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# **Electrochemical Techniques Applied for Industrial Wastewater Treatment: A Review**

Mona A. Abdel-Fatah\*, Marwa M. El Sayed



Chemical Engineering and Pilot Plant Department

Engineering and Renewable Energy Research Institute, National Research Centre, Egypt

\*e-mail [monaamin46@gmail.com] ORCID: 0000-0003-1371-8938

#### Abstract

Electrochemical (EC) innovations for treating mechanical wastewater and potential methods for reusing and reusing this water have been portrayed. In conjunction with financial perspectives on water administration, issues relating to the standards and application of auxiliary and tertiary strategies are altogether inspected. Later improvements in strategies counting coagulation, adsorption, characteristic forms, oxidation, and layer partitions are highlighted since they may help in understanding current forms as well as their heightened for way better effectiveness and economics. This article dives profoundly into a later progression within the field of hydrodynamic cavitation, especially in terms of hardware plan, preparation improvement, and integration with other approaches. Both practicing chemical/environmental engineers and researchers in this subject are likely to discover the survey of later headways within the field of commercial wastewater treatment, reusing, and reuse advertised here to be accommodating. The paper gives an outline of electrochemical advances for mechanical wastewater treatment and investigates potential strategies for reusing and reusing water. It moreover addresses financial contemplations related to water administration.

Keywords: Wastewater treatment; Electrochemical coagulation, adsorption, natural process, oxidation, and membrane separations.

# 1. Introduction

The notion of utilizing electricity to purify water was first proposed in the UK in 1889. In 1904, Elmore patented the use of electrolysis in mineral beneficiation. EC with aluminum (Al) and iron (Fe) electrodes was patented in the USA in 1909. EC was first employed on the large scale in the USA in 1946. Since for the most part costly capital wander and expensive imperativeness supply at the time, electrochemical water or wastewater advancements were not of the foremost portion passed on.

During the next half-century, however, intensive research in the USA and the former Soviet Union yielded a wealth of knowledge. Because of growing drinking water standards and stronger environmental rule controlling wastewater disposal, electrochemical technologies have regained significance across the world in the last two decades.

There are companies that provide services such as metal recovery, drinking water or process water treatment, and electro-photo-oxidation and electro-disinfection for various wastewaters originating from tanneries, electroplating, diary, and textile (Hassani, 2022). It's common known that businesses struggle to meet wastewater discharge regulations, particularly when it comes to dissolved solids, ionic salts, pH, COD, color, and, in rare cases, heavy metals.

The presence of color in textile dye house effluent, as well as the possibility for dyes and dye degradation products to be discharged, is a source of concern. This sort of wastewater is often treated using biological, physical, and chemical treatments, as well as various combinations of these. Traditional

\*Corresponding author e-mail: <a href="monaamin46@gmail.com">monaamin46@gmail.com</a>

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biological treatment procedures have been shown to
be challenging to break down many color complexes.

Because chemical, electricity, and water prices are insectic

always rising, it is more important to reuse this sort of wastewater rather than dispose it after treatment.

Electrochemical oxidation treatment methods have been used to a range of wastewaters (Adesola, 2012); wastewater treatment is becoming a more essential part of industrial production processes. A variety of toxins commonly contaminate this area. This effluent must be appropriately treated before being released into bodies of water. Otherwise, it might be harmful to the environment and human life. Toxic pesticides have become widely utilized across the world to control insect problems. Pesticides are found in food, soil, water, and even breast milk. Hazardous and carcinogenic chemicals may be detected in the effluent from industrial chloro-pesticide intermediate manufacturing.

Furthermore, chloro-pesticide wastewater has a wide range of pH (ether alkaline or acidic, depending on the method), high temperature, high COD, and high suspended solids (SS) contents. Each year,

around half a million people in China are poisoned by pesticide contamination. Inhaling pyrethrins and insecticides, which are commonly used in bug sprays, can cause potentially fatal diseases. Cancer, brain impairment, and reproductive problems are all long-term repercussions of these substances.

Some of the procedures utilized to treat this wastewater include adsorption, reverse osmosis (RO), Nanofiltration (NF), electro-dialysis (ED), membrane distillation (MD), incineration, ozonation/UV radiation, Fenton oxidation, phytoremediation, photocatalytic degradation, and biodegradation. Recent years have seen a significant increase in interest in electrochemical technologies such electro-oxidation (EO), electrochemical coagulation (EC), electrochemical flotation (EF) (Chen, 2004). Many pollutants may be totally degraded before they reach receiving aquatic environment electrochemical procedures, which are quite simple to Shown in Figure (1) summarized classification electrochemical methods of treatment of industrial wastewater. (Abdel-Fatah, 2021).

# **Classification of Electrochemical Methods by the Mechanism of Treatment**

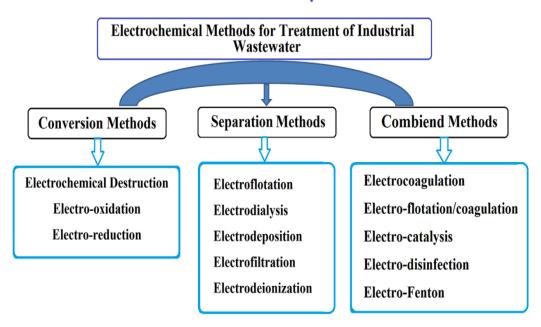


Figure (1) summarized of classification of electrochemical methods

They might also be referred to as "green technology" approaches because they use little, if any, chemicals to aid water treatment. The enhancement of new electrode materials holds a lot of promise in terms of increasing treatment efficiency. Electrochemical approaches can be used to remediate wastewaters, industrial process fluids, and disinfect drinking water more effectively (Yadav, 2022). These methods, on the other hand, are neither cost-effective nor ecologically friendly, and they can't handle low concentrations. Each technique takes a different and unique approach, and some may be more advantageous in some situations than others.

However, when large-volumes of wastewater containing dangerous compounds need to be treated, having a cost-effective solution is essential. In the recent years, there has been a boom in interest in creating environmentally friendly electrochemical technology to remove dangerous organic pollutants from wastewater. Several studies have focused on the usage of EC due to increased environmental laws on effluent waste water (Escobedo, 2022).

### 2. Conventional Methods

# 2.1. Electro-oxidation

EO can totally mineralize contaminants in wastewater by electrolysis using high oxygen overvoltage anodes like PbO<sub>2</sub> and boron doped diamond. PbO2 anode has been used to cure dyestuff by a number of researchers. A 120-minute electrolysis handle utilizing a PbO<sub>2</sub> anode at a current density of 0.2 A cm<sup>-2</sup> was utilized to completely decolorize Orange II in their examination. Other studies looked at the faradic yield and proportion of hazardous intermediates eliminated from the Ti/PbO<sub>2</sub> anode during the electrolysis of 2-cholorophenol. The anode in this experiment was a Ti/PbO<sub>2</sub> anode, which has been extensively investigated and employed in several electrolysis businesses, such as chlorine production plants (Song, 2022).

EO is one of the cutting-edge wastewater treatment techniques that have been researched. It has a number of qualities that can aid in the management of effluents from the food processing industry: When compared to biological systems, small treatment units are easier to build, assemble, operate, and maintain, enabling treatment to take place where the effluent is produced. They are also more versatile, allowing for

simple adjustment of operational variables based on the quality and quantity of the effluent as well as process disruption for seasonal effluent production.

Using EO approach to remediate effluents from the food processing sector has been demonstrated in several papers. Table (1) provides a summary of the research results conducted, as well as the important experimental settings explored and the results acquired (Ganiyu, 2021). The electro oxidation of effluents from food processing facilities has been studied using a variety of anode materials, with boron-doped diamond (BDD) receiving the most attention.

BDD is the most extensively employed anode material in EO research because of its great performance in producing highly reactive species such as hydroxyl radicals and, as a result, its significant potential to remove different organic and inorganic contaminants (Ghazouani, 2017). In addition, BDD electrodes have a wide potential window in both aqueous and non-aqueous electrolytes, corrosion stability in extremely aggressive media, an inert surface with low adsorption properties and a strong tendency to resist deactivation, and extremely low double layer capacitance and back-ground current (Panizza, 2008). In addition to the anode material, other factors like as current density have an influence on the EO process performance.

Lower energy use and improved current efficiency are frequently caused by reduced applied current densities. However, the response rate is faster at greater current densities, cutting down on the operating time. The applied current density in the literature study summarized in Table (1) ranged from 9.1 to 4286 A m<sup>2</sup>. As shown in the EO of brewery wastewater using a BDD anode, increasing current density enhances COD removal rate. COD removal rates were 65, 91, and 98 percent after 6 h treatments at 80, 160, and 240 A m<sup>2</sup>, respectively.

These specialists contend that the rise is the result of higher levels of hydroxyl radicals and other oxidants including chlorine, hydrogen peroxide, chlorine dioxide, and molecular oxygen being produced. However, when energy consumption was assessed, it was found that a rise in current density

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Table (1) summarizes the key research findings previously reported on electrochemical oxidation in the processing sectors

Anode	Supporting	COD/	pН	Applied Current Intensity,	Volume "l"	Time	COD removal	Ref.
Material	Electrolyte	${ m mgL}^{ ext{-}1}$		<b>Current Density or Voltage</b>		"h"	%	
BDD	NaCl	700	7.13	300 Am <sup>-2</sup>	0.6	-	100	Canizares, 2006
	Na <sub>2</sub> SO <sub>4</sub>	15,178	5.76	200 Am <sup>-2</sup>	0.2	7	20.2	Chatzisymeon, 2009
Ti/Pt	NaCl	250,000	5.2	2600 Am <sup>-2</sup>	15	10	93	Israilides, 1997
	NaCl	234,000	5.1	3125 Am <sup>-2</sup>	10	72	50	Kotta, 2007
	-	65000	5.27	350 Am <sup>-2</sup>	0.5	10	55	Belaid, 2013
Ti/Ta/Pt/Ir	NaCl	1475	-	5 V	10	2	5	Gotsi, 2005
	NaCl	18100	5.5	14 V	45	8	58.9	Giannis, 2007
Ti/RuO <sub>2</sub>	NaCl	41,000	4.57	1350 Am <sup>-2</sup>	0.4	7	99.6	Un, 2008
	HClO <sub>2</sub>	1220	-	500 Am <sup>-2</sup>	0.11	5	52	Papastefanakis, 2007
Ti/TiRuO <sub>2</sub>	-	26,750	5	617 Am <sup>-2</sup>	0.4	33	89	Panizza, 2006
BDD	-	3350	2.17	357 Am <sup>-2</sup>	1	6	88	Ghazouani, 2019
BDD	Na <sub>2</sub> SO <sub>4</sub>	12,647	10.4	600 Am <sup>-2</sup>	25	7	81.3	Alvarez-Pugliese, 2011

Electrode	Advantages	Disadvantages	Compared to other electrodes
Ti	Stable	Passive, expensive	
Pt	Inert, low oxygenevolution over potential	Expensive	Poor efficiency in anodic oxidationof organic compounds
PbO <sub>2</sub>	Good current efficiency, cheap, effective in oxidizing pollutants,high oxygen evolution over potential, easy to prepare	Corrosive, toxic Pb <sup>2+</sup> -ions could be released	
DSA electrodes	Supports indirect oxidation, good current efficiency, high oxygen evolution over potential, lowercost, higher availability	Short lifetime, lackof electrochemical stability	
BDD	Inert in tough conditions, high oxygen evolution over potential and electrochemical stability, good current efficiency,high corrosion stability, good conductivity		Higher activity

Table (2) Comparison of electrodes performance in EO treatment

also led to an increase in energy consumption since a greater electrical charge was involved. This resulted in a lower current efficiency when COD was reduced (Zambrano, 2020). Electrochemical oxidation has been used to treat water with a variety of electrodes. Lead (Pb) and lead dioxide (PbO<sub>2</sub>), dimensionally stable anode (DSA) electrodes, graphite, and BDD electrodes are some of the traditional anode materials utilized for water and wastewater treatment.

Pb and PbO<sub>2</sub> have been used as anodes due to their stability, affordability, and high oxygen evolution potential, which delays O<sub>2</sub> evolution and speeds up Cl<sub>2</sub> evolution (Sakka, 2015). A complete mineralization of 1,3,5-tri-methoxybenzene in acid medium has been seen at a Ta/PbO<sub>2</sub> anode. They found that by using carboxylic acids as an intermediary, all oxidation products were ultimately transformed to CO<sub>2</sub>. A lead dioxide electrode's electrocatalytic activity is reliant on the conductive electrolyte. An adherent layer formed on the anode surface, which led them to conclude that electrode poisoning happened in the presence of H<sub>2</sub>SO<sub>4</sub> electrolyte. The solubility of dangerous Pb<sup>2+</sup> ions presents another obstacle to the use of lead and lead

dioxide as anodes. The main advantages and disadvantages of the different electrodes used in EO treatment are listed in Table (2) (Panizza, 2004).

Numerous investigations have demonstrated that the composition of the anode material affects both the process efficiency and electrode selectivity. For instance, "active anodes" with low oxygen evolution over potentials, like IrO<sub>2</sub>, RuO<sub>2</sub>, or Pt, favour partial and selective oxidation of pollutants, whereas "non-active anodes" with complete combustion capabilities, like SnO<sub>2</sub>, PbO<sub>2</sub>, or BDD, are viewed as ideal electrodes for the complete oxidation of organics to CO<sub>2</sub> in wastewater treatment. As illustrated in Figure (2). (Sakka, 2015)

# 2.2 Electro-Reduction

Some electrochemical process, such as metallurgical and electroplating industries, printed circuit boards, and battery manufacture, produce aqueous effluents containing metal pollutants, which require particular treatment to eliminate dangerous metal ions or recycling of valuable material (Darkan, 1992). For a long time, electrometallurgy has been used to recover metals from water via electrochemical means.

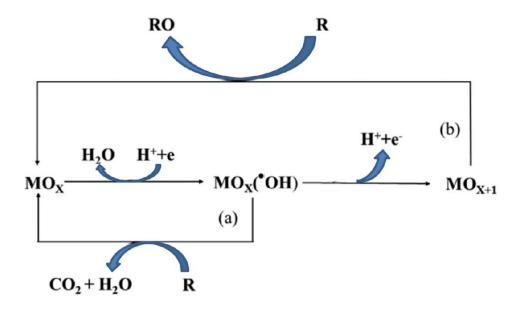


Figure (2) Scheme of the electrochemical oxidation of organic compounds on (a) "active" and (b) "non-active" anodes

The electro-chemical recovery of copper (Cu) from cupriferous mine fluids was the first known case in Europe in the mid-17th century. The catholic deposition electro-chemical method for metal recovery provides an effective approach to remove toxic heavy metals or recover valuable metals from water and wastewater with-out leaving any residues during metals separation (Fleet, 1989).

One example of selective electrochemical metal removal is the recovery of gold-rich alloys utilizing a filter press-type electrochemical flow reactor with highly polished vitreous carbon (VC) and titanium (Ti) flat cathodes. It was discovered that the cathode materials VC and Ti were very effective in recovering gold from gold plating effluent. Both materials are easy to polish and have a wide range of chemical resistances (Spitzer, 2004).

On the Ti cathode, Catholic efficiencies were greater, with 23 percent for a gold-rich alloy recovered at 1.0 V and 15 % when just gold is considered. Aqueous solutions containing chelating agents such as (EDTA), nitrile tri-acetic acid, and citrate can also be used to recover metals. A minimum of 40 % of the metals was recovered using

a two chambers cell with a commercial cation-exchange membrane, with Cu recovering the highest percentage of 90 %. To improve metal recovery, electro-deposition can be used with ultrasound. Copper removal rose to 95.6 %, and EDTA was also removed from the wastewater (84 % COD removal) (Oztekin, 2006).

The fluid mechanical environment also affects reactor efficiency. A hydrodynamic analysis of a bench-scale electrochemical reactor using parallel plates and an inert fluidized bed (glass beads) showed the importance of fluid motion in the removal of Cd and Pb ions from an aqueous synthetic effluent. An electrochemical reactor with rotating cylinder electrode (RCE) and a pH controller were used to optimize the electro-chemical recovery of Ni from a synthetic Ni plating effluent. It was crucial to be able to keep the pH at 4, recover high-quality Ni, and prevent the precipitation of hydroxides and oxides. (Secondly, 2012)

# 2.2.1 Cathodic electrochemical de-chlorination

Many wastewaters include chlorinated organic compounds (COCs), notably those from businesses that utilize solvents and chemical companies that

generate herbicides, fungicides, and insecticides. Because of their toxicity and great stability, the

presence of these COCs in the environment presents a concern to human health. For cleaning COCcontaining wastewaters, a variety of approaches have utilized. Electrochemical reductive dechlorination has evolved as an appealing way to compared conventional remove COCs, to physicochemical, biological, and chemical dehalogenation procedures, due to the moderate reaction conditions and the avoidance of probable secondary pollutants (Li, 2019; Jalil, 2007).

#### 2.2.2. Cathodic electrochemical denitrification

In the recent years, electrochemical reduction of nitrate and nitrite ions has received increased attention, notably for the treatment of nitrate containing ground waters. The structure of the electrode surface determines the nature of the nitrate reduction products, as it does for many other compounds, making this reaction particularly intriguing from a mechanistic standpoint. At 0.1 M nitrate ions in acid solutions, electrochemical nitrate reduction was explored on coinage (copper, silver, and gold) and transition-metal electrodes (ruthenium, palladium, platinum, iridium, and rhodium). (Dima, 2003)

The kinetic order and the influence of coadsorbing anions, the rate-determining step on majority of these electrodes was the reduction of nitrate to nitrite. Current densities for nitrate reduction at specific applied voltages were shown to be substantially dependent on the type of the electrode using cyclic voltammetry. For transition metal electrodes, activities declined in the sequence Rh>Ru>Ir>Pd and Pt, whereas for coinage metal electrodes, activities decreased in the order Cu>Ag>Au. Using transition-metal electrodes, online mass spectrometry studies revealed no production of gaseous products such as nitric oxide (NO), nitrous oxide ( $N_2O$ ), or nitrogen ( $N_2$ ), implying that ammonia and hydroxylamine were the predominant products. This result was consistent with the known NO reduction process, which generates N<sub>2</sub>O or N<sub>2</sub> only when NO is present in solution. The generation of gaseous NO was seen on Cu, which might be explained by the lower binding of NO to Cu compared to transition metals (Hasnat, 2009).

# 2.2.3 Electro-chemical reduction of CO<sub>2</sub>

Recent years have seen a lot of interest in CO2 conversion using electrochemical catalysis methods because of their numerous benefits, including the ability to control the process by electrode potentials and reaction temperature, the ability to fully recycle the supporting electrolytes, which reduces the overall chemical consumption to just water/wastewater, and the ability to obtain electricity without producing any new CO<sub>2</sub>. Even with the use of electro-catalysts and high electrode reduction potential, there are still problems with CO<sub>2</sub> electro-reduction, including slow kinetics, high energy consumption, and low energy efficiency of the process due to parasitic or decomposition reactions of the solvent at high electrode reduction potential (Qiao, 2014).

One of the most notable approaches to CO<sub>2</sub> reduction is electrochemical reduction, which has numerous advantages: (a) Controlling the process is aided by the electrode voltage and reaction temperature. (b) Chemical usage is extremely low, allowing for the recycling of the supporting electrolyte. (c) Renewable energy sources might be used to electrochemically decrease CO<sub>2</sub>. (d) Modifications to electrochemical cells are simple. Depending on the kind of catalyst and supporting electrolyte, CO<sub>2</sub> electro reduction yields a variety of compounds (Al-Rowaili, 2018).

The electrochemical conversion of CO<sub>2</sub> mostly follows reduction routes involving two, four, six, and eight electrons, depending on the reaction media used (gaseous, non-aqueous, and aqueous) and the electrodes used. (Oiao, 2014). During electro reduction, CO<sub>2</sub> works as a C<sup>1-</sup> or C<sup>2-</sup> building block source, producing a variety of important products such as carbon monoxide, formaldehyde, methanol, methane, oxalic acid, ethylene, and ethanol (Back, 2015). Figure (3) is a schematic illustration that shows how the electrochemical reduction process uses CO2 to make methanol. The manufacture of methanol, one of the aforementioned chemical products of CO<sub>2</sub> electro reduction, is particularly important and includes a number of problems (Li, 2017)

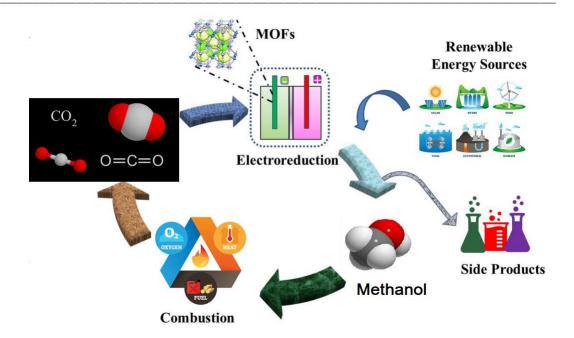


Figure (3) Schematic diagram of the electrochemical reduction of CO<sub>2</sub>

# 3. Separation Methods

### 3.1 Electro-flotation

Flotation is a gravity separation technique that has its origins in mineral processing (termed froth flotation). Flotation is thought to be extremely important to the economics of the entire industrial world. Many common metals and inorganic raw materials would be extremely rare and expensive if not for this separation process. The procedure requires the addition of surfactants or collectors to hydrophobic/surface-inactive remove ions particles from aqueous solutions, followed by the passage of gas bubbles through the solution (Novikov, 2021). Electro-flotation, or maybe more accurately, electrolytic flotation, is an alternative yet successful flotation technique used mostly on a smaller scale. It gets its name from the bubbles generating process it employs, which is electrolysis of the aqueous medium. Some of the technique's advantages should be highlighted: the electrode grids may be set to give adequate coverage of the whole surface area of the flotation tank, resulting in homogeneous mixing of the wastewater and gas bubbles (Kolesnikov, 2021).

The electric field gradient between the electrodes facilitates suspended materials flocculation. When a sacrificial iron or aluminium

anode is used, it dissolves and creates coagulant ions, therefore electrocoagulation takes place before flotation (although the relative costs of the former are a drawback). In the ex-USSR (Union of Soviet Socialist Republics), many electro flotation cell designs were presented, including the notion of consumable anodes (Li, 2021). It is vital to discover electrode materials with appropriate mechanical and electrical qualities and a long life-time before developing a feasible electro flotation method. The importance of the basic information obtained from batch electro flotation tests, as well as the related questions to be answered, was emphasized (Shukhenin, 2021).

# 3.1.1 Technological Basics of Electro-flotation Process

At the core of the electro flotation process are electrochemical events near electrodes and physicochemical phenomena in the liquid being treated when the dispersion phase is present. Examples of electro flotation as a multistage process include the formation of gas bubbles during liquid electrolysis, the formation of disperse phase particles, the formation of particle-gas bubble flotocomplexes, the buoying of flotocomplexes, and the formation of particle-gas bubble-water three-phase froths.

The presence of all five steps is required for the process to be efficient. The creation of particle—gas bubble flotocomplexes is the most crucial stage of the entire process. The stages of the electro flotation

process, as well as the elements that have the greatest impact on it, are described briefly below. When aqueous solutions are electrolyzed, gaseous products are frequently released (hydrogen, oxygen, chlorine, and...etc. The size of bubbles is dependent on the type of the electrode, the voltage, the medium composition, and other characteristics, according to B.N. Kabanov and A.N. Frumkin's basic study (Chen, 2010). The electrolysis process is controlled, the size of the gas bubbles is controlled, and the reaction at the electrodes is controlled schematically in Figure (4).

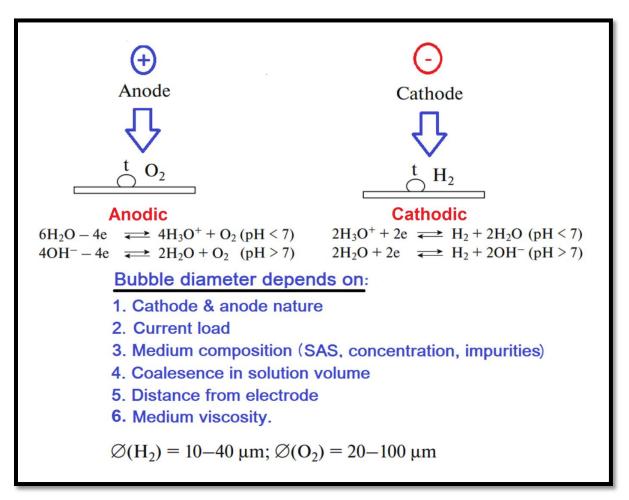


Figure (4) Control of bubble formation

Hydrogen bubbles acquire a negative charge and are repelled from the cathode surface during water electrolysis due to an abundance of OH<sup>-</sup> ions in the near-cap layer. Rapidly developing hydrogen bubbles have a negative charge in alkaline environment, but oxygen bubbles have no charge due to alkali neutralization. Rapidly developing oxygen bubbles have a positive electric charge in acid environments, but hydrogen bubbles have no charge due to acid neutralization (Ksentini, 2014).

In most particle flotation processes, hydrogen bubbles perform the most important function. The diameter of hydrogen bubbles is substantially less than that of oxygen bubbles generated at the anode, as well as the diameter of air bubbles that emerge when alternative liquid aeration methods (50–100 m) are applied (Ren, 2014). The size of bubbles is further influenced by the current density, the characteristics of the electrode surface, their form, the pH and temperature of the medium, and the surface

tension on the electrode–solution phase boundary line. The diameter of hydrogen and oxygen bubbles fluctuates between 10–40 m and 20–100 m, respectively, according to the integral distribution curve (Akarsu, 2021).

The type of the gas-removing medium was discovered to influence the effectiveness of the electro flotation process in a number circumstances. The authors investigated the electro flotation of a variety of metal-containing sediments using hydrogen and oxygen as a gas-removing medium in a unit with split anode and cathode portions, as well as a mixture of hydrogen and oxygen in a unit without membrane (Ren, 2014). As a result, electro flotation extraction of hydroxide sediments with oxygen is less effective than electro flotation extraction of phosphate sediments. Hydrogen extraction improves hydroxide extraction efficiency more than phosphate extraction. The effect of a gas-removing medium influence may only be seen at low current load levels (50-150 A/m<sup>2</sup>), i.e. when gas saturation is low. It should be noted that metallic phosphates are often characterized by a negative value for the particle's potential (Bondarenko, 2021; Kolesnikov,, 2017).

The dispersion composition of gas bubbles may be influenced by the presence of soluble and insoluble contaminants, as well as SAS in water. Impurities diminish the size of the bubbles at first. Second, contaminants reduce the effectiveness of coalescence (coagulation) among bubbles by leveling down the gas-water emulsion. The attachment of released gas bubbles and pollution particles, which happens at the molecular level, is a key stage in the electro flotation process. Particles and bubbles come influence together under the of external hydrodynamic forces. Molecular forces develop when the distance between them is reduced to 10 nm. The act of particle attachment to a bubble is accompanied by a drastic fall in the surface energy of surrounding layers, as well as the appearance of forces that diminish the wetting surface (Deryagin, 1986). Table (3) Illustrates of Efficiency of electro

flotation of hardly soluble compounds of heavy

Table (3) Efficiency of electro flotation of hardly soluble compounds of heavy metals

Me n+	Me(OH) <sub>n</sub>	$Me_x(CO_3)_n$	$Me_x(S)_n$	$Me_x(PO_4)_n$
Al <sup>+3</sup>	high	medium	medium	medium
Cd <sup>2+</sup>	Very high	medium	low	high
Cr <sup>3+</sup>	low	-	-	-
Cu <sup>2+</sup>	high	medium	medium	high
Fe <sup>3+</sup>	Very high	medium	-	medium
Mn <sup>2+</sup>	high	medium	-	medium
Ni <sup>2+</sup>	high	medium	low	medium
$Zn^{2+}$	Very high	medium	medium	high

Additionally, manganese compounds (Mn(II), Mn(III), and Mn(IV)) and hydrometallurgical liquid waste were separated using the electroflotation technique. The efficiency of the process was investigated in relation to the composition of the medium, the pH of the electrolyte, and the addition of flocculants. Under optimal conditions, the extraction percentage is 98–99%, and the residual Mn content is 0.1–1 mg/l (Nepochatov, 2009).

# 3.1.2 Reactor Design

The electrode arrangement, reactor geometry, and flow regime inside the reactor are all part of the electroflotation reactor design. Batch-flow processing has been used in the majority of lab/bench electroflotation research. They are generally made up of a tiny reactor and a few electrodes. A basic and simple design of a batch electroflotation reactor with vertically oriented mono polar electrodes is shown in Figure (5a). Other batch reactors have also been proposed by scientists. Figure (5b) depicts an anode, which is a cylindrical aluminium reactor, and a cathode, which is an aluminium impeller (Un, 2013). Nunez et al. (2011) employed varied diameter iron cylinders as anode and cathode in a cylindrical acrylic cell to remove arsenic from wastewater Figure (5c) (Nunez, 2011).

Power supply

Aluminum Impeller
Cahode

Iron
electrodes

(a)

(b)

(c)

Figure (5) Schematics of: (a) simple batch electro-flotation cell, (b) cylindrical reactor with rotating cathode electrode, and (c) acrylic cylindrical cell with iron cylinder electrodes

In order to address the industrialization's environmental concerns and the world's water demand, wastewater treatment systems (WWTS) must be more effective and efficient. This article investigated the electroflotation treatment of a variety of industrial effluents, including oily wastewater, wastewater from the food and beverage sector, wastewater from the textile industry, and more. The technique is more appealing in terms of capital and operating costs because to the development of modern electrode materials with longer lifetimes and reduced costs. Sacrificial metals, such as Al and Fe, were used as anodes when in-situ coagulation was required to achieve the right effluent concentrations. There will likely be more electroflotation facilities erected in the future since commercialized full-scale electro flotation units, particularly prefabricated package units, have been produced and are being used in a number of industries and countries (Mohtashami, 2019).

# 3.2 Electro-dialysis Process

Electro-dialysis (ED) is a novel sophisticated separation method that is widely used to produce drinking water from bodies of water and to treat industrial effluents. On a commercial scale, the ED method is used. An ion exchange membrane is used in an electro dialysis procedure, and the diving force required for the method's application is electric potential. Ions from one solution are transported to another solution due to the presence of electric

potential after passing through an ion selective membrane barrier. The primary elements that influence the performance of the ED process are ion concentration in raw water, flow rate, feed concentration, current density, membrane characteristics, and cell compartment shape (Akhter, 2018).

# 3.2.1 Electrodialysis working principle

The primary goal of the ED process is to remove salts from aqueous solutions by passing them through an ion exchange membrane shown in Figure (6). An anion and cation exchange membrane is placed between two electrodes functioning as a cathode and anode to split the cell into compartments. Between two electrodes, a direct current is applied. Consider a sodium chloride-containing feed solution that travels through the ED system and focuses on one compartment. Anions are confined while cations flow via the cation exchange membrane. Anion can only flow via an anion exchange membrane, which prevents cations from passing through (Yuzer, 2022).

# 3.2.2 Integrated ED using chemical unit operations

ED is an ion exchange device. In the 1970s, electro deionization (EDI), a hybrid of ED and ion exchange, was proposed and has shown to be a dependable approach for treating low-electrolytecontent solutions. Its primary use is to create ultrapure water for semi-conductor manufacturing

and laboratory testing. Its idea has been documented in a number of patents and academic articles. Unlike traditional electro dialysis, ED fills the dilute cell with mixed-bed ion exchange resins or fibers to promote conductivity in the mostly nonconductive solvent, water. The ED dilute is almost all deionized water. Water is divided at the contact zone between the cation- and anion-exchange resin beds at extremely low salt concentrations, generating protons and hydroxyl ions (Wang, 2019).

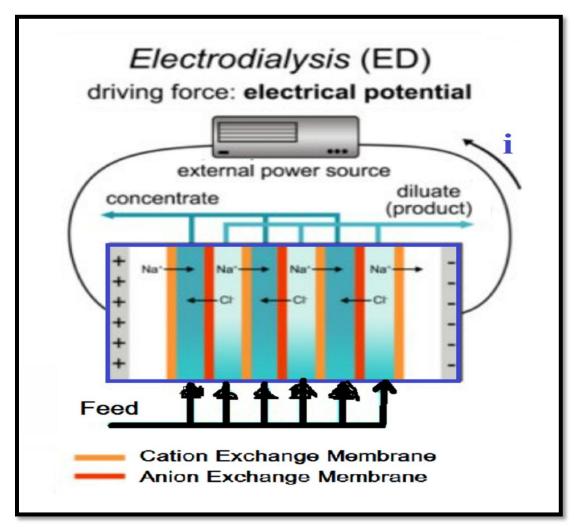
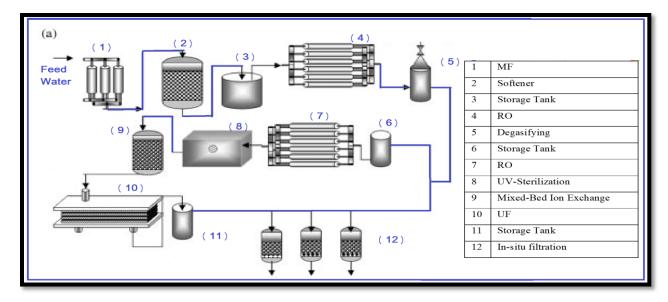
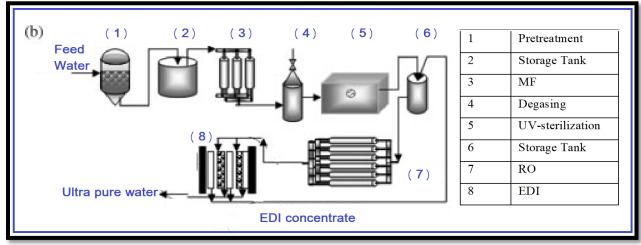


Figure (6) Principle of electro dialysis (ED)

These produced ions will partially replace the salt ions in the resins, allowing the exchange resins to renew in situ. As a result, EDI may be carried out continuously without the requirement for chemical regeneration of ion-exchange resins, saving a significant quantity of acids and bases used in traditional ion exchange procedures. As a result, the

procedure is also known as continuous electro deionization (CEDI). EDI or CEDI has been used to create boiler feed water for power plants or ultrapure water for electronic industries as one of the large-scale uses. Figure (7) shows a comparison of the EDI Figure (7b) and traditional ultrapure water production techniques Figure (7c) (Xu, 2008).





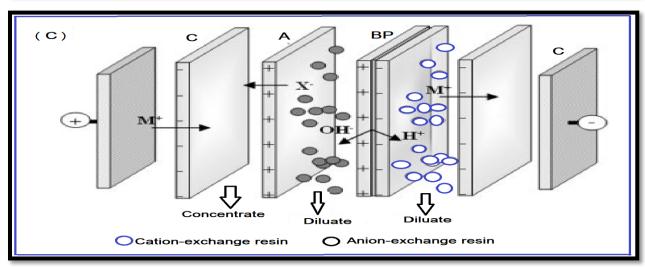


Figure (7) Comparison between (a) conventional technique, (b) EDI, and (c) EDI 1 BMED for production of ultrapure water

<sup>,</sup>Egypt. J. Chem. 67, No. 4 (2024)

Although EDI is a sophisticated process for producing ultrapure water, it still has flaws, such as inadequate weak acid removal, water deionization, and current use (Gurreri, 2019). This method of water splitting cannot produce enough  $H_1$  and  $OH_2$  for resin regeneration due to its low efficiency for cation-exchange membranes, and part of the created  $H_1$  and  $OH_2$  ions recombine before rejuvenating the resins. These limitations can be overcome by combining EDI with bipolar membranes (Bernardes, 2016).

Because BMED has a substantially greater water-splitting efficiency, the supply of H<sub>1</sub> and OH<sub>2</sub> is ensured. Because cation and anion-exchange resins are placed in different compartments, recombination is prevented. Α protective compartment is also put between the dilute and concentrates streams to prevent co-ion leakage and boost the cleanliness of the dilute. In several sectors, such as agro-food, biochemical, and chemical, separation is a required operation. In some cases, such as the separation of cobalt and nickel ions, this procedure is simple, but it can be difficult in others. Cobalt ions and nickel ions have the same charge and sign, as well as similar mobility (limit equivalent

conductance's of cobalt and nickel are 53 and 50 S/cm<sup>2</sup>, respectively; 25°C, aqueous 49), making standard unit procedures like extraction and complication ineffective. This difficulty can be handled if BMED is integrated, as long as BMED obtains selectivity for either Co<sub>2</sub> or Ni<sub>2</sub> (Wang, 2019).

# 3.2.3 Ion exchange membranes applied for ED process.

Based on the type of ionic groups attached to the membrane matrix, ion exchange membranes are categorized as either anion exchange membranes or cation exchange membranes. Cation exchange membranes constituted by negatively charged groups such as:  $-SO_3^-$ ,  $-COO^-$ , $-PO_3^{-2}$ ,  $-PO_3H^-$ ,  $-C_6H_4O^-$ , etc. are attached to the backbone of membranes and reject anions while permitting cation passage.  $-NH^{3+}$ ,  $-NRH^{2+}$ ,  $-NR_2H^+$ ,  $-NR^{3+}$ ,  $-PR^{3+}$ ,  $-SR^{2+}$ , and other charged groups created anion exchange membranes that are attached to the backbone of membranes and reject cations while permitting anions to flow through Figure (8) (Luiz, 2018).

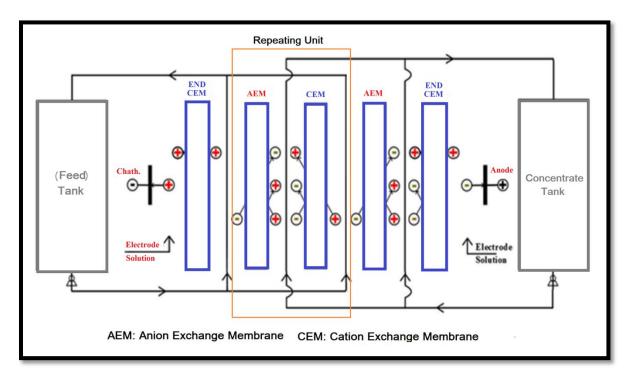


Figure (8) Electro dialysis rig depiction

# 3.2.4 Homogeneous ion exchange membranes

For the manufacture of homogenous ion exchange membranes, many approaches for blending ionic groups are available. The two that are most frequently used are (a) Anionic or cationic exchange groups monomer to form an ion exchange membrane with the aid of copolymerization process; and (b) Polymer film, introduce ionic characters in two ways: directly with functional monomer using grafting process or indirectly monomer non-functional grafting with the aid of functionalization reaction (Dofner, 2011). They are divided into three types based on the starting material membrane.

# 3.2.5 Inorganic-organic ion exchange membranes

Inorganic-organic composite materials, which improve the interaction between the two distinct molecules, are particularly essential due to the extraordinary characteristics inside single molecule composites (Kickelbick, 2003). In compared to refined organic polymer and inorganic materials, these materials possess outstanding mechanical, thermal, electrical, and magnetic characteristics (Mitiz, 2001). High photoconductivity, efficient luminescence, structural flexibility, easy processing, and even metallic properties are all hallmarks of organic polymers. Inorganic compounds have high carrier mobility's, band gap tenability, magnetic field range and dielectric characteristics, as well as thermal and mechanical stability. The interface attraction between the organic and inorganic components of different materials evolves new characteristics by mixing them in different ways (Mauritz, 2004).

# 3.3 Electro-filtration Process

Using this method reduces the amount of chemical additives used and the amount of residuals produced, lowering the cost of chemicals and waste disposal (Li, 2009). Be hold proposed using an electrical field to improve filtration efficiency in 1925 (Ye, 2021), and it was later applied in non-aqueous media, such as separation of small particles from petroleum oil (Permadi, 2010). The use of a high-voltage electrical field to remove airborne particles in processes like electrostatic precipitators (ESPs) is well established; however, technical advancements in filtration operating conditions have made electrofiltration a promising method for water and wastewater treatment. Some research are looking at the reliability of electro filtration for removing

micro-pollutants like personal care products (PCPs) (Chen, 2013) or titanium dioxide (TiO<sub>2</sub>) (Du, 2022) due to strict regulations on the maximum concentration of micro-pollutants. Other motivating factors for incorporating electric technology into traditional sludge treatment and dewatering operations include rising landfilling costs and sludge treatment costs (Villaseñor-Basulto, 2022).

These considerations lead to the use of electrical fields in deep bed filtration, dead-end filtration, and combined filtration with various membrane processes (Song, 2022). This study considers the qualities and advantages of using electrical fields in water and wastewater treatment, as well as the characteristics and advantages of using this technology in media and membrane filtering techniques. Figure (9) depicts a broad perspective of electro filtration setups, which may be classified into two groups (in media and membrane electro filtration).

# 3.3.1 Electrofiltration Principle

Electrofiltration is a method that uses a DC electrical field over the filtration system to reduce membrane fouling. Exceptions aside, practically all colloids and SS, including microbes, have a predominantly negative or positive electrical charge, causing them to deviate in the presence of an electric field. The electrical field may be set up to either attract unwanted particles to media collectors or repel them from the membrane's surface. Various modifications to the aquatic media or electrical field can be used depending on the type of water/wastewater, TSS concentration, or particle charge.

Despite the fact that this sophisticated technique appears to be promising for some types of wastewater, industrial considerations optimization must yet be researched. Gravity separation (sedimentation/flotation) and filtration are two mechanisms for particle removal in media filtration. Chemical additives such as iron or aluminum salts, as well as polymers, can be employed to remove negative charges from particles to increase removal efficiency. Using an electrical field in the filter medium, similar to the action of gravity, increases the chance of particles deposition on the collector surface by increasing the velocity of the charged particles (Pourfadakari, 2021).

Pharmaceutical & Personal products

Bio-products

Timp

Trace organic compounds

Electro-filteration

Advantages

Fouling removal & bachwashing

Turbidity, COD, TOC, and SS reduction

Permeat flux enhancement

Figure (9) Different modes and configurations

### 3.3.2 Effective factors on electrofiltration process

Electrofiltration's ultimate goal, especially in membrane and dead-end filtering, is to reduce the amount of energy required for permeate suction. The quantity of energy utilized by the suction pump, as well as the separation efficiency, are entirely dependent on the TMP. To decrease TMP, certain electrical field strength should be applied to remove the cake layer from the membrane surface (fouling prevention). The membrane flux can even rise tenfold under ideal conditions and correct electrical field strength (EFS), compared to 19 percent flux rate augmentation via electro-osmotic process. The quantity of energy consumed limits the electrical field power.

Electrical power appears to be limitless in extremely conductive suspension (greater than 2000 S/cm). In suspension with low conductivities (20–200 S/cm), on the other hand, the specific energy consumption is strongly influenced by the electrical field strength. Low electrophoretic mobility is frequently linked with high suspension conductivity,

resulting in a significant increase in specific energy consumption. As a result, electro filtering might be regarded a cost-effective alternative for lower conductivity solutions (Le, 2019).

### 3.3.3 Application of electrofiltration

As previously stated, electro filtration is divided into two categories: filter bed and membrane technologies. The latter appears to be more promising; with the bulk of investigations focusing on the separation of highly concentrated biopolymers from the biological process's downstream. Furthermore, a reduction in fouling in an electromembrane bioreactor (MBR) has been reported, as well as an improvement in the separation of tiny fragments from electronic and nanomaterial production effluent. Electrofiltration, which uses various types of filters and optimal applied voltages to separate various sorts of contaminants in water and wastewater, has also lately been introduced. Table (4) summarizes the most recent advancements in this field. For various purposes, electro filtration can use a variety of techniques (Yang, 2015).

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Table (4) Formation potential of some typical chemical reactants vs. normal hydrogen electrode
Adapted from (Singh 2020; Martínez-Huitle & Andrade 2011)

Oxidants Name	Oxidant Chemical Formula	Formation Potential
Hydroxyl radicals	$\mathrm{H_{2}O/\cdot OH}$	2.80
Ozone	O <sub>2</sub> /O <sub>3</sub>	2.07
Peroxodisulfate	$SO_4^{2-}/S_2O_8^{2-}$	2.01
Hydrogen peroxide	$H_2O/H_2O_2$	1.77
Chlorine dioxide	$Cl^-/ClO_2^-$	1.57
Chlorine	$Cl^-/Cl_2$	1.36
Oxygen	$H_2O/O_2$	1.23

To eliminate emerging contaminants, tubular membranes may be used in conjunction with a simultaneous electrocoagulation and electrofiltration process (EC/EF). Some potential approaches are size exclusion, electrostatic repulsion, carbon adsorption, electrocoagulation, and electrofiltration. For the purpose of preventing salt or an ester of alginic acid from interacting with the surface and lowering fouling rates, an electrostatic repelling force partially covers the surface's roughness. The most crucial components in membrane electro filtration (flux and rejection) are membrane structure and performance. The performance of membranes may be assessed using appropriate pore spreading, pore structure, and pore size. In actuality, the atomic force microscope affects the structure of the surface membrane. The main method for removing UV light is known as chemical application to polymer membranes, and size exclusion has a significant impact on separation at a later stage (Yang, 2014).

Furthermore, the process of cross flow filtration is heavily reliant on the interaction of the electrical field with charged colloidal particles, implying that a strong electrostatic field improves particle removal effectiveness. In the presence and absence of an electrical field, Wei, (2015) studied the fouling process of humic compounds and calcium. Adsorption onto the membrane surface and in the pores by hydrophobic interactions was the main mechanism when the electrical field was not applied; however, when the electrical field was applied, attraction by the anode and migration away from the membrane, coordinate bond breaks, and a reduction in fouling were observed. Size exclusion, electrophoresis and electrostatic exclusion,

adsorption, and coagulation are the important separation processes for the simultaneous EC/EF process. When the membrane serves as the anode during wastewater filtration, electrochemical processes and electrophoresis have both been shown to be effective methods for controlling membrane fouling (Le, 2019).

#### 3.4 Electrodeionization Process

Electrodeionization eliminates some of the problems of ion exchange resin beds in water treatment, notably ion dumping as the beds age. In an electro deionization unit, this comprehensive examination examines the theory, principles, and processes of ion movement and separation. It also looked into the design and use, particularly in the removal of heavy metal, as well as contemporary advancements in electro deionization units. Polarity reversal, Resin wafer Electrodeionization, membrane free Electrodeionization, and electrostatic shielding using innovative materials and hybrid technique together with Electrodeionization were discussed. Electrodeionization systems are predicted to improve in efficacy while operating at reduced costs due to lower energy use, making them desirable for industrial scale up across a wide range of applications throughout the world (Rathi, , 2022).

### 3.4.1 Technology overview of electrodeionization

A hybrid ion-exchange resin and electro dialysis approach is termed electrodeionization. Electro deionization has been successfully used in the manufacturing of ultra-pure water, combining the advantages of electro dialysis with classic ion-exchange processes (Hernon, 2010). Given its ability to perform a continuous, thorough deionization

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process without replenishing chemicals, electro deionization has discovered a variety of new exciting applications, including wastewater treatment, bioengineering product extraction, and other promising areas. To improve efficiency, there was a growing interest in the design and configuration of the electro deionization stack (Hakim et al., 2020).

Electrodeionization is able to overcome the apparent drawbacks of each of these approaches by combining them. Due to the presence of diluted compartments ion exchange resins across both membranes in the electro dialysis device, systems with electro deionization have the capacity to continually cure solutions with low conductance. No chemical additives are required since the electrical field continuously supplies the ion exchange resins, which may split water in situ into hydrogen and hydroxyl. More ion exchange resins give more conductance for the diluted section, resulting in speedier, more effective power and comprehensive separation (Zhang and Chen, 2016). In a constantly operating electro deionization machine, three phases run at once. Under equilibrium state and mass transfer circumstances, ions dissolved in the input stream that passes through the rows of ion exchange resins are captured on the cationic and anionic resins. Second, through resins and membrane layers, ions are continually delivered to the concentrated stream. Finally, during the operation of a direct current, resins are continuously replaced by H+ and OH generated by water hydrolysis molecules (Arar et al., 2011).

Water breaking is more likely to occur at the contact sites of various types of resins and membranes, such as anion resins interacting with cation resins and membranes, and cation resins engaging with anion resins or membranes, according to mathematical models (Enciso et al., 2017). Both electro deionization and electro dialysis use the same basic architecture, which consists of two electrodes separated by a layer of alternate liquid chambers split by alternating cation exchange and anion exchange membranes. Ions migrate towards their oppositely charged electrodes as a result of the supplied current. As a result, charged particles are constantly removed from dilute compartments and transferred to adjoining concentrated compartments. The presence

of relatively dense cation and anion resin in the dilute fluid compartment distinguishes electro deionization from electro dialysis. (Palakkal et al., 2020).

Unfortunately, the exchange membranes utilized are prone to clogging since calcium and magnesium hardness ions are more likely to coagulate with hydroxyl in the case of concentration polarization. This is one of the main disadvantages of the electro deionization procedure, which is presently utilized to produce high purity water. The scale that forms on the membrane's surface limits ion exchange efficiency and needs a higher voltage, resulting in greater membrane stack impedance and worse water quality (Liu et al., 2019). The gadget is safe to use since no chlorine is produced at the electrode. It has a long module life and can recover 100% of the water from a continuous electro deionization system.

The resistivity is substantially lower than any commercial device, lowering other consumption and improving safety. The resin bed may be customized to meet the needs of each individual. In fact, one design has generated over 18 M-cm on a regular basis while eliminating over 99.5 percent silica and 99.6% boron (Gifford et al., 2000). The consumption and energy demand are quite modest as compared to conventional nuclear cleaning processes; around 0.3 percent of evaporation. Both inorganic and organic exchange chemicals can be used to attain a high level of selectivity (Enciso et al., 2017).

# 3.4.2 Configuration of electrodeionization module

Electrodeionization is a sophisticated technology that combines electrodialysis with classical ion exchange to produce ultrapure water. It has been used commercially for more than 20 years. Its economic progress is primarily due to the elimination of chemical renewal. The rising popularity of electrodeionization has resulted in the construction of a somewhat large plant as the newest industrial technology, capable of generating 25,000 LPM of freshwater for high-pressure boilers. Electrodeionization technology has recently been revealed to offer a variety of unique and intriguing applications in water purification, biotechnology, and other promising fields (Khoiruddin et al., 2014).

Both cation and anion exchange membrane are inserted amid the electrodes in an electro deionization system, much as they are in an electro dialysis system. A series of cation and anion-exchange membranes alternate in the electrodeionization system, which is made up of concentrated and dilute chambers generated between the electrodes. The schematic depiction of a basic electro deionization setup is shown in Figure (10). The dilution chamber

of an electrodeionization system is filled with mixed resins to lower resistivity and promote anions and cations mobility under voltage difference. Cations go to the cathode and anions move to the anode when feed water enters the dilution chamber and an electrode potential difference is introduced. Hydrogen and hydroxide ions are produced during the electrodeionization system's operation as a result of water breakdown (Zahakifar et al., 2020).

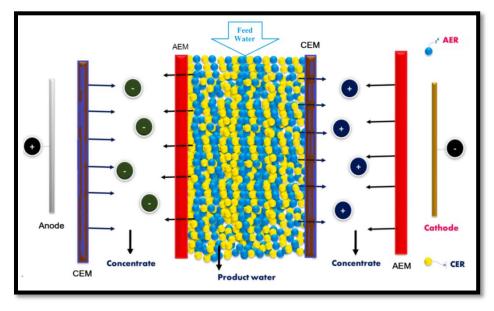


Figure (10) Schematic Representation of simple Electro-deionization set up. AER - Anion Exchange resin,

CER – Cation Exchange resin, AEM - Anion Exchange Membrane and CEM - Cation Exchange Membrane

The protons and hydroxide ions produced can revitalize the resins, allowing for prolonged functioning without the need of chemicals. Because no chemicals are needed to remove resins in the electro deionization technique, this technology is ecologically safe. (Zahakifar, 2017). Scrubbers for stream neutralization after acid and base restoration, and reservoirs for holding high concentration acids and alkaline solutions are not required because the electro deionization invention does not employ chemicals. The related hydraulic equipment and nozzles, as well as the rust-resistant double pipes, considerably minimize both capital and operational costs (Fedorenko, 2004)

# 4. Combined Methods

# 4.1 Electrocoagulation

Over the last decade, electrocoagulation (EC) has gained popularity as a reliable method for a

variety of water treatment applications. EC research has looked at colloidal and organic matter removal and a wide range of applications in urban and industrial wastewater treatment. Additionally, prior to membrane filtration, EC has been proven to be an efficient pretreatment procedure for both flow increases. Despite the growing interest in EC research, the great majority of investigations have been carried out at an applied rather than mechanistic level. Several researches have looked at the mechanics of the process, such as distinguishing between different coagulant species. Chemical flocculation (CF) comparative studies are few and mostly restricted to removal efficiency comparisons. As a result, a more fundamental approach may be required to postulate the relevance of the EC process versus the CF approach in water treatment processes.

In contrast to CC, where chemical coagulants such as metal salts, polymers, and polyelectrolytes are utilized, in EC the active coagulant species are created in situ by electrolytic oxidation of a suitable anode material. The following are the half-cell electrochemical reactions that occur in the EC cell (with an aluminium anode) and their related standard electrode potentials (expressed as reductions by convention):

Aluminium dissolution will ultimately prevail when the half-reaction standard potentials are compared since it has a far lower Gibbs free energy than anodic water reduction. Hydroxyl ions (OH) will be produced in excess at the cathode compared to hydrogen ions (H) at the anode, assuming that only a small portion of the current is used for anodic water reduction. Al<sub>2</sub>(OH)<sub>3</sub> precipitation can remove some

OH, but not enough to counteract the total generation of OH. Even under perfect precipitation conditions, the rate of OH production is greater than the rate of Al<sub>2</sub>(OH)<sub>3</sub> precipitation. This is especially true when one mole of produced aluminium splits into a number of hydrolyzed species, some of which are soluble.

As a result of the overall reactions, there is an excess of OH in solution, which manifests itself as a transient pH rise over time. This phenomenon has been described earlier, and it varies significantly from CF, in which the pH drops. Coagulation mechanisms are largely governed by pH and coagulant dose, which influence the speciation of active mononuclear species; therefore this distinction is critical when comparing the two processes. Disparities in the hydrolysis of the aluminium species may also exist.

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(ag)}$$
  $E^{\circ} = -0.83 \text{ V}$ 

# Anode:

$$O_{2(g)} + 4 H_{(aq)}^+ + 4 e^- \! \to \! 2 H_2 O \quad E^\circ = +1.229 \ V$$

$$Al_{(aq)}^{3+} + 3e^- \!\to\! Al_{(s)} \quad E^\circ = -1.662 \ V$$

# 4.1.1 Electrocoagulation technology and coagulant

An electrolytic cell with one anode and one cathode can be used as the most basic EC reactor. Aluminium and iron are the most commonly used anode metals because they produce the most commonly used ionic coagulants, Al<sup>3</sup> and Fe<sup>3</sup> (or Fe<sup>2</sup>), when electrochemically oxidized. Faraday's Law governs the dissolution of coagulant into solution (units coulombs (C):

$$\omega = \frac{I * t * M}{Z * F}$$

Where

 $\omega$  = metal dissolving (gr M/cm<sup>2</sup>)

I = current intensity (A)

t = time(s)

M = molecular weight of metal (gr/mol)

Z = number of electrons involved in the oxidation/reduction reaction

F = Faraday's constant (96,485 C)

Aluminium hydrolysis and mononuclear species production in response to aluminium dosage have been thoroughly explored by Amirtharajah and O'Melia (1990), The thermodynamic equilibrium that exists between the dominant aluminium species and amorphous aluminium hydroxide, Al<sub>2</sub>(OH)<sub>3</sub>, (the assumed solid form relevant in coagulation processes) at a given pH is known as the aluminium solubility boundary (0.03 mg/l Al<sup>3</sup> at pH 6.3). Although Al<sup>3</sup> hydrolysis products such as dimeric, trimeric, and poly-nuclear can form, they are often overlooked, especially in dilute solutions, and may have no effect on overall speciation (Duan and Gregory, 2003).

# 4.2 Electro-Flotation/Coagulation Process

A two-phase process called flocculation or coagulation eliminates stable particles by generating bigger aggregates that may subsequently be removed from the aqueous phase. The first phase is the coagulation phase, which results in instability either by diminishing repulsive interactions between particles or by entanglement in precipitates. Electrical double layer contact in insoluble particles, such as many minerals (i.e. Kaolin), is the principal cause of inter-particle repulsion.

When soluble ionic species are introduced, adsorption to the particle surface or double layer compression will affect the surface potential of colloidal particles (electrical potential difference between the particle surface and the bulk solution). Ionic species that are preferentially adsorbed at the surface include multivalent cations and anions, ionic surfactants, and, particularly in aquatic systems, hydrogen and hydroxyl ions (Louhichi, 2022).

### 4.3 Electro-catalysis Process

Electro-catalysis is a form of catalysis that alters the pace of an electrochemical reaction taking place on an electrode surface. The relative electrocatalytic characteristics of a collection of materials at a particular temperature and concentration aren't always constant, and they can fluctuate depending on how rates are affected by electrical potential.

Electro-catalysis is a catalytic process that involves the direct transfer of electrons in oxidation and reduction processes, and it necessitates the use of electro-catalysts to reduce the over potential of the reactions. The surface catalytic reaction can be carried out by an electro-catalyst via a variety of reaction routes with varying thermodynamic potentials. A good electro-catalyst can minimize the amount of over potential necessary to drive a certain electrochemical reaction to the absolute minimum.

In photo-catalysis, the process of surface catalytic reactions is very similar to electro-catalysis. In theory, a nanoparticle photo-catalyst may be thought of as an integrated micro-electrochemical cell with cathodes for reduction reactions (such as  $H_2$  evolution sites) and anodes for oxidation reactions (such as  $O_2$  evolution sites). The only difference between the two methods is whether or not the reduction and oxidation reactions are divided onto separate electrodes (Li, 2017).

# **4.4** Electrochemical oxidation of organic pollutants

The electrochemical approach for the oxidation of organic contaminants in waste water treatment has lately received a lot of attention, thanks to the introduction of new efficient anode materials. In reality, it has been shown that organic oxidation is usually accompanied by simultaneous oxygen evolution, which has led to the development of novel anode materials with high oxygen evolution overpotential in order to prefer organic oxidation over the side reaction of oxygen evolution.

A mechanism for the electrochemical oxidation of organics at diverse electrode materials with simultaneous oxygen evolution has been presented in our research Figure (11). The initial stage in all cases is water discharge, which produces hydroxyl radicals '1'. The best activity for the oxidation of organics has been found in BDD electrodes. (Palmas, 2021).

It has also been established that utilizing BDD anodes, full oxidation of organics to CO<sub>2</sub> or partial oxidation to other aromatic compounds may be achieved. Organic oxidation, whether partial or total, is found to be dependent on hydrodynamic circumstances, applied current density, and organic content.

Finally, a model for predicting the evolution of chemical oxygen demand (COD) and instantaneous current efficiency (ICE) during the electrochemical oxidation of organic contaminants on BDD electrodes under Galvano-static circumstances has been suggested. For diverse types of organic molecules (phenol, chloro-phenols, naphthols, pyridines, and soluble polymers) under different experimental settings, there is a good agreement between experimental data and projected values from the model '2' (Martinez, 2018)

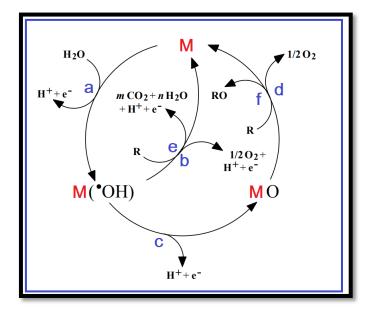


Figure (11) Proposed mechanism for the electrochemical oxidation of organic compounds with simultaneous oxygen evolution.

(a) water discharge to hydroxyl radicals, (b) oxygen evolution by electrochemical oxidation of hydroxyl radicals, (c) formation of the higher metal oxide, (d) oxygen evolution by chemical decomposition of the higher metal oxide (e) oxidation of the organic compound,

R, via hydroxyl radicals; (f) oxidation of the organic compound via the higher metal oxide.

## 4.4.1 Electrode material

The optimal electrode material for the degradation of organic pollutants should be completely stable in the electrolysis medium, cheap, and extremely active for organic oxidation while being inactive for secondary reactions e.g. oxygen evolution reaction (OER). The nature of the electrode material has a significant impact on the process's selectivity and efficiency. Organics DEO at a specific electrode may generally only take occur at high anodic potentials in the water discharge zone at sufficient rates and without electrode deactivation, due to the inclusion of oxygen evolution intermediates. In the last few decades, comprehensive models for organics destruction have been proposed to explain this behavior (Xie, 2021).

# 4.4.2 Classification and activity of anodes

As previously said, the nature of the electrode material has an impact on the selectivity and efficiency of an electrochemical process for the oxidation of organic compounds, and as a result, numerous anodic materials have been investigated in the literature in attempt to discover the best one. Comninellis' model divides anode materials into two categories for ease of understanding: active and non-active electrodes. Changing the electrode material, on the other hand, allows for the formation of various

oxidizing species and hence the modification of the oxidation pathway (Patel, 2013).

Active anodes with low oxygen evolution over potential are effective electro catalysts for the OER, resulting in selective oxidation of organic contaminants. Some electrode materials, including carbon and graphite, platinum-based, iridium-based oxides, and ruthenium-based oxides, can be classified in this way. Non-active anodes, on the other hand, which have a high oxygen evolution over potential, are poor electro catalysts for the OER, and direct electrochemical oxidation is envisaged. They also have no higher oxidation state accessible, thus an adsorbed hydroxyl radical instantly oxidizes the organic molecule, resulting in full combustion. As a result, non-active anodes such as antimony-doped tin oxide, PbO<sub>2</sub>, and BDD are the best for electrochemical combustion processes. Table (4) shows the typical over potential values for the OER (in H<sub>2</sub>SO<sub>4</sub>) found for the most thoroughly examined anode materials, as well as the formation potentials of some common oxidants, in order to better understand the performance of the anodic materials.

# 4.5 The ElectroFenton Method

Its cutting-edge oxidation technique is based on radical reactions. Pharmaceuticals, insecticides, dyes, phenol, and phenolic chemicals are examples of organic pollutants. Hydroxyl radicals have a high standard reduction potential, which is why they are thought to be involved in the majority of chemical degradation. Henry John Horstman Fenton, who discovered the transfer of electrons in particular metals, is known as the inventor of Fenton's reaction. The electro-Fenton procedure can be performed in cells that are divided by a cation exchange membrane or in cells that are not split by a membrane. Lignin and its derivatives, as well as other substances because of the limited degradability of these compounds, we apply the oxidation method.

### 4.6 Electrodisinfection

Compared to the traditional chemical disinfection procedure, it's a lot more efficient. It works on the idea of strong oxidizing agents like  $O_2$ ,  $O_3$ , and hypochlorite being generated anodically during water electrolysis. Electrodisinfection with oxygen gas: the creation of anodic oxygen, which can destroy bacteria to a degree. It is, however, usually suggested for the eradication of water odor.

Activated chlorine is best for destroying bacteria, fungus, and spores in electro disinfection utilizing chlorine gas and hypochlorite ions.  $O_3$  electrodisinfection has a high oxidation potential and can diffuse through cell walls. Microorganisms' cell walls for the extraction of pure metals and organic contaminants, it is a practical approach that requires less chemical reagents.

# 5. Conclusions

To treated wastewater containing heavy metals, technologies provide electrochemical wastewater conditions. For treatment, approaches include separation, conversion, and combination treatments. Separate the required particles from the wastewater using separation. Convert them to a suitable substance during the conversion process. Because of its dual qualities, the combination technique yields promising outcomes. Membranes are one of the most dependable methods for extracting desired ions from a solution. Electrodes are commonly used to accumulate ions based on their charge properties. Electrocoagulation is very useful for collecting waste materials and by-products. offer increased Electrochemical technologies efficiency, economic feasibility, and simple operating and control conditions. As a result, it is always given priority over other wastewater treatment systems.

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