

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/7971546>

The Future for Electrocoagulation as a Localised Water Treatment Technology

ARTICLE *in* CHEMOSPHERE · MAY 2005

Impact Factor: 3.34 · DOI: 10.1016/j.chemosphere.2004.10.023 · Source: PubMed

CITATIONS

243

READS

307

3 AUTHORS, INCLUDING:



[Cynthia A Mitchell](#)

University of Technology Sydney

79 PUBLICATIONS 1,031 CITATIONS

SEE PROFILE

The future for electrocoagulation as a localised water treatment technology

Peter K. Holt ^{a,*}, Geoffrey W. Barton ^a, Cynthia A. Mitchell ^b

^a Department of Chemical Engineering, University of Sydney, NSW 2006, Sydney, Australia

^b Institute for Sustainable Futures, University of Technology Sydney, P.O. Box 123, Broadway, NSW 2007, Sydney, Australia

Received 20 April 2004; received in revised form 15 October 2004; accepted 19 October 2004

Abstract

Electrocoagulation is an electrochemical method of treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors (usually aluminium or iron cations) into solution. Accompanying electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode.

Electrocoagulation has a long history as a water treatment technology having been employed to remove a wide range of pollutants. However electrocoagulation has never become accepted as a ‘mainstream’ water treatment technology. The lack of a systematic approach to electrocoagulation reactor design/operation and the issue of electrode reliability (particularly passivation of the electrodes over time) have limited its implementation. However recent technical improvements combined with a growing need for small-scale decentralised water treatment facilities have led to a re-evaluation of electrocoagulation.

Starting with a review of electrocoagulation reactor design/operation, this article examines and identifies a conceptual framework for electrocoagulation that focuses on the interactions between electrochemistry, coagulation and flotation. In addition detailed experimental data are provided from a batch reactor system removing suspended solids together with a mathematical analysis based on the ‘white water’ model for the dissolved air flotation process. Current density is identified as the key operational parameter influencing which pollutant removal mechanism dominates.

The conclusion is drawn that electrocoagulation has a future as a decentralised water treatment technology. A conceptual framework is presented for future research directed towards a more mechanistic understanding of the process. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Electrocoagulation; Electrochemistry; Coagulation; Flotation; Water treatment

1. Introduction

At the turn of the last century, it was estimated that some 1.1 billion people (one-sixth of the world’s population) were without an ‘improved’ water supply (WHO/Unicef, 2000), while in the foreseeable future the demand for water is only expected to grow as human population and industrialization increases (Asmal, 2000). The right of all people to access suitable water supplies

* Corresponding author. Address: Ecological Engineering, P.O. Box 453, Prahran, VIC 3181, Australia. Tel.: +61 3 9533 8445; fax: +61 3 9533 7781.

E-mail address: peterh@ecoeng.com.au (P.K. Holt).

Nomenclature

A_b	projected bubble area (m^2)	v_b	terminal rise velocity (m s^{-1})
F	Faraday's constant (96486 C/mol)	z	number of electrons
i	current density (A m^{-2})	α_{pb}	particle–bubble attachment efficiency
I	operating current (A)	ε	pollutant removal efficiency
m	mass (g)	η_T	single bubble collector efficiency
M	molecular weight (g mol^{-1})	η_D	Brownian diffusion collector efficiency
N_b	bubble number concentration (m^{-3})	η_I	interception of the particle by the bubble collector efficiency
N_p	particle number concentration (m^{-3})	η_S	sedimentation of the particle onto the bubble collector efficiency
N_{pe}	particle effluent concentration (m^{-3})	η_{IN}	inertial driven contact collector efficiency
N_{pi}	particle influent concentration (m^{-3})		
t	run time (s)		
t_{cz}	contact zone time (s)		

must thus be seen as a global challenge, the solution of which is dependent on the formulation and implementation of sustainable water management strategies.

A sustainable water management approach requires 'fit for purpose' use and reuse of water as shown by the illustrative 'water cascade' in Fig. 1. To reverse this downward trend water must be treated in some way. In many developed countries, large-scale centralised water treatment facilities are both appropriate and highly cost-effective for this purpose. However even in such countries, there are numerous situations where smaller, localised water treatment technologies are preferable to centralised treatment. Indeed the work reported in this paper regarding electrocoagulation was motivated by an approach from the commercial sector within Australia for a widely applicable, low-cost batch water treatment technology.

In essence an electrocoagulation reactor is an electrochemical cell wherein a sacrificial metal anode, usually aluminium but occasionally iron, is used to dose polluted water with a coagulating agent (Vik et al., 1984; Barkley et al., 1993; Matteson et al., 1995; Pouet and Grasmick, 1995; Mameri et al., 1998; Holt, 2003). Elec-

trocoagulation introduces metal cations in situ rather than via external dosing. Simultaneously electrolytic gases (typically hydrogen) are generated at the cathode. Depending on the reactor operating conditions and the pollutant, these bubbles may float some portion of the coagulated pollutant to the surface.

Electrocoagulation is not a new technology. Indeed the literature indicates that it has been regularly 'discovered' over the last hundred years or so, both in batch and continuous applications. For example, during the late 19th century several large-scale water treatment plants were commissioned in London (Matteson et al., 1995), while electrolytic sludge treatment plants were operating as early as 1911 in various parts of the USA (Vik et al., 1984) with similar plants being commissioned to treat municipal wastewater in the following decades. By the 1930s however, all such plants had been abandoned due to higher operating costs and the ready availability of mass-produced alternatives for chemical coagulant dosing. In more recent times, there has been some renewed interest in continuously fed water treatment plants based on electrocoagulation technology (some with sizeable throughputs) for specialised indus-

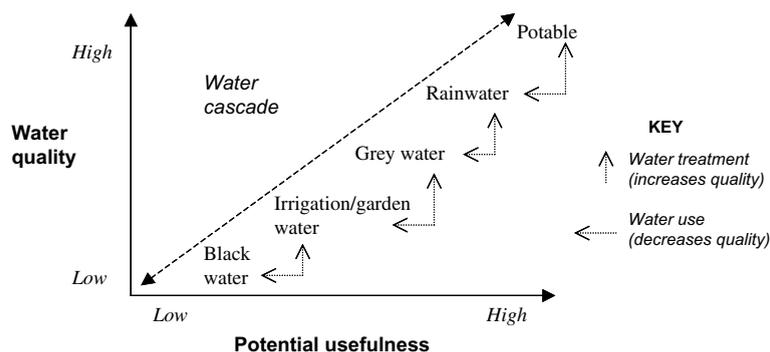


Fig. 1. Cascade relationship between water quality and potential usefulness.

trial applications, such as the removal of fine material from coal wash water. However because of its proven ability to effectively remove an extremely wide range of pollutants, together with its inherent simplicity of design and operation, electrocoagulation is being re-examined as a localised low-cost treatment technology.

In reviewing the future status of electrocoagulation, a number of major deficiencies were identified. The first is that the literature does not reveal any systematic approach to electrocoagulation reactor design and operation. Reported designs range through laboratory, pilot and industrial scales, both as stand-alone reactors through to fully integrated units within a wastewater purification system. Certainly there is no dominant reactor design in use today, while very little is available in the way of comparative reactor performance. This article thus begins (in Section 2) by reviewing the literature on electrocoagulation, seeking to introduce a structured approach to highlight commonalities and differences between the work reported. The second deficiency is the almost complete lack of published data on the operation of batch electrocoagulation reactors, seen as the most likely means of providing a localised water treatment facility. Section 3 thus contains detailed experimental results from a laboratory scale batch reactor, while the following section outlines a simple modelling approach that is consistent with the observed data. The third deficiency is intimately linked with the previous two, in that little guidance is available for a priori reactor design or performance prediction. Thus in Section 5 a framework is proposed as an aid to further understanding of the myriad interactions that can occur between the fundamental processes (i.e. electrochemistry, coagulation, sedimentation and flotation) taking place within an electrocoagulation reactor.

The final deficiency (not specifically considered in this paper) relates to the fact that an electrocoagulation reactor is an electrochemical cell and thus its performance is directly related to the operational state of its electrodes. These vary widely in material used, design and mode of operation from simple vertical plate arrangements to packed-bed style reactors containing various metallic packings (Ogutveren et al., 1992; Barkley et al., 1993). Electrode passivation, specifically of aluminium electrodes, has been widely observed and recognised as detrimental to reactor performance (Osipenko and Pogorelyi, 1977; Novikova et al., 1982). This formation of an inhibiting layer, usually an oxide, on the electrode surface prevents metal dissolution and electron transfer, thereby limiting coagulant addition to the solution. Over time, the thickness of this layer increases, reducing the efficacy of the electrocoagulation process as a whole. The use of new materials, different electrode types and arrangements (Pretorius et al., 1991; Mameri et al., 1998) and more sophisticated reactor operational strategies (such as periodic polarity reversal of the electrodes)

have certainly led to significant reductions in the impact of passivation, although it must be admitted that this issue is still seen as a serious potential limitation for applications where a low-cost, low maintenance water treatment facility is required.

2. Electrocoagulation reactor design and operation

Given the time-scale over which this technology has been utilized, it is somewhat surprising that the available literature does not reveal any systematic approach to electrocoagulation reactor design and operation. The reason for this failure to drive towards some agreed 'best' solution would seem to be the lack of any quantitative understanding of the many interactions that occur within an electrocoagulation reactor, and in particular the ability to predict the relative importance of these interactions for a given situation. The key driver for the development of any particular application of this technology has generally been the removal of a specific pollutant. Such 'pollutant centred' studies have characterised almost all the published research into electrocoagulation. Consequently, despite more than a century's worth of applications, many of them deemed successful, the science and engineering behind electrocoagulation reactor design is still largely empirical and heuristic. These studies invariably prove the viability of the technology, but singularly fail to capitalise on its potential by being incorporated within a broad-based understanding of electrocoagulation technology.

Published electrocoagulation reactor designs may be classified as shown in Fig. 2. The first major distinction between alternative designs is whether a reactor was configured as a batch or a continuous system. It is clear that the majority of applications fall into the latter category, having a continuous feed of wastewater and operating under (pseudo) steady-state conditions. A key advantage for such reactor systems is that their coagulant requirements are essentially fixed, a major advantage in terms of both design and operation. Batch reactor applications on the other hand typically operate with a fixed wastewater volume per treatment cycle but suffer from the perceived disadvantage (from a design and operational standpoint) that conditions within the reactor change with time. This dynamic behaviour is clearly illustrated in Section 3 where experimental data are given for the removal of suspended solids (i.e. clay) from a synthetic wastewater. Here the time dependent behaviour results from the fact that the coagulant precursor (i.e. aluminium cations) is continuously 'fed' to the reactor as the anode corrodes. The aluminium cations are hydrolysed to a form capable of aggregating the pollutant which is then removed from solution by sedimentation and/or flotation. As a result, both pollutant and coagulant levels shift over time as material is

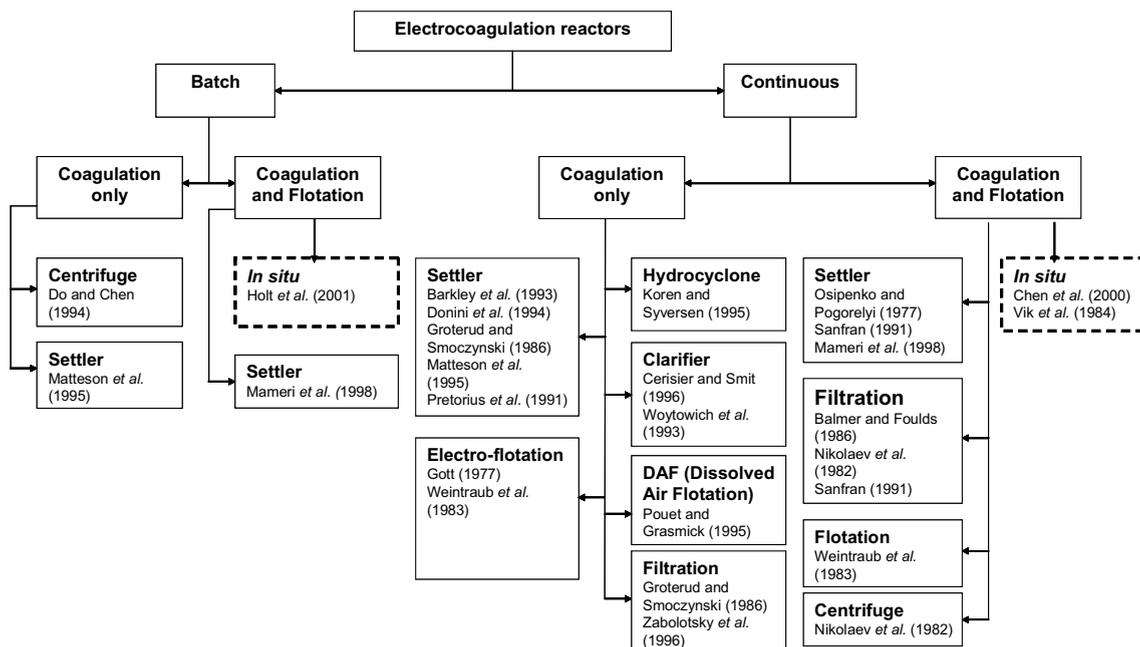


Fig. 2. Classification of electrocoagulation reactor systems. See above-mentioned references for further information.

added to the solution, is modified within the solution, and is removed from solution.

The second major distinction between alternative reactor designs is the role of flotation. Reactors that do not exploit the separation of aggregated pollutant via electrochemically generated bubbles are labelled in Fig. 2 as ‘coagulation only’ processes, while reactors that integrate flotation into their design and operation are classed as ‘coagulation and flotation’ processes. If no additional separation process is required (i.e. separation occurs within the electrocoagulation reactor itself), relevant references are cited directly below (being connected by a vertical arrow and a dashed box). Otherwise, the additional separation processes are reported in bold with relevant references grouped accordingly. Integrated units have two main pollutant removal paths—flotation and settling (Holt et al., 2001). Separation by settling is the more common option, with the fact that electrolytic gases are also being produced simultaneously with the dosing process often viewed as an unnecessary operational complication (Mameri et al., 1998). The prime differentiator between pollutant removal by settling or flotation would seem to be the current density employed in the reactor. A low current produces a low bubble density, leading to a low upward momentum flux—conditions that encourage sedimentation over flotation (Holt et al., 2002). As the current is increased, so the bubble density increases resulting in a greater upwards momentum flux and thus more likely removal by flotation.

‘Coagulation only’ processes can be further differentiated on the basis of the type of aggregated pollutant separation technology used. As shown, electrocoagulation dosing has been combined with most common separation technologies including dissolved air flotation, electroflotation, filtration and clarification. Basically, pollutant separation is either integrated into the reactor’s design, or else occurs in a separate (downstream) unit.

The value of the hierarchic structure shown in Fig. 2 is that it succinctly summarises previous electrocoagulation reactor design practice and demonstrates that it is possible to reduce a myriad applications to combinations of just three core design decisions.

- Batch or continuous operation.
- The role played by electrolytically generated bubbles.
- The means of separating out the aggregated pollutant.

For example, the applications shown in Table 1 (for removing suspended solids) may be readily differentiated from each other on the basis of these design decisions. Similar tabulations (Holt, 2003) related to the removal of heavy metals and ionic species, colour dyes and organic material (including fats, oils and greases) confirm the value of classifying diverse applications on this simple basis. Consequently the design of any future localised water treatment facility built around electrocoagulation technology may be simplified by making initial reactor

Table 1
Summary of electrode properties for suspended solids removed by electrocoagulation

Reference	Pollutant	Electrical requirement ^a	Electrodes ^b	Electrode type	Pollutant removal	Reactor type
Abuzaid et al. (1998)	Bentonite	0.2–1 A	A = SS C = SS	Plates	Settling (implied)	Batch (4l)
Avetisyan et al. (1984)	Carbon	120–170 A m ⁻²	A = Al C = Fe	Plates	Flotation	Continuous
Belongia et al. (1999)	Silica, alumina	2.5–10.0 V cm ⁻¹	A = SS C = SS	Mesh	Settling	Batch (3l)
Holt et al. (2001)	Clay	3.4–27 A m ⁻²	A = Al C = SS	Plates	Flotation and settling	Batch (7l)
Ivanishvili et al. (1987)	Suspended solids	5–50 A m ⁻²	A = Al C = Fe	Plates	Settling	Continuous
Matteson et al. (1995)	Kaolinite	0.01 A m ⁻²	A = SS C = SS	Mesh	Settling	Stirred batch (and series of batch reactors)
Syrbu et al. (1986)	Suspended solids	50–70 A m ⁻²	A = Al C = SS	Plates	Flotation (inseparate chamber)	Continuous

^a Reactor electrical requirements are reported with appropriate units indicated.

^b A and C refer to anode and cathode, respectively and SS refers to stainless steel.

design and operation considerations as combinations of these three design decisions.

3. Operation of a batch electrocoagulation system

Based on the previous review of reactor design and operation, it seems clear that the simplest option for a low-cost localised water treatment facility involves a batch reactor system with vertical plate electrodes where separation of the aggregated pollutant is integral to the reactor design with use being made of electrolytic gas flotation. The fact that surprisingly few such cases have been reported in the literature (see Table 1) may be attributed to the supposed 'complexity' introduced by the time dependent nature of such systems and, as noted, the almost complete lack of dynamic experimental data

from such systems. This section reports on the experimental setup and data from one such reactor system.

The reactor system used (see Fig. 3) was constructed of Perspex and had a maximum capacity of 7.1l. The 'pollutant' used was a potter's clay. Details of the size distribution and material composition of this material have been reported elsewhere (Holt et al., 2002). Five stainless steel cathodes were interspersed with four aluminium anodes, with brass rods used to connect the parallel plate electrodes. The electrodes have an active surface area of 732 cm² with a surface area to volume ratio of 10.5 m² m⁻³ which falls within the range reported in the literature.

Electrical conductivity, total dissolved solids, salinity and temperature were all measured using a WTW LF340 probe, while pH was measured in a flow-through cell drawing solution from the reactor at a rate of

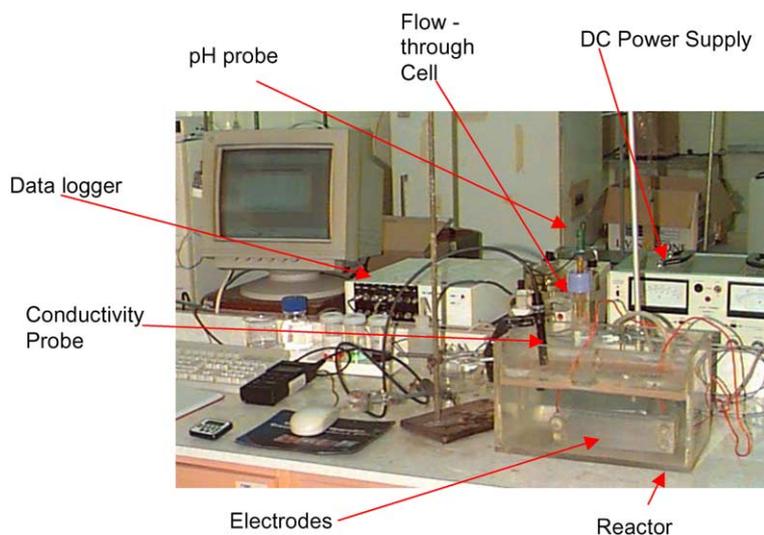


Fig. 3. Batch electrocoagulation reactor system.

0.301min^{-1} using a peristaltic pump. The current flowing through the cell and the voltage across the electrodes were both recorded using a data logger. The current was held constant for each run, being varied over the range $0.25\text{--}2.0\text{A}$ (i.e. equivalent to a current density of $3.4\text{--}27\text{A m}^{-2}$). Aluminium concentration was measured using a varian atomic absorption spectrophotometer, while turbidity and zeta potential were measured off-line using a Merck Turbiquant 1500T (tungsten lamp) and Malvern Zetasizer, respectively.

All runs were conducted with an initial clay loading in the range $0.1\text{--}1.6\text{g l}^{-1}$ using 6l of de-ionised water. Sodium chloride was added to adjust solution conductivity and allow the requisite current to pass through the reactor. Initial results indicated that above $350\mu\text{S cm}^{-1}$ (equivalent to a concentration of 0.15g l^{-1}) there was no change in the system's response. Consequently to remove the influence of conductivity a 'standard' concentration of 0.20g l^{-1} sodium chloride was used for all subsequent electrocoagulation experiments. It should be noted that this level of 200mg l^{-1} is less than the ionic concentration of 'fresh' water (at most about 1000mg l^{-1}) and substantially less than the concentration of sea-water (some 35000mg l^{-1}).

Fig. 4 is a typical plot showing the dynamic nature of this batch reactor system. Note that turbidity has been normalised (against its initial value) to aid comparisons between runs. Three stages can clearly be identified—namely, a lag, a reactive and a stabilising stage. Little or no turbidity change is observed in the lag stage with the majority ($\sim 95\%$) of the turbidity removal occurring during the reactive stage. As time progresses, the rate of turbidity reduction decreases and the turbidity levels out during the stabilising stage. The solution pH was monitored rather than controlled and stabilised to about 8.5 after 10min operation.

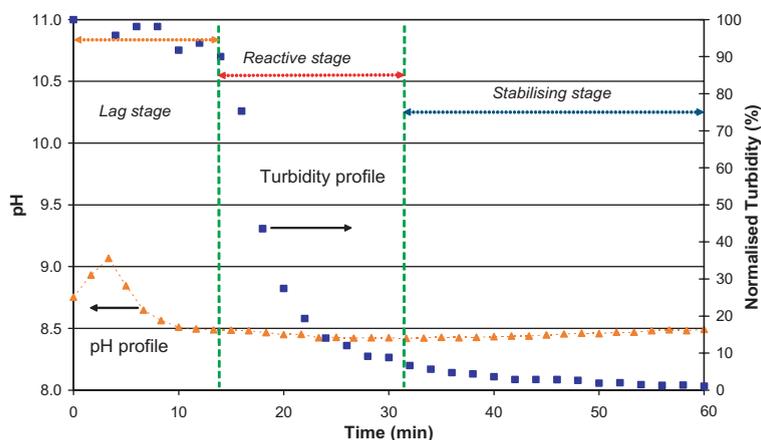


Fig. 4. Dynamic response of batch reactor; [clay] = 0.8g l^{-1} ; initial turbidity = 631 NTU ; $i = 6.8\text{A m}^{-2}$.

3.1. Impact of pollutant loading

Fig. 5(a) presents normalised turbidity results for pollutant loadings over the range $0.1\text{--}1.6\text{g l}^{-1}$ at a constant current density of 14A m^{-2} . Note that as a reproducibility check one set of conditions was repeated a number of time ($n = 4$), with the averaged response being shown here. The response for all pollutant loadings was similar with some difference observed in the residual normalised turbidity levels. However, when compared on an absolute turbidity basis, 1.6g l^{-1} and 0.1g l^{-1} pollutant loading levels gave almost identical residual values of 4.3 and 3.6 NTU, respectively. Thus, for this system at least, the extent of turbidity removal was essentially independent of the initial pollutant load—a result that hinted strongly at a dominant removal mechanism that was independent of pollutant loading.

Dynamic mass balance results were also conducted on the runs shown in Fig. 5(a) and are reported here in two ways. Firstly the cumulative mass removed at the surface of the reactor (i.e. transported by the hydrogen bubbles generated at the cathodes) is presented in Fig. 5(b) as a function of time and initial pollutant loading. Alternatively the mass balance data over a 1h period are presented in Table 2. It should be noted that the mass added to the reactor was a combination of initial pollutant (i.e. clay) loading and coagulant addition, with 1h operation at 14A m^{-2} generating a calculated 0.97g of aluminium hydroxide. Thus at the lowest pollutant loading (0.1g l^{-1}), a greater proportion of the final total mass in the system was actually the result of coagulant generation (53%) than was initially present as pollutant. Subsequent runs to investigate the impact of the operating current on the dominant removal mechanism (i.e. settling or flotation) were carried out at a pollutant

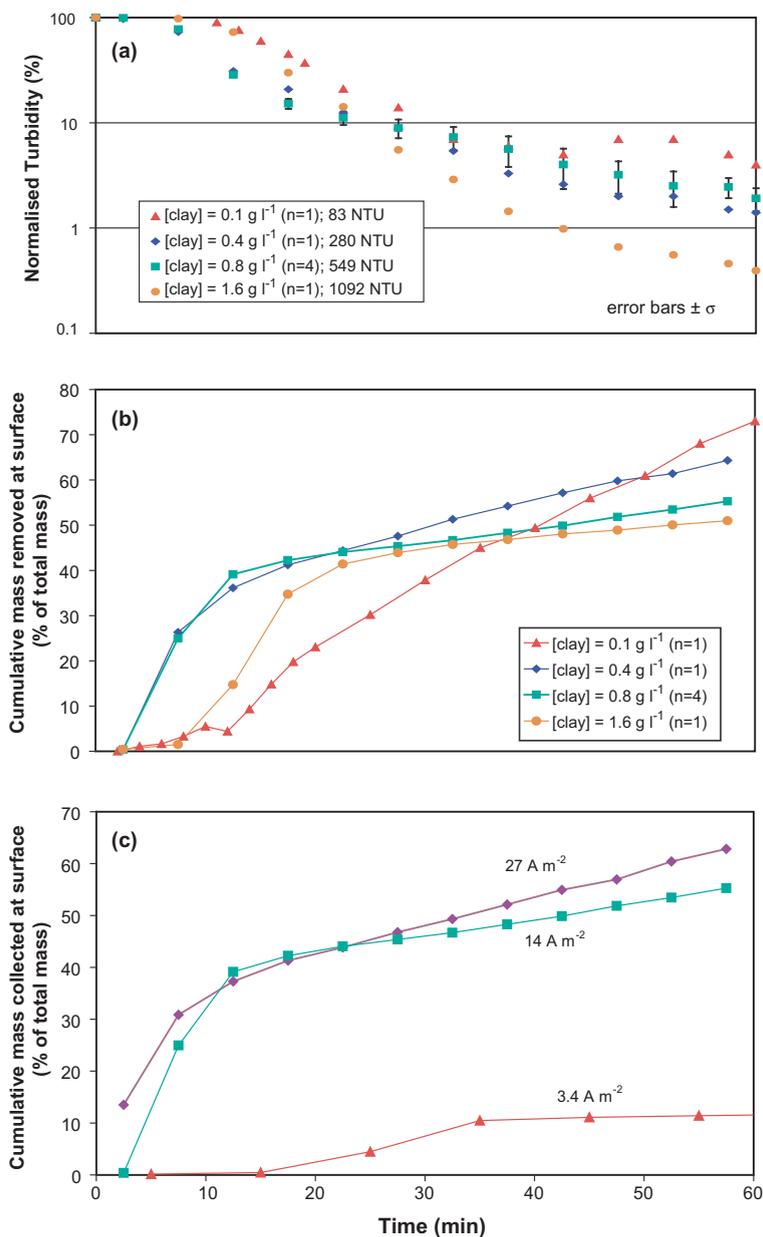


Fig. 5. (a) Normalised turbidity as a function of time and pollutant loading; $i = 14 \text{ A m}^{-2}$. (b) Cumulative mass collected at the surface as a function of time and pollutant loading; $i = 14 \text{ A m}^{-2}$. (c) Cumulative mass collected at the surface as a function of time and current density; $[\text{clay}] = 0.8 \text{ g/l}$.

loading of 0.8 g l^{-1} , thus limiting this potential source of experimental inaccuracy. Experimental details of the mass balancing procedures are given elsewhere (Holt, 2003).

In terms of evaluating batch electrocoagulation as a candidate technology for providing low-cost, low maintenance localised water treatment, these preliminary experiments clearly demonstrated that the performance

of such a system can be quite robust (i.e. insensitive to large operational changes) with respect to both solution conductivity and pollutant loading.

3.2. Operating current density

Operating current density is critical in batch electrocoagulation, as it is the only operational parameter that

Table 2

Mass balance breakdown over an hour of operation; [clay] = 0.1–1.6 g/l; $i = 14 \text{ A m}^{-2}$

Loading (g/l)	Mass in ($t = 0 \text{ min}$)			Mass out ($t = 60 \text{ min}$)		
	Total, g	Total clay, g (% total)	Total Al(OH) ₃ , g (% total)	At surface, g (% total)	At base, g (% total)	In bulk solution, g (% total)
1.6	12.00	11.03 (92%)	0.97 (8%)	6.12 (51%)	5.62 (47%)	0.26 (2%)
0.8	6.49	5.52 (85%)	0.97 (15%)	3.59 (55%)	2.63 (41%)	0.27 (4%)
0.4	3.76	2.79 (74%)	0.97 (26%)	2.42 (64%)	1.20 (32%)	0.14 (4%)
0.1	1.82	0.85 (47%)	0.97 (53%)	1.33 (73%)	0.50 (27%)	0.0 (0%)

can be controlled directly. In this system electrode spacing is fixed and current is a continuous supply. Current density directly determines both coagulant dosage and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes. Thus a set of experiments were carried out to quantify the impact of operating current on reactor performance. This was done on two related bases—a dynamic (or time dependent) basis and an equivalent aluminium concentration basis. Fig. 5(c) and Table 3 present results in an analogous fashion to that employed above for pollutant loading. Both presentations show clear differences between the three current density levels used.

The mass balance data show that at the lowest current density (3.4 A m^{-2}), only 26% of the total mass input to the system had been transported to the surface by flotation after 4 h operation, with some 73% of the total mass reporting to the base of the reactor. Settling of the aggregated pollutant was clearly the dominant removal mechanism at this low current density where fewer bubbles were produced at the cathode, resulting in a decrease in solution mixing and material uplift. Conversely, at the highest current density (27 A m^{-2}), 63% of the total mass had reported to the surface after just 1 h. Flotation was clearly favoured here by the higher bubble density and coagulant dosage rate occurring at this current density.

Faraday's law may be used to relate the mass (m) of electrolytically generated aluminium going into solution to the operating current (I) and the run time (t). In this relationship, M is the atomic weight of aluminium, z is the number of electrons transferred in the anodic dissolution (here $z = 3$), while F is Faraday's constant (96486 C mol^{-1}).

Table 3

Mass balance breakdown as a function of current density; [clay] = 0.8 g/l

Current density, A m^{-2}	Time, min	Mass in			Mass out		
		Total, g	Total clay, g (% total)	Total Al(OH) ₃ , g (% total)	At surface, g (% total)	At base, g (% total)	In bulk solution, g (% total)
3.4	240	6.49	5.52 (85%)	0.97 (15%)	1.68 (26%)	4.76 (73%)	0.05 (1%)
14	60	6.49	5.52 (85%)	0.97 (15%)	3.59 (55%)	2.63 (41%)	0.27 (4%)
27	60	7.48	5.54 (74%)	1.94 (53%)	4.70 (63%)	2.93 (39%)	-0.15 (-2%)

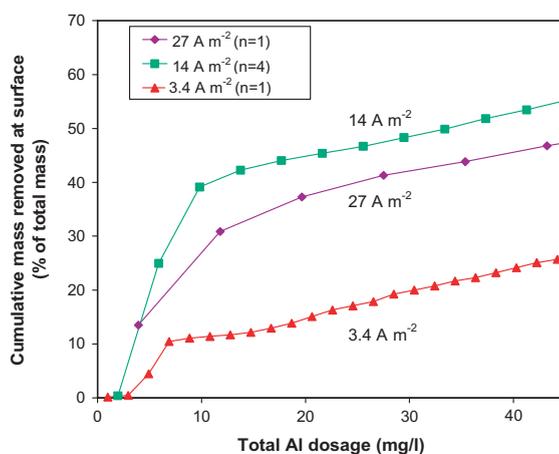


Fig. 6. Cumulative mass collected at the surface as a function of coagulant addition and operating current; [clay] = 0.8 g/l.

$$m = \frac{ItM}{zF}$$

Using this equation, the amount of coagulant delivered to the solution may be calculated. Thus Fig. 6 shows the system's response not on a simple time basis but as a function of the total amount of coagulant put into solution—the latter being quoted as an equivalent aluminium concentration. When plotted in this way, the results were somewhat counter-intuitive. As expected, the lowest current density (3.4 A m^{-2}) removed the least mass to the surface as aluminium concentration increased, primarily due to the dominance of settling. Operation at 27 A m^{-2} (which had the highest coagulant and hydrogen bubble generation rates) might be ex-

pected to achieve the greatest mass removal to the surface. Yet on an aluminium basis, it was the mid-range current density case (14 A m^{-2}) that resulted in the greatest mass reporting to the surface. In other words, a current density of 14 A m^{-2} resulted in the most efficient usage of the available coagulant, if efficiency is defined as the pollutant mass removed to the surface per unit of coagulant provided.

In terms of evaluating batch electrocoagulation as a candidate technology for providing low-cost, low maintenance localised water treatment, this set of experiments clearly demonstrated two important results. Firstly, that operating current density is the key operational parameter, affecting not only the system's response time but also strongly influencing the dominant pollutant separation mode. Secondly however, these results would also seem to indicate that running the reactor at the highest allowable current density may not be the most efficient mode of operation. For any specific application, the 'optimal' current density will invariably involve a trade-off between operational costs and efficient use of the introduced coagulant.

4. Modelling batch electrocoagulation behaviour

For the batch electrocoagulation system presented in the previous section, the dominant removal mechanism (i.e. enhanced pollutant settling or flotation to the surface) was largely set by the current density. Although the use of batch electrocoagulation as a favoured water treatment technology is not dependent on our ability to carry out a priori modelling, it would seem reasonable that its wider acceptance can only be accelerated by the promise of likely advances in this area. Consequently, this section sets out to explore via mathematical modelling the reasons for the strong impact of operating current density on the dominant pollutant removal mechanism.

An insight into the competing removal processes in electrocoagulation can be made using the white water collector efficiency (WCE) model (Edzwald et al., 1991; Edzwald, 1995; Gregory et al., 1999) used to describe dissolved air flotation (DAF). This model treats each bubble as an individual collector of particles, considers all such bubbles as a 'white water' blanket, and divides a DAF unit into two zones. The reaction zone encourages contact between bubbles and particles, while the separation zone promotes clarification as particle–bubble aggregates float to the surface. Here the entire volume of our batch reactor was considered as comprising the 'reaction zone' with the WCE model being applied to the reactor as a whole. It is assumed here that the flotation process occurring within a DAF reactor is mechanistically similar to that in our electrocoagulation reactor.

The WCE model describes the transport mechanisms that result in attachment between an individual particle and a bubble. The total single bubble collector efficiency (η_T) is taken as comprised of a linear combination of Brownian diffusion (η_D), interception of the particle by the bubble (η_I), sedimentation of the particle onto the bubble (η_S) and inertial driven contact (η_{IN}):

$$\eta_T = \eta_D + \eta_I + \eta_S + \eta_{IN}$$

Each term in this equation can be readily calculated using particle (i.e. aggregated pollutant) and fluid properties.

Fig. 7 shows the calculated single collector collision efficiency for our electrocoagulation reactor conditions based on a mean electrolytic hydrogen bubble diameter of $20 \mu\text{m}$ (Fukui and Yuu, 1980). η_T is dominated by Brownian diffusion for particles below about $0.8 \mu\text{m}$ with interception and sedimentation together controlling removal above this level. Note that before any particle coagulation occurs, the majority of the clay pollutant lay within the $0.5\text{--}15 \mu\text{m}$ range (Holt et al., 2002).

The WCE model builds upon the concept of a single bubble collector efficiency by extension to a blanket of bubbles. A particle removal rate equation can be obtained by considering removal by a white water blanket in the contact zone containing a bubble number concentration N_b and a particle number concentration N_p (Gregory et al., 1999) with A_b being the projected bubble area.

$$\frac{dN_p}{dt} = -(\alpha_{pb}\eta_T)N_p(A_b v_b N_b)$$

The particle–bubble attachment efficiency (α_{pb}) describes the fraction of the collisions between bubbles and particles that results in attachment. A conservative value for α_{pb} of 0.1 was used here. The terminal rise velocity (v_b) for a $20 \mu\text{m}$ hydrogen bubble was calculated as $2.5 \times 10^{-4} \text{ m s}^{-1}$. The mean bubble path (taken from

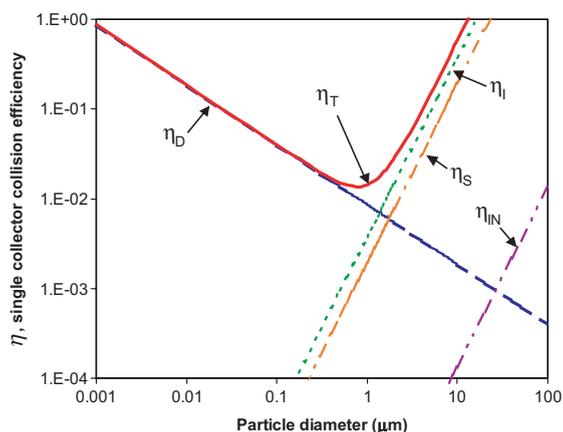


Fig. 7. Single collector efficiency as a function of particle size.

the middle of an electrode to the surface) was 130 mm and hence the average rise time was 8.9 min for an unhindered bubble. The mean bubble rise time was equated to the contact zone time (t_{cz}) in the WCE model.

The bubble number concentration (N_b) can be estimated using the mean rise time, the hydrogen mass generation rate (noting that the generation rate is directly proportional to current according to Faraday's Law) and the bubble diameter. For an operating current density of 14 A m^{-2} and $20 \mu\text{m}$ bubbles, N_b was estimated to be $2.5 \times 10^{12} \text{ m}^{-3}$.

Upon integration of the particle removal rate equation, an expression can be derived relating the particle effluent concentration (N_{pe}) to the particle influent concentration (N_{pi}). Note that the 'effluent' should be thought of as what leaves the WCE reaction zone, after particles have been removed by bubble attachment and flotation to the reactor surface.

$$\frac{N_{pe}}{N_{pi}} = \exp(-\alpha_{pb}\eta_T t_{cz} A_b v_b N_b)$$

This expression can be used to predict pollutant removal efficiency (ϵ) by flotation assuming the electrocoagulation reactor acts as a white water collector, as shown in Fig. 8. Bubble attachment calculations (similar to those presented by Edzwald, 1995) showed that the number of bubbles attached per floc and the estimated density of the aggregate did not strongly influence the overall floc removal rate by flotation. Rather these calculations showed that the most likely source of error in these estimates was associated with the probability of particle–bubble attachment (α_{pb}).

Fig. 8 relates the effective flotation removal efficiency (ϵ) to the aggregate size. Coagulant addition results in aggregation with an increase in 'particle' size to within

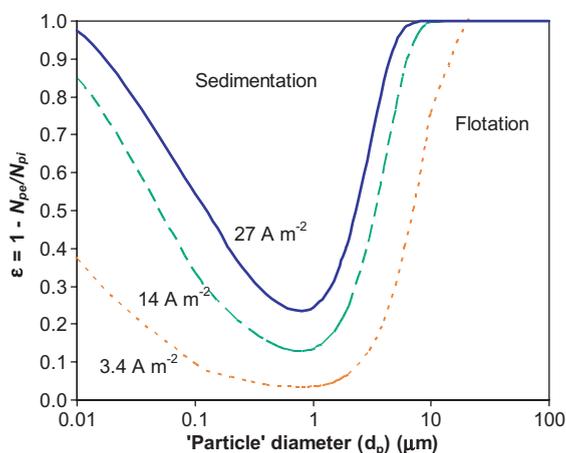


Fig. 8. Removal efficiency (by flotation) as a function of particle diameter and operating current density.

the range $5\text{--}20 \mu\text{m}$ where the bulk of the pollutant is readily removed by flotation. Operation of the electrocoagulation reactor at higher current densities (27 A m^{-2}) also increases the bubble number concentration (N_b). This combination of increased aggregation and an increased bubble number concentration is the reason for the dominance of flotation as the removal mechanism at high currents in this reactor. The reactor is operating in the 'coagulation and flotation' mode identified earlier (see Fig. 2). At low current density (3.4 A m^{-2}), aggregation still occurs (but on a longer time scale) but the bubble number concentration is insufficient to ensure high flotation rates, hence making sedimentation the dominant removal mechanism. This reduction in flotation effectiveness for low current density is clearly seen in Fig. 8. Under these conditions, the electrocoagulation reactor is primarily operating as an electrochemical dosing device (i.e. in the 'coagulation only' mode shown in Fig. 2).

5. A framework for future research of electrocoagulation

Electrocoagulation is an enigmatic technology. Despite having been widely used for over a century, there appears to be no real consensus on the most appropriate approach for any given application, little in the way of systematic reactor design rules, and almost nothing in the way of a generic a priori modelling approach. The root cause of this situation seems to be that electrocoagulation is a technology that lies at the intersection of three more fundamental technologies—electrochemistry, coagulation and flotation. Each of these is well-studied in its own right. However, it is clear from the published literature that what is lacking is a quantitative appreciation of the way in which these technologies interact to provide an electrocoagulation system. For electrocoagulation to play a wider role as an accepted and dependable water treatment technology, research is required that focuses neither on simply making a specific (pollutant-centred) application work nor on any one of the foundation technologies, but rather the emphasis needs to be on explaining and quantifying the key interactions between electrochemistry, coagulation and flotation.

One possible conceptual framework is shown in Fig. 9. Each foundation area brings a certain perspective to electrocoagulation, as represented by each lobe of this Venn diagram. The aim here is to show how electrocoagulation's complexity can be simplified using a reductionist approach. Relevant phenomena, characterisation methods and tools are highlighted in each lobe. Information presented in the intersection between two lobes represents knowledge that links the foundation areas. For example, thermodynamic modelling of the solution chemistry of hydrolysed metal cations links the electro-

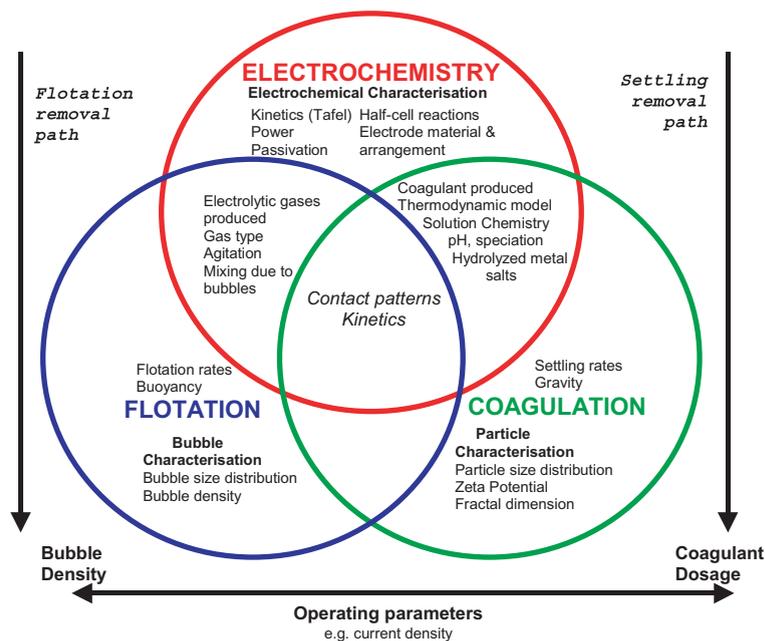


Fig. 9. Conceptual framework for electrocoagulation as a 'synthesis' technology.

chemistry and coagulation lobes. Central to understanding and describing electrocoagulation as a whole are the contact pattern (i.e. mixing) and process kinetics. The first of these describes how the various species (coagulant, pollutant particles, bubbles) move and are brought into proximity with each other, while the latter describes the rate at which interactions between the various species occurs. Hence, these aspects are placed at the intersection of all three lobes.

As shown in Sections 3 and 4, it is a combination of physico-chemical processes occurring within an electrocoagulation reactor that shifts the dominant pollutant separation mechanism between (gravity driven) settling and (buoyancy driven) flotation. The vertical arrows in Fig. 9 represent these two removal paths with the relative importance of each being set by a combination of reactor design and operating parameters. As an example, current density (represented by a double-headed arrow at the base of Fig. 9) shifts the relative importance between the flotation and coagulation lobes, as it determines both the coagulant dosage and bubble production rates, as well as influencing the extent of mixing within a reactor. The message here is that decisions about reactor design cannot be made in isolation, as there is an inseparable link between design and operational parameters brought about by the complex interactions between the three foundation technologies.

In many areas of engineering, short-cut methods (such as the correlation of experimental data via dimensionless analysis) have been successfully employed as design/operational tools long before a process has been

understood at a mechanistic level. However the electrocoagulation literature is almost completely devoid of such short-cut (or scale-up) methods, a testimony to the complexity of the process and the myriad possible interactions occurring within. Indeed it is the authors' view that meaningful short-cut methods will never be developed for general application to electrocoagulation and that in terms of research effort it would be a mistake to pursue such a goal. Rather electrocoagulation is a process where some level of mechanistically based mathematical modelling is almost certainly required for the technology to progress beyond its present state of 'enlightened empiricism'. Thus the future focus should be on quantifying the interactions that occur between each of the three underlying technologies (i.e. the lobes in Fig. 9) for a range of systems where the pollutant itself can be readily quantified.

6. Conclusions

Without doubt the provision of an adequate water supply suitable for a diversity of uses by the world's growing population is one of the 21st century's more pressing challenges. Even in developed countries, the use of large-scale, continuous throughput water treatment plants is not the complete solution. There is a growing awareness that localised plants (each tailored to a particular region and application) have a significant role to play in the overall solution strategy. This article addresses electrocoagulation's surprising lack of

acceptance as a mainstream option and puts forward the following reasons for this failure by identifying deficiencies in a number of key areas:

- The lack of any systematic evaluation of existing applications leading to an agreed set of guidelines suitable for the design/operation of new applications.
- An almost complete lack of detailed experimental data on the operation of batch electrocoagulation reactors, one of the more suitable options for (modest size scale) localised water treatment.
- No widely applicable mechanistically based approach to the mathematical modelling of electrocoagulation reactors.
- Failure to fully appreciate that the performance of an electrocoagulation reactor is largely determined by the interactions that occur between the three 'foundation technologies' of electrochemistry, coagulation and flotation.
- No generic solution to the problem of electrode passivation.

This paper has attempted to demystify electrocoagulation by showing that it is possible to classify a wide diversity of reactor systems on a simple basis, to obtain and interpret detailed dynamic data from a batch reactor system, and to show that the complexity of electrocoagulation is a natural (and understandable) consequence of the interactions between a number of processes occurring in parallel. It is hoped that this evaluation will play its part in focussing attention on electrocoagulation as a viable localised water treatment technology in the near future.

Apart from a technical focus on quantifying interactions between the foundation technologies and an economic focus on the relative cost of electrocoagulation, future research also needs to examine reliable means of reducing electrode passivation.

References

- Abuzaid, N.S., Bukhari, A.A., Al-Hamouz, Z.M., 1998. Removal of bentonite causing turbidity by electrocoagulation. *J. Environ. Sci. Health, Part A* A33, 1341–1358.
- Asmal, P.K., 2000. Water is a catalyst for peace. In: Stockholm Water Symposium Laureate Lecture World Commission on Dams, Stockholm.
- Avetisyan, D.P., Tarkhanyan, A.S., Safaryan, L.N., 1984. Electroflotation-coagulation removal of carbon black from acetylene production wastewaters. *Sov. J. Water Chem. Technol.* 6, 345–346.
- Balmer, L.M., Foulds, A.W., 1986. Separating oil from oil-in-water emulsions by electroflocculation/electroflotation. *Filtr. Sep.* 23, 366–370.
- Barkley, N.P., Farrell, C.W., Gardner-Clayson, T.W., 1993. Alternating current electrocoagulation for superfund site remediation. *Air Waste* 43, 784–789.
- Belongia, B.M., Haworth, P.D., Baygents, J.C., Raghavan, S., 1999. Treatment of alumina and silica chemical mechanical polishing waste by electrodecantation and electrocoagulation. *J. Electrochem. Soc.* 146, 4124–4130.
- Cerisier, S.D.M., Smit, J.J., 1996. The electrochemical generation of ferric ions in cooling water as an alternative for ferric chloride dosing to effect flocculation. *Water SA* 22 (4), 327–332.
- Chen, X., Chen, G., Yue, P.L., 2000. Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep. Purif. Technol.* 19, 65–76.
- Do, J.-S., Chen, M.-L., 1994. Decolourization of dye-containing solutions by electrocoagulation. *J. Appl. Electrochem.* 24, 785–790.
- Donini, J.C., Kan, J., Szykarczuk, J., Hassan, T.A., Kar, K.L., 1994. Operating cost of electrocoagulation. *Can. J. Chem. Eng.* 72, 1007–1012.
- Edzwald, J.K., 1995. Principles and applications of dissolved air flotation. *Water Sci. Technol.* 31, 1–23.
- Edzwald, J.K., Malley, J.P., Yu, C., 1991. A conceptual model for dissolved air flotation in water treatment. *Water Supply* 9, 141–150.
- Fukui, Y., Yuu, S., 1980. Collection of submicron particles in electro-flotation. *Chem. Eng. Sci.* 35, 1097–1105.
- Gregory, R., Zabel, T.F., Edzwald, J.K., 1999. Sedimentation and flotation. In: Letterman, R.D. (Ed.), *Water Quality and Treatment: A Handbook of Community Water Supplies*. McGraw-Hill, New York, pp. 7.1–7.87.
- Gott, R., 1977. Development of waste water treatment at the Climax Mine. *Amer. Mining Cong. J.* 64 (4), 28–34.
- Groterud, O., Smoczynski, L., 1986. Phosphorus removal from water by means of electrolysis. *Water Res.* 20 (5), 667–669.
- Holt, P.K., 2003. Electrocoagulation: unravelling and synthesising the mechanisms behind a water treatment process, PhD thesis, Faculty of Engineering, The University of Sydney.
- Holt, P.K., Barton, G.W., Mitchell, C.A., 2001. The role of current in determining pollutant removal in a batch electrocoagulation reactor. In: 6th World Congress of Chemical Engineering Conference Media CD, Melbourne, Australia.
- Holt, P.K., Barton, G.W., Wark, M., Mitchell, C.A., 2002. A quantitative comparison between chemical dosing and electrocoagulation. *Colloids Surf. A* 211, 233–248.
- Ivanishvili, A.I., Przhedorlinskii, V.I., Kalinichenko, T.D., 1987. Comparative evaluation of the efficiency of electrocoagulation and reagent methods of clarifying waste water. *Sov. J. Water Chem. Technol.* 9, 468–469.
- Koren, J.P.F., Syversen, U., 1995. State-of-the-art electroflocculation. *Filtr. Sep.* 32 (2), 153–156.
- Mameri, N., Yeddou, A.R., Lounici, H., Belhocine, D., Grib, H., Bariou, B., 1998. Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes. *Water Res.* 32, 1604–1612.
- Matteson, M.J., Dobson, R.L., Glenn, R.W.J., Kukunoor, N.S., Waits, W.H.I., Clayfield, E.J., 1995. Electrocoagulation and separation of aqueous suspensions of ultrafine particles. *Colloids Surf., A* 104, 101–109.
- Nikolaev, N.V., Kozlovskii, A.S., Utkin, I.I., 1982. Treating natural waters in small water systems by filtration with

- electrocoagulation. *Sov. J. Water Chem. Technol.* 4 (3), 244–247.
- Novikova, S.P., Shkorbatova, T.L., Sokol, E.Y., 1982. Purification of effluents from the production of synthetic detergents by electrocoagulation. *Sov. J. Water Chem. Technol.* 4, 353–357.
- Ogutveren, U.B., Goenen, N., Koparal, S., 1992. Removal of dye stuffs from waste water: Electrocoagulation of Acilan Blau using soluble anode. *J. Environ. Sci. Health, Part A* A27, 1237–1247.
- Osipenko, V.D., Pogorelyi, P.I., 1977. Electrocoagulation neutralization of chromium containing effluent. *Metallurgist* 21, 44–45.
- Pouet, M.F., Grasmick, A., 1995. Urban wastewater treatment by electrocoagulation and flotation. *Water Sci. Technol.* 31, 275–283.
- Pretorius, W.A., Johannes, W.G., Lempert, G.G., 1991. Electrolytic iron flocculant production with a bipolar electrode in series arrangement. *Water SA* 17, 133–138.
- Sanfan, W., 1991. Studies on economic property of pretreatment process of brackish water using electrocoagulation (EC) method. *Desalination* 82 (1–3), 365–373.
- Syrbu, V.K., Drondina, R.V., Romanov, A.M., Ershov, A.I., 1986. Combined electroflotocoagulation apparatus for water purification. *Elektronnaya Obrabotka Materialov (Electron treatment of metals)*, 57–59.
- Vik, E.A., Carlson, D.A., Eikun, A.S., Gjessing, E.T., 1984. Electrocoagulation of potable water. *Water Res.* 18, 1355–1360.
- Weintraub, M.H., Gealer, R.L., Golovoy, A., Dzieciuch, M.A., Durham, H., 1983. Development of electrolytic treatment of oily wastewater. *Environ. Prog.* 2, 32–37.
- WHO/Unicef, 2000. Global water supply and sanitation assessment 2000 report. World Health Organization and United Nations Children's Fund, USA.
- Woytowich, D.L., Dalrymple, C.W., Gilmore, F.W., Britton, M.G., 1993. Electrocoagulation (CURE) treatment of ship bilgewater for the US coast guards in Alaska. *Mar. Technol. Soc. J.* 27, 62–67.
- Zabolotsky, V.I., Nikonenko, V.V., Pismenskaya, N.D., Istoshin, A.G., 1996. Electrodialysis technology for deep demineralization of surface and ground water. *Desalination* 108 (1–3), 179–181.