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Journal of Hazardous Materials B84 (2001) 29–41

**Journal of
Hazardous
Materials**

www.elsevier.nl/locate/jhazmat

Electrocoagulation (EC) — science and applications

M. Yousuf A. Mollah¹, Robert Schennach,
Jose R. Parga², David L. Cocke*

Gill Chair of Chemistry & Chemical Engineering, Lamar University, Beaumont, TX 77710, USA

Received 23 July 2000; received in revised form 22 December 2000; accepted 23 December 2000

Abstract

Although electrocoagulation 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. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrocoagulation; Wastewater; Physico-chemical processes

1. Introduction

One of the major challenges facing mankind today is to provide clean water to a vast majority of the population around the world. The need for clean water is particularly critical 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

* Corresponding author. Tel: +1-409-880-1862; fax: +1-409-880-8374.

E-mail address: cockedl@hal.lamar.edu (D.L. Cocke).

¹ Present address: Department of Chemistry, Dhaka University, Dhaka 1000, Bangladesh.

² Present address: Instituto Tecnológico de Saltillo, Mexico City, Mexico.

processes are filtration, air stripping, ion-exchange, chemical precipitation, chemical oxidation, carbon adsorption, ultrafiltration, reverse osmosis, electrodialysis, volatilization and 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 electrocoagulation [1], electroflotation [1], electrodecantation [2–4], and others [5]. Even though one of these, electrocoagulation, has reached profitable commercialization, it has received very little scientific attention. 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 [6]. It has also been noted [6] 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 [7], oil wastes [7–10], dyes [11], suspended particles [12–16], chemical and mechanical polishing waste [17], organic matter from landfill leachates [16], defluorination of water [18], synthetic detergent effluents [19], mine wastes [20] and heavy metal-containing solution [21–25]. 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 electrocoagulation

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 $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ 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 [26,27]. 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 enough for van der Waal's forces to hold them together and allow aggregation. The reduction of the surface charge is a consequence of the decrease of the repulsive potential of the electrical double layer by the presence of an electrolyte having opposite charge. In the EC process, the coagulant is

generated in situ by electrolytic oxidation of an appropriate anode material. In this process, charged ionic species — metals or otherwise — are removed from wastewater by allowing it to react (i) with an ion having opposite charge, or (ii) with floc of metallic hydroxides generated within the effluent.

The EC technology offers an alternative to the use of metal salts or polymers and poly-electrolyte addition for breaking stable emulsions and suspensions. The technology removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species. These species neutralize the electrostatic charges on suspended solids and oil droplets to facilitate agglomeration or coagulation and resultant separation from the aqueous phase. The treatment prompts the precipitation of certain metals and salts. The advantages and disadvantages of EC technology are discussed below.

4. Advantages of EC

1. EC requires simple equipment and is easy to operate with sufficient operational latitude to handle most problems encountered on running.
2. Wastewater treated by EC gives palatable, clear, colorless and odorless water.
3. Sludge formed by EC tends to be readily settleable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.
4. 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.
5. 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.
6. 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.
7. 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.
8. 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.
9. The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance.
10. 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

1. The ‘sacrificial electrodes’ are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.

2. The use of electricity may be expensive in many places.
3. An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.
4. High conductivity of the wastewater suspension is required.
5. Gelatinous hydroxide may tend to solubilize in some cases.

6. Description of the technology

In its simplest form, an electrocoagulating 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 Fig. 1.

It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a dc power source as shown in Fig. 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 Fig. 2. As can be seen from Fig. 2, each pair of 'sacrificial electrodes' is internally connected with each other, and has no interconnections with the outer electrodes. This arrangement of

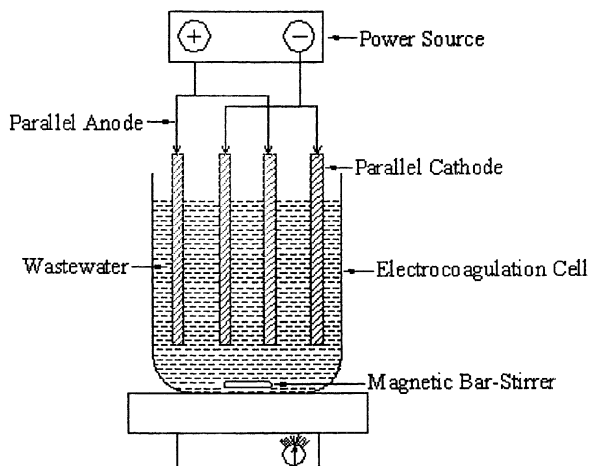


Fig. 1. Bench-scale EC reactor with monopolar electrodes in parallel connection (after [28]).

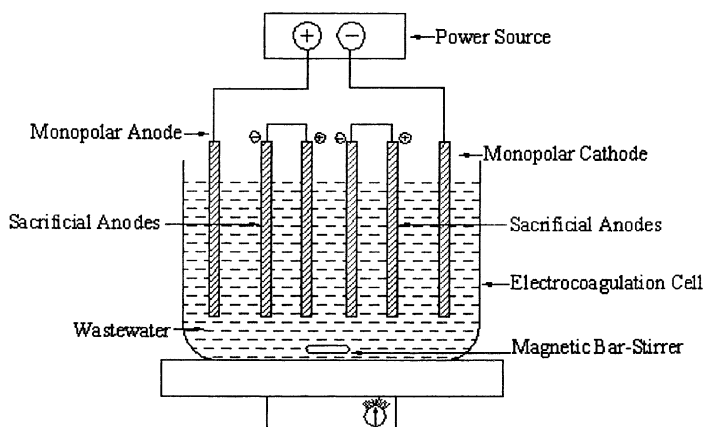


Fig. 2. Bench-scale EC reactor with monopolar electrodes in series connection (after [28]).

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. [28] for discussion of the parallel and series arrangements of monopolar cells.

Some authors [18,29] have, however, used bipolar electrodes with cells in parallel. In this case, the sacrificial electrodes are placed between the two parallel electrodes without any electrical connection as shown in Fig. 3. Only the two monopolar electrodes are connected

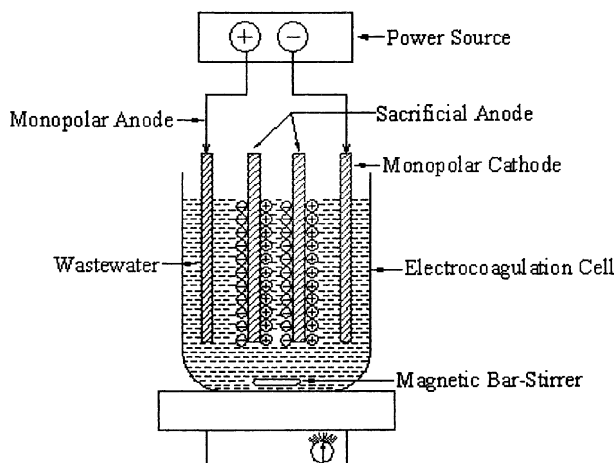


Fig. 3. Bench-scale EC reactor with bipolar electrodes in parallel connection (after [28]).

to the electric power source with no interconnections between the sacrificial electrodes. This cell arrangement provides a simple set-up, which facilitates easy maintenance during use. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it. The sacrificial electrodes in this case are also known as bipolar electrodes.

Thus, during electrolysis, the positive side undergoes anodic reactions, while on the negative side, cathodic reaction is encountered. Consumable metal plates, such as iron or aluminum, are usually used as sacrificial electrodes to continuously produce ions in the system. The released ions neutralize the charges of the particles and thereby initiate coagulation. The released ions may remove the undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce and then removed by electrolytic flotation. In addition, as water containing colloidal particulates, oils, or other contaminants move through the applied electric field, there may be ionization, electrolysis, hydrolysis, and free-radical formation which may alter the physical and chemical properties of water and contaminants [6]. As a result, the reactive and excited state causes contaminants to be released from water and destroyed or made less soluble. Inert electrodes, such as titanium and the passage of alternating current, have been observed to remove metal ions from solution and to initiate coagulation of suspended solids. To ensure more effective removal of the undesirable ions, wastewater may be passed through a series of cells containing electrodes made up of various metals. In such cases, the contaminated wastewater is passed through the annular spaces between the electrodes and is exposed to sequential positive and negative electrical fields. To optimize the removal efficiencies, the water characteristics such as pH, oxidation–reduction potential, and conductivity can be adjusted for specific contaminants.

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 electrocoagulation

The direct current electrocoagulation (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 electrocoagulation (ACE) technology [32]. 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 electrocoagulation (ACE)

The US EPA has applied ACE technology for remediation of aqueous waste streams at Superfund Sites [30]. The ACE separator designed by EPA consists of either a parallel electrode unit in which a series of vertically oriented aluminum electrodes form a series of monopolar electrolytic cells through which the effluent stream passes, or a fluidized bed unit with nonconductive cylinders equipped with nonconsumable 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 and 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 nonconsumable metal electrodes is shown in Fig. 4. As can be seen from Fig. 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 dissolves from the fluidized bed and neutralizes the charges on suspended or emulsified particles. Once the charged species are electrically neutralized, they tend to coagulate and separate from the aqueous phase. The treated water is then transferred to a product separator where the water and solid phases are removed separately for reuse, recycling, additional treatment or disposal. One of the advantages of the ACE process is that attrition

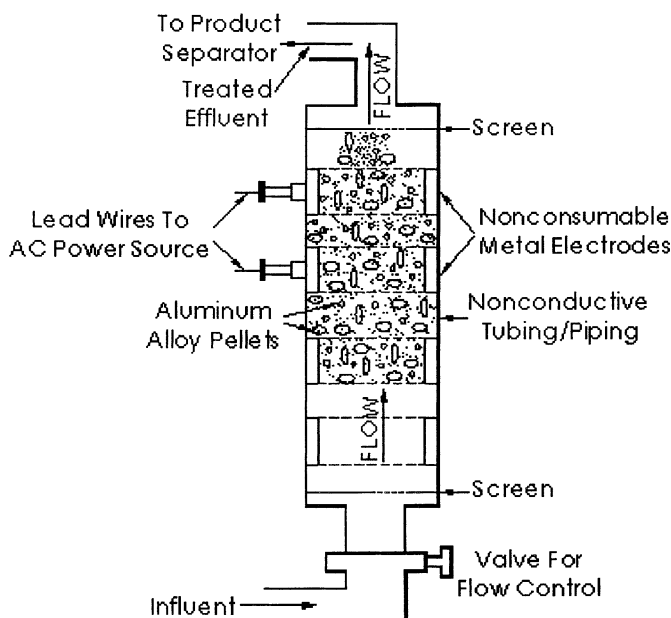


Fig. 4. Flow diagram of a typical ACE fluidized separator (based on Recra Environmental Inc., USA).

scrubbing of the fluidized bed pellets within the cell inhibits the buildup of scale or coating on the aluminum pellets and the face of the electrodes. In a recent publication, Mills [31] has described a new process for electrocoagulation. In this process, the electrocoagulation unit is made up of a ladder series of electrolytic cells containing iron anodes and stainless-steel cathodes. The electrolytic cells are constructed in such a way that a narrow concentric gap is maintained 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 [6,32]. It is 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:

1. 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.
2. 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.
3. 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.

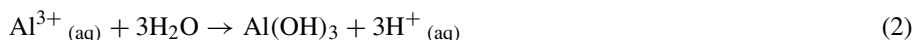
10. Reaction types involved in the EC process

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.

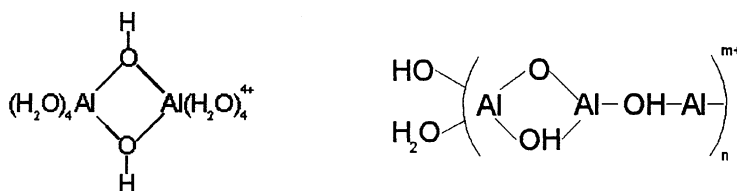
10.1. Aluminum

Electrocoagulation of wastewater using an aluminum electrode has been reported by a number of authors [33–37]. The electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as Al^{3+} and $\text{Al}(\text{OH})_2^+$ at low pH, which at appropriate

pH values are transformed initially into $\text{Al}(\text{OH})_3$ and finally polymerized to $\text{Al}_n(\text{OH})_{3n}$ according to the following reactions:



However, depending on the pH of the aqueous medium other ionic species, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}(\text{OH})_4^-$ may also be present in the system. Examination of the pE–pH equilibrium diagram reveals that under appropriate conditions various forms of charged multimetric hydroxo Al^{3+} species may be formed. For example, the structures of dimeric and polymeric 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. [37] have reported the defluorination of water by electrolysis using aluminum electrodes. According to the proposed mechanism the Al^{3+} ions under high F^- concentration may be induced to form AlF_6^{3-} which was transformed to insoluble salt Na_3AlF_6 by adding sodium ions according to the following reactions:



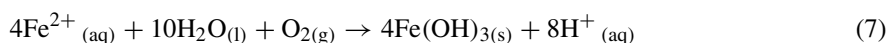
The insoluble Na_3AlF_6 salt was then separated by decantation. Mameri et al. [18] have successfully applied this technology to defluoridation of septentrional Sahara water of North Africa.

10.2. Iron

Iron upon oxidation in an electrolytic system produces iron hydroxide, $\text{Fe}(\text{OH})_n$, where $n = 2$ or 3. Two mechanisms have been proposed for the production of $\text{Fe}(\text{OH})_n$ [38–40].

• Mechanism 1

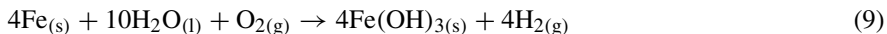
Anode:



Cathode:

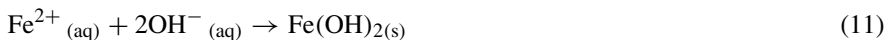


Overall:



• Mechanism 2

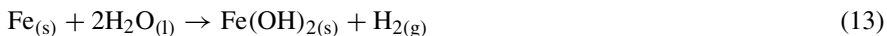
Anode:



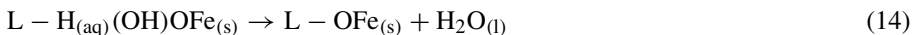
Cathode:



Overall:

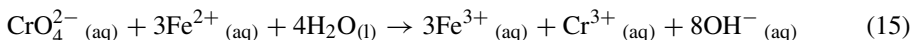


The $\text{Fe}(\text{OH})_{n(\text{s})}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation [41]. In the surface complexation mode, the pollutant acts as a ligand (L) to chemically bind hydrous iron:



The prehydrolysis of 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 ([42] and references therein).

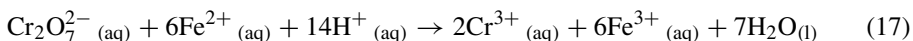
Wastewater containing Cr^{6+} (CrO_4^{2-}) ions can be removed by the EC technique using iron as the sacrificial anode [43,44]. The ferrous ion (Fe^{2+}) generated by electrooxidation of the iron anode can reduce Cr^{6+} to Cr^{3+} under alkaline conditions and is itself oxidized to ferric (Fe^{3+}) ion according to



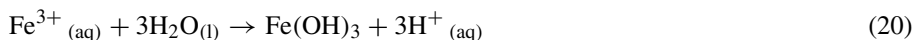
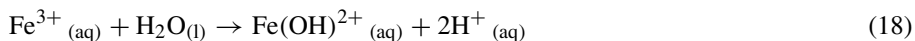
or



The $\text{Cr}^{3+}_{(\text{aq})}$ ion is then precipitated as $\text{Cr}(\text{OH})_{3(\text{s})}$ by raising the pH of the solution. The $\text{Fe}^{2+}_{(\text{aq})}$ ions can also reduce $\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})}$ under acidic conditions according to the following reaction:



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 $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_3$ species may be present under acidic conditions. The reactions involved are



Under alkaline conditions, $Fe(OH)_6^-$ and $Fe(OH)_4^-$ 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+} hydroxide complexes has been extensively reported ([45] 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 [46].

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, electrofiltration, sludge dewatering, thermo-oxidation and other conventional technologies to enhance the recovery of fine particles and metal ions from wastewater. Belongia et al. [17] have investigated the waste streams from chemical mechanical operations by electrocoagulation with electrodecantation (EC/ED) techniques. Removal of coloring materials from dyestuffs using EC with electroflotation has been reported by Ibanez et al. [41]. Pouet and Grasmick [29] and Beck et al. [7] 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 [47]. EC has also been used in conjunction with filtration to remove silica and suspended solids that tend to foul reverse osmosis membranes [48,49].

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 overpotential for electrocoagulation performance, η_n , is the result of three components [34], $\eta_n = \eta_k + \eta_m + \eta_{IR}$ where η_k is the kinetic overpotential which may have several contributions (e.g.

gas evolution), η_m the mass transfer overpotential, and η_{IR} the IR-drop due to solution and electrode deposits. The solution part of the η_{IR} is controlled by $\eta_{IR} = I(d/A\kappa)$ where I is the current (A), d the distance between the electrodes, A the active electrode surface area, and κ the specific conductivity (10^3 m S m^{-1}). The IR drop is reduced by lowering d and increasing A and κ . 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 study. 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 electrocoagulation 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 overpotential of hydrogen evolution. At the same time, an anode would have to carry out several fundamental processes at highest efficiencies. These include a corrodable part, that supplies the polyvalent coagulant ions to the solution at the lowest overpotential, 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.

Acknowledgements

The authors are grateful for the financial support of the Robert A. Welch Foundation (Houston, TX) under Grant No. V-1103, the Texas Advanced Technology Research Program #003581004 and the Gulf Coast Hazardous Substance Research Center under Grant No. EPA-118LUB. We thank Mr. Paul Morkovsky of KASELCO for useful suggestions.

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