THE INFLUENCE OF ELECTRODE COMBINATIONS ON THE KINETICS REMOVAL OF ORGANIC SUBSTANCES FROM THE PRINTING EFFLUENT

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Abstract
In this research, the electrocoagulation/flotation (ECF) reaction kinetics of organic substances removal from the waste fountain solution was investigated. The ECF reaction kinetics of the organic substances removal from the printing effluent can be described by a pseudo-second rate equation. Obtained results have shown that the trend of decrease in pseudo-second order constant for organic substances removal follows the trend of decrease in the efficiency of electrode combinations (Fe(-)/Al(+) > Al(-)/Fe(+) > Al(-)/Al(+) > Fe(-)/Fe(+)) and current density (8 > 4 > 2 mA cm^{-2}) of the ECF treatment.

Key words: Electrocoagulation/flotation, waste fountain solution, kinetics

Introduction

The environment is, due to the technological development of the offset printing production, being faced with an extensive amount of printing waste and later with the problem of their disposal. The offset printing wastes may contain various inorganic and organic pollutants, potentially dangerous to the environment, which comes from dyes and pigments, fillers, stabilizers, varnishes, adhesives, etc. [1].
Sheet-fed offset printing process is based on the interaction of printing ink and fountain solution with the process materials. The fountain solution usually contains plate preservative agents, wetting agents, isopropyl alcohol or glycol-based surfactants, buffer substances, and antimicrobial additives [2]. After the printing process, the fountain solution changes its chemical composition due to direct contact with different printing materials (plates, inks, paper, etc.) and becomes enriched by metals, dust consisting of paper fibers and fillers, and organic compounds from printing inks and surface coated offset plates. Following current ecology standards, the offset printing effluents must be adequately treated before they are flushed into the sewage system or a natural recipient.
ECF technique has many advantages when compared to the conventional methods: easier operation, simpler equipment, lower retention time, better safety, selectivity, flexibility, cost effectiveness, and lower sludge production [3]. Also, ECF treatment has been an environmentally friendly process implemented to remove different types of pollutants (dyes, heavy metals, organic substances, etc.). The ECF process involves three successive stages [4]:

1. Production of coagulants in “in situ” by electrolytic oxidation of the sacrificial electrodes;

2. Destabilization of the contaminants or particulates suspension and breaking of emulsions by insoluble hydroxides;

3. Aggregation of destabilized phase and formation of flasks.

As well, the ECF process can be described as equations (1) - (3)[5, 6]:

At the anode:

$$M \rightarrow M^{n+} + ne^{-} \quad (1)$$

At the cathode:

$$nH_2O + ne^{-} \rightarrow n/2\ H_2 + nOH^{-} \quad (2)$$

Where M is the anode of aluminum or iron and n is the stoichiometric number of electrons within the oxidation or reduction reaction.

Soluble metal (Fe or A1) ions (produced at the anode) react with the hydroxide ions (formed at the cathode) and generated insoluble hydroxides (equation (3)) that adsorb the pollutants and eliminate them from the solution.

$$M^{n+} + nOH^{-} \rightarrow M(OH)\ n \quad (3)$$

The literature shows that the kinetic studies of the ECF treated different types of wastewaters have been conducted in order to study the rate of removal of organic pollutants as well as the impact of the ECF operational variables (current density, interelectrode distance, etc.) on reaction rate constant [6, 7, 8, 9, 10].

In this paper, a kinetic study of the ECF treatment was performed to define the rate of removal of organic substances from the waste fountain solution. Also, the correlations between the reaction rate constant and electrode combinations were examined.

Experimental

ECF treatment of waste fountain solution

Four sets of the ECF experiments have been performed with different electrode combinations: (1) four iron electrodes (Fe(-)/Fe(+)), (2) four aluminum electrodes (Al(-)/Al(+)), (3) two aluminum (one was anode) and two iron electrodes (Al(-)/Fe(+)), and (4) two iron (one was anode) and two aluminum electrodes (Fe(-)/Al(+)). The electrodes were prepared appropriately to ensure electrode surface reproducibility. Before each run, the electrode surface has: (i) mechanically polished with abrasive paper, (ii) rinsed with deionized water, (iii) immersed for 10 min in a 5M solution of hydrochloric acid (35%), (iv) washed again with deionized water, (v) and dried [3].

The total area of electrodes is 100 cm^2 (the effective area being 40 cm^2) and the gap between the electrodes is 0.5 cm. Electrodes are connected in a bipolar mode to a digital DC power supply (DF 1730LCD) equipped with potentiostatic or galvanostatic operational options. The ECF process was carried out at a current density of 2, 4 and 8 mA/cm^2. The ECF unit is made of borsilicate glass with the volume of 250 cm^3. 220 cm^3 of waste fountain solution has been stirred at 150 rpm by a magnetic stirrer (IKA color squid). 15 cm^3 of electrolyte samples have been taken at a particular operating time (1, 5, 10, 20, 40 and 60 minutes). All collected samples have been centrifuged for 10 minutes at 2000 rpm. Supernatant has then been used for

the analyses of organic substances quantities. The content of organic substances present in waste fountain solution is determined by measurement of UV_{326} absorbance.
The UV_{326} absorbance measurements of organic substances have been performed before and after the ECF treatment in accordance with standard methods [11] by UV-1800 SHIMADZU spectrophotometer at a wavelength of 326 nm with a 1 cm quartz cell.

The kinetic study of the ECF treatment
The reaction rate of organic substances removal from the waste printing effluent by applying the ECF treatment can be presented as an equation of the *n*-order rate (1) [6, 7]:

$$\frac{dC}{dt} = -k \cdot C^n \qquad (1)$$

Where: C – content of organic substances, n - reaction order, k – reaction rate constant, and t – operational time of the ECF treatment. For the reactions of the pseudo-first and pseudo-second order of organic substances removal from the waste fountain solution by the ECF treatment, the equation (1) turns into equations (2) and (3), respectively, by integration:

$$\ln\left(\frac{C_t}{C_o}\right) = -k_1 \cdot t \qquad (2)$$

$$\frac{1}{C_t} - \frac{1}{C_o} = k_2 \cdot t \qquad (3)$$

Where: C_o – the initial content (the absorbance at λ = 326 nm) of organic substances in the waste fountain solution before the ECF treatment, C_t – content of organic substances in the waste fountain solution at a particular ECF time t (min), k_1 – reaction speed constant of the pseudo first-order rate (min^{-1}), and k_2 – the pseudo second-order rate constant (min^{-1}). The value of the constant k_1 is calculated from the slope of the plot of dependence $ln(C_t/C_o) = f(t)$. The slope of the plot of dependence $1/C_t = f(t)$ determines the constant k_2.

Results and discussion
The rate of organic substances removal from the ECF treated waste fountain solution can be expressed by a pseudo-second order equation [9, 10]. The results obtained in the kinetic study point out that the pseudo-second order rate constants for organic substances removal with tested electrode combinations decrease as the efficiency of electrode combinations decreases: k_2 for Fe(-)/Al(+) > k_2 for Al(-)/Fe(+) > k_2 for Al(-)/Al(+) > k_2 for Fe(-)/Fe(+). It can also be seen that kinetic constants of pseudo-second order for organic substances removal follow the trend of decrease in organic substances removal efficiency with current density (8 > 4 > 2 mA cm^{-2}) (Figure 1). According to the literature, [12, 13] data k_2 increases together with the increase in current density because by increasing the current density coagulant forming reaction rate is also increased, as well as the rate constant. Thus for the most efficient Fe(-)/Al(+) electrode combination, interelectrode distance of 0.5 cm and increase in current density from 2 to 8 mA cm^{-2}, k_2 value for the removal of organic substances from the ECF-treated waste fountain solution are in the interval from 1,42 10^{-3} to 1,53 10^{-3} min^{-1}. The dependences of the plot $ln(C_t/C_o) = f(t)$ are linear with correlation coefficients R^2 at intervals:

from 0.95 to 0.98 for Fe(-)/Al(+), from 0.93 to 0.97 for Al(-)/Fe(+), from 0.94 to 0.97 for Al(-)/Al(+), and from 0.93 to 0.95 for Fe(-)/Fe(+) combinations of electrodes.

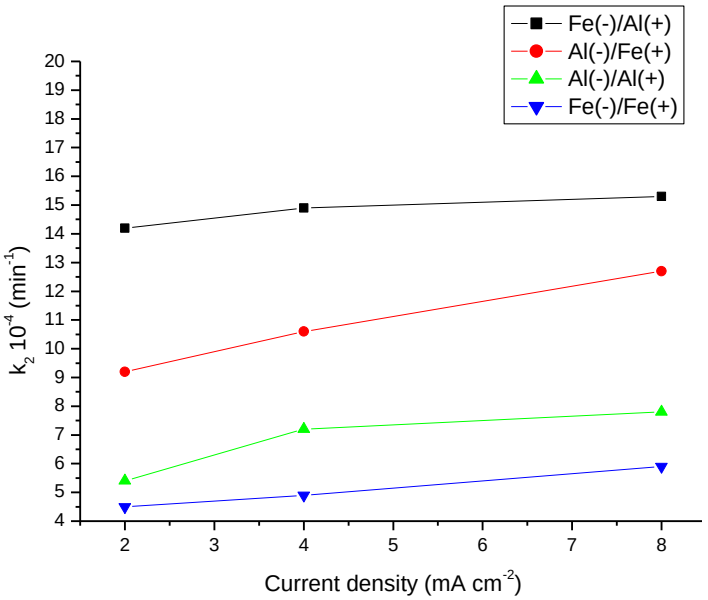

Figure 1. The pseudo second-order rate constant at current densities of 2, 4 and 8 mA cm^{-2} (four electrode combinations and interelectrode distances of 0.5 cm)

Conclusion

The rate of organic substances removal from the ECF-treated waste fountain solution can be expressed by a pseudo-second order equation. Also, the results obtained have shown that the trend of decrease in pseudo-second order rate constant for organic substances removal follows the trend of decrease in the efficiency of electrode combinations and current of the ECF treatment. Thus, for the highest ECF efficiency of the organic substances removal from the waste fountain solution under the best operational conditions (Fe(-)/Al(+), 8 mA cm^{-2} and 0.5 cm) the highest ECF reaction pseudo-second order rate constant is also obtained.

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