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Modeling Studies for Electrocoagulation

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Abstract**—**Synthetic oily wastewaters were prepared from metal working fluids (MWF). Electrocoagulation experiments were performed under constant voltage application. The current, conductivity, pH, dissolved oxygen concentration and temperature were recorded on line at every 5 seconds during the experiments. Effects of applied voltage differences, electrode materials and distance between electrodes on removal efficiency have been investigated. According to the experimental results, the treatment of MWF wastewaters by iron electrodes rather than aluminum and stainless steel was much quicker; and the distance between electrodes should be less than 1cm. The electrocoagulation process was modeled by using block oriented approach and found out that it can be modeled as a single input and multiple output system. Modeling studies indicates that the electrocoagulation process has a nonlinear model structure.

Keywords**—**Electrocoagulation, oily wastewater, SIMO systems.

I. Introduction

METALWORKING FLUIDS (MWF) are widely used in metal forming, metal cutting, and in the galvanic industry where cooling, lubrication and rust control are important in operations. MWFs are classified as water insoluble, water dispersible, and water composite fluids. The group of water dispersible cooling lubricants is subdivided into emulsions and cooling lubricant solutions. Oil based MWFs are commonly formulated as oil in water emulsions. The oil phase of the emulsion reduces the friction between the machine tool and work piece, and the aqueous phase dissipates the heat generated by friction. Additionally, MWF flushes away the created fines and chips from the nascent metal surface, preventing rewelding [1]. The metalworking oils are degraded by usage and have to be disposed after being used for some time. However, these oils are classified as hazardous wastes and the treatment to remove the emulsified oil is generally complex and expensive. In addition to that often emulsion breaking (destabilization) is needed before the oil can be successfully removed.

The treatment of MWF wastewaters has been addressed by different techniques, but the most commonly used are membrane processes [2], chemical destabilization [3] and electrochemical destabilization (electrocoagulation) [4]. Since MWFs contain biocides (such as heterocyclic sulphur and nitrogen compounds) to prevent their degradation and sometimes biological processes can be used as well. In addition, when the effluent is highly polluted with soluble compounds and they cannot be removed by other techniques, distillation [5] can be an attractive alternative, despite of its high operation-cost.

Most of the chemical processes can be represented by block oriented nonlinear models [6], [7]. Among these models, Wiener and Hammerstein models are the popular ones and they consist of two blocks in series (linear dynamics and nonlinear static functions) [8]. In this study electrocoagulation process has been modeled as a single input and multiple output system. The input variable was selected as the voltage difference applied to the electrodes and current, conductivity, turbidity and pH were taken as the output variables. First, a linear model was obtained by analyzing experimental results applying output error approach. Then, a block oriented nonlinear model (Hammerstein-Wiener) was developed. Finally, the predictions of output variables from the linear and nonlinear models were compared to the experimental values.

II. Material and Methods

A. Preparation of Synthetic Wastewaters

In this study, electro-coagulation experiments have been performed by using synthetic wastewaters produced from two commonly used MWFs in industry. Taptamic Dual Action Plus 1 is used for all metals other than aluminum (EAL). On the other hand, Taptamic Dual Action 2 is applied for aluminum (FAL). Both MWF is composed of mainly from alkanes and forms emulsions when they are mixed by water (Table I).

TABLE I
Chemical Compositions of Metalworking Fluids

Trade Name	Code	Composition
Taptamic Dual Action Plus 1	EAL	Chlorinated alkane (40%-60%) Chlorinated paraffin (20%-40%) Not soluble in water
Taptamic Dual Action 2	FAL	Aliphatic hydrocarbons Not soluble in water

The synthetic wastewaters were prepared by mixing EAL or FAL to tap water at a volume percentage of 2; then the mixture was stirred mechanically for 30 minutes. The chemical oxygen demands (COD) for EAL and FAL wastewaters were measured by titrimetric method and evaluated as 150mg/L and 250mg/L, respectively.

B. Experimental Set-Up

A photograph of the experimental set-up where electrocoagulation experiments were performed was shown in

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Fig. 1. It consists of an electrokinetic unit (1.75L), a power supply (40V, 5A), probes (conductivity, pH and dissolved oxygen), a data logger and a peristaltic pump. The electrodes were 13cm in length, 2cm in width and 0.3cm in thickness. Tests were performed by using stainless steel, aluminum and iron plate electrodes. The distance between electrodes was 1cm. The applied voltages to the electrodes were kept constant during the experiments and the studied voltage differences were 10, 20, 30 and 40V. Conductivity, dissolved oxygen and pH were measured online (Mettler Toledo) and recorded at every 5 seconds. The system was at batch mode since water was recirculated to the electrokinetic unit by a peristaltic pump at a flow rate of 20mL/min. The time duration for each experiment was 120 minutes and removal efficiency was calculated by measuring turbidity (Aqualytic AL450T-IR).

Fig. 1 Electrocoagulation set-up

III. Discussions and Results

A. Electrocoagulation Experiments

Effects of applied voltage differences, electrode materials and distance between electrodes on removal efficiency have been investigated by performing electrocoagulation experiments using MWFs. Similar to the observations presented in the literature [9], [10], the removal efficiency increased as the applied voltage difference to the electrodes was increased. The highest applied voltage difference (40V) results in higher removal efficiency (99%) for EAL and FAL wastewaters.

The studied electrode materials were aluminum, iron and stainless steel. The variations in turbidity with respect to time for the treatment of EAL wastewaters by electrocoagulation were shown in Fig. 2. It was observed that three electrode materials result in almost the same removal efficiency after 60 minutes. However, the change in turbidity was much quicker for iron electrodes. For example, turbidity values dropped from 960 NTU to 97, 35 and 303 NTU for aluminum, iron and stainless steel electrodes in the 30 minutes of treatment, respectively. In addition, when the distance between electrode pairs (L) was increased from 1 to 4cm it was observed that variation in turbidity becomes more sluggish (Fig. 3). Turbidity almost stayed constant at L= 3cm and L= 4cm for the first 60 minutes of treatment. All the electrocoagulation experiments were also performed by using FAL wastewaters and similar results were obtained.

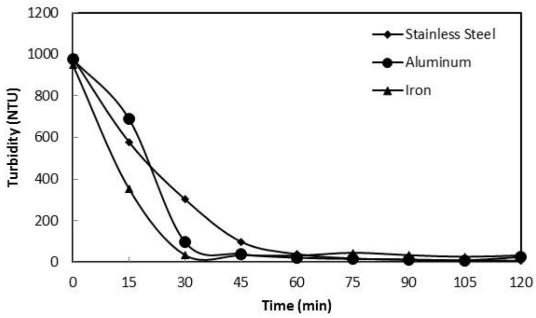

Fig. 2 Turbidity variations with respect to time during the treatment of EAL wastewaters (V=40V, L= 1cm)

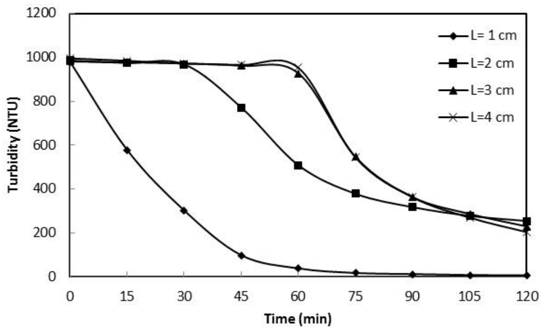

Fig. 3 Turbidity variations with respect to time during the treatment EAL wastewaters (V=40V, L=1cm)

B. Modeling Studies

Physical, chemical and electrochemical processes are taken place at the same time during electrocoagulation and, therefore, it is a complex process and difficult to model. In order to remove MWFs from wastewater, first, metals (coagulants) from electrodes should pass to water by the application of voltage; then oil droplets should be destabilized as a result of changes in surface charges and finally droplets should be adsorbed by coagulants and settle down.

The results of electrocoagulation experiments showed that the voltage difference applied to electrodes was the main parameter that can be controlled. The current, conductivity, turbidity and pH depend on it. Since the applied voltage difference was kept at a constant value during the electrocoagulation experiments, the measured parameters become the output responses of the process to a step function. When the step response of a system is known it is possible to obtain the impulse response of the system and the transfer function that presents a relation between input and output parameters of the system [8].

A linear model for electrocoagulation has been developed by analyzing experimental results applying output error approach. According to this approach, the transfer function of a process can be defined as a polynomial function and the coefficients can be evaluated by minimizing the difference between the model output predictions and the experimental values [8]. The least square minimization was applied in this study. The linear model was evaluated as a fourth order polynomial transfer function for voltage to current and a second order for voltage to turbidity.

On the other hand a block oriented (Hammerstein-Wiener) nonlinear model has been developed to model electro-coagulation process. As for the linear model, fourth order and second order polynomial transfer function was used in the dynamic linear block of nonlinear model structure. Both polynomial and saturation functions were used for the static nonlinear block of nonlinear model.

A set of electrocoagulation experiments has been performed in modeling studies in order to identify system parameters.

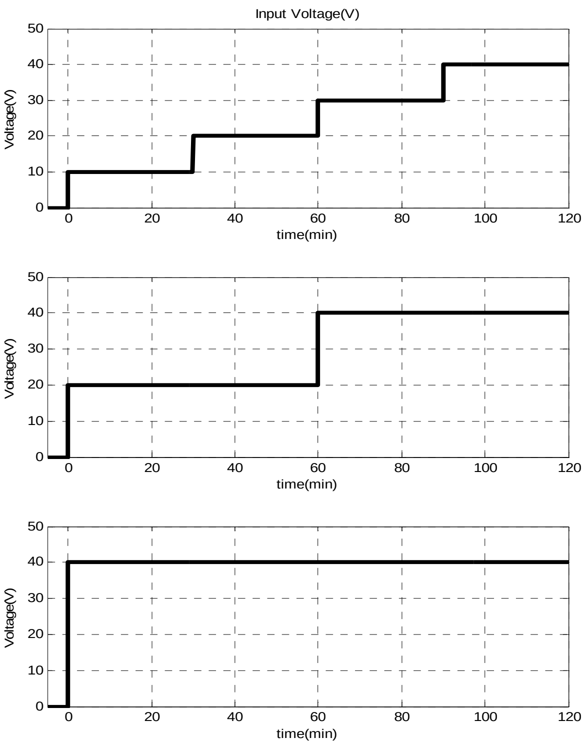

Fig. 4 The applied voltage differences to the electrodes as step functions

Experiments were performed by using 2% (v/v) EAL and FAL wastewaters. The current passing through the electro-coagulation unit was recorded at every 1 minutes but turbidity was read in every 15 minutes. Since the voltage difference was selected to be the controlled variable it was set to 40V and applied to the electrodes as step changes (Fig. 4). It can be seen that 40V was reached as a single, double and four step functions and the total duration was 120 minutes.

The current and turbidity measurements for EAL wastewaters were given in Figs. 5 and 6, respectively. Both the linear and the nonlinear models predict the current values very close the measured values for a single step function, as it was expected. However, as the number of step function increases better predictions for the currents were calculated from the nonlinear model. The performance of nonlinear model can be pointed out much better in turbidity predictions (Fig. 6). It can be seen that the predicted turbidity values from the linear model were much lower than the actual values when 40V was applied as in the form of two step functions. Even though there were some deviations in the predictions of current for the nonlinear model as well, the predictions were certainly much closer to the measured values. Similarly, the predictions of turbidity from the nonlinear model were in good agreements with the measured values for the treatment of FAL wastewaters (Fig. 7). On the other hand, the linear model predictions were much lower than the experimental values.

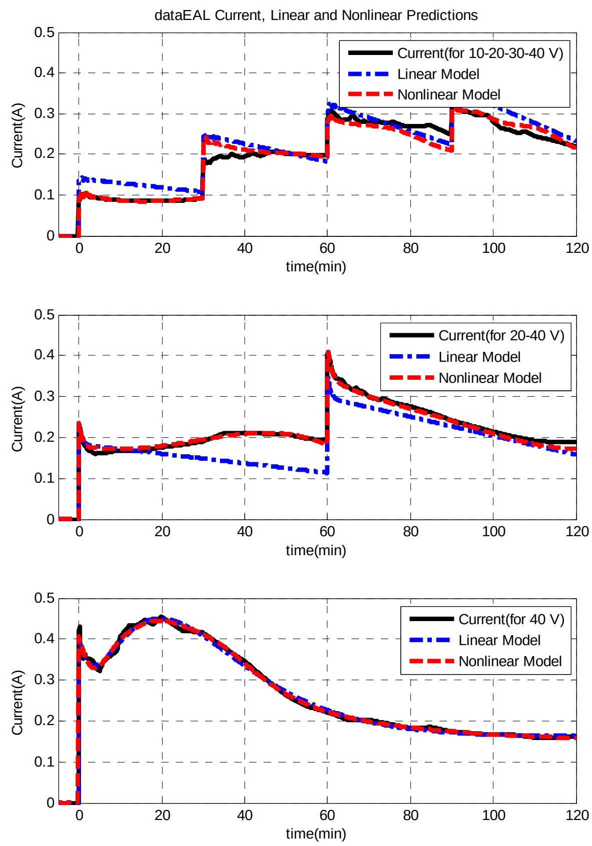

Fig. 5 The current measurements and the linear and nonlinear model predictions (EAL wastewater)

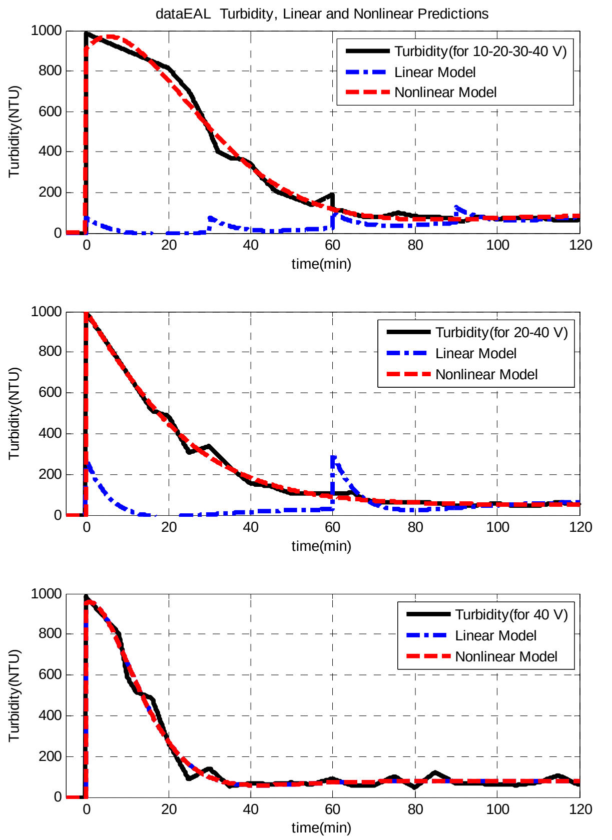

Fig. 6 The turbidity measurements and the linear and nonlinear model predictions (EAL wastewaters)

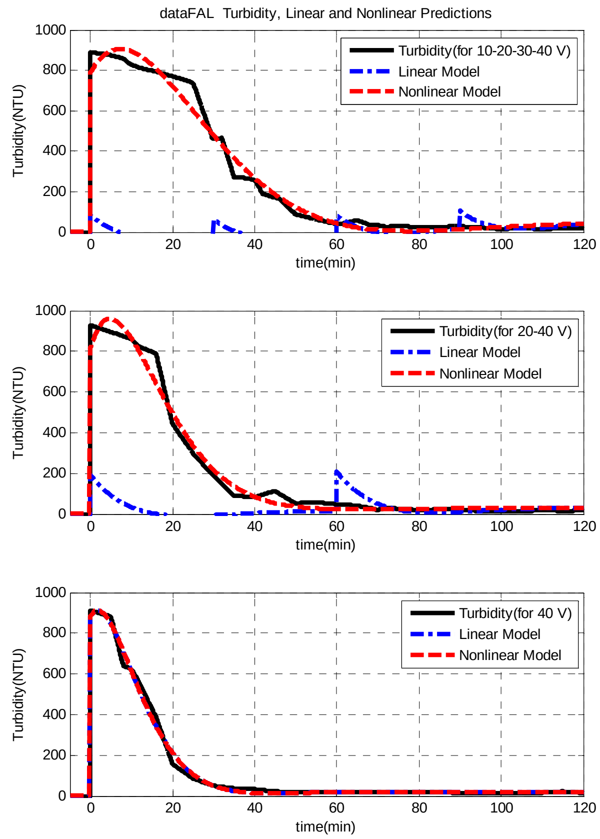

Fig. 7 The turbidity measurements and the linear and nonlinear model predictions (FAL wastewaters)

IV. Conclusion

Metalworking fluids (MWF) form stable emulsions in water and cannot be separated easily by using traditional methods such as gravity or air flotation. In this study, electro-coagulation was applied as the separation method of MWF from water. Based on the results of the experiments and the modeling studies the following conclusions are drawn:

- As the applied voltage difference to the electrodes increases removal efficiency of MWFs increases.
- Iron electrodes give much quicker response than aluminum and stainless steel electrodes.
- The distance between iron electrodes should be less that 1cm in order to reach 98% removal efficiency
- The electrocoagulation process has a nonlinear structure and can be represented successfully by using a block oriented nonlinear model.

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