Theoretical considerations on electrocoagulation/flotation process

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ABSTRACT

This paper presents a general theoretical consideration of the electrocoagulation/flotation (ECF) process with an electrochemical mechanism occurring in the reactor. To understand how the ECF process works it is important to discuss the mechanism of water electrolysis and other related chemical reactions. The first section presents a synthesis of the ECF technology and mechanism associated with water electrolysis. Several sections discuss information regarding the chemistry and kinetics of removing pollutants when three different mechanisms including, electrode oxidation, gas bubble generation, and flotation and sedimentation of flocs formed, interact in the ECF processes. It was found that the kinetics of de-pollution follows the exponential law with time. Towards the end of this research, information regarding the basic equations is included to present a theoretical, as well as empirical model for prediction pollutant removal by the EC process. The chemical theory of batch reactor is used as the basis for development of the empirical model in the following paper.

KEYWORDS

Electrocoagulation/flotation (ECF) process; Theoretical consideration; Empirical modeling approach.

INTRODUCTION

The ECF process is an electrochemical technique in which a variety of unwanted dissolved particles and suspended matter can be effectively removed from an aqueous solution by electrolysis of the electrodes\textsuperscript{[1]}. In a general sense, electrocoagulation or electroflotation are technologies based on the concepts of electrochemical cells, specifically known as “electrolytic cells”. In an electrolytic process a source of direct current is connected to a pair of electrodes immersed in a liquid that serves as the electrolyte. To understand the electrochemical behaviour of the system, it is important to describe the general electrolytic reactions. The basis of electrocoagulation is the in situ formation of a coagulant species that can remove various pollutants from the water and wastewater being treated. There are three main mechanisms in the whole of electrocoagulation-flotation process:

- Electrode oxidation
- Gas bubble generation
- Flotation and sedimentation of flocs formed

The total processes in ECF can be summarised in Figure 1.

The mechanism for removing pollutants is based on hydrolysis reaction and the coagulation-flotation mecha-
nism in the ECF reactor. Application of direct electric current through electrodes induces electrolysis reactions, as presented in the following pages.

**THEORETICAL CONSIDERATION**

**Hydrolysis reaction**

Electrolytic dissolution of the metal anode (M) in water produces aqueous M$^{n+}$ species:

Anodes: $\text{M}_{(s)} \rightarrow \text{M}^{n+} + ne^- \quad (1)$

Reduction takes place at the cathodes which results in hydrogen bubbles being produced by the following reaction:

Cathodes: $6\text{H}_2\text{O} + 6e^- \rightarrow 3\text{H}_2(g) + 6\text{OH}^-$

$E_0^C = -0.83 \text{ V} \quad (2)$

where $E_0^C$ is standard cathode potential. A significant factor for operating EC technology and its field of application depends on many factors on the right choice of electrode material, especially the anodes. An anode must be easily treated, and also cheap and long lasting. Electrodes must have adequate mechanical strength and an extended operating life. The choice of material is limited to dissolved and undissolved materials. Iron and aluminium electrodes will dissolve and are suitable for many applications but materials such as platinum, carbon, and graphite are used as sources of undissolved anodes. Aluminium is the most commonly used material and is used in this research. The effluent with aluminium electrodes was very clear and stable but appear greenish with iron electrodes and then turn yellow and turbid because of formation of Fe (II) and Fe (III) ions into solution.

**Charge loading**

In order to use Faraday’s law, the relationship between current value, electrolysis time, and the amount of electric charge that flows through a circuit must be recognised. By definition one coulomb of charge transferred when a 1-amp current flows for 1 second (1 C = 1 A.s), the following relations demonstrate the direct proportionality between current (I) and electrolysis rate:

$I = \frac{dQ_e}{dt} \quad (3)$

$Q_e/zF = N_e \quad (4)$

where $Q_e$ and $N_e$ are quantity of electricity and mol electrolysed in the electrode reaction, respectively. From Eq. 3 and 4, Eq. 5 can be expressed as:

$\text{Rate(mol/s)} = \frac{dN_e}{dt} = \frac{1}{zF}$

(5)

An electrode process is a heterogenous reaction which occurs in the interfacial area between electrode and solution. A heterogeneous charge-transfer reaction means a charge-transfer reaction, with the charge transferred across a phase boundary, typically between a solid and liquid phase. Since electrode reactions are heterogenous, their reaction rates are usually described in units of mol/s per unit area. From Eq. 5, Eq. 6 can be expressed as:

$\text{Rate(mol/s.m}^2) = \frac{1}{zFA} = \frac{i}{zF}$

(6)

where $i$ is the current density (A/m$^2$). In most electrochemical processes the current density is the most important parameter for controlling the reaction rate, as the process at constant current density a steady dissolution of aluminium and hydrogen generation rate are certified. Faraday’s law has been experimentally shown to explain the dissolution of aluminium in an electrocoagulator. Thus, Faraday’s law describes the coagulant and hydrogen generation rate as follows:

$r_{Al^{3+}} (g \text{Al}^{3+} \text{ s}^{-1}) = \frac{I(AW)}{ZF}$

(7)

$r_{H^+} (g \text{H}^+ \text{ s}^{-1}) = \frac{I(MW)}{ZF}$

(8)
where AW and MW are the atomic weight and molecular weight respectively. Thus, operation at constant current density a constant dissolution of aluminium and hydrogen generation rates is ensured.

**Operational cell potential of EC reactor**

Based on the primary half-cell equations (Eq. 2) for the EC system, the standard equilibrium potential (Eq. 9) was +0.83 V (at 298.15 °K, 1 atm, and 1 molar solution). Note that these values were relative to the standard hydrogen electrode (SHE)[5].

\[ E_{\text{cell}}^0 = E_c^0 - E_a^0 \]  

where \( E_{\text{cell}}^0 \) is standard cell potential. This provides a minimum cell potential for the EC reactor and variations in solution conditions including pH and total concentration of aluminium. In an electrolytic cell the energy source is provided by a direct current power supply. As for the EC process, the actual cell potential was measured at constant currents. Figure 2 shows the resultant potential difference for the batch monopolar electrocoagulation reactor in the range of loading different pollutants in this research.

As seen, the cell potential increased as the current increased. A potential cell range was observed for each current. A higher potential was detected in all cases. This high potential overcomes a range of resistances including electrode spacing, conductivity, and surface resistance. The cell potential stabilised within one minute after operation under a wide range of operational conditions including pH, conductivity, and the initial pollutant concentrations.

**Coagulation-flotation process**

Three basic sciences in the ECF process including electrochemistry, coagulation, and flotation may interact to make it work[6-12]. The fundamental electrocoagulation reactions at the anodes and cathodes were given in equations 1 and 2. The dissolution of the metal anode allows floc formation, while the \( \text{H}_2 \) bubbles float and drive the flotation process. The bubbles float to the top of the tank, collide with suspended particles on the way up, adhere to them, and float them to the surface of the water. The \( \text{M}^{m+} \) ions further react as shown in Eq. 10 to form solid \( \text{M} (\text{OH})_n \) precipitate.

\[ \text{M}^{m+} + n\text{H}_2\text{O} \rightleftharpoons \text{M}(\text{OH})_n\text{s(s)} + n\text{H}^+ \]  

The metal hydroxides [\( \text{M} (\text{OH})_n \)] react as coagulants, destabilise and aggregate suspended particles or precipitate, and adsorb dissolved contaminants.

The electrode material determines the coagulant type. By passing a steady electric current through a solution and aluminium electrodes, the dissolution of the aluminium anodes allow floc formation, while the production of hydrogen bubbles at the cathode traps flocs and other suspended matter, bringing them to the surface as a float[13-14]. From Eq 10, the formation of a floc by electrocoagulation (using sacrificial aluminium electrodes) is given in the following equation[15-16]:

\[ 2\text{Al}^{m+} + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_3\text{ss} + 6\text{H}^+ \]  

Some of the possible reactions and mechanisms occurring in the boundary layer between the electrode and bulk of the liquid have been summarised in Figure 3. To oxidise a soluble electrode (e.g. aluminium) in the electrochemical cell, current value and potential differences across the electrodes are required.

It is believed that precipitation or adsorption reaction may occur when aluminium electrode is used for fluoride removal by ECF process. The only mathematical model of electroflotation was reported by Matis and Zouboulis[17], who used a macroscopic approach to evaluate the overall kinetic for removing paint in an electro-flotation cell. They removed pollutant to the surface using a first order kinetic expression to describe flotation. Various kinetic approaches are available that could describe the electrocoagulation-flotation mechanism. Also, Mameri et al[18], derived a first-order kinetic model for removing fluoride from water by electrocoagulation. Therefore, the chemical batch reactor theory, material balances, and reaction kinetics concepts involving the coagulation-flotation mechanisms are
used as a basis for developing the empirical modelling efforts in the following pages.

\[ [\text{Accumulation}] = -[\text{Decrease due to reaction}] (13) \]

The fundamental equitation for the design of the reactors is the rate equation and the equation for the law of conservation of mass. Starting at an initial pollut-ant concentration of \( C_0 \), the rate equation for the vari-ous reaction orders is given[19]:

\[ (\frac{dC}{dt})V = -rV = -(KC_i)V \]  

where “\( n \)” is the reaction order, “\( r \)” is the rate of re-moval of the pollutant by reaction (ML\(^{-3}\)T\(^{-1}\)), and K is the reaction rate constant (M\(^{1-n}\)T\(^{-1}\)). \( C_i \) is the concentr-ation of the pollutant at any time, \( t \), during the reaction and \( V \) is the reactor volume that remains constant in CMBR reactor. Chemical kinetics is concerned with the rate at which reactions occur. Consider a batch re-actor with a first order reaction (\( n=1 \)), the accumula-tion term is \( \frac{dC}{dt} \) and the reaction term is \( KC_i \); thus the mass balance equation, Eq. 14, becomes:

\[ \int_0^t \frac{dC}{C_i} = -KC_i \]  

Integrating the last equation (Eq. 15) between theinitial and final concentrations, and treatment time, leads to the following expression:

\[ \ln\left(\frac{C_i}{C_0}\right) = -Kt \text{ or } \ln\left(\frac{C_i}{C_0}\right) = Kt \]  

Eq. 17 can be rewritten to Eq. 18, as follows:

\[ C_i = C_0 e^{-Kt} \]  

For example for defluoridation by ECF process, As noted in previous researches[20-27], the highest cur-rent (2.5A) removed fluoride quickest due to the readyavailability of Al\(^3+\) ions in the solution. However at higher currents more coagulant (aluminium) is available per unit time, which may be unnecessary, because not only is excess residual aluminium unsafe for drinking water, high current is also uneconomic in terms of energy consump-tion. In this batch ECF the minimum electrolysis time required to reduce the fluorine concentration to the NHMRC and ARMCANZ[28]; and WHO[29] drinking
water guidelines (0.5 < \( F \leq 1.5 \) mg/L) is defined as the detention time (\( t_d \)). The detention time was experimentally determined to achieve the desirable fluoride concentration range in the electrocoagulator. From Eq. 18, the detention time can be expressed as:

\[
t_d = \frac{1}{K} \ln\left(\frac{C_t}{C_i}\right)
\]  

When the fluoride concentration (\( C_t \)) reaches to 1 mg/L, the optimal detention time (\( t_{do} \)) can be expressed as Eq. 20:

\[
t_{do} = \frac{1}{K} \ln(C_s)
\]  

The overall fluoride removal efficiency (\( R_{ef} \)) in batch reactor may be obtained using the following expression:

\[
R_{ef} = \frac{(C_s - C_t)}{C_s} = 1 - \frac{C_t}{C_s}
\]  

From Eq. 18, Eq. 21 can be rearranged to Eq. 22, as follows:

\[
R_{ef} = 1 - e^{-k.t}
\]  

**Continuous flow reactor**

Continuous reactors can be classified according to the mixing regime. Mixing in a continuous system is determined by the residence time (\( t_r \)) and flow rate (\( Q \)). Residence time is a function of reactor volume and flow rate (\( t_r = V/Q \)). A plug flow reactor (PFR) is one type of continuous reactor which behaves mathematically like a batch reactor. In perfect plug flow there is no mixing and they have the same residence time. A plug flow reactor operated at steady state is shown in Figure 5, the feed and its composition, the discharge and its composition, and the composition at any point in the reactor are constant with respect to time.

In the plug flow reactor, the concentration within the reactor is a function of the distance along the reactor, thus the composition of the fluid varies from point to point along the flow path. Therefore, the mass balance for a reaction component must be made for a differential volume, \( dV_r \), as was shown in Figure 5. From Eq. 12, the mass balance equation for PFR in steady state, there is no accumulation, is given:\n
\[
\text{[Input]} = \text{[Decrease due to reaction]} + \text{[Output]}
\]  

The mass balance in the differential reactor volume, \( dV_r \), becomes:

\[
QC_i = Q(C_s - dC_i) + rdV_r
\]  

which gives:

\[
QdC_i = rdV_r
\]  

Since a plug flow reactor with a first order reaction is considered, substituting of the reaction rate (\( r = -KC_t \)) in Eq. 25 gives:

\[
QdC_i = -(KC_t)dV_r
\]  

Integrating the Eq. 26, leads to the following expression:

\[
\int_{C_i}^{C_e} \frac{C}{C_e} dV_r = -\frac{K}{Q} \int dV_r
\]  

which gives:

\[
\ln\left(\frac{C_e}{C_i}\right) = -\frac{K}{Q} V_r
\]  

where \( C_i \) is the effluent or final concentration. Since \( V_r = Qt_r \), substituting of \( V_r \) in Eq. 28 provides Eq. 29:

\[
\ln\left(\frac{C_e}{C_i}\right) = -K.t_r
\]  

or

\[
C_e = C_s.e^{-K.t_r}
\]  

where \( t_r \) is mean residence time of the fluid. Eq. 30 can be rewritten to Eq. 31, as follows:

\[
t_r = \frac{1}{K} \ln\left(\frac{C_s}{C_i}\right)
\]  

When the final fluoride concentration (\( C_e \)) reaches to 1 mg/L, Eq. 31 can be rearranged to Eq. 32:

\[
t_{ro} = \frac{1}{K} \ln(C_s)
\]  

where \( t_{ro} \) is optimum residence time. The overall fluoride removal efficiency (\( R_{ef} \)) in continuous flow reactor may be obtained using the following expression:

\[
R_{ef} = 1 - e^{-K.t_r}
\]  

Since Eq. 32 for a plug flow reactor is the same as Eq. 20 for a batch reactor, a plug flow reactor will have the same performance as a batch reactor if the detention and residence times are the same.
RESULTS AND DISCUSSION

Solution scheme

A solution and application of Eq. 18 will be presented here for modelling purposes. The initial analysis of the solution procedure is based on showing how Eq. 18 fits with the experimental data collected. Thus, the first step is to plot the experimental data by calculating the \(-\ln \left(\frac{C_t}{C_o}\right)\) versus electrolysis time. Based on the plotted data, it appears that the points may be fitted by a linear regression. A first order behaviour for the process is appeared. In the procedure, the slope of each line represents an experimentally determined rate constant \(K_{\exp}\) for the process. Concerning the approach and data analysis, the experimentally determined constant results are attached to independent important variables\(^{25-27}\), including current concentration \(I/V\), initial pollutant concentration \(C_o\), pH of the solution, distance between electrodes \(d\), and ion competition effects. The \(K_{\exp}\) can be expressed as a function of \(I/V\), \(C_o\), \(d\), \(pH\), and ion concentration, as follows:

\[
K_{\exp} = f(I/V, C_o, d, pH, \text{ion})
\]

where current concentration \((I/V)\) is the ratio between the current flowing through a compartment of an electrochemical cell and the volume of that compartment. The appropriate correlations between an experimentally determined constant with different corresponding independent values need to be found separately.

Empirical model

A schematic diagram of the empirical modelling approach is presented in Figure 6.

The chemical batch reactor theory can be used as the basis for developing the empirical model, including statistical scheduling of the experimental data gathered\(^{25}\). Based on the theoretical background and experimental removal rate \(K_{\exp}\), an empirical rate constant is developed for the process. A primary analytical tool for correlating the experimental data is used by the SPSS package. A multiple regression analysis is used by SPSS package to estimate the coefficients of the linear equation, involving one or more independent variables. In fact the model is developed to predict the removal of pollutant. Development of the empirical model will be needed.

CONCLUSIONS

The total process of removing pollutants is based on three mechanisms in the whole ECF process including electrode oxidation, gas bubble generation, and the coagulation-flotation mechanism. Application of direct electric current through electrodes induces electrolysis reactions. The metal hydroxides \([M(\text{OH})_n]\) react as coagulants, destabilise and aggregate suspended particles or precipitate, and adsorb dissolved contaminants. The chemical batch reactor theory, material balances, and reaction kinetic concepts were used as a basis for developing the empirical modelling efforts. The model presented in this manuscript was based on the concept of kinetics for conservative substances reacting in the reactors. In the process, not only mass balance and flow models are important, but also the rate at which the process occurs determines the size of the treatment facilities that must be provided. The overall rate constant for the entire ECF process is determined experimentally \(K_{\exp}\) and included in a model. A multiple regression analysis can be used by SPSS package to estimate the coefficients of the linear equation, involving...
one or more independent variables. An empirical model using critical parameters can be developed for the process, when the experimental rate constant depends on some operating important parameters including current concentration (I/V), initial pollutant concentration \( C_0 \), distance between electrodes (d), pH of the solution, and ion competition effects (ion).

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