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OPTIMIZATION OF OPERATIONAL PARAMETERS OF ELECTROCOAGULATION PROCESS FOR TREATING METALWORKING FLUIDS

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ABSTRACT

Study aims on optimization of two operational parameters of electrocoagulation process (EC) used for treating metalworking fluids (MWF). First, we focused on the selection of the type and amount of saltadded to the solution to increase its conductivity. TOC concentration decrement of total organic carbon was evaluated to determine the optimal dose of added salt. Both types of salt – NaCl, KCl, have similar effect on TOC concentration decrement. Optimal dosage of salt is 7.5 g. Γ^1 . Second parameter was value of applied current. Most significant decrease of TOC concentration (87,7%) occurred at current value of 5A.

KEY WORDS

metalworking fluid (MWF), electrocoagulation, conductivity, electric current

Introduction

Most commontechnologies used for treatment of spent MWF are membrane separation (ultrafiltration, reverse osmosis), incineration and chemical coagulation. They are basically used as a primary step of treatment, followed by secondary or tertiary stages of treatment.

Electrocoagulation (EC) is one of electro-chemical methods used for treating water and wastewater. It has been successfully used and implemented in the process of purification of drinking water and in past years also for treating industrial wastewaters obtained from many branches of industry. It has been also used for removing heavy metals, arsenic, boron and sulphur, sulphide and sulphite ions. It is also widely used for removing turbidity and colour from wastewaters from textile and paper industry.^[1,3,4,6,7,8,9,11,12]

EC was also studied as a method of treatment of spent metalworking fluids, mainly oil-in-water (O/W) emulsions and polysynthetic fluids. These fluids are designed to form stable emulsion by adding special chemical substances – emulsifiers. MWFs have high concentrations of chemical and biological oxygen demand (COD, BOD) and total organic carbon (TOC). Therefor they need to be treated prior to their discharge into environment.

Electrocoagulation process is method based on adding positive charged ions of particular metals (AI, Fe, Cu) to solution as in conventional coagulation process. In conventional coagulation process these metal species are provided by addition of metal salts into the solution, while in electrocoagulation these species are generated in-situ, by dissolution (oxidation) of positively charged electrode (anode) immersed in the solution. Main goal for using EC is to destabilize O/W emulsion, which then breaks down to two phases – oil phase and aqueous phase.

In ECprocess, electric current from external power supply is applied to appropriate set of metal electrodes immersed in solution. Current passing through negatively charged cathode causes the reduction(electrolysis) of water thus generating gaseous H_2 and hydroxyl ions (OH⁻) according to chemical reaction^[1]:

These hydroxyl ions react with metal ions generated by electro-oxidation of sacrificial anode, forming various monomeric or polymeric species of metal hydroxyl ions which are in the endtransformed to metal hydroxides, in dependence on pH of the solution^[13].

$M \rightarrow M^+ + ne^-$

Moreover, the reduction of water occurs on anode, depending on pH of the solution. This process can be not welcomed because of faster passivation of the anode, on the other hand produced O_2 supports the flotation process.^[2]

Metal hydroxides act like coagulant agents, forming flocks (flocculation) with large surface area and positive surface charge. Depending on the presence of the type of produced metal ions or hydroxides, and pH of the solution, there can be two mechanisms of flocculation, namely adsorption and precipitation. Metal hydroxides have large surface area, thus good adsorption properties. They can bound the pollutants to their surface (bridge coagulation) or form large complexes (flocs) that sweep through the solution and entrap colloid particles (sweep coagulation). Moreover, positive charge of these speciesreduce interparticle repulsion forces by neutralization of the charge of some counter anionic groups (carboxyl or hydroxyl) of organic pollutants which subsequently precipitate into insoluble flocs with neutral net charge.^[1]



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Formed flocs then settle down or are floated on the surface depending on their size. Bubbles of H_2 generated on the cathode or O_2 generated on the anode support flotation of flocs, so they can be easily removed from the surface of solution by one of the mechanical methods.

The electrocoagulation process is dependent on various internal and operating factors, which have direct or indirect influence on efficiency of the EC process. Internal factors include mainly physicochemical properties of the treated wastewater, such as pH of the solution, composition and conductivity. Operational factors are current density, intraelectrode gap, operational time, material and setting of used electrodes. *Current density*

Current density has direct effect on the effectivity of EC process as it determines the floc dosage and bubble generation rates. It is defined as:

$$i = \frac{I}{A_{eff}} \left[Am^{-2}\right]$$

where I is electric current [A], A_{eff} is effective area of electrode (area of electrode immersed in the solution).^[10] According to Faraday's Law it determines the amount of dissolved metal ions from anode. Besides this, it also affects size growth and morphological structure of produced flocs, thus improving destabilization of the emulsion.^[3]

$$m_{metal} = \frac{i \times t \times M}{n \times z} [g]$$

Higher applied current also increases amount of produced H_2 on cathode and reduce the size of its bubbles, which have positive influence on flotation of flocs.^[3]

On the other hand, higher values of applied current may have negative impact on the efficiency of the process, mainly because of reactions on anode when O_2 is produced instead metal ions and generation of heat. Higher values of current also decrease the life of electrodes (passivation) and increases total cost of the operation (depending on the conductivity of solution) so the optimal value of current density should be determined for specific treated wastewater.^[3] *Effect of pH*

Initial pH of solution has significant effect affecting the effectiveness of EC process. According to ^[5]the optimal value of pH during EC is 5 – 9. While in this range, most species generated by electrolysis are polymeric hydroxyls or amorphous hydroxides, which have the best ability to destabilize O/W emulsion. Outside this range more monomeric species of metal captions are formed, and as it was described they do not have ability to successfully break down the emulsion.^[5]

Material and methods

The aim of this paper was to choose the optimal values of some parameters of EC process i.e. type of salt, amount of salt added to solution and electric current applied on the electrodes (current density). Total organic carbon (TOC) was chosen as monitored parameter.

Electrocoagulation process was carried out in the batch reactor consisting of glass cylindrical vessel (V=0,55I, d=10cm) which contains 0,4l of treated MWF.Electric current from adjustable DC power supply *BK Precision 1696* (V=0–20V, I=0–10A) was applied to pair of electrodes, connected in monopolar mode. Power supply was connected to PC via RS-232 port to log out parameter values to worksheet. This allows continuous measuring of passing electrical current, voltage and output power, which can be used for evaluation of costs.

Pair of aluminium electrodes was used in this test. Dimensions of the electrode were $100 \times 40 \times 2$ mm, with total area of $0.00856m^2$. Total active area (area immersed in the solution) was $0,00302 \text{ m}^2$. After 5 runs the polarity of current was inverted to prevent the passivation of the electrodes. After each run electrodes were cleaned with acetone, rinsed in distilled water and dried in order to be weighed out, so the weight reduction can be determined. Gap between electrodes was set to 10mm. Solution was stirred by magnetic stirrer. Each run lasted for 15 minutes.

TestedMWF was prepared as O/W emulsion (5%/95% tap water), without adding any others additives. Initial pH of the solution was 8,5 which is in the range proposed to be most efficient for EC process. Sample of nontreated MFW was taken to measure initial TOC on TOC Analyzer V-CPN. Initial concentration of TOC (without added salt) in solution was 40065 mg. l^1 .

Results and discussion

Type and amount of the salt

In first experiment, two different types of salts (NaCl. KCl) weretested to increase the conductivity of treated MWF.Required quantity of salt was weighted on analytical balance Satorius BP 110S. Salt was added to the solution and stirred for 5 minutes to dilute completely. Weight of added salt was 1 g. I^{-1} , 2.5 g. 1^{-1} , 5 g. 1^{-1} , 7.5 g. 1^{-1} and 10 g. 1^{-1} (0.4 g, 1 g, 2 g, 3 g and 4 g per 400ml of solution). Applied electric voltage and current was set to 20V and 7.5A, which represent the



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current density of i=0,25 $A.cm^{-2}$. After electrocoagulation, solution was left standing still for 24 hours due to the sedimentation of generated flocs. After 24 hours sample of treated solution was collected to evaluate TOC. Fig.1 shows the dependence of TOC concentration on the concentration of added salt.



Figure 1 TOC concentration with different doses of NaCl and KCl

Optimal concentration of added salt was 7.5 g.l⁻¹, at which the concentration of TOC decreased to 5637 mg.l⁻¹ for NaCl, and 5465 mg.l⁻¹ for KCl. Higher dose of salt (10 g.l⁻¹) was ineffective, as the decrease of TOC concentration was negligible. Figure 2 shows treated MWF with different doses of NaCl. Figure 3 shows treated MWF with different doses of KCl.



Figure 2 MWF treated with EC with different doses of NaCl



Figure 3 MWF treated with EC with different doses of KCl



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Effect of applied electric current

In the next set of measurements, effect of applied current on TOC concentration was investigated. 400 ml of chosen MWF was poured into the five reactors. Small sample of it was collected to measure the initial TOC concentration. 7,5 g.l⁻¹ (3 g per 400 ml) of NaCl was added to each sample a nd then stirred for 5 minutes to completely dilute. Every sample was treated for 15 minutes with different current applied on electrodes. Applied currents were 1 A, 3 A, 5 A, 7 A and 9 A. Treated MWFs were left standing still for 24 hours and the samples were taken subsequently to determine TOC concentration. Effect of applied current is shown on Figure 4.



Figure 4 Effect of applied electric current on TOC concentration

Graph shows that with increasing current there is decrement in TOC concentration of solution up to the value of current of 5A. TOC concentration is merely the same for higher values of current (7A, 9A). Therefore, current of 5A is most effective due to the lower operational costs and longer lifetime of electrodes.

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