

ELECTROCOAGULATION AS A WASTEWATER TREATMENT

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ABSTRACT

Coagulation and flocculation are traditional methods for the treatment of polluted water. Electrocoagulation presents a robust novel and innovative alternative in which a sacrificial metal anode doses water electrochemically. This has the major advantage of providing active cations required for coagulation, without increasing the salinity of the water.

Electrocoagulation is a complex process with a multitude of mechanisms operating synergistically to remove pollutants from the water. A wide variety of opinions exist in the literature for key mechanisms and reactor configurations. A lack of a systematic approach has resulted in a myriad of designs for electrocoagulation reactors without due consideration of the complexity of the system. A systematic, holistic approach is required to understand electrocoagulation and its controlling parameters. This will enable *a priori* prediction of the treatment of various pollutant types.

KEYWORDS

Electrocoagulation, electroflotation, wastewater treatment, sacrificial electrodes.

INTRODUCTION

The natural resources of Australia are limited, and as such the use and reuse of water is becoming an increasing concern. Cost-effective methods are required to treat a wide range of wastewater pollutants in a diverse range of situations.

Coagulation and flocculation are traditional methods for the treatment of polluted water. In these processes, coagulating agents (e.g. alum or ferric chloride) and other additives (e.g. polyelectrolytes) are dosed to produce larger aggregates, which can be separated physically. This is a multi-stage process that requires considerable land area and a continual supply of chemicals. A more cost-effective method to clean a wide range of polluted water, on-site, and with minimal additives, is required for sustainable water management. Electrocoagulation treatment of water may fit this description.

Electrocoagulation involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions and hydrogen gas occurring at the cathode. Electrocoagulation has been proposed since before the turn of the century with Vik *et al.* (1984) describing a treatment plant in London built in 1889 (for the treatment of sewage by mixing with seawater and electrolyzing). In 1909, in the United States, J.T. Harries (Vik *et al.*, 1984) received a patent for wastewater treatment by electrolysis with sacrificial aluminium and iron anodes. Matteson *et al.* (1995) describe a device of the 1940's, the "Electronic Coagulator" which electrochemically dissolved aluminium (from the anode) into solution, reacting this with the hydroxyl ion (from the cathode) to form aluminium hydroxide. The hydroxide flocculates and coagulates the suspended solids purifying the water. A similar process was used in Britain in 1956 (Matteson *et al.*, 1995) for which iron electrodes were used to treat river water.

Presently electrocoagulation is marketed by a small number of companies around the world. A variety of designs have been employed with no dominant design. Often the electrocoagulation units are used simply as a replacement for chemical dosing systems and do not take advantage of the electrolytic gases produced in the electrocoagulation process.

It is clear that electrocoagulation has the capability to remove a large range of pollutants under a variety of conditions ranging from: suspended solids (Matteson *et al.* 1995); heavy metals (Osipenko

and Pogorelyi, 1977); petroleum products (Amosov *et al* 1976); colour from dye-containing solution (Do and Chen, 1994); aquatic humus (Vik *et al.* 1984); and defluoridation of water (Mameri *et al.* 1998).

POSSIBLE MECHANISMS

The pH, pollutant type and concentration, the bubble size and position, floc stability and agglomerate size all influence the operation of the electrocoagulation unit. The complexity and number of possible interactions are highlighted in Figure 1. The overall mechanism is a combination of mechanisms functioning synergistically. The dominant mechanism may vary throughout the dynamic process as the reaction progresses. The dominant mechanism will almost certainly shift with changes in operating parameters and pollutant types.

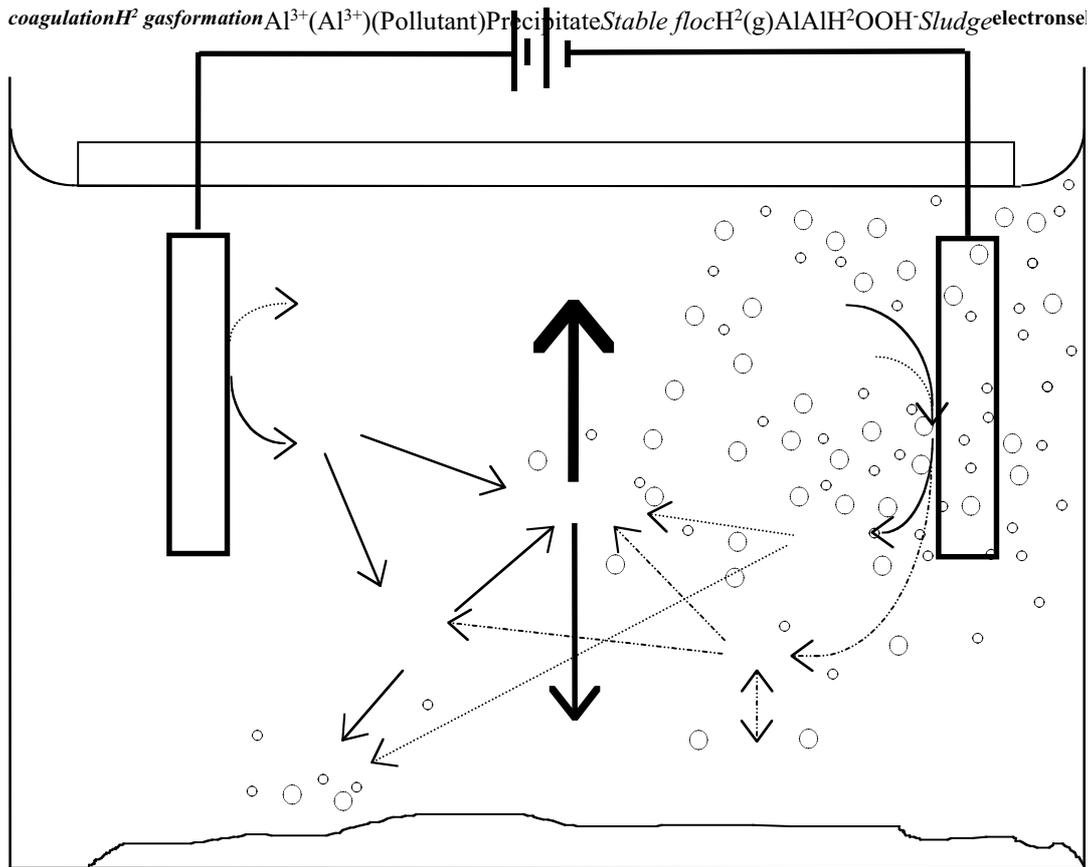
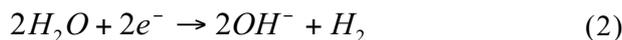
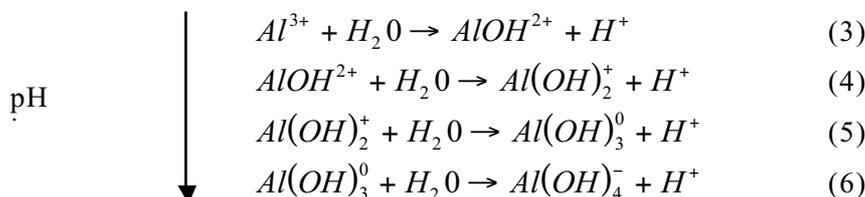


Figure 1. Interactions within the electrocoagulation process

A current is passed through a metal electrode, oxidising the metal (M) to its cation (Mⁿ⁺) (Equation 1). Simultaneously, water is reduced to hydrogen gas and the hydroxyl ion (OH⁻) (Equation 2). Electrocoagulation thus introduces metal cations *in situ*, electrochemically, using sacrificial anodes (usually aluminium or iron).



The cation hydrolyzes in water forming a hydroxide with the dominant species determined by solution pH. Equations 3 – 6 illustrate this in the case of aluminium.



Highly charged cations destabilize any colloidal particles by the formation of polyvalent polyhydroxide complexes. These complexes have high adsorption properties, forming aggregates with pollutants. Evolution of hydrogen gas aids in mixing and hence flocculation. Once the floc is generated, the electrolytic gas creates a flotation effect removing the pollutants to the floc - foam layer at the liquid surface.

There are a variety of ways in which species can interact in solution:

1. Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralisation.
2. The cation or hydroxyl ion (OH^-) forms a precipitate with the pollutant.
3. The metallic cation interacts with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation).
4. The hydroxides form larger lattice-like structures and sweeps through the water (sweep coagulation).
5. Oxidation of pollutants to less toxic species.
6. Removal by electroflotation and adhesion to bubbles.

The inherent complexity of the process makes it difficult to model and control. Adequate scaleup parameters, a systematic approach to the optimization and *a priori* prediction for the performance of the electrocoagulation reactor are yet to be established. The literature reveals that previously each "new" system has been considered separately on an individual basis. There has been little or no attempt to provide a holistic approach to electrocoagulation. In order to understand the mechanisms behind electrocoagulation, and thus control the system better, a holistic approach is required.

DESIGN ISSUES

The lack of mechanistic understanding of electrocoagulation is reflected in the design of reactors. No single empirical or systematic approach has emerged over the years in the design of electrocoagulation reactors. It is therefore difficult to compare the performance of reactors. This literature review aims to highlight commonalities (or lack of such) between reactors. In this analysis, the discussion is separated in to two main sections; physical and chemical design issues. Obviously, chemical and physical design aspects interact and the division is simply to highlight key features of the system.

PHYSICAL DESIGN ISSUES

There has been a range of laboratory, pilot and industrial scale electrocoagulation units produced. The designs range from fully integrated units to stand alone reactors.

The electrocoagulation process has been combined with many units including microfiltration, dissolved air flotation (DAF), sand filtration and electroflotation. Obviously, pre- and post- water treatment impacts significantly on the performance of the electrocoagulation reactor.

The design of the electrocoagulation process influences its operation and efficiency. The design phase should consider the following physical factors:

- Continuous versus batch operation
- Reactor geometry
- Reactor scale-up
- Current density

Geometry

Geometry of the reactor affects operational parameters including bubble path, flotation effectiveness, floc formation, fluid flow regime and mixing/settling characteristics. From the literature, the most common approach involves plate electrodes (aluminium or iron) and continuous operation. Water is dosed with dissolved metal ions as it passes through the electrocoagulation cell. A downstream unit is often required to separate pollutant and water.

Scale-up Issues

One of the cornerstones of chemical engineering is to establish key scale-up parameters to define the relationships between laboratory and full-scale equipment.

The surface area to volume ratio (S/V) was anticipated as being a significant scale-up parameter. Electrode area influences current density, position and rate of cation dosing, as well as bubble production and bubble path length. Mameri *et al.* (1998) reported that as the S/V ratio increases the optimal current density decreases.

However, the S/V ratio was not widely reported. Only three values, other than the experimentation by Mameri *et al.* (1998), are available in the literature.

Table 1. Comparison of surface area to volume ration (S/V)

Reference Author	Year	S/V (m ² /m ³)
Osipenko and Pogorelyi	1977	18.8
Novikova <i>et al.</i>	1982	42.5
Amosov <i>et al.</i>	1976	30.8

The values reported for the S/V ratio in Table 1 are all of the same order of magnitude. However, a more rigorous and consistent approach is clearly required to establish a set of design characteristics for electrocoagulation reactors.

Zolotukhin (1989) scaled up an electrocoagulation-flotation system from laboratory to industrial scale. The following dimensionless scale-up parameters were chosen to ensure correct sizing and proportioning of the reactors:

- Reynolds number – indication of the fluid flow regime;
- Froude number – indication of buoyancy;
- Weber criteria – indication of the surface tension;
- Gas saturation similarity;
- Geometric similarity.

Current Density

Current density (*i*) is the current delivered to the electrode divided by the active area of the electrode. Varying the current easily controls this parameter. Current density determines both the rate of electrochemical metal dosing to the water and the electrolytic bubble density production.

Current densities ranging from 10 to 2000 A m⁻² have been reported from 16 literature sources (limited space to report all references in this paper). The majority of the sources report a current density in the range 10 – 150 A m⁻². Different current densities are desirable in different situations. High current densities are desirable for separation processes involving flotation cells or large settling tanks, while small current densities are appropriate for electrocoagulators that are integrated with conventional sand and coal filters. A systematic analysis is required to define and refine the relationship between current density and desired separation effects.

CHEMICAL ISSUES

The control, operation and chemical interactions of the system affect performance and reliability. The first section of the literature review discussed the possible pollutant removal mechanisms and their interactions. Adding to complexity, the chemical interactions of the pollutants (type and concentration) with the electrode material, electrode passivation and operational region should also be considered. Literature has not revealed a systematic approach to these issues, and this is reflected in the variety of reactor designs and methods used for passivation control.

Electrode Material

The electrode material impacts markedly on the performance of the electrocoagulation reactor. The anode material determines the cation introduced into solution. Several researchers have studied the

choice of electrode material with a variety of theories as to the preference of a particular material. The most common electrodes were aluminium or iron plates as described by Vik *et al.* (1984) and Novikova *et al.* (1982).

Do and Chen (1994) compare the performance of iron and aluminium electrodes for removing colour from dye-containing solutions. Their conclusion was that the optimal electrocoagulation conditions varied with the choice of iron or aluminium electrodes, which in turn is determined by:

- Initial pollutant concentration;
- Pollutant type;
- Stirring rate.

One group (Baklan and Kolesnikova, 1996) investigated the relationship between “size” of the cation introduced and removal efficiency of organic waste. The size of the cation produced (10-30 μm for Fe^{3+} compared to 0.05-1 μm for Al^{3+}) was suggested to contribute to the higher efficiency of iron electrodes. Their conclusion is based on a single experiment, however, using chemical absorption of oxygen as their only measure.

Hulser *et al.* (1996) observes that electrocoagulation is strongly enhanced at aluminium surfaces in comparison to steel. This is attributed to a higher efficiency due to the *in situ* formation of dispersed aluminium-hydroxide complexes through hydrolysis of the aluminate ion, which does not occur with steel electrodes.

Passivation

One of the greatest operational issues with electrocoagulation is electrode passivation. The passivation of electrodes is concern for the longevity of the process. Passivation of aluminium electrodes has been widely observed in the literature (Nikolaev *et al.* (1982), Novikova *et al.* (1982), Osipenko and Pogorelyi (1977)). The latter also observed that during electrocoagulation with iron electrodes, deposits of calcium carbonate and magnesium hydroxide were formed at the cathode and an oxide layer was formed at the anode.

Nikolaev *et al.* (1982) investigated various methods of preventing and / or controlling electrode passivation including:

- Changing polarity of the electrode;
- Hydromechanical cleaning;
- Introducing inhibiting agents;
- Mechanical cleaning of the electrodes.

According to these researchers, the most efficient and reliable method of electrode maintenance was to periodically mechanically clean the electrodes which for large-scale, continuous processes is a non-trivial issue.

Solution pH

Solution pH determines the speciation of metal ions. The pH influences the state of other species in solution and the solubility of products formed. Thus, solution pH influences the overall efficiency and effectiveness of electrocoagulation.

The pH of the solution can easily be altered. An optimal pH seems to exist for a given pollutant, with optimal pH values ranging from 6.5 to 7.5.

CONCLUSIONS

Electrocoagulation has successfully treated a wide range of waste streams. Previous research has focused on the application of electrocoagulation to a particular situation (plant and waste stream). On-site optimization and process "tuning" had limited success, but *a priori* prediction for reactor operation has not been reported. Mechanisms are expected to change through the process but the dominant mechanisms and their role are yet to be identified.

The lack of a methodical approach on a mechanistic level is reflected by the lack of similarities in reactor design. No dominant reactor design exists, adequate scale-up parameters have not been defined, materials of construction are varied and operational regions fuzzy. A logical, systematic approach to a fundamental understanding of electrocoagulation is clearly required. The design phase can then proceed on solid scientific and engineering knowledge.

A large number of key mechanisms are dependent on a few operating parameters. Individual "optimizations" exist, that is, for pH and speciation of the coagulant ion (Fe^{3+} or Al^{3+}) but this often conflicts with other localised optimal conditions. The electroflotation mechanism, passivation of the electrodes, economic considerations all have their own operating pH. A trade-off between the competing factors must be evaluated to provide a global optimum operating condition.

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