IS ELECTROCOAGULATION (EC) A SOLUTION TO THE TREATMENT OF WASTEWATER AND PROVIDING CLEAN WATER FOR DAILY USE

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ABSTRACT

Although electro coagulation is an evolving technology that is being effectively applied today for wastewater treatment, the paucity of scientific understanding of the complex chemical and physical processes involved is limiting future design and hindering progress. The objective of this review through a survey of the literature is to bring the chemistry and physical processes involved into perspective and to focus attention on those areas critically needing research.

Keywords: electro coagulation, wastewater, physico-chemical processes.

1. INTRODUCTION

Around the world, one of the major challenges facing mankind today is to provide clean water to a vast majority of the population mostly in third world countries. Rivers, canals, estuaries and other water-bodies are being constantly polluted due to indiscriminate discharge of industrial effluents as well as other anthropogenic activities and natural processes. In the latter, unknown geochemical processes have contaminated ground water with arsenic in many countries? Highly developed countries, such as the US, are also experiencing a critical need for wastewater cleaning because of an ever-increasing population, urbanization and climatic changes. The reuse of wastewater has become an absolute necessity. There is, therefore, an urgent need to develop innovative, more effective and inexpensive techniques for treatment of wastewater. A wide range of wastewater treatment techniques are known which includes biological processes for nitrification, denitrification and phosphorous removal; as well as a range of physico-chemical processes that require chemical additions. The commonly used physico-chemical treatment processes are (a) filtration, (b) air stripping, (c) ion-exchange, (d) chemical precipitation, (e) chemical oxidation, (f) carbon adsorption, (g) ultra filtration, (h) reverse osmosis, (i) electro dialysis, (j) volatilization and (k) gas stripping. A host of very promising techniques based on electrochemical technology are being developed and existing ones improved that do not require chemical additions.

These include electro coagulation [45], electro flotation [45], electro decantation [46,47,48], and others. Even though one of these, electro coagulation, has reached profitable commercialization, it has received very little scientific attention [49]. This process has the potential to extensively eliminate the disadvantages of the classical treatment techniques. Moreover, the mechanisms of EC are yet to be clearly understood and there has been very little consideration of the factors that influence the effective removal of ionic species, particularly metal ions, from wastewater by this technique. In this brief review, we wish to address these issues.

2. TECHNOLOGY

Treatment of wastewater by EC has been practiced for most of the 20th century with limited success and popularity. In the last decade, this technology has been increasingly used in South America and Europe for treatment of industrial wastewater containing metals [1]. It has also been noted [1] that in North America EC has been used primarily to treat wastewater from pulp and paper industries, mining and metal-processing industries. In addition, EC has been applied to treat water containing foodstuff wastes [2], oil wastes [2-5], dyes [6], suspended particles [7-11], chemical and mechanical polishing waste [12], organic matter from landfill leachates [11], defluorination of water [13], synthetic detergent effluents [14], mine wastes [15] and heavy metal-containing solution [16-20]. Typically, empirical studies are done on EC to define major operating parameters for broad classes of contaminated water or waste streams. The technology has been optimized to minimize electrical power consumption and maximize effluent throughput rates. This approach, which provides little insight into the fundamental chemical and physical mechanisms, does not allow modeling of the process or the design of improved systems, process control and optimization from fundamental physico-chemical principles.

3. COAGULATION AND ELECTRO COAGULATION

Coagulation is a phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with counter ions and are agglomerated, followed by sedimentation. The coagulant is added in the form of suitable chemical substances. Alum [Al2(SO4)3·18H2O] is such a chemical substance which has been widely used for ages for wastewater treatment. The mechanism of coagulation has been the subject of continual review [21, 22]. It is generally accepted that coagulation is brought about primarily by the reduction of the net surface charge to a point where the colloidal particles, previously stabilized by electrostatic repulsion, can approach closely
4. ADVANTAGES OF EC

a) EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
b) Wastewater treated by EC gives palatable, clear, colorless and odorless water.
c) Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.
d) Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
e) EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
f) The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
g) The EC process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used.
h) The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
i) The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance.
j) The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

5. DISADVANTAGES OF EC

a) The ‘sacrificial electrodes’ are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.
b) The use of electricity may be expensive in many places.
c) An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.
d) High conductivity of the wastewater suspension is required.
e) Gelatinous hydroxide may tend to solubilize in some cases.

6. DESCRIPTION OF THE TECHNOLOGY

In its simplest form, an electro coagulating reactor may be made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. But, this arrangement is not suitable for wastewater treatment, because for a workable rate of metal dissolution, the use of electrodes with large surface area is required. This has been achieved by using cells with monopolar electrodes either in parallel or series connections. A simple arrangement of an EC cell with a pair of anodes and a pair of cathodes in parallel arrangement is shown in Figure-1.

![Figure-1. Bench-scale EC reactor with monopolar electrodes in parallel connection (after [23]).](attachment:image.png)

It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a dc power source as shown in Figure-1. The experimental set up also requires a resistance box to regulate the current density and a multimeter to read the current values. The conductive metal plates are commonly known as ‘sacrificial electrodes’. The ‘sacrificial anode’ lowers the dissolution...
potential of the anode and minimizes the passivation of the cathode. The sacrificial electrodes may be made up of the same or of different materials as the anode.

An arrangement of an EC cell with monopolar electrodes in series is shown in Figure-2. As can be seen from Figure-2 each pair of ‘sacrificial electrodes’ is internally connected with each other, and has no interconnections with the outer electrodes. This arrangement of monopolar electrodes with cells in series is electrically similar to a single cell with many electrodes and interconnections.

In series cell arrangement, a higher potential difference is required for a given current to flow because the cells connected in series have higher resistance. The same current would, however, flow through all the electrodes. On the other hand, in parallel arrangement the electric current is divided between all the electrodes in relation to the resistance of the individual cells. The readers are referred to an article by Pretorius et al., [23] for discussion of the parallel and series arrangements of monopolar cells.

In the EC process, an electric field is applied to the medium for a short time, and the treated dispersion transferred to an integrated clarifier system where the water-contaminant mixture separates into a floating layer, a mineral-rich sediment, and clear water. The aggregated mass settles down due to gravitational force. The clear water can be extracted by conventional methods.
7. AC VERSUS DC ELECTRO COAGULATION

The direct current electro coagulation (DCE) technology is inherent with the formation of an impermeable oxide layer on the cathode as well as deterioration of the anode due to oxidation. This leads to the loss of efficiency of the EC unit. These limitations of the DCE process have been minimized to some extent by the addition of parallel plate sacrificial electrodes in the cell configuration. However, many have preferred the use of alternating current electro coagulation (ACE) technology [25]. It is believed that the ac cyclic energization retards the normal mechanisms of electrode attack that are experienced in DCE system, and thus, ensure reasonable electrode life. In addition to that, since the ac electric fields in an ACE separator do not cause electrophoretic transport of the charged particles due to the frequent change of polarity, it can induce dipole-dipole interactions in a system containing nonspherical charged species. As a result, the ac electric fields may also disrupt the stability of balanced dipolar structures existing in such a system. This is, however, not possible in a DCE separator using dc electric fields.

8. ALTERNATING CURRENT ELECTRO COAGULATION (ACE)

The US EPA has applied ACE technology for remediation of aqueous waste streams at Superfund Sites [26]. The ACE separator designed by EPA consists of either a parallel electrode unit in which the effluent stream passes, or a fluidized bed unit with conductive cylinders equipped with nonconductive metal electrodes between which a turbulent fluidized bed of aluminum pellets is maintained. Compressed air is introduced into the EC cell to maintain a turbulent fluidized bed to enhance the aluminum dissolution efficiency by increasing the anodic surface area. The basic flow diagram for the ACE separator with fluidized bed of aluminum alloy pellets entrained between a series of nonconductive metal electrodes is shown in Figure-4. As can be seen from Figure-4, an ac electric field is applied to the aqueous stream as it flows through the unit. As a result, a low concentration of aluminum ions is generated by dissolution of the sacrificial electrode. These counter ions reduce the electrical double-layer charge concentration and separate the aqueous phase. The treated water is then transferred to a product separator where the water and solid phases are separated for reuse, recycling, additional treatment or disposal. One of the advantages of the ACE process is that attrition scrubbing of the fluidized bed pellets within the cell inhibits the build up of scale or coating on the aluminum pellets and the face of the electrodes. In a recent publication, Mills [27] has described a new process for electro coagulation. In this process, the electro coagulation unit is made up of a series of electrolytic cells containing iron anodes and stainless-steel cathodes. The electrolytic cells are constructed in such a way that a narrow gap between the central anode and the surrounding cathode. Wastewater is allowed to flow through the ladder of cells, by way of a labyrinth of holes in the cathodes. Application of a low-voltage dc source to the cells produces iron hydroxide flocculant.

9. THEORY OF EC

The theory of EC has been discussed by a number of authors [1, 25]. It’s generally accepted that the EC process involves three successive stages: (a) formation of coagulants by electrolytic oxidation of the ‘sacrificial electrode’; (b) destabilization of the contaminants, particulate suspension, and breaking of emulsions; (c) aggregation of the destabilized phases to form flocs. The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions has been described in broad steps and may be summarized as follows:

a) Compression of the diffuse double-layer around the charged species, which is achieved by the interactions of ions generated by dissolution of the sacrificial electrode, due to passage of current through the solution.

b) Charge neutralization of the ionic species present in wastewater, which is caused by the counter ions, produced by the electrochemical dissolution of the sacrificial electrode. These counter ions reduce the electrostatic interparticle repulsion sufficiently so that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.

c) Floc formation, and the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles that have not been complexed.

Details of these steps are lacking and require further study.
10. REACTION TYPES INVOLVED IN THE EC PROCESS

The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the EC process. The mechanisms of removal of ions by EC will be explained with two specific examples involving aluminum and iron, since these two metals have been extensively used to clarify wastewater.

10.1 Aluminum

Electro coagulation of wastewater using an aluminum electrode has been reported by a number of authors [28-32]. The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as $\text{Al}^{3+}$ and $\text{Al(OH)}_2^{4-}$ at low pH, which at appropriate pH values are transformed initially into $\text{Al(OH)}_3$ and finally polymerized to $\text{Al}_n(\text{OH})_3n$ according to the following reactions:

$$\text{Al} \rightarrow \text{Al}^{3+} (aq) + 3e^- \tag{1}$$

$$\text{Al}^{3+} (aq) + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ (aq) \tag{2}$$

$$n\text{Al(OH)}_3 \rightarrow \text{Al}_n(\text{OH})_3n \tag{3}$$

However, depending on the pH of the aqueous medium other ionic species, such as $\text{Al(OH)}_2^{5-}$, $\text{Al}_2(\text{OH})_2^{4-}$ and $\text{Al(OH)}_4^-$ may also be present in the system. Examination of the pE-pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimeric hydroxo $\text{Al}^{3+}$ species may be formed. For example, the structures of dimeric and polymeric $\text{Al}^{3+}$ hydroxo complexes are shown below:

These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate. Ming et al., [32] have reported the defluorination of water by electrolysis using aluminum electrodes. According to the proposed mechanism the $\text{Al}^{3+}$ ions under high F- concentration may be induced to form $\text{AlF}_6^{3-}$ which was transformed to insoluble salt $\text{Na}_3\text{AlF}_6$ by adding sodium ions according to the following reactions:

$$\text{Al}^{3+} + 6\text{F}^- \rightarrow \text{AlF}_6^{3-} \tag{4}$$

$$6\text{AlF}_6^{3-} + 3\text{Na}^+ \rightarrow \text{Na}_3\text{AlF}_6 \tag{5}$$

The insoluble $\text{Na}_3\text{AlF}_6$ salt was then separated by decantation. Mameri et al., [13] have successfully applied this technology to defluoridation of septentrional Sahara water of North Africa.

10.2 Iron

Iron upon oxidation in an electrolytic system produces iron hydroxide, $\text{Fe(OH)}_n$ where $n = 2$ or 3. Two mechanisms have been proposed for the production of $\text{Fe(OH)}_n$ [33–35].

- **Mechanism 1**
  - **Anode**
    $$4\text{Fe}(s) \rightarrow 4\text{Fe}^{2+} (aq) + 8e^- \tag{6}$$
    $$4\text{Fe}^{2+} (aq) + 10\text{H}_2\text{O} (l) + \text{O}_2 (g) \rightarrow 4\text{Fe(OH)}_2(s) + 8\text{H}^+ (aq) \tag{7}$$
  - **Cathode**
    $$8\text{H}^+ (aq) + 8e^- \rightarrow 4\text{H}_2 (g) \tag{8}$$

- **Overall**
  $$4\text{Fe} (s) + 10\text{H}_2\text{O} (l) + \text{O}_2 (g) \rightarrow 4\text{Fe(OH)}_2(s) + 4\text{H}_2 (g) \tag{9}$$

- **Mechanism 2**
  - **Anode**
    $$\text{Fe}(s) \rightarrow \text{Fe}^{2+} (aq) + 2e^- \tag{10}$$
    $$\text{Fe}^{2+} (aq) + 2\text{OH}^-(aq) \rightarrow \text{Fe(OH)}_2(s) \tag{11}$$
  - **Cathode**
    $$2\text{H}_2\text{O} (l) + 2e^- \rightarrow \text{H}_2 (g) + 2\text{OH}^- (aq) \tag{12}$$

- **Overall**
  $$\text{Fe}(s) + 2\text{H}_2\text{O} (l) \rightarrow \text{Fe(OH)}_2(s) + \text{H}_2 (g) \tag{13}$$

The Fe (OH) $n$s) formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [36]. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:

$$\text{L - H} (aq) \text{OFe(s)} \rightarrow \text{L - OFe(s)} + \text{H}_2\text{O} (l) \tag{14}$$

The prehydrolysis of $\text{Fe}^{3+}$ cations also leads to the formation of reactive clusters for water treatment. Structural models for these oxyhydroxy iron cations have been extensively reported in the literature ([37] and references therein).

Wastewater containing $\text{Cr}^{6+}$ ($\text{CrO}_4^{2-}$) ions can be removed by the EC technique using iron as the sacrificial anode [38, 39]. The ferrous ion ($\text{Fe}^{2+}$) generated by electrodissolution of the iron anode can reduce $\text{Cr}^{6+}$ to $\text{Cr}^{3+}$ under alkaline conditions and is itself oxidized to ferric ($\text{Fe}^{3+}$) ion according to:

$$\text{CrO}_4^{2-} (aq) + 3\text{Fe}^{2+} (aq) + 4\text{H}_2\text{O} (l) \rightarrow 3\text{Fe}^{3+} (aq) + \text{Cr}^{3+} (aq) + 4\text{OH}^- (aq) \tag{15}$$

or

$$\text{CrO}_4^{2-} (aq) + 3\text{Fe}^{2+} (aq) + 4\text{H}_2\text{O} (l) + 4\text{OH}^- (aq) \rightarrow 3\text{Fe} (OH)_3 \downarrow + \text{Cr (OH)}_3 \downarrow \tag{16}$$

The $\text{Cr}^{3+} (aq)$ ion is then precipitated as $\text{Cr (OH)}_3(s)$ by raising the pH of the solution. The $\text{Fe}^{2+} (aq)$ ions can also reduce $\text{Cr}_2\text{O}_7^{2-} (aq)$ under acidic conditions according to the following reaction:
Cr$_2$O$_7^{2-}$ (aq) + 6Fe$^{2+}$ (aq) + 14H$^+$ (aq) → 2Cr$^{3+}$ (aq) + 6Fe$^{3+}$ (aq) + 7H$_2$O (l)  \hspace{1cm} (17)

The H$_2$ produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation. However, the Fe$^{3+}$ ions may undergo hydration and depending on the pH of the solution Fe (OH)$_2^{2+}$, Fe (OH)$_3$ and Fe (OH)$_4$ species may be present under acidic conditions. The reactions involved are:

Fe$^{3+}$ (aq) + H$_2$O (l) → Fe (OH)$_2^{2+}$ (aq) + 2H$^+$ (aq) \hspace{1cm} (18)
Fe$^{3+}$ (aq) + 2H$_2$O (l) → Fe (OH)$_3$ (aq) + 2H$^+$ (aq) \hspace{1cm} (19)
Fe$^{3+}$ (aq) + 3H$_2$O (l) → Fe (OH)$_4$ (aq) + 3H$^+$ (aq) \hspace{1cm} (20)

Under alkaline conditions, Fe (OH)$_5^-$ and Fe (OH)$_6$ ions may also be present. It is, therefore, quite apparent that EC of both anionic and cationic species is possible by using an iron plate/rod as a sacrificial electrode.

The adsorption and absorption of heavy metals by polymeric Fe$^{3+}$ and Al$^{3+}$ hydroxo complexes has been extensively reported \cite{40}, and references therein which is beyond the scope of the current review. It should, however, be pointed out that the use of Fe$^{3+}$ as flocculation agent in water treatment has considerable advantage because of its innocuity compared to Al$^{3+}$ ions, which exhibits some toxic effects \cite{41}.

11. HYBRID PROCESS

Sometimes it becomes necessary to use two or more methods of treatment, i.e., hybrid processes, to ensure efficient treatment of wastewater. The EC technology can be designed into water treatment systems to include membrane separation, reverse osmosis, electro filtration, sludge dewatering, thermo-oxidation and other conventional technologies to enhance the recovery of fine particles and metal ions from wastewater. Belongia et al., \cite{12} have investigated the waste streams from chemical mechanical operations by electro coagulation with electro decantation (EC/ED) techniques. Removal of coloring materials from dyestuffs using EC with electro filtration has been reported by Ibanez et al., \cite{36}. Pouet and Grasmick \cite{24} and Beck et al., \cite{2} have reported the uses of EC with dissolved air flotation (DAF) for treatments of urban wastewater. Continuous treatment of textile wastewater by combining electrochemical oxidation, coagulation and activated sludge has been reported by Lin and Peng \cite{42}. EC has also been used in conjunction with filtration to remove silica and suspended solids that tend to foul reverse osmosis membranes \cite{43, 44}.

12. OPEN QUESTIONS

EC is a very complex chemical and physical system that has not been delineated. The voltage ranges used are not commonly used in fundamental electrochemical studies. These voltage ranges are found in anodization and electrolysis. There is a need for fundamental electrochemical studies of both the interfacial reactions affecting the electrodes and the multiphase reactions in the voltage range from 10 to 60 V. The necessary over potential for electro coagulation performance, $\eta_{co}$, is the result of three components \cite{29}. $\eta_{co} = \eta_k + \eta_m + \eta_R$ where $\eta_k$ is the kinetic over potential which may have several contributions (e.g., gas evolution), $\eta_m$ the mass transfer over potential, and $\eta_R$ the IR-drop due to solution and electrode deposits. The solution part of the $\eta_{co}$ is controlled by $\eta_{co} = I (d/AK)$ where $I$ is the current (A), $d$ is the distance between the electrodes, $A$ is the active electrode surface area, and $K$ is the specific conductivity ($10^5$ m Sm$^{-1}$). The IR drop is reduced by lowering $d$ and increasing $A$ and $K$. The effects of these changes need to be documented for specific types of chemical and physical species in aqueous solutions. The detailed effects of the electric field gradient on the relevant interfacial and solution reactions need to be studied. The nature of the deposits on the electrodes need better characterization and the influences of pH and electrochemical potentials on both solution phase and interfacial reactions need further study. Experimentation and modeling of the reactions need to be done to establish steady-state and equilibrium status. Reactions under kinetic control need to be established and their controlling parameters defined.

13. CONCLUSIONS

The fact that electro coagulation is being successfully applied to contaminated water is testament to its potential which is yet to be fully realized. Clearly more fundamental information is needed on the physical chemistry involved. From the electrochemical, surface and interfacial chemical and aqueous chemical perspective there appear to be several approaches that can be taken based on fundamental principles. Hydrogen evolution would have to be controlled by the size of the cathodic reaction area and the electrode over potential of hydrogen evolution. At the same time, an anode would have to carry out several fundamental processes at highest efficiencies. These include a corroding part that supplies the polyanion coagulant ions to the solution at the lowest over potential, a part that must be an efficient electro-oxidation catalyst to form charged organics by partial oxidation, and an oxygen evolution part, that must generate the oxygen at the highest efficiency but in controlled amounts. The latter may be achieved by limiting the oxygen evolution electrode area. Electro-oxidation catalysts are available for shallow oxidation. These may be achieved by composite electrodes or unique multi-electrode arrangements. In addition, the presence of sacrificial surfactants at low concentration may be helpful to improve the efficiency of the coagulation process and ad/absorption processes. In addition the ionic make-up of the solution may be adjustable for optimization of the processes involved.

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