American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)
ISSN (Print) 2313-4410, ISSN (Online) 2313-4402

http://asrjetsjournal.org/

Advanced Electrochemical Technologies in Wastewater Treatment Part I: Electrocoagulation

Irena Mickova *

Faculty of Technology and Metallurgy, University "Ss Cyril and Methodius"
Skopje 1000, Republic of Macedonia
Email: mickova@tmf.ukim.edu.mk

Abstract

This paper aims to provide an overview of electrochemical technologies in wastewater treatment. Part I focuses on the basic theory development and application of electro-coagulation. Electrocoagulation is advanced and innovative method which involves direct interaction between the ions of sacrificial metal anode and the pollutants in the water. The dissolved metal ions from sacrificial anode release in wastewater, coagulate with pollutant in wastewater in a manner similar to the traditionally one where chemicals are added for coagulation. The traditionally used chemicals, alum and ferric salts, liberate both, cations and anions. In electrocoagulation there is no supplemental addition of anions and therefore, no increase in salinity of the treated water. The quantity of sludge produced is smaller than that produced during chemical treatment. In the first part of the paper is given the importance for saving the fresh water and cleaning of wastewater using traditionally methods as: physical/mechanical methods, chemical methods and biological methods. In the second part the structure of colloids and traditional coagulation widely using in nowadays is presented. In the third part, an overview of detailed electrocoagulation theory, supported by literature survey for application in wastewater treatment plants, is given

Keywords: electrocoagulation; structure of colloids; wastewater; electrochemical reactions.

1. Introduction

With rapid growth of the world population water consumption increases rapidly and so does water pollution. Rivers, canals, estuaries and other water bodies are being constantly polluted due to discharge of untreated industrial and municipal wastewaters. Water is the source of all life in the world and covers about 70% of the Earth's surface.

---

* Corresponding author.

It exists on Earth as a solid (ice), liquid (oceans, seas, lakes, rivers, streams and groundwater), or gas (clouds and water vapor), with a total quantity that does not change. Unfortunately the water pollution affects drinking water, groundwater, rivers, lakes, seas and oceans, as well as ponds and short-term water collecting areas. The cleaning of these polluted waters is often very difficult and hard renewable whereas the polluted industrial waters released in the oceans consisting of: heavy metals, some of organic and inorganic compounds, make the ocean water non-renewable.

Literature data suggests that the total water resources supply in the world is about 1386 million cubic kilometers, with little over 96% of it being saline and the rest freshwater [1]. By definition, freshwater is water that contains less than 1 milligram per liter of dissolved solids, most often salts. Out of the total quantity of freshwater available (about 3%), over 68% is locked up in ice and glaciers. The rest, less than 31%, is in the ground. Fresh surface-water sources such as rivers, streams and lakes, constitute only about 93100 cubic kilometers, which is about 0.3 % of freshwater, or about 0.007% of the total water on Earth. Finally, rivers and lakes are water resources that people in the world use the most every day.

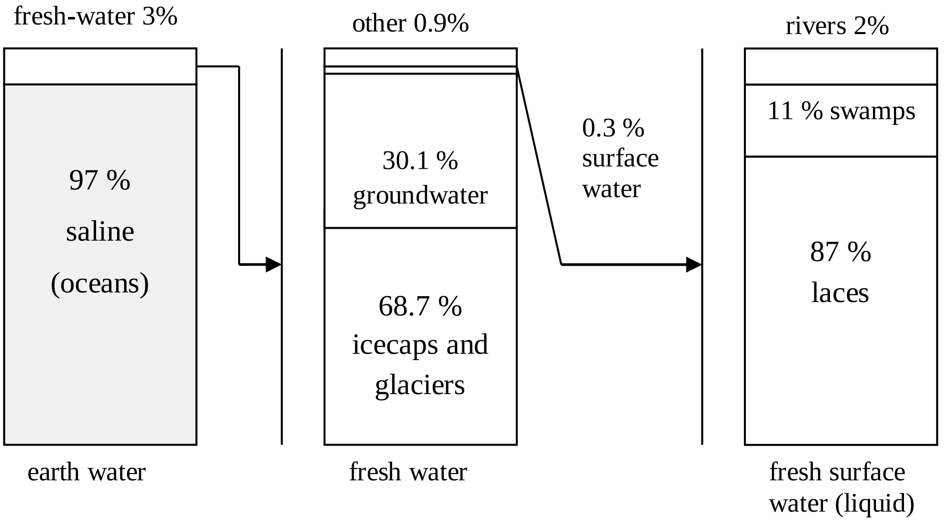


Figure 1: Global distribution of Earth's water

Virtually all types of water pollution are harmful to the health of humans, animals and the environment. The non-degradable pollutants created by human activity, generally become deposited on the bottom of the water system and their accumulation interferes with aquatic ecosystems. The conventional wastewater treatment widely used nowadays over all the world includes: physical/mechanical, chemical and biological treatment methods to remove suspended solids, biodegradable organic matters, inorganic matter and nutrients.

Physical/mechanical methods include processes where no noticeable chemical or biological changes are carried out and strictly physical phenomena are used to treat or improve the quality of the wastewater. These processes are: *sedimentation, screening, aeration, filtration, flotation and skimming, degasification and equalization.*

Chemical methods include the use of chemical processes to improve the water quality. These processes are: *chlorination, ozonation, neutralization, coagulation, adsorption and ion exchange. Chlorine,* a strong oxidizing chemical, kills bacteria and slows down the rate of decomposition of the waste in the wastewater. Another strong oxidizing agent that has also been used as an oxidizing disinfectant is *ozone*. *Neutralization* is a commonly used chemical process in many industrial wastewater treatment operations. It consists of the addition of acid or base to adjust pH levels back to neutrality. But it should be pointed out that certain processes may be physical and chemical in nature. For example coagulation consists of the addition of the chemicals that, through chemical reactions, form insoluble products that can be easily removed from wastewater by physical methods.

Biological methods involve: the use of microorganisms (some kind of bacteria) to degrade natural organic waste resulting in *DO*, *BOD* and *COD* reduction.

DO (Dissolved oxygen) represents the amount of microscopic bubbles of oxygen gas (O_2) that is dissolved in water and refers to the oxygen volume contained in the water. Just as we and terrestrial animals need air to breathe, aquatic organisms need dissolved oxygen to respire. It is also needed for the decomposition of organic matter and it is particularly important in limnology (aquatic ecology). Oxygen enters water through the air-water interface, by direct adsorption and diffusion from the atmosphere. With rapid movement or mixing of the surface water by wind and wave action, which create more surface area, the rate of oxygen adsorption and its diffusion into the water increases. Microbes play a key role in the loss of oxygen from surface waters. Microorganisms use organic matter as a food source through oxidation and consume oxygen in the process. They also use oxygen as energy in order to break down long-chained organic molecules into water and to form more stable end products such as carbon dioxide and water. The basic reaction for biochemical oxidation may be written as

$$\text{Oxidable material} + \text{bacteria} + \text{nutriente} + O_2 \rightarrow CO_2 + H_2O$$

Since all natural waterways contain bacteria and nutrients, almost any waste compounds introduced into such waterways will initiate a biochemical reaction.

BOD (Biochemical Oxygen Demand) is a measure of the amount of total oxygen that is required by bacteria, fungi, and other biological organisms, to degrade/oxidize all organic compounds present in water/wastewater. Organic waste in wastewater treatment plants acts as a food source for water-borne bacteria. Bacteria decompose these organic materials using dissolved oxygen.

COD (Chemical Oxygen Demands) is a measure of the amount of total oxygen that is required to degrade/oxidize all organic (biodegradable) and inorganic (non-biodegradable) matter present in water and wastewater. It is based on a chemical reaction (oxidation) using a strong chemical agent, such as potassium bi-chromate, which is one of the strongest oxidizing agents. Generally any oxidable material present in a natural waterway or in an industrial wastewater will be oxidized by both, biochemical (bacterial) and chemical processes. The main focus of wastewater treatment plants is to reduce the *BOD* in the effluent discharge to levels similar to natural waters.

Wastewater treatment plants are designed to function as bacteria farms, where bacteria are fed oxygen and organic waste. The excess bacteria grown in the system are removed as sludge, and this solid waste is then deposed on land. The advantage of biological treatment is the great adaptability of microorganisms to a wide variety of wastewater content, but this is a long lasting treatment requiring a large physical area and very often leads to generation of non-biodegradable residues [2, 3].

All of the mentioned conventional wastewater treatment technologies have some disadvantages such as: they are time consuming, require extensive land area and demand determination of methods for further use or neutralization of disposed waste. Improper disposal of these aqueous wastes may increase the probability for contamination of other water resources which will influence human health and environment pollution. Therefore, there is an urgent need to develop innovative, less expensive and more effective advanced technologies for wastewater treatment.

2. Electrochemical treatments

Advanced wastewater treatment technologies, which include the use of electricity, have been practiced in the second part of the 20th century [4]. The first water treatment using electricity was carried out in a plant built in 1889 in the UK where sewage treatment had been conducted by mixing the domestic wastewater with sea water, as reported in ref. [5]. The first use of electricity in wastewater treatment in the USA started in the late 1900s as reported in ref. [2]. The capital investment and the electricity costs necessary for the application of this new technology were so high that they were not widely used in that period. Additionally, electrochemical techniques were difficult to control which made it difficult to obtain reliable results. However, later on, extensive research produced by more developed countries had accumulated useful amount of knowledge, and allowed the applications of electrochemical technologies to be restarted and practiced during the past four decades. At nowadays the costs of electrochemical treatments are comparable to the costs of other wastewater treatment technologies. It should be noted that in some cases electrochemical treatment is more efficient than other conventional technologies. The process does not require additional consumption of chemicals and only electrons are added to the processes to stimulate reactions. Electrochemical processes include: electro-coagulation, electro-flocculation, electro flotation, electro-deposition, electro oxidation, electro-disinfection, electro-reduction etc. The first part of this paper focuses on electrocoagulation, whereas the second part on electro-flocculation and electro-flotation.

2.1. Colloids

Natural waters and wastewater always contain dissolved and small solid particles. These particles can be classified into several categories depending on their size; type of solution, colloids and suspensions, as presented in table 1. The colloidal pollutants in wastewater contain: organic materials, metal oxides, insoluble toxic compounds, stable emulsions and biotic materials including; viruses, bacteria and algae.

Colloids are a type of mixture that appears to be a solution, but is actually a mechanical mixture. Each colloid system consists of two separate phases: a dispersed phase and a continuous phase.

The dispersed phase is made up of tiny particles or droplets that are distributed evenly throughout the continuous phase. The size of the dispersed-phase particles ranges between 1 nm and 100 nm in at least one dimension. The colloid particles consist of atoms and molecules. They have surface charges which can be positive or negative. Those charges can come from: ionized groups (amino or hydroxyl groups), lattice imperfections in the crystal due to replacement of an atom by an ion that has a different amount of electrons which results in a charged surface and ionic species that can become adsorbed onto the surface of the colloids [3]. Examples of colloidal systems include: milk (liquid fat droplets emulsified in water), paints (small pigment particles dispersed in a carrier fluid), aerosols (liquid droplets dispersed in air) and blood (the cells that flow through our veins are colloidal particles)

Table 1: Characteristics of particles dispersed in water

System	Particle size	Particle visibility	Particle movement
Solution	<1 nm	Invisible	Kinetic
Colloid	1 – 100 nm	Ultra-microscope	Brownian
Suspension	> 100 nm	Microscope	Convective

2.1.1. Structure of colloids

Colloids can be: *hydrophilic* (proteins), and *hydrophobic* (clays, metal oxides). *Hydrophilic colloids* are typically formed by large organic molecules. The charge on these molecules originates from the presence of ionized groups on the molecules that transform the molecules into colloids when placed in solution. As a result of these charges, the colloidal particles become significantly hydrated and form hydrophilic colloids which are thermodynamically stable in their hydrated form. *Hydrophobic colloids* are composed of small particles with no affinity for water. Their stability is due to the existing charge which attracts other ionic species present in the water, resulting in the formation of an electrically charged layer around the colloidal particles. If these charged layers are removed, the particles become thermodynamically unstable and tend to agglomerate spontaneously.

In wastewater, colloids generally have a negative charge and are stable. The charged colloidal particles affect the ions in the surrounding media causing oppositely charged ions to be attracted towards the surface of the particle, and the ions of the same charge to be repelled from the surface of the particle. This separation of charges on the particle surface, results in formation of an electrical double layer, presented in figure 2. The electrical double layer has been explained by various models from: Helmohltz [4], Stern, Gouy and Chapmen [5]. Today a combined model is widely accepted.

According to this model, ions with a charge opposite to that of the negatively charged particles' surface are tightly attached to the particle by electrostatic forces forming a first inner layer named the Stern or Helmohltz layer [6]. This layer with fixed charges has a thickness of a single hydrated ionic layer. Additional ions with a charge opposite to that of the colloid particles, accumulate on the surface of the outer layer (fixed layer), but are less tightly bound to the colloidal particle and move under the influence of diffusion.

The Nernst potential is the electrical potential difference between the particle surface and the bulk of the solution. *Zeta* potential is the electrical potential difference between the Stern layer and the bulk solution. Measured *zeta* potential is defined as the electrical potential difference between the shear plane and the bulk solution.

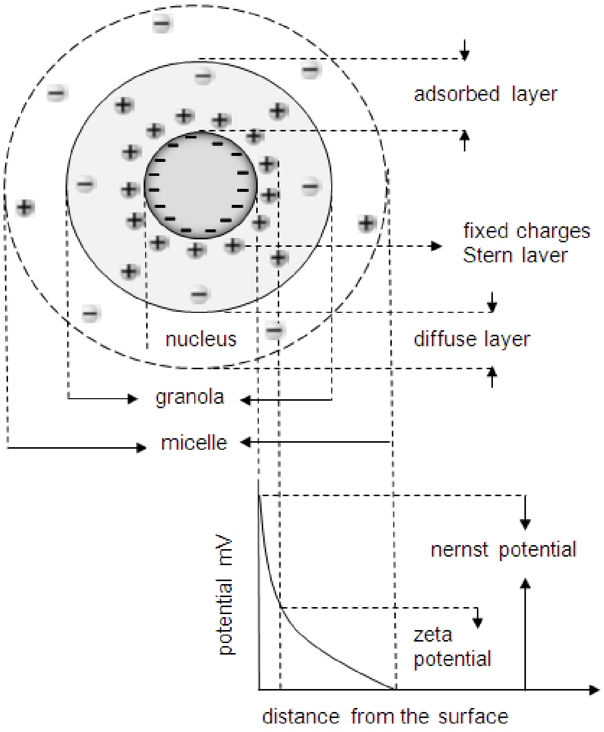


Figure 2: Distribution of charges in electrical double layer

In other words, *zeta* potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. It should be pointed out that the *zeta* potential is an indirect measure of the electrical charge of the colloidal particle. It can be experimentally measured using a microscope to determine the velocity of a particle moving under an applied electrical potential of known intensity.

$$\psi_m = \frac{4\pi \cdot v}{\varepsilon \cdot V_a} = \frac{4\pi \cdot \mu \cdot EM}{\varepsilon} \qquad (1)$$

Ψ_m – zeta potential

v – particle velocity

ε – dielectric constant of the medium

Va – applied potential per unit length

EM – electrophoretic mobility

When the colloidal particles are surrounded by enough counter ions they become electrically neutral.

This point is called the *isoelectric point* and at the *isoelectric point* the *zeta* potential is zero. By definition, *isoelectric point* is the value of pH at which a particle carries no net electrical charge. A classic example in colloid chemistry is the measurement of *zeta* potential vs. pH to determine the conditions under which the *zeta* potential reaches zero. Stable colloids are those that remain fully dispersed over time, with no degradation or sedimentation. The stability of colloids comes from electrostatic repulsion between the particles, and it prevents the aggregation of those particles as well as other particles [7]. Colloid particles do not settle out and cannot be removed from wastewater by conventional physical treatment processes. To remove the colloids from wastewater, repulsion must be overcome and the particles must become unstable

2.1.2. Coagulation.

The dictionary definition of coagulation is “to make liquids solid”. For example blood coagulates when it clots. Eggs coagulate when they are cooked. In principle coagulation is destabilization of colloids by neutralizing the forces that keep them apart trough introduction of an opposite charge. It is a phenomenon that occurs when the existing charged particles in the colloidal suspension are neutralized by mutual collision with counter ions added to the solution that further promote contact between the charged particles.

Once the charge is neutralized the colloidal particles are capable of sticking together. i.e. coagulate. In order to achieve good coagulation, rapid mixing of the suspension is needed to properly disperse the coagulant and promote particle collision. There are three main types of coagulants that are used to neutralize the repulsive forces of particles and allow them to come closer together, i.e. to aggregate. These three main types are: inorganic electrolytes (alumina, lime, ferric chloride, ferric sulfate etc.), organic polymers and synthetic poly-electrolytes with cationic and anionic functional groups.

There are four main mechanisms of destabilization of colloids which provoke coagulation:

(i) Compression of electrical double layer. The increase of counter ion concentration in the bulk solution causes compression of the electrical double layer of the colloidal particles. As the thickness of the electrical double layer decreases the colloidal particles can come close together more easily and aggregate. Optimal destabilization is achieved when the zeta potential is close to 0 mV.

(ii) Adsorption. This type of destabilization occurs when oppositely charged ions or polymers are adsorbed onto the surface of colloidal particles. The oppositely charged ions reduce the surface charge and the repulsive forces among the particles. Destabilization occurs when the zeta potential is close to 0 mV.

(iii) Inter particle bridging. When one polymer chain is adsorbed onto multiple particles, bridging occurs and molecular weight increases. The zeta potential of destabilized particles is typically not close to 0 mV

(iv) Precipitation. Precipitation means making soluble species insoluble. This type of destabilization occurs when high concentration of metal counter ions in wastewater form insoluble hydrolysis products. These products sorb to the colloidal particles and neutralize the surface charge.

Traditionally the most widely used counter ions in waste and drinking water treatment, which result from dissociation of added chemicals are: aluminum sulfate $Al_2(SO_4)_3 18H_2O$, ferric sulfate $Fe_2(SO_4)_3$, ferrous sulfate $FeSO_2 7H_2O$ and ferric chloride $FeCl_3$. These chemicals are called coagulants and they produce positive charges. The positive charge of coagulants neutralizes the negative charge of the colloid particles suspended in the water. Coagulation occurs when the net surface charge of the particle is reduced to a critical point where the colloidal particles previously stabilized by electrostatic repulsion can approach each other close enough to allow Van der Waal’s forces to hold them together and initiate aggregation. It should be pointed out that records have been found which indicate that old Egyptians and Romans used these techniques of coagulation with Al-hydroxide and Fe-hydroxide 2000 years before Christ.

For example when $Al_2(SO_4)_3 18H_2O$ is added to water, hydrolysis occurs and insoluble aluminum hydroxide is formed

$$Al_2(SO_4)_3 18H_2O + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-} + 18H_2O \qquad (2)$$

The insoluble $Al(OH)_3$ is responsible for coagulation

If $FeCl_3$ is added the following reaction occurs

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + 3Cl^- \qquad (3)$$

The coagulation occurs between the addition of $FeCl_3$ and the formation of $Fe(OH)_3$. Coagulation can successfully remove a large amount of organic compounds present in the water as dissolved organic carbon (*DOC*), suspended particles of inorganic precipitates, parts of viruses (27 – 84%) and bacteria (32 – 87%) [8-10]. In a wastewater treatment facility, the coagulant is added to the wastewater and it is rapidly mixed, so that the coagulant is circulated throughout the entire volume of the water. The colloids begin to agglomerate, then flocculate and finally settle to the bottom of the tank.

2.2. Electrocoagulation

Electrocoagulation EC is not a new technique. The process was originally developed and patented in 1906 by Dietrich to treat bilge water from ships [11]. However, this process was never adopted due to lack of legislation concerning marine discharges. Later, in 1909, electrocoagulation with aluminum and iron electrodes was patented in the USA, as described in ref. [2].

The treatment of wastewater by electrocoagulation was increasingly practiced in the 20th century, but with limited success and popularity. Some new theoretical knowledge of EC was reported in 1946 [12] and in 1947 [13]. In the last decade, electro-coagulation has been optimized to minimize electrical power consumption and minimize effluent throughput rate [14-19].

This technology has been increasingly used for treatment of different types of industrial wastewater containing: suspended particles [20-22], clay and clay minerals [23,24], chemical and mechanical polishing waste in wastewater [25,26], organic compounds: fats, oils, alcohols and grasses [27-31], foodstuff [32,33], synthetic detergent effluents [34], heavy metals [35-39], bacteria, algae and larvae [40,41], textile wastewater [42,43], latex particles [44], laundry wastewater [45], decolourization of dye and cotton dye [46,47], *COD*, *BOD* and *TOC* reduction [48-50], tannery wastewater [51] wastewater from slaughter-houses [52], for removing metals such as: Mn, Cu, Zn, Ni, Al, Fe, Co, Sn, Mg, Se, Mo, Ca etc., [53-55]. EC has also been used in removing anions such as: CN^-, PO_4^{3-}, SO_4^{2-}, NO_3^-, F^- and Cl^- [56-59]. Electrocoagulation generally refers to the electrolytic generation ofcoagulating metal ions, Al and Fe, which make colloidal particles larger so they can be filtered out fromthe water. The gas (H_2) released at the cathode plays no part in the pollutant removal. Electrodes which produce coagulants into water are made either from aluminum or iron. The principle of electro-coagulation is the same as in chemical coagulation [60]. The difference is only in the way that the coagulant is added. In the electro-coagulation process the coagulant is generated in situ by electrolytic oxidation and reduction occurring at the appropriately chosen electrodes in an electrochemical reactor. The system is connected to an external power source and as the process of oxidation occurs sacrificial anodes are corroded and release coagulant cations in the reactor where wastewater is the electrolyte. In reality electrocoagulation is the electrochemical production of destabilization agents such as Al and Fe ions that neutralize the electric charge of the colloidal particles.

Aluminum cations dissolve from the anode according to the reactions [61]

Anode

$$Al_{(s)} \rightarrow Al_{aq}^{3+} + 3e^- \tag{4}$$

Cathode

$$3H_2O_{(l)} + 3e^- \rightarrow 3OH^-_{(aq)} + 3/2H_{2(g)} \tag{5}$$

The evolution of hydrogen bubbles serves to promote flotation in EC reactors. The electrolytic dissolution of the Al anode produces Al^{3+} ions which immediately undergo spontaneous hydrolysis reactions that generate various monomeric species according to the following reactions, governed by solution pH

In acidic electrolytes

$$Al^{3+} + H_2O_{(l)} \rightarrow Al(OH)^{2+}_{(aq)} + H^+_{(aq)}$$

$$Al(OH)^{2+}_{(aq)} + H_2O_{(l)} \rightarrow Al(OH)^+_{2(aq)} + H^+_{(aq)} \tag{6}$$

$$Al(OH)^{+}_{2(aq)} + H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + H^{+}_{(aq)}$$

Or overall reaction is

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^{+}_{(aq)} \qquad (7)$$

In alkaline electrolytes

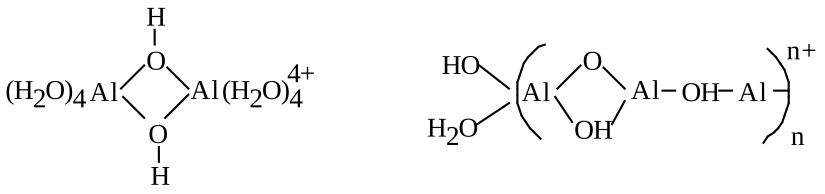
$$Al^{3+}_{(aq)} + 3(OH)^{-} \rightarrow Al(OH)_{3(s)} \qquad (8)$$

If the initial pH is about 9 or higher, it will decrease during the EC process due to the formation of aluminate $Al(OH)^{-}_{4}$ which is an alkalinity consumer [32,33]

$$Al(OH)_{3(s)} + OH^{-}_{(aq)} \rightarrow Al(OH)^{-}_{4(aq)} \qquad (9)$$

Highly charged cations destabilize any colloidal particle by forming polyvalent poly-hydroxide complexes. These complexes have high adsorption properties and form aggregates with pollutants. The hydrolyzed Al ions can form large networks of Al-O-Al-OH that can chemically adsorb pollutants. Under appropriate conditions

can form large networks of Al-O-Al-OH that can chemically adsorb pollutants. Under appropriate conditions various forms of charged multimeric hydroxo Al^{3+} species may be formed as well. For example the structure of dimeric and polymeric Al^{3+} hydroxo complexes are shown below



(10)

The gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization.

For an iron anode two mechanism have been proposed for the production of $Fe(OH)_n$ where n = 2 or 3 [41,60]

Mechanism 1

Anode

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^{-} \qquad (11)$$

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^{+}_{(aq)} \quad (12)$$

Cathode

$$8H^{+}_{(aq)} + 8e^{-} \rightarrow 4H_{2(g)} \quad (13)$$

Overall

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \quad (14)$$

Mechanism 2

Anode

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \quad (15)$$

Bulk solution reaction

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (16)$$

Cathode

$$2H_2O_{(l)} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \quad (17)$$

Overall

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad (18)$$

The $Fe(OH)_{n(s)}$ remains in the aqueous phase as a gelatinous suspension, which can remove the pollutants from the wastewater by either complexation or by electrostatic attraction followed by coagulation. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron

$$L - H_{(aq)}(OH)OFe_{(s)} \rightarrow L - OFe_{(s)} + H_2O_{(l)} \quad (19)$$

The H_2 produced from redox reactions can remove organic pollutants or any suspended materials by flotation. In acidic electrolytes and in the presence of oxygen, Fe^{3+} ions can be formed

$$Fe^{2+}_{(aq)} + O_2 + 2H_2O \rightarrow 4Fe^{3+}_{(s)} + 4OH^- \quad (20)$$

The pre-hydrolysis of Fe^{3+} cations also leads to the formation of reactive clusters for wastewater treatment. Fe^{3+} cations may also undergo hydration and depending on the pH of the solution the following species can be formed:

$$\begin{aligned} &Fe^{3+}_{(aq)} + H_2O_{(l)} \rightarrow Fe(OH)^{2+}_{(aq)} + 2H^+_{(aq)} \\ &Fe^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow Fe(OH)^+_{2(aq)} + 2H^+_{(aq)} \\ &Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_3 + 3H^+_{(aq)} \end{aligned} \quad (21)$$

The formed amorphous $Fe(OH)_3$ has a large surface area which is beneficial for rapid adsorption of soluble organic and inorganic compounds and trapping of colloidal particles.

In alkaline electrolytes

$$Fe^{2+}_{(aq)} + 3OH^- \rightarrow Fe(OH)_{2(s)} \quad (22)$$

Under alkaline conditions $Fe(OH)^-_6$ and $Fe(OH)^-_4$ ions may be also present. The nascent ions of Al^{3+} and Fe^{2+} are very active coagulants for colloidal suspensions and for particulates flocculating. In addition, the oxygen evolution reaction occurs which is more accentuated for Al than for Fe anode [63]. Then, particles bond together like small micro-magnets and form an agglomerated mass. During the electrocoagulation there are multiple electrochemical processes occurring simultaneously at the anodes and cathodes [64]. Evolution of gaseous bubbles, i.e. oxygen at the anode and hydrogen at the cathode, occurs as a result of water decomposition.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (23)$$

The reaction of the cathode is

$$2H_2O \rightarrow H_2 + 2OH^- - 2e^- \quad (24)$$

These electrode reactions also produce the highly chemically reactive OH^- ions and superoxide HO_2 radicals (which react with metal ions and form hydroxides) [65,66]

2.2.1. Parameters affecting electrocoagulation

In order to select the use of electrocoagulation, the method must be more cost-effective when compared to other classical processes for wastewater treatment. In electrocoagulation there are various parameters that affect the efficiency of the process, some more than others.

But the key parameters are: electrode materials, pH of the solution, concentration of anions, current density, electrode potential, concentration of pollutants, temperature and time of treatment. There also are some less influential parameters.

(i) *Electrode materials* define the type of electrochemical reaction that will occur in the EC processes. The anode can be Al or Fe plate whereas the cathode is an inert material such as: steel, stainless steel, platinum coated titanium etc. [67]. In some cases the anode and cathode are built from the same material; Al or Fe [68]. The influence of different combinations of Al and Fe electrodes on the EC efficiency has been studied by the authors in ref. [69]. The electrode material impacts the performance of the EC reactor, especially the anode, which determines the type of cations released into the solution. However, in literature data, there is still controversy with respect to the dissolution mechanism of the anode. In all existing publications Al dissolves as Al (III), whereas Fe dissolves either as Fe (II) or Fe(III) [70,71]. The authors in ref. [72] reported that Fe(III) is a much better coagulant compared to Fe (II) due to lower solubility of the hydroxides and a higher positive charge. It is difficult to determine which electrode material is superior. In some cases Al electrodes are superior, whereas in other cases iron anodes are superior. It seems that the optimal selection of the electrode material depends on the type of pollutant present in the wastewater. From literature review it appears that Al is superior compared to Fe, but Al is more expensive that Fe. The relationship between the size of the cations released in solution and the efficiency of the removal of organic waste was reported in ref. [73]. The Authors concluded that the size of the Fe^{3+} ions is bigger (10 – 30 μm) compared to Al^{3+} (0.01–1 μm). It was also shown that there was a positive correlation between the ion size and the removal efficiency. The efficiency of iron, aluminum and stainless steel electrodes in the removal of cooper(II), chromium(VI) and nickel(II) from metal plating effluent was studies in ref. [74]. It was also reported that Cr(III) precipitation was due to the presence of $Fe(OH)_3$ and its removal could be facilitated by the electro-generated Fe(II), reduced at the cathode. The removal efficiency of color and COD has been studied using Al and stainless steel electrodes [75]. The authors reported that electrical energy consumption and sludge production rate were lower for stainless steel (8 KWh and 700 g/m^3) compared to Al (17 KWh and 8200 g/m^3).

The sulfides removal from wastewater from a fowl slaughterhouse using inexpensive cast-iron and more expensive Al anodes, as well as a combination of cast-iron and Al plates has been studied by the authors in ref. [76]. They noticed that the strong odor of the wastewater disappeared only when the cast-iron electrodes were used. During electrolysis the anodic plates undergo corrosion, liberating Fe (II) ions which react with the sulfide ions, producing a black precipitate of Fe (II) sulfide.

$$Fe^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow FeS_{(s)} \qquad (25)$$

This reaction explains that in the first few minutes of electrolysis the color of the wastewater, which was initially pale yellow, changed to grey, due to the black color of the Fe (II) sulfide. The color change coincides with the disappearance of the strong odor. After about 15 min. of electrolysis, the color continues to change and becomes reddish, due to the formation of iron (II) hydroxide. The reddish corrosion products are reported in more detail in ref. [63]. An experimental study of the sulfides removal from aqueous solution by electrocoagulation was also described in ref. [77].

In this ref. two types of anode material, aluminum and mild steel, were investigated in relation to anodic dissolution, removal efficiency and energy consumption. It was shown that compared to aluminum, iron based anodes provide higher removal efficiencies, and have lower energy requirements and electrical operating costs. The other authors reported that the best sulfate removal efficiency was achieved with six plate aluminum electrodes in an electro-coagulator reactor with a voltage of 30 V, pH = 11 and time of treatment of 30 min. [78]. The advantage of the Al electrode for removal of Zn(II), Cu(II), Ni(II), Ag(I), Cr(VI) from wastewater by EC was also proposed in ref. [53]. All these cations were removed by hydrolysis and co-precipitation. For example Cr(VI) was first reduced to Cr(III) and then precipitated as a hydroxide.

(ii) *pH and concentration of anions.* Some of the most important parameters in EC are the pH of the solution and the concentration of the anions [79,80]. These two parameters affect the conductivity of the solution, the dissolution of electrodes and formation of hydroxides [76]. In contrast to chemical coagulation, in EC treatment with Al electrodes the value of pH increases when the wastewater is in an acidic, neutral or slightly alkaline regime. This pH increase is due to reactions between Al^{3+} and other anions present in the wastewater, as well as the formation of $Al(OH)_3$ near the anode surfaces. The increase of pH is also due to evolution of hydrogen on the cathode. In stronger acidic mediums (pH about 2), the produced alkalinity by the EC is not sufficient enough to increase the pH of the solution significantly, whereas at higher pH (about 3), the alkalinity rises measurably during the treatment [81].

There are some pollutants, such as phosphorous and some metal cations, which have a specific efficiency of removal that depends on the pH, [82]. The highest removal efficiency was observed at pH = 3. When Fe electrodes were used for pH values higher than 3, the removal rate was very slow due to the formation of $Fe(OH)_4^-$ and the increased solubility of $FePO_4$. For higher pH values, more OH^- ions are present to compete with PO_4^{3-} and therefore less $FePO_4$ is formed [83]. According to authors in ref. [80], pH increases more in sulfate than in chloride solutions. Sulfate can replace hydroxyl ions in the hydroxide precipitates and therefore less hydroxyl ions are bound to hydroxides. The relationship between the increase of pH and alkalinity with increase in temperature and the time duration of electrolysis was investigated by the authors in ref., [84]. They reported that during the EC, de-colorization and *COD* removal were 75.4% and 84.6% respectively, for a treatment time of 25 min. According to the authors in ref. [85], in general, for EC processes, the optimal pH values of wastewaters range from 6.5 to 7.5. The formation of Al or Fe dimers from the monomer on pollutants in the water is most efficient at $pH \approx 5.5$ to 7.

(iii) *Current density and time of treatment.* Current density and time of treatment are two parameters which define a quantity of electricity that has passed through the electrocoagulation reactor, which is directly related to the quantity of dissolved Al^{3+} and Fe^{2+} ions from the corresponding electrodes, and the cost of the process. The current density is directly proportional to the rate of the electrochemical reactions and has an influence on the voltage between the anodes and cathodes. The efficiency of the current density can be calculated using Faraday's law. For Al and iron anodes, dissolution is the primary reaction when pH is neutral or slightly acidic [86]. For alkaline solutions the dissolution rate of iron anodes can be lower than the theoretical value calculated using Faraday's law. This indicates that other side reactions occur [86].

The current density influences the design of the reactor dimensions as well. For higher current densities the reactor dimensions are smaller. However, very high current densities diminish the process efficiency because a major part of the electricity is transformed into heat energy causing temperature increase of the treated wastewater.

It should be noted that the total amount of coagulant dissolved electrochemically can include also chemical dissolution of electrodes at low pH values. Several studies have reported current yields higher than 100% for dissolving Al electrodes where Al plates were used for both the anode and cathode [64]. This is probably due to the dissolution of the cathode during the EC process and it can occur when the pH on the cathode surface decreases as a result of the formation of OH^- or it can be caused by the consumption of hydronium ions.

At higher pH aluminum dissolves as aluminate

$$2Al_{(s)} + 6H_2O + 2OH^-_{(aq)} \rightarrow 2[Al(OH)_4]^-_{(aq)} + 3H_{2(g)} \qquad (26)$$

Comparative studies of hydrogen evolution from Al and stainless steel cathodes have shown that hydrogen evolution on stainless steel followed Faraday's law. On the other hand, tests with Al cathodes have shown that hydrogen evolution is higher due to the chemical dissolution of Al according to reaction (27). For example the current efficiency at the Al electrode could be 120% - 140% as a result of pitting corrosion in the presence of Cl^- It is recommended that for EC a current density between 20 and 25 A/m^2 should be applied. At these current densities the EC system will operate for a long period of time without requiring maintenance. However, the recommended current densities are not universal and should be changed depending on the type of cations and anions present in the wastewater. The authors in ref. [87] concluded that in EC processes the Cr was completely removed from solution after 45 min. at a lower current of 0.05 -0 1 A. At higher currents, 1–3 A, Cr concentrations decreased at a slower rate. The removal of Cr, Pb and Zn from wastewater in the billet industry has an efficiency of 99% for a current density of 98 A/m^2, pH =5 and 30 min. of electrolysis time [45]. Using Al and stainless steel electrodes, the authors in ref. [88] studied color and *COD* removal from a disperse dye bath using chemical and electrochemical processes. The EC treatment removed the color and *COD* instantaneously at a pH of 7 and a current density of 44 mA/cm^2. The successful reduction of heavy metals: Cr, Cu and Ni by treating galvanized wastewater has been realized for pH values higher than 5. The current used in this treatment was 0.2 A for Fe electrodes and 1.5 A for Al electrodes with a power consumption of 9 KWh/m^3 [87]

(iv) Temperature can have a negative or a positive effect on the removal efficiency of pollutants in the EC processes. The effects of temperature have been studied in a few articles [69,89,91]. In general, higher temperatures resulted in higher conductivity of the wastewater and consequently smaller energy consumption during the electrolysis. The Authors in ref. [69] have reported a negative effect of temperature on the removal efficiency of an electrocoagulation process used in the treatment of heavy metals containing solution. In most cases where temperature is being considered as an electrocoagulation factor, it is important to find out what factors contribute temperature change during the process, especially when it is carried out at ambient temperature.

For example the removal of phosphate from wastewater by EC, using aluminum, aluminum alloy and mild steel anodes was studied by authors in ref. [90]. These authors have found that the removal efficiency was 29% lower at 20 ^{O}C than at higher temperatures. This could be attributed to the low dissolution rate of anodes at lower temperature. For wastewaters containing oils it was found that the smallest energy consumption occurred at temperatures close to 35 ^{O}C. The effect of temperature on electrocoagulation was investigated in ref. [92] by electrocoagulation and coagulation during the pretreatment of palm oil mill effluent. It was shown that the temperature can affect the electrocoagulation process in many ways such as rate of reactions, solubility of metal hydroxides, liquid conductivity, and kinetics of gas bubbles, or small colloidal particles. Temperature is not straightforward because there are many competing mechanisms in an electrocoagulation process. The bubble formation was one of the major characteristics of electrocoagulation treatment and an increase in temperature might be expected to have a negative effect due to a corresponding increase in kinetic energy and random motion of the gas bubbles. The increase in the random motion of the gas bubbles and small colloidal particles could interfere with the processes of oil droplet coalescence and attachment of oil onto flocks. The effect of varying temperature from 20 to 50 ^{O}C has been studied in ref. [93]. It was observed that the increase in temperature causes an increase in removal efficiency for phosphate from wastewater using Al electrodes. This may be attributed to the increase in the mass transferred of A^{l3+} from the anode surface to the solution bulk and the increase of the rate of Al^{3+} hydrolised to $Al(OH)_3$. But increasing the temperature above 50 ^{O}C was found to be uneconomic as there was a slight change in the rate of the reaction and the percentage of removal.

2.3. Limitation and open questions

Today electro-coagulation EC technique is widely used in treating industrial, rural, and sewage wastewater, remediation of surface and groundwater effluents as well as landfill leachate, but with variable success and certain limitation, especially in optimization and processes tuning. This technique is also used for cleaning of drinking water in smaller cities where the installment of big equipment's has not economic justification. EC demonstrate superior performance for treatment of different types of industrial wastewater as: electroplating, foodstuff and nutrients, slaughterhouse, textile, cosmetic, distillery, tannery, pulp and paper industry, synthetic detergent effluents, heavy metals etc. It is also very efficacy in removal of day and colored water, oil, grasses, inorganic and organic pollutants and pathogens.

In many cases this process has capability to overcome the disadvantage of the other treatment technologies. EC is still an emerging technology which contains complex and multitude of mechanisms operating synergetically in combination with electrochemistry, polymer and surface chemistry, physicochemical properties of pollutants and effluents etc. However, a quantitative appreciation of the mechanisms of interaction between these branches of industrial technologies employed in an EC system generally is absent. So far many works have been consecrated to the EC operating conditions. These conditions mostly depend on the chemical constituents and their concentrations containing wastewater, conductivity of wastewater, pH, particle size, types of electrode used, applied voltage, current density, retention time between electrode plates, plate spacing and number of electrodes. Oppositely, the works consecrated to the EC application in industry is limited.

However in any case the range of feasible EC applications is in progress and expanding. In a vast majority of studies the optimal parameters are proposed as: (i) optimal treatment time in the range 5-60 min (the time of sedimentation is not taking into account), (ii) optimal current density more varied and to be in the range 10-150 A/m^2, (iii) optimal pH range was mostly founds to be close to the neutrality, (iv) the most used electrodes are Al and Fe. (iv) For lowering the cost of EC process it is necessary to minimize the current IR drop for enhancing the current efficiency.

The open questions and limitation for larger application of EC process still are:

- It is still empirically optimized process. For each type of wastewater it is necessary firstly in laboratory conditions to optimize the working parameters. There is no yet generally the basic fundamental knowledge how to optimize the working parameters for each type of wastewater.
- No clear which electrode materials should be used. For the removing the same pollutants from wastewater various electrode materials have been proposed
- No dominant reactor design exists. Materials for construction varied and adequate scale-up parameters have not been yet defined.
- There is no a logical systematic approach to the mathematical modeling of EC reactors
- No detailed effects of the electrical field gradient on the interfacial and solution reactions were determined.
- No generic solution with passivation of electrodes. The formed passive films on electrode surfaces have semi-conducting properties and diminished the current efficiency

The potential of EC technology as a waste water treatment alternative is not yet fully realized. More fundamental knowledge for engineering design is required. In any case this technology will continue to make inroads into the waste water treatment because it is eco-friendly technology and has numerous advantages.

3. Conclusion

From the presented theoretical and practical literature knowledge of some electrochemical methods in wastewater treatment, the following conclusions can be drawn:

- The application of advanced electrochemical technologies in wastewater treatment in many countries is still in an embryonic phase, but the significant progress achieved in the last 20 years is evident. These technologies in many cases become alternative, more efficient, faster and chipper than the classical ones. The advantages of electrochemical technologies are: simple equipment, smaller processing area, convenient operation, clean energy conversion, using renewable energy sources, and no chemical requirements for coagulation, sedimentation, floc generation and flotation.
- Of all the electrochemical technologies used in wastewater treatment, electrocoagulation is the most efficient method with many advantages, and disadvantages that have a lesser effect.

The main advantages are: (i) Simple equipment, small land area, low initial investment, low operational costs and easy to operate. (ii) The electrolytic process is easily controlled only by varying the applied voltage and current density. (iii) Lower maintenance requirements (iv) Low quantities of produced sludge, which is easy to dewater and it tends to be readily settable. (v) High efficiency in removing the smallest colloidal particles due to the applied electrical field that sets them in faster motion and thereby facilitates coagulation (vi) Possibility for removal of a large variety of multiple contaminants in wastewater. (vii) Rarely requires small quantities of chemicals, only for augmentation of the conductivity, so there is no problem with neutralization of excess chemicals and secondary pollutants. The main Disadvantages are: (i) Depending on the electrode material, oxide films can form on the cathode which reduce the active electrode surface area and conductivity, reducing the process efficiency. (ii) High conductivity of wastewater is required. To lower the cost of electrocoagulation, electro-flocculation, and electro-flotation, it is necessary to minimize the IR drop which will enhance the current efficiency. The IR drop should be minimized by decreasing the distance between the electrode plates, i.e. using a higher number of plates positioned at smaller distances. (iii) Maintenance and regular replacement of the sacrificial anodes. (iv) Evolution of oxygen at the anodes sometimes represents unwanted leakage of current. This problem can be minimized by the choice of an anodic material that has high over potential for oxygen evolution. (v) In some countries the use of electricity may be expensive.

References

[1] P. Gleick. *Water Resource Management in Encyclopedia of Climate and Weather,* vol. 2 ed. ,S. Schneider; Ed. Oxford University Press, New York, 1996 pp. 817-823

[2] E. Vik, D. Carlson A, Eikun, E. Gjessing. “Electro-coagulation of Portable Water.” *Water Research,* vol. 18 pp. 1355-1361, Iss: 11,1984

[3] R. Hughes. “*An Introduction to Colloids in Colloid Science: Principles, Methods and Applications,* 2nd ed., T. Cosgrove; Ed. Wiley-Blackwell, London, 2005 pp. 394

[4] H. Helmholtz. “Ueber Einige Gesetze der Vertheilung Elektrischer Ströme in Körperlichen”. *Ann Physik,* vol. 89, pp. 211-233, 1853

[5] K. Oldham. “A Gouy-Chapman-Stern Model of the Double Layer at a Metal/ionic Liquid Interface”. *Journal of Electroanalytical Chemistry,* vol. 613, pp. 131-138, Feb. 2008

[6] Z. Stojek. *The Electrical double layer and its structure in Electro-analytical Methods, Guide to Experiments and Applications,* ed. F. Scholz, Ed. Springer Werlag Berlin Heidelberg, 2010, pp. 3-9

[7] J. Overbeek. “Recent Developments in the Understanding of Colloid Stability”. *Journal of Colloid and Interface Sci*ence, vol. 58, pp. 408–422, Feb. 1977

[8] P. Moussas, A. Zouboulis. “A new Inorganic-organic Composite Coagulant Consisting of Polyferric Sulphate (PFS) and Polyacrylamide (PAA). *Water Research,* vol. 43, pp. 3511-3524, Aug. 2009

[9] Y. Matsui, T. Matsushita, S. Sakuma, T. Gojo, T. Mamiya, H. Suzuoki, T. Inoue. “Virus Inactivation in Aluminum and Polyaluminum Coagulation”. *Environmental Science and Technology*, vol. 37, pp. 5175–5180, Iss: 22, Oct. 2003

[10] I. Xagoraraki, G. Harrington. “Zeta Potential, Dissolved Organic Carbon and Removal of Cryptosporidium Oocytes by Coagulation and Sedimentation”. *Journal of Environmental Engineering*, vol. 130, pp. 1424-1432, Dec. 2004

[11] A. Dietrich. “Electric Water Purifier, U. S. Patent No. 823, 671, Jun. 19 (1906)

[12] F. Stuart. “Electronic Water Purification; Progress Report on the Electronic Coagulator, a New Device Which Gives Promise of Unusually Speedy and Effective Results”. *Water and Sewage*, vol. 84, pp. 24-26, 1946

[13] C. Bonilla. “Possibilities of the Electronic Coagulator for Water Treatment”. *Water and Sewage*, vol. 85, pp. 21-22, 1947

[14] P. Holt, G. Barton, C. Mitchell. “The Future of Electrocoagulation as a Localized Water Treatment Technology. *Chemosphere*, vol. 9, pp. 335-367, Apr. 2005

[15] P. Canizares, F. Martinez, C. Jimenez, C. Saez, M. Rorigo, “Technical an Economic Comparison of Conventional and Electrochemical Coagulation Processes”. *Journal of Chemical Technology and Biotechnology*, vol. 84, pp. 702-710, May. 2009

[16] W. Chou, C. Wang, K. Huang. “Effect of Operating Parameters on Indium (III) Ion Removal by Iron Electrocoagulation and Evaluation of Specific Energy Consumption”. *Journal of Hazardous Materials*, vol. 167, pp. 467-474, Aug. 2009

[17] A. Dalvand, M. Gholami, A. Joneidi, N. Mahmoodi, “Dye Removal, Energy Consumption and Operating Cost of Electrocoagulation of Textile Wastewater as a Clean Process”. *CLEAN - Soil, Air, Water*, vol. 39, pp. 665-672, Jul. 2011

[18] C. Escobar, C. Soto-Salazar, M. Toral. “Optimization of the Electrocoagulation Process for the Removal of Copper, Lead and Cadmium in Natural Waters and Simulated Wastewater”. *Journal of Environmental Management*, vol. 81, pp. 384–391, Dec. 2006

[19] N. Tambo. “Basic Concepts and Innovative Turn of Coagulation/flocculation”. *Water Supply*, vol. 9, pp. 1–10, Iss: 1, 1991

[20] S. Khoufi, F. Feki, S. Sayadi. “Detoxification of Olive Mill Wastewater by Electrocoagulation and Sedimentation Processes”. *Journal of Hazardous Materials*, vol. 142, pp. 58–67, Apr. 2007.

[21] A. Bukhari. “Investigation of the Electrocoagulation Treatment Process for the Removal of Total Suspended Solids and Turbidity from Municipal Wastewater”. *Bioresource Technology*, vol. 99, pp.9 14-921, Iss. 5, Mar. 2008

[22] S. Zodi, O. Potier, F. Lapicque, J. Leclerc. “Treatment of the Industrial Wastewater by Electrocoagulation: Optimization of Couple Electrochemical and Sedimentation Processes”. *Desalination*, vol. 261, pp. 186-190, Oct. 2010

[23] P. Canizares, F. Martinez, M. Rodrigo, C. Jimenez, C. Saez, J. Laboto. “Modeling of Wastewater Electro-coagulation Processes: Part I. General Description and Application to Kaolin-polluted Wastewaters”. *Separation and Purification Technology*, vol. 60, pp. 155-161, Apr.2008

[24] M. Kilic, C. Hosten. “A Comparative Study of Electrocoagulation and Coagulation in Aqueous Suspensions of Kaolinite Powders”. *Journal of Hazardous Materials*, vol. 176, pp. 735-740, Apr. (2010)

[25] I. Heidmann, W. Calmano. “Removal of Ni, Cu and Cr from a Galvanic Wastewater in an Electro-coagulation System with Fe and Al Electrodes”. *Separation and Purification Technology* vol. 71, pp. 308-314, Mar. (2010)

[26] F. Akbal, S. Camc. “Copper, Chromium and Nickel Removal from Metal Plating Wastewater by Electrocoagulation”. *Desalination*, vol. 269, pp. 214–222, Mar. 2011

[27] O. Abdelwahab, N. Amin, E. Ashtoukhy. “Electrochemical Removal of Phenol from Oil Refinery Wastewater”. *Journal of Hazardous Materiaols*, vol. 163, pp.711-716, Apr. 2009

[28] G. Sleptsov, A. Gladkii, E. Sokol, S. Novikova. “Electrocoagulation Treatment of Oil Emulsion Wastewaters of Industrial Enterprises”. *Elektronnaya Obrabotka Materiajalov*, vol. 6, pp. 69-72, 1987

[29] L. Chou. “Removal and Adsorption Characteristics of Polyvinyl Alcohol from Aqueous Solutions Using Electrocoagulation”. *Journal of Hazardous Materials*, vol. 177, pp. 842-850, Iss: (1-3), 2010

[30] M. Chen, G. Chen, P. Yue. “Separation of Pollutants from Restaurant Wastewater by Electrocoagulation”. Separation and Purification Technology, vol. 19, pp. 65-76, Iss. 1-2, 2000

[31] Z. Murthy, C. Nancy, A. Kant. Separation of Pollutants from Restaurant Wastewater by Electrocoagulation”. *Separation Science and Technology*, vol. l42, pp. 819-833, Mar. 2007

[32] M. Kobya, H. Hiz, E. Senturk, C. Aydiner, E. Demirbas. “Treatment of Potato Chips Manufacturing Wastewater by Electrocoagulation”. *Desalination*, vol. 190, pp. 201–211, Apr. 2006

[33] M. Kobya,S. Delipinar. “Treatment of Baker’s Yeast Wastewater by Electrocoagulation”. *Journal of Hazardous Materials*, vol. 154, pp. 1133-1140, Jun. 2008

[34] S. Novikova, T. “Purification of Effluents from the Production of Synthetic Detergents by Electro-coagulation”. *Soviet Journal of Water Chemistry and Technology*, vol. 4, pp. 353-357, Iss: 3, 1982

[35] C. Petsriprasit, J. Namboonmee, M. Hunsom. “Application of the Electrocoagulation Technique for Treating Heavy Metals Containing Wastewater from the Pickling Process of a Billet Plant. *Korean Journal of Chemical Engineering*, vol. 27, pp. 854-861, Iss: 3, 2010

[36] C. Nanseu-Njiki, S. Tchamango, P. Ngom, A. Darchen, E. Ngameni. “Mercury(II) Removal from Water by Electrocoagulation Using Aluminum and Iron Electrodes”. *Journal of Hazardous Materials*, vol. 168, pp. 1430–1436, Iss: 2, 2009

[37] A. Golder, A. Samanta, S. Ray. “Removal of Trivalent Chromium by Electrocoagulation”. *Separation and Purification Technology*, vol. 53, pp. 33–41, Feb. 2006

[38] I. Zongo, J-Pierre Leclerc, H. Maiga, F. Lapicque. “Removal of Hexavalent Chromium from Industrial Wastewater by Electrocoagulation. A Comprehensive Comparison of Aluminum and Iron Electrode”. *Separation and Purification Technology*, vol. 66, pp.159-166, Apr. 2009

[39] N. Balasubramanian, T. Kojima, C. Basha, C. Srinivasakannan. “Removal of Arsenic from Aqueous Solution Using Electrocoagulation”. *Journal of Hazardous Materials*, vol. 167, pp. 966–969, Iss: 1, 2009

[40] K. Castro-Ríos, G. Taborda-Ocampo, R. Torres-Palma. “Experimental Design to Measure Escherichia Coli Removal in Water through Electrocoagulation”**.** *International Journal of Chemical Science*, vol. 9, pp. 610 – 617, 2014

[41] G. Azarian, A. Mesdaghinia, F. Vaezi, R. Nabizadeh, D. Nematollahi. “Algae Removal by Electro-coagulation Process; Application for Treatment of the Effluent from an Industrial Wastewater Treatment Plant”. *Iranian Journal of Public Health*, vol. 36, pp. 57-64, Iss: 4, 2007

[42] M. Kobia, O. Can, M. Bayramoglu. “Treatment of Textile Wastewaters by Electrocoagulation Using Iron and Aluminum Electrodes”. *Journal of Hazardous Materials*, vol. B100, pp.163-178, Jun. 2003

[43] S. Zodi, O. Potier, F. Lapicque, J. Lecrerc. “Treatment of the Textile Wastewaters by Electrocoagulation; Effect of Operating Parameters on the Sludge Settling Characteristics”. *Separation and Purification Technology*, vol. 69, pp. 29-36, Sep. 2009

[44] O. Larue, E. Vorobiev, C. Durand. “Electrocoagulation and Coagulation by Iron of Latex Particles in Aqueous Suspensions”. *Separation and Purification Technology*, vol. 31, pp.177-192, May 2003

[45] F. Janpoor, A. Torabian, V. Khatibikamal. “Treatment of Laundry Wastewater by Electrocoagulation”. *Journal of Chemical Technology and Biotechnology*, vol. 86, pp.1113-1120, Aug. 2011

[46] F. Zidane, P.Drogui, B. Lekhliv, J. Bensaid, J. Blais, S. Belcadi, K. Kacemi. "Decolourization of Dye-containing Effluent Using Mineral Coagulants Produced by Electrocoagulation". *Journal of Hazardous Materials*, vol. 155, pp. 153-163, Jun. 2008

[47] R. Ahlawat, V. Srivastava, I. Mall, S. Sinha. "Investigation of the Electrocoagulation Treatment of Cotton Blue Dye Solution Using Aluminum Electrodes *CLEAN-Water, Air Soil*, vol. 36, pp. 863-869, Iss: 10-11, 2009

[48] K. Animes, A. Golder, A. Harsh, N. Amar, A. Samanta, R. Subhabrata. "Color Diminution and COD Reduction in Treatment of Colored Effluent by Electrocoagulation". *International Journal of Environmental Engineering,* vol. 2, pp. 228-238, Iss: 1-3, 2010

[49] A. Moghadam, H. Amiri. "Investigation of TOC Removal from Industrial Wastewaters Using Electro-coagulation Process". *Iranian Journal of Health and Environment*, vol. 3, pp. 185-194, Issu: 2, 2010

[50] A. Chopra, A. Sharma. "Removal of Turbidity, COD and BOD from Secondarily Treated Sewage Water by Electrolytic Treatment". *Applied Water Science*, vol. 3, pp.125-132, Issu: 1, 2013

[51] S. Kongjao, S. Damronglerd, M. Hunsom. "Simultaneous Removal of Organic and Inorganic Pollutants in Tannery Wastewater Using Electrocoagulation Technique". *Korean Journal of Chemical Engineering*, vol. 25, pp. 703–709, Jul. 2008

[52] M. Bayramoglu, M. Kobya, M. Eyvaz, E. Senturk. "Technical and Economic Analysis of Electro-coagulation for the Treatment of Poultry Slaughterhouse Wastewater". *Separation and Purification Technology*, vol. 51, pp. 404-408, Oct. 2006

[53] I. Heidmann, W. Calmano. Removal of Zn(II), Cu(II), Ni(II), Ag(I), Co(II) and Cr(VI) Present in Aqueous Solutions by aluminum Electrocoagulation". *Journal of Hazardous Materials,* vol. 152, pp. 934–941, Apr. 2008

[54] Ö. Hanay Ö, H. Hasar. "Effect of Anions on Removing Cu^{2+}, Mn^{2+} and Zn^{2+} in Electrocoagulation Process Using Aluminum Electrodes". *Journal of Hazardous Materials,* vol. 189, pp. 572–576, May 2011

[55] A. Shafaei, E. Pajootan, M. Nikazar, M. Arami. "Removal of Co(II) from Aqueous Solution by Electrocoagulation Process Using Aluminum Electrodes". *Desalination*, vol. 279, pp. 121–126, Sep. 2011

[56] M. Murugananthan, G. Bhaskar Raju, S. Prabhakar. "Removal of Sulfide, Sulfate and Sulfite Ions by Electrocoagulation". *Journal of Hazardous Materials,* vol. 109, pp. 37–44, Jun. 2004

[57] V. Khatibikamal, A. Torabian, F. Janpoor, G. Hoshyaripour. "Fluoride Removal from Industrial Wastewater Using Electrocoagulation and its Adsorption Kinetics". *Journal of Hazardous Materials,* vol. 179, pp. 276-280, Jul. 2010

[58] S. Irdemez, Y. Sevki Yildiz, V. Tosunoglu. "Optimization of Phosphate Removal from Wastewater by Electrocoagulation with Aluminum Plate Electrodes". *Separation and Purification Technology,* vol. 52, pp. 394–401, Dec. 2006

[59] E. Lacasa, P. Cañizares, C. Sáez, F. Fernández, M. Rodrigo. "Removal of Nitrates from Groundwater by Electrocoagulation". *Chemical Engineering Journal*, vol. 171, pp. 1012–1017, Jul. 2011

[60] M. Mollah, R. Schennach, J. Parga, D. Cocke. "Electrocoagulation Science and Applications". *Journal of Hazardous MaterialsB,* vol. 84, pp.29–41, Jun. 2001

[61] Y. Meas, J. Ramirez, M. Villalon, W. Chapman. "Industrial Wastewaters Treated by Electrocoagulation". *Electrochimica Acta*, vol. 55, pp. 8165-8171, Nov. 2010

[62] G. Chen. Electrochemical Technologies in Wastewater Treatment". *Separatation and Purification Technology,* vol. 38, pp. 11-41, Jul. 2004

[63] H. Moreno, D. Cocke, J. Gomes, P. Morkovsky, J. Parga, E. Peterson, C. Garcia. "Electrochemistry behind Electrocoagulation Using Iron Electrodes". *ECS Transactions*, vol. 6, pp.1-15, Iss: 9, 2007

[64] T. Picard, G. Cathalifaud-Feuillade, M. Mazet, C. Vandensteendam. "Cathodic Dissolution in the Electrocoagulation Process Using Aluminum Electrodes". *Journal of Environmental Monitoring,* vol. 2, pp. 77–80, 2000

[65] T. Matsue, M. Fujhira, T. Osa. "Oxidation of Alkylbenzenes by Electrogenerated Hydroxyl Radical". *Journal of the Electrochemical Society (IJMER),* vol. 128, pp. 2565-2569, Iss: 12, 1981

[66] S. Chaturvedi. "Electro-coagulation: A Novel Wastewater Treatment Method". *International Journal of Modern Engineering Research*, vol. 3, pp. 93-100, Iss: 1, Jan.-Feb. 2013

[67] I. Linares-Hermandez, C. Barrera-Diaz, G. Roa-Morales, B. Bilyeu, F. Urena-Ninez. "Influence of the Anodic Material on Electrocoagulation Performance". *Chemical Engineering Journal*, vol. 148, pp. 97-105, May 2009

[68] B. Krishna, U. Murthy, B. Manoj Kumar, K. Lokesh. "Study of the Electrochemical Process for Distillery Wastewater Treatment". *Journal of Environmental Research and Development*, vol. 5, pp. 134-140, Iss: 1, 2010

[69] R. Katal, H. Pahlavanzadeh. "Influence of Different Combination of Aluminum and Iron Electrode on Electrocoagulation Efficiency: Application to the Treatment of Paper Mill Wastewater". *Desalination*, vol. 265, pp. 199-205, Jan. 2011

[70] I. Alill, V. Gupta V, T. Khan, M. Asim. "Removal of Arsenate from Aqueous Solution by Electro-coagulation Method Using Al-Fe Electrodes". *International Journal of Electrochemical Science*, vol. 7, pp. 1898-1907, Mar. 2012

[71] H. Moreno, D. Cocke, J. Gomes, P. Morkovsky, J. Parga, E. Peterson, C. Garcia. "Electrochemical Reactions for Electrocoagulation Using Iron Electrodes". *Industrial & Engineering Chemical Research*, vol. 48, pp. 2275-2282, Iss: 4, 2009

[72] A. Bagga, S. Chellam, D. Clifford. "Evaluation of Iron Chemical Coagulationand Electrocoagulation Pretreatment for Surface Water Microfiltration". *Journal of Membrane Science*, vol. 309, pp. 82–93, Feb. 2008

[73] V. Baklan, I. Kolsenikova. "Influence of Electrode Material on the Electrocoagulation". *Journal of Aerosol Science*, vol. 27, pp. S209-S210, Iss. 1, 1996

[74] N. Beyazit. "Copper(II), Chromium(VI) and Nickel(II) Removal from Metal Plating Effluent by Electrocoagulation" . *International Journal of Electrochemical Science*, vol. 9, pp. 4315-4330, May 2014

[75] I. Arslan-Alaton, I. Kabdash, Y. Sahin. "Effect of Operating Parameters on the Electrocoagulation of Simulate Acid Dye Bath Effluent". *The Open Environmental & Biological Monitoring Journal*, vol. 1, pp. 1-7, 2008

[76] J. Marconato, E. Bidola, R. Rochia-Filho. "Electrolytic Treatment of Wastewater from a Fowl Slaughter House Using Cast-iron Electrodes". *Bulletin of Electrochemistry*, vol. 14, pp. 228-230, jun-Jul. 1998

[77] M. Secula, I. Cretescu, S. Petrescu. "Electrocoagulation Treatment of Sulfide Wastewater in a Batch Reactor: Effect of Electrode Material on Electrical Operating Costs". *Environmental Engineering and Management Journal*, vol. 11, pp. 1485-1491, Aug. 2012

[78] A. Mahvi, H. Mansoorian, A. Rajabizadeh. "Performance Evaluation of Electrocoagulation Process for Removal of Sulfate from Aqueous Environments Using Plate Aluminum Electrodes". *World Applied Science,* vol. 7, pp. 1526-1533, Iss: 12, 2009

[79] P. Cañizares, C. Jiménez, F. Martínez, M. Rodrigo, C. Sáez. "The pH as a Key Parameter in the Choice Between Coagulation and Electrocoagulation for the Treatment of Wastewaters". *Journal of Hazardous Materials*, vol. 163, pp. 158–164, Apr. 2009

[80] J. Trompette, H. Vergnes. "On the Crucial Influence of Some Supporting Electrolytes During Electrocoagulation in the Presence of Aluminum Electrodes". *Journal of Hazardous Materials*, vol. 163, pp. 1282–1288, Apr. 2009

[81] M. Mollah, P. Morkovsky, J. Gomes, M. Kesmez, J. Parga, D. Cocke. "Fundamentals, Present and Future Perspectives of Electrocoagulation". *Journal of Hazardous Materials*, vol. 114, pp. 199–210, Oct. 2004

[82] S. Irdemez, N. Demircioglu, Y. Yildiz. "The Effects of pH on Phosphate Removal from Wastewater by Electrocoagulation with Iron Plate Electrodes". *Journal of Hazardous Materials,* vol. 137, pp. 1231–1235, Iss. 2, 2006.

[83] M. Yu, J. Koo, G. Myung, Y. Cho “Evaluation of Bipolar Electrocoagulation Applied to Bio-filtration for Phosphorus Removal. *WaterScience and Technology*, vol. 51, pp. 231–239, Iss: 10, 2005

[84] X. Wang, H. Li, D. Su, T. Sun. “Treatment of Printing and Dyeing Wastewater by Electrocoagulation Method”. *Environmental Science & Technology*, vol. 33, pp. 150-153, 2010

[85] P. Holt, G. Barton, C. Mitchell. “Electrocoagulation as a Wastewater Treatment”. The III Annual Australian Environmental Engineering Research. 23-26 November (1999) www.isf.uts.edu.au/publications, last accessed 12/06/2013http://cfsites1.uts.edu.au/find/publications/search.cfm?year=1999&UnitId=139

[86] G. Mouedhen, M. Feki, M. De Petris Wery, H. Ayedi. “Behavior of Aluminum Electrodesin Electrocoagulation Process”. *Journal of Hazardous Materials*, vol.150, pp. 124–135, Jan. 2008

[87] I. Heidmann, W. Calmano. “Removal of Cr(VI) from Model Wastewater by Electrocoagulation with Fe Electrodes”. *Separation and Purification*, vol. 61, pp. 15-21, Jun. 2008

[88] I. Arslan-Alton, G. Turkoglu. “Treatability of a Simulated Spent Disperse Dye Bath by Chemical and Electro-chemical Processes”. *Environmental Engineering and Science*, vol. 25, pp. 295-308, Apr. 2008

[89] A. Yilmaz, R. Boncukcuoglu, M. Kocakerim, M. Yilmaz, C. Paluluoglu. “Boron Removal from Geothermal Waters by Electrocoagulation”. *Journal of Hazardous Materials*, vol. 153, pp. 146–151, May 2008

[90] S. Vasudevan, J. Lakshmi, J. Jayaraj, G. Sozhan. “Remediation of phosphate contaminated water by electrocoagulation with aluminum, aluminum alloy and mild steel anodes”. *Journal of Hazardous Materials*, vol. 164, pp. 1480–1486, Iss: 2-3, 2009

[91] S. Giwaa , K. Polatb and H. Hapoglua. “The Effects of Operating Parameters on Temperature and Electrode Dissolution in Electrocoagulation Treatment of Petrochemical Wastewater”. *International Journal of Engineering Research & Technology (IJERT)*, vol. 1, pp. 2278-0181, Dec. 2012,

[92] C Phalakornkulea, , J Mangmeemak , K Intrachod , B Nuntakumjorna. “Pretreatment of Palm Oil Mill Effluent by Electrocoagulation and Coagulation”. *Science Asia*, vol. 36, pp. 142-149, 2010

[93] A. Shalaby, E. Nassef, A. Mubark, M. Hussein, “Phosphate Removal from Wastewater by Electrocoagulation Using Aluminum Electrodes”. *American Journal of Environmental Engineering and Science*, vol. 1, pp. 90-98, Oct. 2014 (http://www.openscienceonline.com/journal/ajees).