

CEE 597T
Electrochemical Water and Wastewater Treatment

UNIT 3
ELECTRO-FENTON

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What is Electro-Fenton?

- **Electro-Fenton (EF)** process is an advanced oxidation process (AOP) that is able to mineralize organic pollutants such as pharmaceuticals, pesticides, dyes, phenols, and phenolic compounds through radical reactions.
- EF process is a modification of conventional Fenton reaction (a synergetic action of H_2O_2 and iron catalysts) by means on in situ electrogeneration of Fenton's reagent.

What is Fenton Reaction?

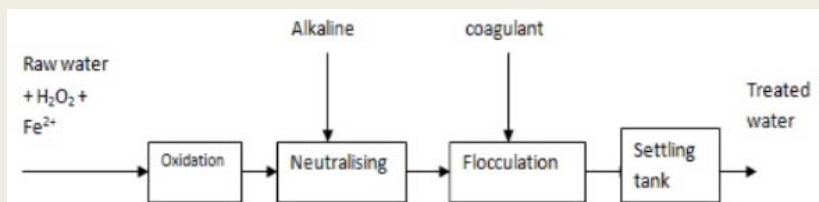
- Advanced Oxidative Degradation Processes (AOPs) comprise of techniques such that, under certain conditions, it could transform the vast majority of organic contaminants into carbon dioxide, water, and inorganic ions as a result of oxidation reactions.
- The oxidation of organic substrates by iron (II) and hydrogen peroxide is called the “Fenton Reaction” or “Fenton reagent”.
- The Fenton's reaction is used to treat a large variety of water pollution such as phenols, formaldehyde, pesticides, and rubber chemicals and so on.
- The high efficiency of this technique can be explained by the formation of strong hydroxyl radical ($\text{OH}\cdot$) and oxidation of Fe^{2+} to Fe^{3+} . Both Fe^{2+} and Fe^{3+} ions are coagulants, so the Fenton process can, therefore, have dual function, namely oxidation and coagulation, in the treatment processes.

How does the Fenton's reaction work ?

- The mixture of FeSO_4 or any other ferrous complex and H_2O_2 (Fenton's reagent) at low enough pH, results in Fe^{2+} catalytic decomposition of H_2O_2 and proceeds via a free radical chain process that The generated ferric ions can be reduced by reaction with excess hydrogen peroxide to form again ferrous ion and more radicals
- In the Fenton reaction hydroxyl radicals are generated from the reduction of hydrogen peroxide.
- $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}\cdot + \text{OH}^-$

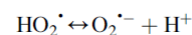
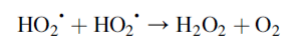
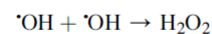
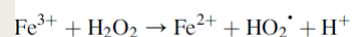
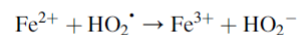
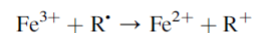
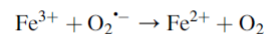
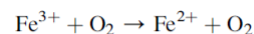
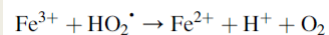
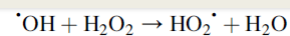
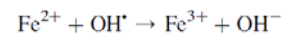
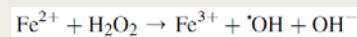
Hydroxyl radicals have extremely high oxidizing ability and could oxidize hard to decompose organic compounds in a short time.

- $\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OOH}\cdot + \text{H}^+$
This reaction is called Fenton-like reaction and slower than Fenton reaction, and allows Fe^{2+} regeneration in an effective cyclic mechanism. In Fenton like reaction, apart from ferrous ion regeneration, hydroperoxyl radicals ($\text{OOH}\cdot$) are produced. The hydroperoxyl radicals may also attack organic contaminants, but they are less sensitive than hydroxyl radicals.
- The iron added in small amount acts as a catalyst while H_2O_2 is continuously consumed to produce hydroxyl radicals.



- Hydroxyl radicals can oxidize organics (RH) by abstraction of protons producing Organic radicals (R•), which are highly reactive and can be further oxidized.
- $RH + OH\cdot \rightarrow H_2O + R\cdot \rightarrow \text{further oxidation}$
- **$\cdot OH + \text{Organic pollutant} \rightarrow \text{Primary intermediates}$**
- If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2 , water and in the case of substituted organics, inorganic salts if the treatment is continued.

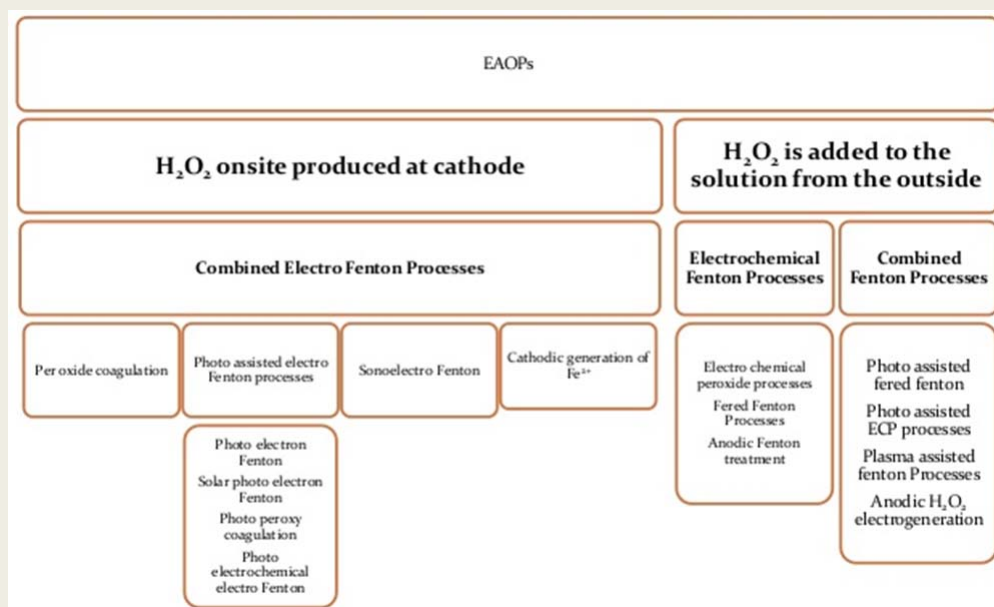
Primary intermediates + $\cdot OH \rightarrow CO_2 + H_2O + \text{inorganic ions}$



Electro-Fenton

- Hydrogen peroxide can be generated at the cathode when bubbling oxygen gas through the acidic solution followed by its reduction to H_2O_2
- Electrochemical generation of Fe(II) ion occurs through the reaction of anodic material dissolution or cathodic reduction of Fe(III) ions. In general, there are four combinations of

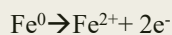
Classification of Electro-Fenton



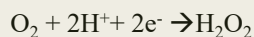
How does the Electro-Fenton's reaction work ?

- **Type I: Peroxi-coagulation (PC) process:** H_2O_2 and Fe^{2+} are generated in situ by means of an oxygen sparging cathode and a sacrificial iron anode.

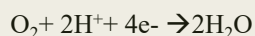
Anode:



Cathode:



Reaction of cathodic H_2O_2 formation in acidic conditions can compete with the reaction of oxygen reduction to water by the following half-reaction:



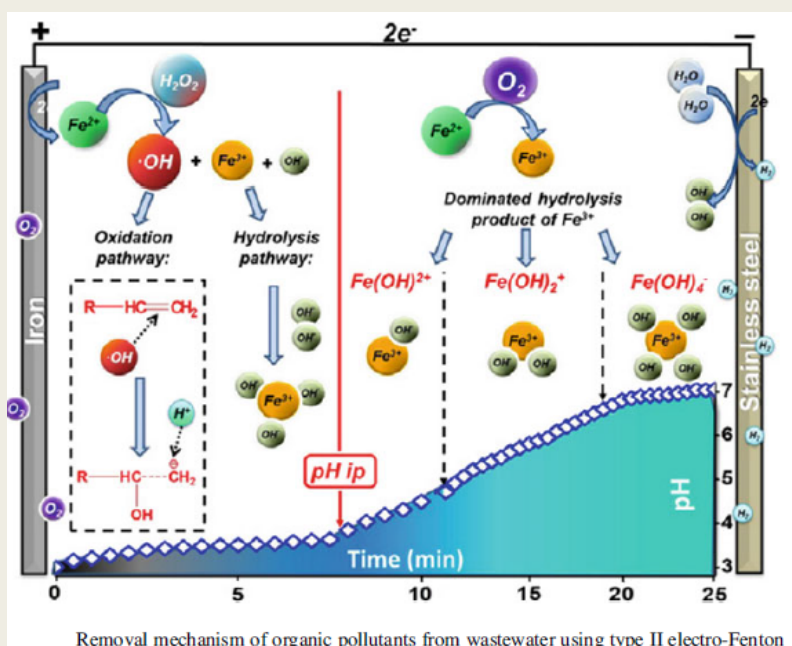
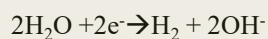
Type II: Peroxi-electro-coagulation (PEC) process or anodic Fenton treatment (AFT) process:

Fe^{2+} is continuously supplied by a sacrificial iron anode while H_2O_2 is added externally.

Anode:

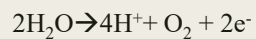


Cathode:

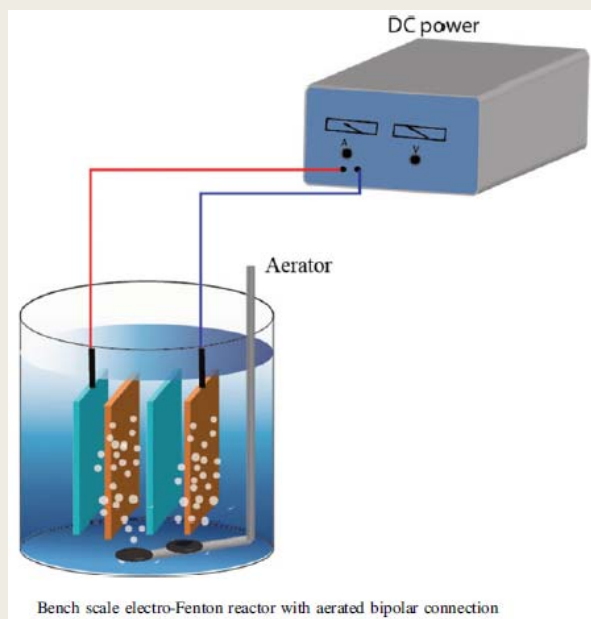
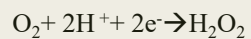


Type III: H_2O_2 is continuously electrogenerated on an oxygen sparging cathode while Fe^{2+} is externally added. This option is considered as a conventional EF process, in which anodic and cathodic processes can be described by the following reactions:

Anode:

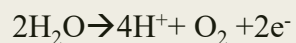


Cathode:

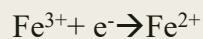


Type IV: This type is similar to type III but differs in that Fe^{2+} is regenerated through the reduction of Fe^{3+} on the cathode.

Anode:

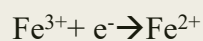


Cathode:



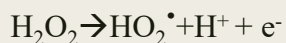
Type V: Fered-Fenton process: both H_2O_2 and Fe^{2+} are externally supplied with in situ regeneration of Fe^{2+} through the reduction of Fe^{3+} at the cathode.

Cathode:



In undivided cells:

H_2O_2 can be also consumed by parasitic anodic reactions such as



Moreover, Fe(II) can be oxidized to Fe(III) in undivided cells



Advantages of Electro-Fenton over convention Fenton reaction

- In situ generation of reaction reagents eliminates necessity to have storage and dosage facilities for those chemicals.
- Anodic dissolution of iron electrode is possible to conduct at neutral pH; however, the problem of excessive ferric hydroxide sludge generation will still be present.
- Ease of implementation and automation.
- Continuous cathodic regeneration of Fe^{3+} to Fe^{2+} .
- Higher mineralization rates of organic compounds compared with conventional Fenton reaction process due to additional $\cdot\text{OH}$ radical electrocatalytic generation at the anode.

Disadvantages of EF process

- Corrosive acidic environment of the process, which requires corrosion resistant electrodes. Acidic media is a preferable condition for electrogeneration of H_2O_2 because in alkaline media the reduction of O_2 occurs through the following reactions:

$$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$$

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$$
- Formation of iron(III) oxide-hydroxide sludge. In this regard, the option of in situ reduction of Fe(III) to Fe(II) would be the most preferable to avoid excessive sludge production. However, the reaction rates are only reasonable at pH below 2.5. Another way to reduce sludge generation is to use solid iron catalyst in the form of sieves, particles, and iron oxides, which can be easily removed from treated solution.
- Relatively low rates of electrochemical generation of H_2O_2 , which however can be improved by some type of electrodes, as for example porous gas dispersion electrodes.
- High acidity of the treated water, which should be neutralized and requires additional chemicals use.

Electrode Materials Used in Electro-Fenton Process

Electrodes should have

- high chemical stability toward corrosive acidic environment,
- high overpotential toward hydrogen and oxygen evolution reaction,
- high surface area,
- good mechanical stability,
- high sorption capacity, and conductivity.

The higher the surface area of the electrodes, the faster the H_2O_2 and Fe^{2+} generation and consequently the greater generation of hydroxyl radicals.

Electrode Materials

■ Most commonly used materials for cathodes

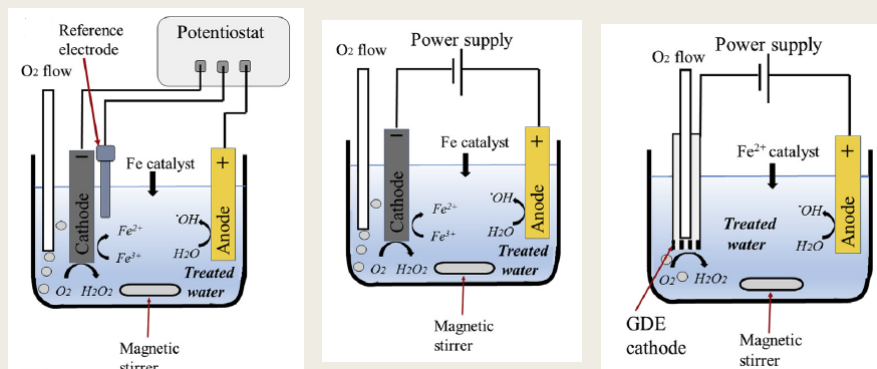
- **Carbon electrodes** such as graphite, activated carbon, carbon nanotubes and sponges, vitreous carbon, and gas diffusion electrode (GDE) : This is explained by the chemical inertness, nontoxicity, high conductivity properties, high overpotential toward HER, low activity toward H_2O_2 decomposition, and high porosity of these electrodes. GDE is a thin porous carbon plate, which allows gas bubbles pass through its porous structure, thus significantly intensifying the generation of hydrogen peroxide.

■ Most commonly used materials for anodes

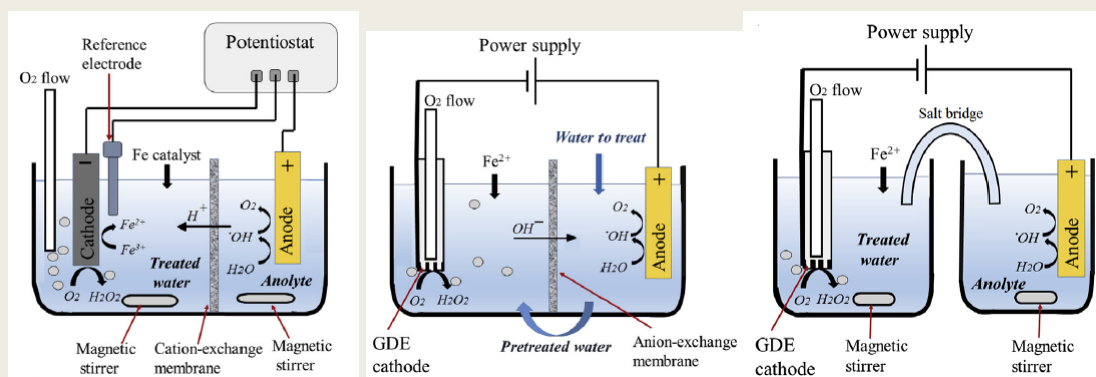
- Boron-doped diamond electrode (BDD),
- mixed-metal oxide,
- Pt, and
- graphite electrodes

Types of Electrochemical Cells Configurations in Electro-Fenton Process

■ Undivided Cells



■ Divided cells



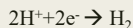
- Cells work under potentiostatic or galvanostatic conditions.
- **Potentiostatic electrolysis** is conducted under constant potential, which is set up by a potentiostat or power supply, whereas **galvanostatic electrolysis** is conducted under a CC, which is applied to the system by means of a power supply.
- Advantage of potentiostatic mode is the generation of high amounts of H_2O_2 .
- The optimum value of applied potential depends on the electrode material and is determined experimentally.
- Galvanostatic mode is mostly used in two-electrode cells and provides higher degradation rates of organic compounds at higher current density applied. However, higher currents lead to smaller current efficiencies. There is an optimum value of current density, above which degradation rates start to decrease.

Effect of Operating Parameters

Electro-Fenton combines two processes: electrochemical control and Fenton reaction; therefore, all influencing factors relative to the two processes could affect the efficiency by which pollutants are degraded.

pH

- Solution pH: pH is the critical control factor during homogeneous EF. The pH solution in EF has to adjust from ca. 2–4 in order to maintain the EF pollutant removal efficiency. This pH adjustment keeps the ferrous ion stable, which reacts with H_2O_2 to form HO^\bullet in the solution. The resistance of the solution is also low and favourable for the EF treatment. Moreover, the production of H_2O_2 in EF types I, III and IV is accelerated at an acidic medium. However, an extremely low pH (< 2) enhances H_2 evolution at the cathode as a following reaction, therefore significantly reducing the formation of H_2O_2 .



- It is optimal at pH 2.8 but the process can be performed properly at the range $2.5 < pH < 3.5$. Higher pH values provoke catalyst loss by the precipitation of ferric iron while low pH values lead to the formation of peroxonium ion ($H_3O_2^+$) from protonation of H_2O_2 . This species is electrophilic and is less reactive toward Fe_2^+ .
- The stirring (or liquid flow) rate: The stirring rate depends on the cell design and volume; it should be set to ensure mass transport to the electrodes.
- Air (or O_2) feeding: The air (or O_2) feeding flow rate should be set in order to saturate the solution in dissolved O_2 (carbon-felt cathode cells) or to feed suitable gas diffusion electrode (GDE) cells.

Current density

- Generally, with an increase in power of the current density, the dissolution rate of the anode and H_2O_2 generation on the cathode. The current (I) and voltage between electrodes (U) have significant effects on the release of H_2O_2 and Fe^{2+} concentration during the EF process. This is enhanced through Faraday's law.

$$C(gFe/m^3) = \frac{I \cdot t \cdot M}{z \cdot F \cdot V} \times 10^3$$

where F is Faraday's constant (96,485 Coulomb/mol); t is operation time (s); M is the molecular weight of iron (56 g/mol); z is the number of an electron transfer (assumed here $Z_{Fe} = 2$); V is the treated volume (L); and I is the electric current (A).

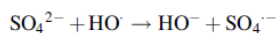
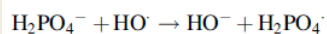
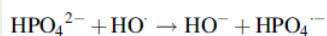
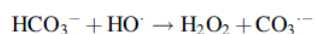
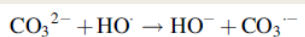
- However, an increase in current density leads to an increase in the EF energy. The energy consumption per cubic meter of wastewater can be calculated by the following equation

$$\text{Energy consumption (kWh/m}^3\text{)} = \frac{U \cdot I \cdot t}{3.6 \times 10^3 \cdot V} \quad U = I \cdot R \text{ (R is the resistance of wastewater)}$$

- The greater use of energy leads to an increase not only in temperature but also in treatment cost. Moreover, the increase in energy could accelerate a more complex reaction that could result in the reduction of the treatment capacity
- Applied current (or potential): Apart from pH, the most important operating parameters of the EF process are the applied potential (three-electrode cells) or current (two-electrode cells) and catalyst nature and concentration. In the first case, the potential of the cathode is set to a value on the plateau corresponding to a two-electron reduction wave of O_2 to form H_2O_2 in an optimal way. This value is dependant on the nature of the cathode used, that is, to H_2 evolution overpotential and H_2O_2 reduction potential.

Presence of anions

- Experiments have been generally carried out in the presence of 0.05 M Na_2SO_4 as a supporting electrolyte. Perchlorate and nitrate salts have also been tested. The use of chloride salt leads to the formation of active chlorine species and can affect the oxidation/mineralization efficiency of the process.
- The key degrading factor of EF is the oxidation capacity of a free radical, particularly HO^\bullet ; any presence of HO scavengers (mostly anion ions) will reduce the treatment efficiency of EF due to the many interference reactions.



- Most anions normally improve solution conductivity or decrease the resistance of a solution that may improve current density as explained by Ohm's Law
- Some investigations noted that the supplement of adequate SO_4^{2-} and NO_3^- ions could improve the degradation of pollutants. However, too much SO_4^{2-} and NO_3^- supplement also decrease the treatment capacity as a reaction to HO scavengers

Temperature

- The activation energy of Fenton's reaction being low, mostly ambient temperatures are employed. An increase to 35–40°C was found to slightly increase the mineralization efficiency while higher temperatures are detrimental because of the decrease in O_2 solubility and decomposition of H_2O_2 .
- When temperature increases, the ion and electron in a solution will be more flexible or reduce resistance (R) of the solution, which gives the Fe^{2+} a greater chance for reacting with H_2O_2 .
- However, this increase also reduces the O_2 concentration in wastewater by Henry's law, which results in a decrease of H_2O_2 concentration in an electrolysis solution. At a high temperature, H_2O_2 also favours the decomposition of O_2 and H_2O . This trade-off effect of temperature could be found in many studies, and the suitable temperature for EF ranges from 20 to 30 °C

Fe^{2+} concentration

- Fe^{2+} concentration plays an important role for EF. Generally, an increase in Fe^{2+} concentration causes an increase in EF efficiency because Fe^{2+} directly conducts the formation of HO.
- However, the increase in Fe^{2+} concentration also redundantly releases Fe^{3+} , which produces iron sludge during neutral step. An increment of Fe^{3+} also consumes more H_2O_2 that leads to a reduction in EF efficiency.
- The optimal Fe^{2+} concentration can vary between wastewaters depending on the organic load, the concentration of H_2O_2 , and the presence of scavengers (e.g., inorganic ions to the generation of HO).

H₂O₂ concentration

- The optimum H₂O₂ is crucially important for achieving high efficiency in the EF process because H₂O₂ directly produces HO[•]. The increment of the initial H₂O₂ concentration enhances oxidation during the EF process up to a certain point, at which H₂O₂ begins inhibiting the elimination of pollutants. At a higher H₂O₂ acting as an HO[•] scavenger, below reaction becomes more important, and a less reactive HO₂[•] radical is formed.



- In EF systems type I, III and IV, excluding type II and V, the produced H₂O₂ concentration could be estimated directly from the sparging of oxygen or air. However, many studies show that a significant O₂ had been wasted in an H₂O₂ production process. Therefore, current density (CE) equation for producing H₂O₂ from O₂ is suggested.

$$\text{CE} = \frac{nFC_{\text{H}_2\text{O}_2}V}{\int_0^t I dt} \times 100\%$$

where n is the number of electrons transferred for oxygen reduction to H₂O₂ (normally 2), and C_{H₂O₂} represents the molar concentration of H₂O₂ (moles per litre).

- As indicated in Reaction, the applied current (or current density) of EF systems significantly affects the produced H₂O₂. Moreover, the cathode material and designed reactor are the most influential factors affecting H₂O₂ production rate.

Electrode distance

- Normally, the greater the distance between electrodes results in a greater decrease in voltage or current during EF. Essentially, the gap increase between an electron or ion makes reaching the opposite electrode difficult, which consequently decreases the U and I in a solution.

Electrode arrangements

- The electrode arrangements could affect removal efficiency and energy consumption. The pollutant removal efficiency and energy consumption of monopolar and bipolar configurations have been compared in several studies. They found that a monopolar configuration has a lower operating cost; however, in some cases, a higher removal of pollutants could be achieved with the bipolar configuration, possibly due to additional side reactions.

References

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