Comparison of CO₂ and oxygen DC submerged thermal plasmas for decomposition of carboxylic acid in aqueous solution

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Abstract. The feasibility of the carboxylic acid decomposition with two different direct current (DC) thermal plasma torches was investigated. An oxygen DC submerged thermal plasma torch and a newly designed submerged DC plasma torch operating with a mixture of carbon dioxide and methane (CO₂/CH₄) were used. Sebacic acid was selected as a representative of pollutants in the most wastewater produced by chemical process industries. The effect of different operational conditions including treatment time, the reactor pressure as well as the role of oxidizing agents such as (H₂O₂) were investigated on the decomposition rate of sebacic acid. Concentration of sebacic acid was quantified by Ion Chromatography/Mass Spectrometry (IC/MS). The oxygen plasma showed higher decomposition rate in basic medium. Adding H₂O₂ into aqueous solution enhanced the sebacic acid decomposition rate with the CO₂/CH₄ plasma up to the same decomposition rate of the oxygen plasma. Increasing the pressure also increased the decomposition rate for both plasmas with an increase twice higher for the CO₂/CH₄ plasma than that of the oxygen plasma. This work therefore presents the conditions in which these plasmas can provide the same decomposition rate for contaminants in aqueous solution.

1. Introduction
The increase in the world’s population and at the same time, changes in our lifestyles along with industrialization, especially in developing countries, are leading to increase the amounts of wastewaters and contaminated aqueous solutions. This ongoing increase in the amounts of wastewater raises the risk of discharging the polluted water into the natural environment. The nature of the contaminants is different. A significant amount of pollutants in wastewater of chemical process industries, such as dyes, pigments, paints, and petrochemicals, are carboxylic acids [1]. They also form a significant part of organic contaminants in process liquors in some industries, such as the aluminum industry (Bayer process) [2]. A large amount of solubilised and built up carboxylic acids in process liquors and wastewaters has negative effects on the environment and the production efficiency of these industries. Therefore, demands for effective and environmentally friendly technologies for aqueous solution treatment have increased [2]. Among different types of thermal plasma, direct current (DC) arc plasma is a common type of thermal plasma for treating liquids and solutions [2]. DC submerged thermal plasma reactor is a specific type of DC thermal plasma reactors because it can offer a direct contact between the plasma and solution [3]. The advantages of the submerged thermal plasma also include the presence of steep thermal gradients, the photolysis reaction as a result of UV radiation of...
plasma, ability to treat high volumes of wastewater, and proper mixing between solution and plasma [4]. In the case of DC plasma torches, different plasma gases can lead to different decomposition rates of the treated material depending on their reactive species, enthalpy and thermal conductivity. They also have a direct effect on the electrode life-time, which is an important issue for DC plasma torches [2]. Air, oxygen, argon, and nitrogen are considered as common plasma gases [5]. Carbon-containing molecular gases, such as CO₂-based gas mixtures, are recently presented by Mostaghimi et al. [6] as plasma gases for a newly designed DC plasma torch. This new DC plasma torch shows some advantages compared to DC plasma torches with common plasma gases. It can efficiently transfer heat to the treated waste due to its high plasma enthalpy and high thermal conductivity. Moreover, it produces a positive carbon ion current, which can be deposited on the surface of a negatively charged cathode. This carbon deposition protects the electrode from erosion and increases the electrode life-time. Furthermore, CO₂ can be found in almost pure form as a waste gas in certain chemical industries [7]. Therefore, using easily available plasma gas like CO₂ along with a long-life electrode makes this torch valuable. However, the performance of this new DC thermal plasma torch has not been yet compared with common DC thermal plasma torches for treatment of organic contaminants in solutions and liquids.

Therefore, the scope of this study is to investigate the comparison between the performances of CO₂-based gas mixture thermal plasma torch and oxygen thermal plasma torch in a submerged mode at different operational conditions for decomposition of carboxylic acid in aqueous solution. Sebacic acid, a typical organic contaminant in Bayer liquor, was selected as a representative of organic contaminant. The effectiveness of the process was therefore defined by decomposition rate of sebacic acid. The operational parameters such as treatment time, and reactor pressure as well as the role of hydrogen peroxide as an oxidizing agent were investigated on the decomposition of sebacic acid for both plasmas.

2. Material and methods

Figure 1 shows a photo of the apparatus used in this work. This apparatus was initially designed by Bernier et al. [3] based on a submerged thermal plasma system. In this study, two different direct current (DC) plasma torches using CO₂-CH₄ and O₂ gases were separately used to generate thermal plasma at the bottom of the reactor. A DC plasma torch designed and built in the Centre for Advanced Coating Technology at University of Toronto with a 39 kW power (60% thermal efficiency), and a graphite cathode was used while the plasma gas was CO₂ and CH₄ in a volume ratio of (CO₂/CH₄= 1.875). The presence of CH₄ in plasma gas composition produces a protective graphite deposition on the surface of the negatively charged graphite cathode protecting the cathode form erosion. Therefore, the cathode will be operational as long as the CH₄ is present in the plasma gas composition. Another 39 kW DC plasma torch with a copper cathode, around 60% thermal efficiency, and oxygen as plasma gas designed and built in the thermal plasma laboratory at Université de Sherbrooke was also used for generation of thermal plasma. The operating procedure for the decomposition of sebacic acid by submerged thermal plasma was as follows: 20 L of distilled water and 4.5g/L of sebacic acid (supplied by Alfa Aesar®) and known amount of sodium hydroxide (97%, from Alfa Aesar®) for changing the solution pH were placed in the solution tank. The solution was stirred before injecting into the reactor for making homogenous solution. The solution was injected into the reactor via the solution pump after preheating to 50 °C. Totally dry CH₄ (99.99% pure) and CO₂ (99.99% pure) in a volume ratio of (CO₂/CH₄= 1.875), and dry oxygen (99.99 % pure) were used as plasma gases for the experiments. Plasma gas (CO₂/CH₄ or oxygen) were then injected into the discharge region of the torch. The beginning of the treatment process (t=0) was set with the starting of the plasma ignition. The solution samples were then taken periodically from the sampling line at the middle of the reactor for analytical characterization. IC/MS (A Dionex ICS-3000 ion chromatography system equipped with a Thermo Scientific MSQ Plus Mass Detector) was used to quantify sebacic acid present in the sample. More details about the analytical characterization can be found in [5].
The emission of UV radiation (UVB and partially UVC) from plasma in the submerged mode was quantified by means of an IL-1700 research radiometer with SED240 narrow-band germicidal light probe (International Light, Inc., Newburyport, Mass.) as can be seen in figure 1b. The zero point for the detector of radiometer was set at the room light. The organic compounds in the solution absorb the major amount of UV radiation [8]. Therefore, to measure and compare the intensity of UV radiation from the CO₂-based gas mixture plasma and the oxygen plasma in the submerged mode, the blank experiments were performed with distilled water, without adding sebacic acid.

Figure 1. (a) The experimental set-up (b) Magnified zone of location A shown in figure 1 (a) with UV probe for plasma radiation measurement.
3. Result and discussion

3.1. Decomposition vs. treatment time
Decomposition rate of sebacic acid with the oxygen and the CO\textsubscript{2}/CH\textsubscript{4} plasmas in basic medium is shown in figure 2. It is observed that the decomposition of sebacic acid is feasible with both plasmas. However, the decomposition rate of sebacic acid with the CO\textsubscript{2}/CH\textsubscript{4} plasma is lower than that of the oxygen plasma in basic medium. The higher decomposition rate of sebacic acid via the oxygen plasma can be attributed to the higher amount of contributing plasma oxidant species in the decomposition of sebacic acid. The presence of CO\textsubscript{2} in the CO\textsubscript{2}/CH\textsubscript{4} plasma leads to the production of dissolved bicarbonate and carbonate species upon contact with the solution, without any sebacic acid decomposition. These species can act as scavenger of oxidant species, which decrease the amount of oxidant species contributing in the decomposition of sebacic acid with the CO\textsubscript{2}/CH\textsubscript{4} plasma. Therefore, lower decomposition rate of sebacic acid with the CO\textsubscript{2}/CH\textsubscript{4} plasma compared to the oxygen plasma in basic medium can be due to high amount of bicarbonate and carbonate species in solution as well as low amount of plasma oxidant species.

![Figure 2. Sebacic acid concentration versus treatment time, solution pH=12.5, \( C_{\text{Sebacic acid}} = 4.5\text{g/l}, \text{CO}_2/\text{CH}_4=1.875, \) reactor pressure = 1 atm (108 kPa).](image)

3.2. Decomposition rate in the presence of hydrogen peroxide
The role of hydrogen peroxide as an oxidizing agent on decomposition of sebacic acid is illustrated in figure 3 for the oxygen, and the CO\textsubscript{2}/CH\textsubscript{4} submerged thermal plasmas. Hydrogen peroxide is a common industrial oxidizing agent and is easy to provide. Hydrogen peroxide was added through the make-up water (5% volume of make-up water) to the solution during the treatment. As observed in figure 3, adding H\textsubscript{2}O\textsubscript{2} has a significant positive effect on further decomposition of sebacic acid with the CO\textsubscript{2}/CH\textsubscript{4} plasma. It can be attributed to the high amount of UV radiation of the CO\textsubscript{2}/CH\textsubscript{4} plasma.

However, adding H\textsubscript{2}O\textsubscript{2} does not make any difference on decomposition rate of sebacic acid with the oxygen plasma. The UV emission detected by UV detector from the oxygen plasma in submerged mode was (4.26E-06 (W/cm\textsuperscript{2})), which is much lower than that of the CO\textsubscript{2}/CH\textsubscript{4} plasma 5.63E-04 (W/cm\textsuperscript{2}). The UV radiation leads to the production of hydroxyl radicals via cleavage of the hydrogen peroxide molecule (equation (1)).

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2\text{HO}^* \tag{1}
\]
The positive effect of adding hydrogen peroxide on decomposition rate of sebacic acid with the CO\textsubscript{2}/CH\textsubscript{4} plasma is therefore attributed to the formation of hydroxyl radicals, which is a highly oxidant specie, through the photolysis of H\textsubscript{2}O\textsubscript{2}. As seen in figure 3, the addition of H\textsubscript{2}O\textsubscript{2} in the solution treated by the CO\textsubscript{2}/CH\textsubscript{4} plasma increases the sebacic acid decomposition rate up to the same decomposition rate with the oxygen plasma. The high intensity of UV radiation of CO\textsubscript{2} plasma, which leads to photolysis of hydrogen peroxide and formation of hydroxyl radical, has positive effect on sebacic acid decomposition. Therefore, the CO\textsubscript{2}/CH\textsubscript{4} plasma in the presence of hydrogen peroxide can be suitable choice as the oxygen plasma for the treatment of contaminated solution containing sebacic acid.

3.3. Decomposition rate at non-atmospheric pressure
The effect of non-atmospheric pressure on decomposition of sebacic acid with both plasmas was investigated by performing the experiments at atmospheric and non-atmospheric (10 psig equivalent to 1.7 atm) pressure. The comparison of sebacic acid decomposition rate at atmospheric and non-atmospheric pressure for both plasmas is shown in figure 4. It can be seen that higher pressure leads to higher decomposition rate of sebacic acid regardless of the plasma gas type. However, the increase in sebacic acid decomposition rate is lower for the oxygen plasma than that of the CO\textsubscript{2}/CH\textsubscript{4} plasma. It has been shown that the intensity of UV radiation from plasma could be increased by increasing pressure [4, 8, 9]. The higher UV radiation resulting from higher reactor pressure leads to producing higher amount of hydroxyl radicals (equation (2)), and subsequently higher sebacic acid decomposition rate.

\[
H_2O + OH^- \xrightarrow{hv} H^+ + HO^- + e^-
\] (2)

Furthermore, as shown in figure 4, the treatment time for the same amount of sebacic acid decomposition at non-atmospheric pressure with the CO\textsubscript{2}/CH\textsubscript{4} plasma is higher compared to that with the oxygen plasma. This again indicates the lack of oxidizing hydroxyl radicals present in the solution treated by CO\textsubscript{2}/CH\textsubscript{4} plasma due to the formation of bicarbonate and carbonate species.
4. Conclusion
The performance of oxygen direct current (DC) thermal plasma torch and a newly designed carbon dioxide based gas mixture DC plasma torch has been studied for treatment of an aqueous solution containing carboxylic acid. Sebacic acid was selected as a representative of high molecular weight carboxylic acid contaminant in wastewater. The feasibility study confirmed the decomposition of sebacic acid in aqueous solution with both plasma torches. However, the oxygen plasma showed higher conversion rate in basic medium. The results also revealed the positive role of H₂O₂ in the sebacic acid decomposition rate with the CO₂/CH₄ plasma due to synergetic effect between H₂O₂ and UV radiation. It was observed that, by adding H₂O₂ to the solution treated by the CO₂/CH₄ plasma, decomposition rate can attain to the same decomposition rate of the oxygen plasma. Increasing the pressure also enhanced the decomposition of sebacic acid for both plasmas. However, the increasing tendency is lower for the oxygen plasma than that of the CO₂/CH₄ plasma. This work therefore not only shows the difference between the performance of two plasma torches at different operational conditions, but also presents the condition in which these plasmas can provide the same decomposition rate for contaminants in aqueous solution.

Acknowledgments
This study was funded by NSERC (Natural Sciences and Engineering Research Council of Canada) discovery grant. We are grateful for the support of NSERC for funding this research.

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