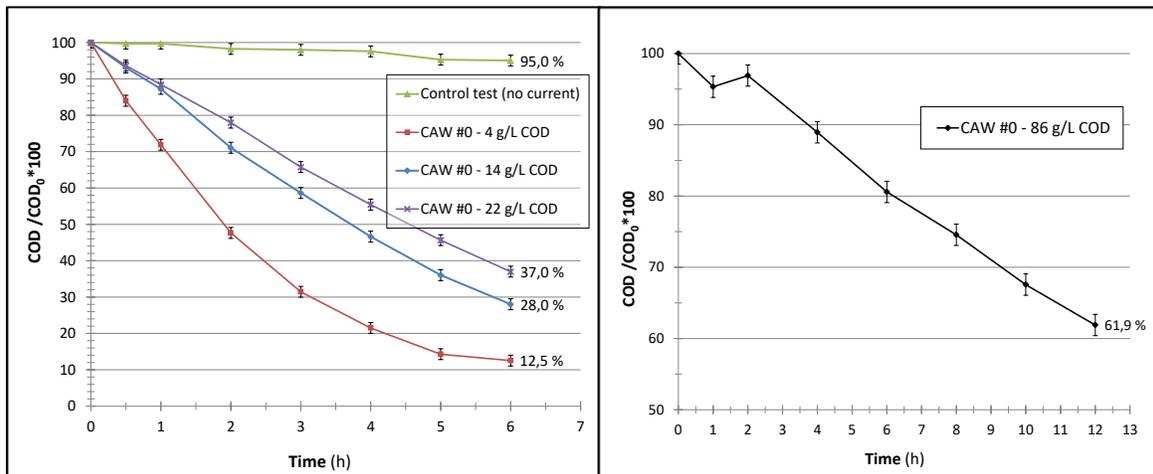


Figure 6: EO of CAW #0 : effect of initial concentration on COD removal rate

COD removal yield was highly affected by initial COD of samples: for a duration of six hours, 87.5% COD removal was obtained at 4 g/L initial COD, as opposed to 20% COD removal at 86 g/L. From these results, rate law calculations have shown that EO acts as a first order reaction for initial COD concentrations lower than ≈ 22 g/L, and as a zero order reaction for higher concentrations. These observations are consistent with literature: at low organic concentrations, EO oxidation kinetic is said to be limited by current, as opposed to limited by mass transfer at higher concentrations, where oxidation rate tends to cap at a certain level [4]. This phenomenon is due to the fact that OH• radicals are generated at the electrode surface, which has a finite dimension. Thus, for CAW concentrations higher than ≈ 22

g/L COD, raising up the surface/volume ratio of this particular EO setup (i.e. more electrodes) would efficiently enhance the reaction rate.

Comparison between both processes

For WAO, oxidation rates are proportional to initial CODs. Hence, oxidation yields at higher concentrations can be estimated with simple linear regression. As for EO, oxidation rates tend to cap at ≈ 27 g DCO/h and this value would rise proportionally with surface/volume ratio. Figure 7 shows oxidation rates that could theoretically be achieved for CAW concentrations up to 200 g DCO/L, with a hypothetical 10 L WAO reactor (to compare with same volume EO equipment).

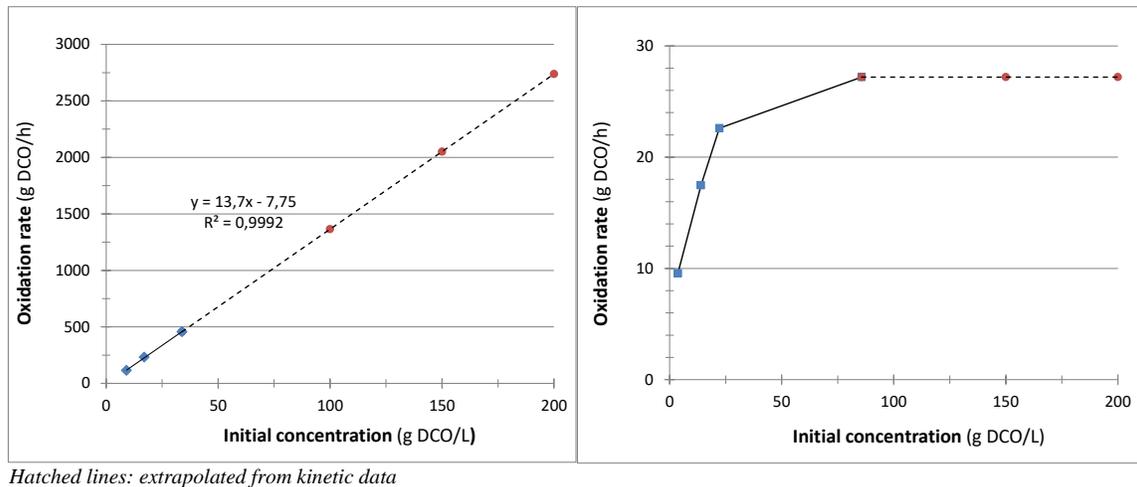


Figure 7: Comparison of oxidation rates between a 10 L WAO reactor and a 10 L EO equipment

These results show that WAO oxidation rates faster than EO for highly concentrated industrial wastes, when considering an equipment of same volume capacity, for these specific operation parameters. However, WAO is known to require high investment costs and could be more expensive than EO for an equipment of similar volume capacity. In order to efficiently support industries with their choice of technology, further modeling of each operational parameter and their effect on oxidation yield (ex.: temperature and pressure for WAO, current intensity and electrode surface for EO), coupled with techno-economic data, would be necessary. This complete tool would be greatly useful for industries aiming to identify the best technology at lower cost, for a particular stream of CAW. Moreover, EO shows a great potential for the post-treatment of CAW after WAO treatment. Known refractory compounds that are generated by WAO (ex.: ammonia, acetic acid) [7] could be efficiently removed by EO, since secondary oxidation reactions with various oxidative species (e.g. persulfate, perchlorate) renders this process less vulnerable to a specific refractory compound [4].

CONCLUSION

Both WAO and EO processes have shown great capacity to oxidize real CAW streams in lab-scale batch equipment, with COD removal about 90%. While substantial COD removal is obtained as fast as in 15 min for WAO regardless of waste initial concentration, such COD removal with EO would require a few hours of treatment time, depending on initial COD, current density and surface/volume ratio. In conjunction with techno-economic analysis, kinetic data that was obtained would be greatly useful to industries aiming to identify the best technology at lower costs for a particular waste stream.

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