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Application of a combination of electrooxidation and ozonation as a sustainable wastewater treatment process

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ABSTRACT

Traditional wastewater treatments involve the addition of chemicals or the use of microorganisms. However, the limitation in both the processes is sludge generation. The sludge management and final disposal could represent up to 50% of the total wastewater treatment plant cost. Therefore, the use of advanced oxidation processes (AOPs) could represent an interesting option for treating wastewater with less or without sludge production. The final goal of advanced oxidation processes is the complete degradation of the pollutants present in wastewater aiming at its complete mineralization. Electrooxidation use one of the cleanest reagents: the electrons. Since the electrons are used in the oxidation process, it becomes sustainable. It is considered a robust technology and is easy to use. Therefore, it has been used for a diversity of wastewater treatments. The main advantages of this technology over other conventional treatments are: the addition of chemicals is not required and this process is carried out at room temperature and atmospheric pressure. Ozone is a powerful oxidant produced in gas phase and a mass transfer occurs to aqueous solution by means of a diffuser. A main advantage of using ozonation is that it oxidizes organic compounds without producing residual sludge. However, when both electrooxidation and ozonation processes take place at the same time, a synergy occurs and the process reaction time is decreased. It implies that the ozone dosage and electricity consumption is also reduced. This review paper gives the application of a combination of electrooxidation and ozonation as a sustainable approach for treatment of different types of wastewaters.

1. Introduction

Water quality and availability is a challenging problem for the societies all over the world. Conventional biological, physical and chemical methods of wastewater treatment have limited success when applied to the treatment of industrial effluents since wastewater contains stable refractory organic compounds (Bernal-Martinez et al. 2010). These processes also tend to generate large amount of sludge which require treatment before final disposal. The costs involved in sludge management and final disposal could be up to 50% of the total wastewater treatment plant cost. Therefore, there is a requirement of novel processes to deal with this issue.

Recently, attention has focussed on advanced oxidation processes (AOPs) to reduce the refractory organic pollutants in wastewater effluents. AOPs are oxidation processes in which the generation of hydroxyl radicals occurs to affect the chemical transformation of contaminants. They are aimed at complete mineralization of the pollutants present in the wastewater. They are also involved in less or no sludge generation and solve the problem of sludge disposal. These processes can reduce the toxicity and increase the biodegradability of recalcitrant organic pollutants (Carbajal et al. 2016).

The electron is the main reagent used in electrochemical oxidation processes. These processes become green and sustainable due to the use of the electrons as the cleanest reagents. These processes include the application of an external source of energy into an electrochemical cell that contains electrodes. A reduction reaction occurs at the cathode whereas the oxidation reactions occur at the anode. Some advantages of using this technology include no addition of chemicals and its application at room temperature and atmospheric pressure.

The ozonation process implies the use of ozone as a strong oxidant that oxidizes organic pollutants. Ozone is produced in gas phase and transferred to the liquid phase by means of a diffuser. This process has the advantage of being applied when the flow rate and/or composition of the effluents is fluctuating (Bernal-Martinez et al. 2013). It also offers the advantage of no residual sludge production.

Mass transfer limitations are one of the limitations during the application of ozonation and electrooxidation processes. However, a synergistic effect occurs when both the processes occur at the same time. The combined process offers the advantages of lesser reaction time, lower ozone consumption rate as well as reduced electricity consumption. This review paper describes the applicability of the combined treatment as a sustainable approach for wastewater treatment.

2. Hydroxyl radical

The formation of hydroxyl ($OH^·$) radicals is the basis for advanced oxidation processes (AOPs). The $OH^·$ radical is a highly reactive radical (E^0 = 2.80 V) which is able to react unselectively and rapidly with recalcitrant organic pollutants. The greener technology to produce hydroxyl radicals is its electrochemical production from the treated water. The Boron Doped Diamond (BDD) anodes have acted as the most efficient electrodes for the production of $OH^·$ radicals.

Some of the characteristics of hydroxyl radicals include: (i) powerful oxidant, (ii) highly reactive, (iii) easily generated, (iv) non-selective, (v) short reaction time and (vi) harmless.

3. Ozonation

Ozone is a pale blue gas generated from oxygen. The most common method used for generating ozone on both laboratory and industrial scale is the electrical discharge method. The electrical discharge generates ionized oxygen atoms which react with oxygen molecules to produce ozone. It is a powerful oxidant ((E^0 = 2.80 V). However, it should be generated in situ prior to its application in wastewater treatment because it is highly unstable. After ozone production, a diffuser is used to transfer the ozone gas to the aqueous solution through a mass transfer process.

The two main advantages of ozonation in wastewater treatment is that it completely degrades organic materials and does not generate sludge as well. The oxidation of organics by the application of ozone occurs through two different pathways: direct and indirect ones. In the direct pathway, the molecules react directly with the ozone molecules. In the indirect pathway, the ozone molecules react to generate oxidant species which carry out the oxidation process. The oxidation pathway depends upon the reaction rate of the ozone and the organics.

The decomposition of ozone in water to form hydroxyl radicals is shown below:

$$O_3 + OH^- \longrightarrow O_2 + HO_2^- \quad (1)$$

$$O_3 + HO_2^- \longrightarrow HO_2^· + O_3^{·-} \quad (2)$$

$$HO_2^· \longrightarrow H^+ + O_2^{·-} \quad (3)$$

$$O_2^{·-} + O_3 \longrightarrow O_2 + O_3^{·-} \quad (4)$$

$$O_3^{·-} + H^+ \longrightarrow HO_3^· \quad (5)$$

$$HO_3^· \longrightarrow OH^· + O_2 \quad (6)$$

4. Electrooxidation

Since electrochemical oxidation is considered to be a robust and easy to use technology, it has been used widely for treating different wastewaters. The main advantages of this technology are:

- Electron is the main reagent
- A simple electrochemical cell is required
- No addition of chemicals is required
- The process is carried out at room temperature and atmospheric pressure

Among the various oxidation processes, the electrochemical advanced oxidation processes (EAOPs) have been used for wastewater treatment recently. In case of direct electrooxidation, the pollutants in the bulk of the wastewater must reach the electrode surface and the oxidation reaction takes place. The electrode materials influence the efficiency and selectivity of the oxidation process. Mass transfer becomes very important in this process. The oxygen evolution potential of some electrode materials is shown in Table 1.

Table 1: Oxygen evolution potential of some electrode materials

Material	Oxygen evolution potential (V)
Pt	1.6
Graphite	1.7
SnO_2	1.9
PbO_2	1.9
Boron doped diamond	2.3

An example of electrochemical reactor is a reactor which contains an anode made of boron doped diamond and cathode made of stainless steel. Hydroxyl radicals are produced at the anode whereas water reduction occurs at the cathode. The main reactions involved in the hydroxyl radicals production through boron doped diamond (BDD) are:

$$BDD + H_2O \longrightarrow BDD\,(OH^{\cdot}) + H^+ + e^- \quad (7)$$

$$BDD\,(OH^{\cdot}) + R \longrightarrow BDD + mCO_2 + nH_2O \quad (8)$$

$$BDD\,(OH^{\cdot}) \longrightarrow BDD + 1/2O_2 + H^+ + e^- \quad (9)$$

The main advantages of BDD anodes are:

- Robustness
- High efficiency
- Good integration capability

The formation of hydroxyl radicals in these electrochemical reactors is limited to the anodic surface and by the mass transfer from the liquid to the electrode.

5. Integrated Ozonation-Electrooxidation

In order to have a synergistic effect of the two processes Ozonation and Electrooxidation, a coupled treatment is more effective. It involves the introduction of the electrodes inside the ozone reactor. For example, the two electrodes are introduced in the ozone bubble column reactor. In this type of reactor, the ozonation and electrochemical oxidation reaction takes place at the same time. Thus, the hydroxyl radical concentration is enhanced and mass transfer limitation is also reduced. At the same time, the bubbles generated by the addition of ozone in the bottom of the reactor allows a complete mixing of the solution inside the reactor.

The variables to control in the integrated process include:

- Electrodes type
- Interelectrode distance
- Current density
- Salt concentration (it determines conductivity)
- Ozone flow rate

With a set of well optimized parameters, there is an improvement in the results obtained through the integrated treatment as compared with the two separate treatment methods. The integrated treatment might result in a significant improvement in the quality of the treated wastewater.

Bernal-Martinez et al. (2010) studied the effectiveness of electrochemical, ozonation and integrated electrochemical-ozonation processes on the treatment of industrial wastewater receiving discharge from 144 different facilities. Electrochemical treatment using iron electrodes under optimum conditions (i.e. pH = 7, current density = 40 mA/cm^2) reduced the chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) by 42% and 43% respectively. Ozonation (mean ozone concentration = 5 mg/L) reduced both COD and BOD_5 by 60%. Integration of the two processes under optimum conditions (i.e. pH = 7, current density = 20 mA/cm^2 and ozone concentration = 5 mg/L) resulted in the reduction of COD and BOD_5 by 84% and 79% respectively. It indicated that the integrated process was more efficient in industrial wastewater treatment due to higher COD and BOD_5 removals whereas it was more cost effective as well due to application of lower current density resulting in lower energy consumption.

The effectiveness of a combination of electrooxidation and ozonation processes for the treatment of industrial wastewater receiving discharge from 144 different facilities was also studied by Garcia-Morales et al. (2013). Electrooxidation using BDD electrodes resulted in COD removal by more than 99% but it took a long reaction time of 140 min. Ozonation resulted in maximum COD removal of 45% within the same reaction time. The coupled electrooxidation-ozonation process under optimum conditions (i.e. current density = 30 mA/cm^2 and ozone concentration = 5 mg/L) resulted in more than 99% COD removal within 60 min reaction time. It indicated the cost-effectiveness as well as higher efficiency of the coupled treatment.

An evaluation into the effectiveness of an integrated electrochemical-ozone reactor was done for the treatment of an industrial wastewater receiving discharge from 144 different industries (Bernal-Martinez et al. 2013). The electrochemical treatment using iron electrodes resulted in 30% COD removal within 48 min reaction time whereas ozonation resulted in 55% COD removal within a reaction time of 20 min. The integrated electrochemical-ozone reactor under optimum conditions (i.e. current density = 66 mA/cm^2 and ozone concentration = 5 mg/L) resulted in a COD removal of 79% within 20 min reaction time. It indicated that the integrated treatment was more efficient as well as cost effective.

Qiu et al. (2014) investigated the synergistic effect of a combination of electrolysis and ozonation for treatment of wastewater contaminated with para-nitrophenol (PNP). Electrolysis using BDD electrode was found to give only 20% total organic carbon (TOC) removal whereas ozonation was found to give only 44% TOC removal. Under similar reaction conditions (i.e. electrolyte = 0.1 M NaCl, current = 100 mA, ozone concentration = 75 mg/L, gas flow rate = 0.2 L/min), 91% TOC removal was obtained within 60 min reaction time of the combined electrolysis-ozonation treatment. It indicated that when electrolysis and ozonation were applied simultaneously, a synergistic effect for PNP mineralization was obtained. The synergistic effect can be attributed to: (a) the rapid degradation of PNP to carboxylic acids by O_3 and (b) the effective mineralization of the ozone-refractory carboxylic acids to CO_2 by $OH^{\cdot}$ radicals generated from multiple sources in the electrolysis-O_3 system. The improvement in performance of the synergistic treatment may be mainly attributed to the fact that electrolysis and ozonation can compensate for each other's disadvantages (i.e. mass transfer limitations inherent to electrode kinetics in electrolysis and selective oxidation in ozonation).

Carbajal et al. (2016) evaluated the effect of adding electrochemically generated copper (III) ions into an ozonation reactor for the treatment of wastewater receiving discharge from 144 different industries. The COD removal in 60 min reaction was found to be 60% and 52% respectively, by electrochemical addition and ozonation respectively. The combination of both processes resulted in COD removal of 83% in only 15 min reaction time. In the same time period, TOC and colour removals of 78% and 93% respectively, were also obtained. It clearly indicated that the combined treatment is more efficient as well as cost effective due to lesser reaction time requirement.

6. Conclusions

Coupling electrooxidation with ozonation has the potential to improve the process efficiency of the already existing electrooxidation and ozonation processes for treating wastewaters contaminated with recalcitrant pollutants. The coupled process has a better performance as compared to the individual processes in terms of COD, TOC and BOD removals due to the compensation of mass transfer limitations in the individual processes. The coupled process is green since it does not produce residual sludge as well as sustainable due to the reduction in electricity consumption.

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