Metallurgy and materials

Metalurgia e materiais

Organic matter removal from oil-water emulsions by electrocoagulation. 2 - Mathematical model

Remoção de matéria orgânica de emulsões óleo-água por eletrocoagulação. 2 - Modelo matemático

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Abstract

A mathematical model of the organic matter (chemical oxygen demand - COD) removal from synthetic oil-water emulsions by the electrocoagulation process was developed to evaluate the COD abatement. The model comprises the three fundaments of electrocoagulation: electrochemistry, coagulation and flotation. By comparing the experimental and calculated values of COD, it was found that the model was able to adequately predict the concentrations of organic matter (COD) present in the emulsions and satisfactorily describe the electrocoagulation process.

Keywords: electrocoagulation, oil-water emulsions, organic matter (COD), mathematical model.

Resumo

Um modelo matemático da remoção de matéria orgânica (demanda química de oxigênio - DQO) de emulsões sintéticas água-óleo pelo processo de eletrocoagulação foi desenvolvido para avaliar a redução da DQO. O modelo compreende os três fundamentos da eletrocoagulação: coagulação, eletroquímica e flotação. Ao comparar os valores experimentais e calculados de DQO, verificou-se que o modelo foi capaz de predizer a concentração de matéria orgânica (DQO) presente nas emulsões e descrever satisfatoriamente o processo de eletrocoagulação.

Palavras-chave: eletrocoagulação, emulsões óleo-água, matéria orgânica (DQO), modelo matemático.

1. Introduction

Oil-water emulsions are widely used in metal industries in processes such as rolling, forging and shaping. These emulsions have oil contents in the range 0.1 - 30 kg.m-3, depending on the specific application, are toxic and must be treated so that recycling of water is possible.

Several electrochemical methods have been studied over the years for the separation of oil-water emulsions (Yang, 2007; Cañizares et al., 2008, Ibrahim et al., 2001, Kramer et al., 1979). Electroflotation was one of the first processes developed in which oil is removed from emulsions previously destabilized by chemical additives. More recent efforts have been focused on the application of electrochemical techniques to destabilize ("break") the emulsion and separate the destabilized oil without the addition of chemical reagents. The key process involved in most of these techniques is electrocoagulation. Cañizares et al. (2008) observed that the gas bubbles generated in electrocoagulation (oxygen at the anode and hydrogen at the cathode) promote the coalescence (electrofloculation) and the separation of coalesced droplets, which may be carried to the top of the emulsion and then collected and removed.

In this work, a mathematical model to predict the organic matter removal (drop of COD) from synthetic oil-water emulsions by electrocoagulation was developed.

2. Materials and Methods

The oil-water emulsions and the experimental apparatus and procedure were described in part 1 of this work.

3. Results

The experimental results indicated that the oil-water emulsions presented good stability for initial pH values above 5, with average values of zeta potential around -75 mV. For initial pH below 5 the stability of the emulsions decreased as the average values of zeta potential were approximately -40 mV. The values of conductivity were close to -0.6 S.m-1, except for experiments performed with NaCl electrolyte concentration of 1.0 kg.m-3. These values are suitable for the implementation of electrocoagulation. Regarding the kinetics, the higher the applied current density, the faster was the removal of organic matter from the emulsion. Due to the fact that the current density is related to rate of production of Al3+ species, higher current densities led to shorter periods of latency and hence to lower total times to obtain high removals (over 95%).

4. Mathematical Model

The mathematical model involved the three fundamentals of electrocoagulation: electrochemistry (represented by Faraday's law to predict the amount of aluminum cations generated at the anode as a function of time), coagulation (represented by the chemical equilibrium between the organic matter and the Al^{3+} species) and flotation (represented by electroflotation during the inertia stage and flotation of the complexes during the reactive stage).

The curves of COD abatement versus time exhibit three stages: a period of inertia in which the species Al^{3+} accumulated in the circuit and contributed to the reduction of the Zeta potential of the dispersed matter surface; a reactive stage where there was an increase in the COD removal probably due to low values of Zeta potential and possible agglomeration of the dispersion of Al^{3+} complexes; a threshold for which additional addition of Al^{3+} species did not allow further treatment.

The current density had a major effect on the COD removal rate, with higher values of current density resulting in shorter periods of inertia and hence in lower total times for the electrocoagulation process. It is well known that the effect of current density is associated with the rate of Al^{3+} species production.

The mathematical model took into account the following simplifying assumptions:

i) Existence of a minimum concentration of aluminum, $C_{Al,min,}$ necessary to start the electrocoagulation process, and a corresponding minimum time for the occurrence of such concentration, t_{min}. The minimum concentration of aluminum and the minimum time are related by Faraday's law, i.e., $C_{Al,min}= (\eta M\,I\,t_{min})/(z\,F\,V)$, where M is the atomic mass of aluminum, I is the applied current, z is the number of electrons involved in the electrode reaction, is the Faraday's constant and V is the volume. Thus, it is considered that the amount of aluminum (Al^{3+}) that is produced in the cell is η times the value predicted by Faraday's law, although in reality the oxidation of aluminum occurs in two ways: electrochemical oxidation and chemical reaction at the anode (when the cathodes are not aluminum but an inert material such as stainless steel).

The minimum concentration of aluminum was expressed by the correlation:

$$C_{Al,min}=A+B\,pH_o+C\,C_{Oo} \tag{1}$$

where pHo is the initial pH of the emulsion, COo is the initial oil concentration and A, B and C are constants determined by the experimental data.

(ii) For aluminum concentrations lower than CAl,min and thus for times lower than tmin, the COD decrease does not occur, which is characterized by a horizontal plateau in the curves. However, if there is an excess of surfactant it was assumed that only the COD related to the surfactant was reduced by electroflotation of that compound. Given that in the inertia stage the curves of COD abatement resemble straight lines with non-zero slopes, a zero-order kinetics was assumed for the electroflotation, i.e.: $COD= COD_o- k\,t$, where COD_o is the initial COD and k is the rate constant which depends on the experimental variables.

In the inertia stage the COD follows the correlation:

$$COD= COD_o-(A+ B\ pH_o+ C\ j+D\ C_{Oo}+ E\ C_E+ F\ \delta\ )\ t \qquad (2)$$

where j is the current density, C_E is the electrolyte concentration, δ is the distance between electrodes, t is time and A, B, C, D, E and F are constants determined by the experimental data.

The statistical analysis of the data revealed that the contribution of the variables δ and C_{Oo} to equation (2) is negligible.

(iii) The organic matter contained in the emulsion was expressed in the model in terms of the amount of COD by the function Q(t). It was considered that the quantity of organic matter that cannot be removed by electrocoagulation is negligible. Hence the stabilization stage is characterized by very low values of COD (less than 0.05 kg/m^3). This assumption implies that all organic matter can be treated by electrocoagulation after addition of coagulant and that at time zero, $COD_o = Q(0) = Q_0$.

(iv) The electrocoagulation occurs by complexation of organic matter, Q, by Al^{3+} species through the "chemical equilibrium":

$$Q+n\ Al=X \qquad (3)$$

where n is an overall coefficient (mg O2/mg Al3+) and X is the complex formed, which will be subsequently removed by flotation. Due to the unity of n the above equation cannot be regarded as a real chemical process, but simply as a phenomenological description of the complexation of organic matter by aluminum species. Such description is adequate since the kinetic analysis revealed that the reaction rate depends on the concentrations of organic matter and aluminum (Rangel, 2008).

An overall "equilibrium" constant, K, was defined by:

$$K = [X]/[Q]\ [Al] \qquad (4)$$

where [Al] is the concentration of free aluminum species and [X] the concentration of aluminum in a complex form.

The coefficient n was not included in the expression for the equilibrium constant, since reaction (3) cannot be deemed as an elementary process at equilibrium.

For times greater than the minimum time, $t > t_{min}$, a mass balance on dissolved aluminum gives:

$$C_{Al}= C_{Al,min}+ [Al]+\ 1/n\ \ [X] \qquad (5)$$

Substituting [Al] obtained by equation (4) in equation (5) the concentration of complex X is given by:

$$[X]=\ (n\ K\ [Q]\ \ (C_{Al}- C_{Al,min}\ ))/(n+K\ [Q]\ ) \qquad (6)$$

(v) The complex formed by organic matter and the Al3+ species was carried to the surface of the cell by hydrogen microbubbles generated on the stainless steel cathodes. The mechanism of organic matter removal by sedimentation will be completely disregarded in view of the fairly high values of current density used in the experiments. The flotation of the complexes to the surface followed a first order kinetics since this kinetics best represented the electrocoagulation data.

$$-\ d[X]/dt= K'\ [X] \qquad (7)$$

where K' is the rate constant for the complex flotation.

Integration of equation (7) from tmin and the corresponding concentration of the complex X, [X]min, not necessarily equal to 0 gives:

$$[Q]\ = \frac{n\ [X]_{min} \exp\{-K'(t-t_{min})\}}{n\ K\ (C_{Al}- C_{Al\ min})\ -\ K[X]_{min} \exp\{-K'(t-t_{min})\}} \qquad (8)$$

Equation (8) provides a mathematical expression for the variation of the organic matter concentration with time as a function of the complexation "equilibrium" constant, K, the flotation rate constant, K', the minimum time for the onset of the reactive stage, t_{min}, the minimum aluminum concentration necessary for initiating the electrocoagulation process, $C_{Al,min}$, and the initial concentration of the complex, $[X]_{min}$.

The methodology used for adjusting the model to the experimental results is described below.

It was not possible at first to identify the exact time (t_{min}) where the change from the inertia to the reactive stage took place, i.e., the instant in which the COD drop was no longer linear in time and begun to follow equation (8). The time interval for which this change (inflection) has happened was then determined for each experiment. After establishing this time interval, the fitting of the model regarding the inertia stage was performed by equation (2) with:

$$k= A+ B\ pH_o+ C\ j+D\ C_{Oo}+ E\ C_E+ F\ \delta \qquad (9)$$

The rate constant k was determined using the numerical package Microsoft® Solver, which uses the least squares method to fit the experimental data. The constants A, B, C, D, E and F were determined using a multiple linear regression of the experimental variables. Therefore, COD values related to the inertia stage were obtained and compared with those experimentally measured.

For the reactive stage, it was essential to evaluate the minimum time, tmin, and the minimum aluminum concentration, CAl,min. For this the numerical package Solver was again utilized. The value of tmin that provided the best fit of the experimental data with equation (8) within the predetermined time interval was determined.

After finding out the inflection point (tmin, CAl,min) the parameters K, K', [X]min and n that best matched the experimental data were assessed by the least squares method (Solver). These parameters were correlated to experimental variables studied.

Finally, the same procedure was repeated for the inertia stage and for the whole model, i.e., considering the two stages in sequence.

5. Model Results

Equation (10) gives the correlation between the rate constant, k, and the experimental variables during the inertia stage. The correlation coefficient was 0.831.

$$k= 14.917- 5.479\ pH_o + 16.847\ j + 9.530\ C_{Oo} + 2.499\ C_E - 0.920\ \delta \qquad (10)$$

As expected, the rate constant increased with increasing current density, oil and electrolyte concentration, and decreased with increasing initial pH and distance between electrodes.

The “equilibrium” constant, K, presented the following dependence on the initial pH (correlation coefficient 0.9995) for the pH range 4-12. The contribution of the other variables was insignificant.

$$K=0.0941\ pH_o^{-5.967} \qquad (11)$$

According to equation (11) the complexation reaction becomes increasingly difficult as the initial pH of the emulsion increases. This finding is consistent with the Eh-pH diagrams in aqueous medium.

During the reactive stage, and especially within its first few minutes, the ratio between the concentration of aluminum in a complex form and the concentration of free aluminum species is greater than 1. This means that during the electrocoagulation process the dissolved aluminum is primarily in the form of a complex with the organic matter. In addition, to begin the flotation of the complex, it is necessary to reach a minimum concentration of the complex, $[X]_{min}$, which must obviously be less than the instantaneous concentration calculated from equation (6).

Correlations between the model parameters K', $[X]_{min}$, n and $C_{Al,min}$ and the experimental variables were obtained. Given that most of the experiments was conducted with I = 2.0 A, $\delta = 0.01$ m, $C_{Oo} = 3.0$ kg.m^{-3} and $C_E = 3.0$ kg.m^{-3}, the pH should be the variable presenting the greatest impact on the model parameters since it varied in the 4-12 range.

The rate constant for the complexes flotation, K', was within the range -10^{-2} and -10^{-4} min^{-1}. The negative sign is due to the fact that [X] needs to be greater than [X]min to occur the flotation of the complexes, as stated above. In another words, the negative sign of K' signifies that the rate of formation of the complexes is higher than the rate of their removal from the solution by flotation, which also seems to be quite reasonable. It was also found that the dependency of K' with pH could be expressed through a sixth degree polynomial with a correlation coefficient of 0.9418.

The minimum concentration of complex required for the onset of flotation, $[X]_{min}$, presented values betweeen 10^{-4} and 10^{-6} kg.m^{-3} and was, for all experiments, always lower than [X] calculated by equation (6). $[X]_{min}$ was also pH dependent, the dependency being expressed by a third degree polynomial with a correlation coefficient of 0.9850. Generally, $[X]_{min}$ decreased with increasing pH. As [X] also decreased with increasing pH, the reaction given by equation (3) is favored at lower pHs, as expected.

The overall coefficient, n, showed values in the range 10^{-4} a 10^{-2} mg O2/mg Al^{3+} except for experiments with pH 4.1, 10.8 and 12.1 for which the values were -5.53×10^{12}, 2.24x107 and 2.86×10^{7} mg O2/mg Al^{3+}, respectively. These exceptions indicate that at acid pHs complexation occurs without the need for aluminum (very high and negative values of n) whereas at pHs (above 10.0) complexation would be very difficult requiring large amounts of coagulant. This result is consistent with the literature and confirms that the model is adequately describing the physical behavior of electrocoagulation. Usually the overall coefficient increased with increasing pH implying that the higher the pH, the greater the amount of coagulant necessary to electrocoagulation. The overall coefficient was correlated to the pH by a third degree polynomial with a correlation coefficient of 0.9957.

The minimum concentration of aluminum for the onset of the reactive stage, CAl,min, displayed values of about 0.02 kg.m^{-3} (pH 4.1), 0.03 kg.m^{-3} (pH 7.2), 0.06 kg.m-3 (pH 8.0), from 0.09 to 1.00 kg.m^{-3} (pH between 8.5 and 9.5) and 1.10 kg.m^{-3} (pH between 10 and 12). Therefore, the higher the pH, the higher the $C_{Al,min}$, which reflects a greater ease for the occurrence of complexation in slightly acid and neutral media and greater difficulty in strongly alkaline media. The minimum concentration was found to be effectively dependent on pH, being expressed by a sixth order polynomial with a correlation coefficient of 0.9524. Both the time required for the onset of the reactive stage and the duration of this stage decreased with increasing current density without influencing the concentration of aluminum required for the initiation of complexation with the organic matter. Accordingly, the minimum concentration should not be dependent on the current density.

To illustrate the application of the model five experiments involving different initial oil concentrations, current and initial pH were selected and are summarized in Table 1. The surfactant concentration was 1.0 kg.m^{-3}, the electrolyte concentration was 3.0 kg.m-3 and the distance between electrodes was 0.01 m.

Experiment	C_{Oo} (kg.m^{-3})	I (A)	pH_o
1	3.0	4.0	9.56
2	3.0	8.0	9.30
3	3.0	2.0	7.21
4	0.5	2.0	8.79
5	10.0	2.0	8.70

Table 1
Selected experiments to illustrate the application of the model.

Figures 1-5 present the results of the comparison between the experimental values of COD and those calculated by the model for the selected experiments. It is evident that the model adequately predicted the concentrations of organic matter (COD) present in the emulsions. Similar results also occurred for all the other experiments.

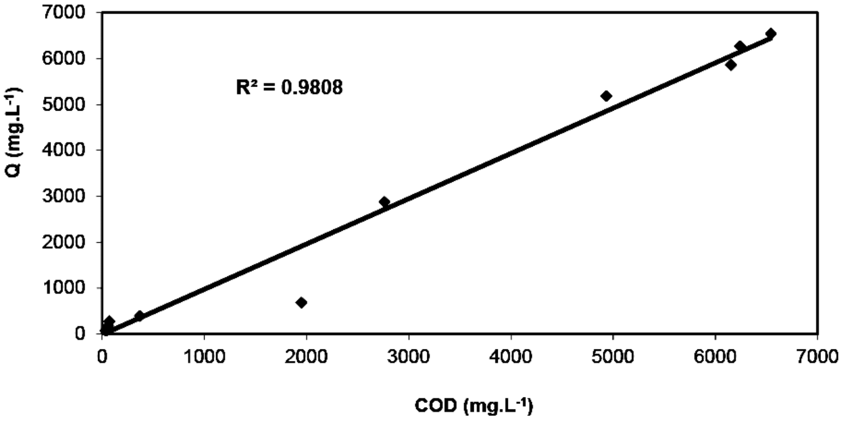

Figure 1
Comparison between measured and calculated COD (Q) for experiment 1.

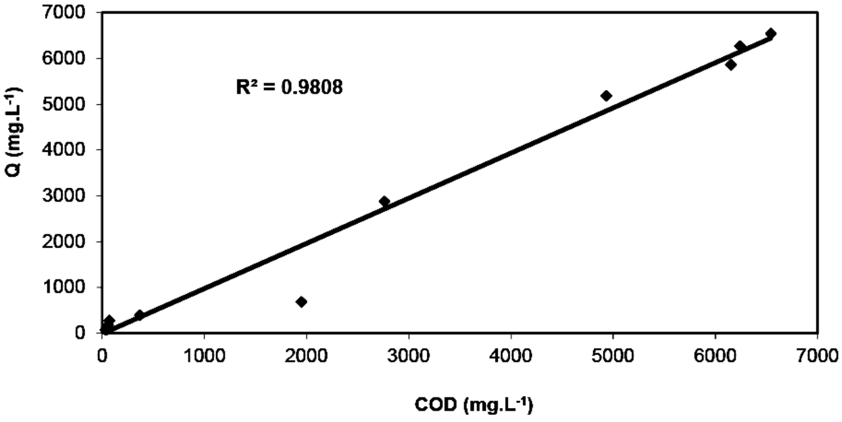

Figure 2
Comparison between measured and calculated COD (Q) for experiment 2.

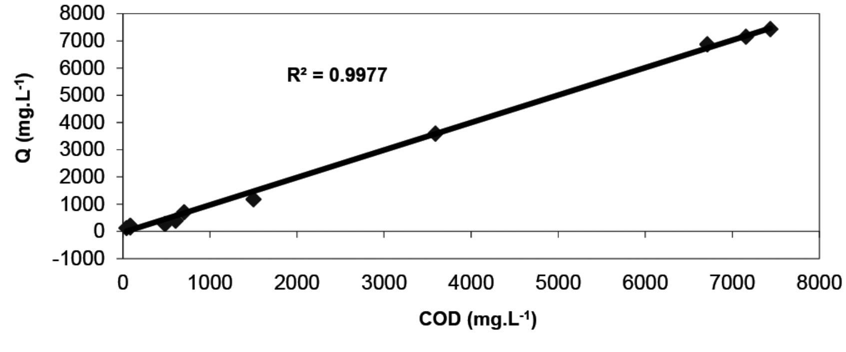

Figure 3
Comparison between measured and calculated COD (Q) for experiment 3.

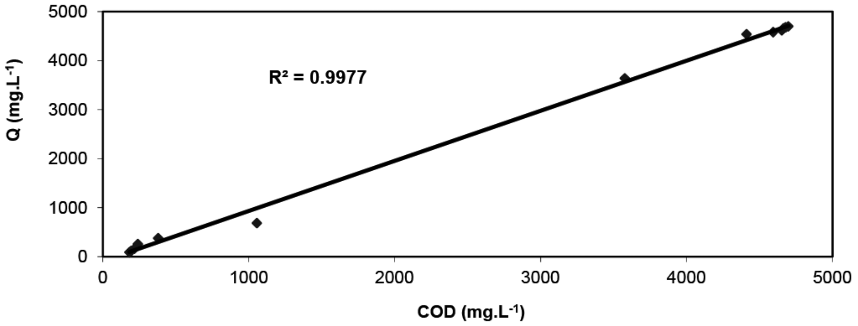

Figure 4
Comparison between measured and calculated COD (Q) for experiment 4.

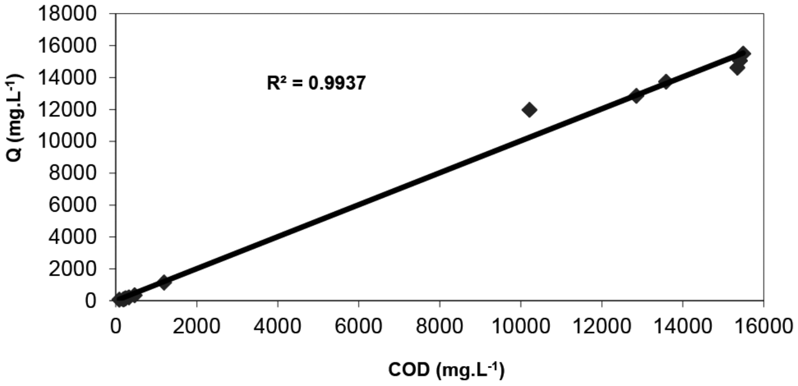

Figure 5
Comparison between measured and calculated COD (Q) for experiment 5.

6. Conclusions

The synthetic oil-water emulsions exhibited good stability for initial pH values above 5. The stability decreased for pHs lower than 5. The higher the value of current density, the faster is the removal of organic matter from the solution, allowing shorter latency stages and therefore lower total times to attain high removals (over 95%). This result was ascribed to the fact that the current is related to the rate of production of Al3+ species.

The comparison between the experimental values of COD and those calculated by the mathematical model substantiates its capacity to properly predict the concentrations of organic matter (COD) present in synthetic oil-water emulsions and satisfactorily describe the electrocoagulation process.

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