Removal of Copper Ions Present in Waste Offset Printing Developer by Electrocoagulation–Electroflotation Process

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Abstract: *The offset printing processes produce large amounts of waste liquids (printing developers, fountain solution, cleaning solvents and inks) which can be damaging for the environment if not monitored in the appropriate manner. The application of electrocoagulation–electroflotation process helps monitor the concentration levels of copper ions in waste offset printing developer. Purpose of this study was to investigate the effects of current density on removal of copper ions from a waste offset printing developer in the batch electrocoagulation–electroflotation process. The electrochemical process was investigated at current densities of 2, 4 and 8 mA/cm2 (corresponding to 0.08, 0.16 and 0.32 A, respectively) for the contact time of 1, 5, 10, 20, 40, and 60 minutes, respectively. The results show that, for a given time, the removal efficiency of copper ions increases significantly with the increase of current density. The current density of 2 mA/cm2 produces the slowest treatment with 90.18% of copper ions reduction which occurs after only 20 minutes. The removal efficiency of copper ions at a current density of 4 mA/cm2 was 92.44% after 10 minutes. The kinetics of electrocoagulation–electroflotation process at a current density of 8 mA/cm^2 is very fast (5 minutes), and the removal rate reached 92.02%. The electrocoagulation–electroflotation process was successfully applied to the purification treatment of waste offset printing developer where an effective reduction of copper ions concentration under prescribed limits was obtained. The conclusion has been drawn that the electrocoagulation–electroflotation process has a future as a printing effluents treatment technology.*

Keywords: *Electrocoagulation–electroflotation process, offset printing developer, waste, copper ions*

1. Introduction

Offset printing is clearly the most competitive and relevant printing activity. It is also the most attractive to new investors, mainly due to its versatility, speed, quality and cost-effectiveness [1, 2]. The offset printing process can be classified into three modules, namely pre-printing, printing and post-printing. All these steps generate waste streams: volatile organic compounds (evaporated from the developing baths, solvents and inks), other mainly waste chemicals such as offset printing developers, fixer or ink residues, polluted water from washing, dirty wiper and hazardous solid waste (empty cartridges and used contaminated metallic and plastic containers). As hazardous waste producers, the offset printing sites should apply measures that would primarily be focused on monitoring and prevention and then on preparation for re-use [1]. Abiding by the requirements, the life of offset printing developer baths can be extended by adding specific chemicals which control the pH of the solution and make up the offset printing developer for its re-use. On the other hand, ion exchange resins can be used to remove halide ions and to regenerate the waste offset printing developer. Furthermore, the electrocoagulation–

electroflotation systems have been successfully employed in removing metals, suspended particles, clay minerals, tannin and organic dyes, and oils and greases, from a variety of industrial effluents. In this process, a potential is applied to the metal anodes, typically made out of either iron or aluminum [3, 4]. The advantages of electrocoagulation–electroflotation include high particulate removal efficiency, compact treatment facility, relatively low cost, and a possibility of complete automation [5].

The application of electrocoagulation–electroflotation process helps monitor the concentration levels of copper ions in the waste offset printing developer. The purpose of this study was to investigate the effects of current density on removal of copper ions from a waste offset printing developer in the batch electrocoagulation–electroflotation process.

2. Materials and Methods

2.1. Waste offset printing developer

The waste offset printing developer was collected from the offset printing facility in Novi Sad, Republic of Serbia. The main characteristics of the waste offset printing developer used in this research are presented in Table 1. A digital calibrated pH-meter (EC30 pH meter) and a conductivity-meter (Cond 3210 conductimeter) were used to measure the pH and the electrical conductivity of the waste offset printing developer.

Table 1: Characteristics of waste offset printing developer

Characteristics	Value
t [°C]	25±1
pH	11.81
Electrical conductivity [mS/cm]	0,77
Electrical conductivity [mS/cm] with NaCl	16,31
C(copper ions) [mg/L]	23,95

2.2. Electrocoagulation–electroflotation procedure

The experiment was conducted in an electrocoagulation cell, with the capacity of 250 mL, made out of borosilicate glass. The electrodes used in this study consisted of aluminum plates of 99% purity. Plates' dimensions of 100 mm in length, 50 mm in breadth and 1 mm of thickness provided an effective electrode area of 40 cm2. The gap between the electrodes has been maintained at 4 mm. The electrodes were connected to a digital DC power supply (DF 1730LCD).

Before each run, the aluminum electrodes were mechanically polished with abrasive paper, rinsed with distilled water, dried and dipped for 10 min in a 5 M solution of hydrochloric acid.

All measurements have been carried out at the ambient temperature (25±1°C), with 220 mL aliquots of waste offset printing developer into which 0.5 g of potassium chloride has been added. The addition of halide salts will: (1) avoid excessive ohmic drop, (2) limit the formation of the passivation layer on aluminum electrodes, (3) decrease the energy consumption and (4) limit the temperature variations, due to the Joule effect [6].

To follow the progress of the electrocoagulation–electroflotation treatment, samples of 15 mL were periodically taken from the electrocoagulation cell at a certain operating time (1, 5, 10, 20, 40 and 60 minutes). All collected samples were centrifuged for 10 minutes at 2000 rpm.

2.3. Analytical procedure and calculation

The residual concentrations of copper ions have been determined by atomic absorption spectrophotometer (PerkinElmer, model Analyst 700).

The percentage removal efficiency of copper ions (E) was evaluated by the following equation [7]:

$$E\,(\%) = \frac{C_0 - C_t}{C_0} \cdot 100 \qquad (1)$$

Where C_0 - initial concentration of copper ions in waste offset printing developer, C_t - concentration of copper ions at a certain operating time (1, 5, 10, 20, 40 and 60 minutes).

3. Results and Discussion

Three batch electrocoagulation–electroflotation treatments have been carried out at appropriate current densities (2, 4 and 8 mA/cm^2). The densities have been kept constant for different operating times of 1, 5, 10, 20, 40 and 60 minutes.

The current density represents the amount of current per area of the electrode. Current density not only determines the amount of aluminum coagulant produced in the electrocoagulation–electroflotation process but also affects the reducing reaction of copper ions. The results showed that as current density increases, reduction and removal of copper ions also increases (Table 2).

Table 2: Percentage of copper ions removal during electrocoagulation–electroflotation process while using aluminum electrodes at 2, 4 and 8 mA/cm^2 (Initial concentration = 23.95 mg/L)

Current density (mA/cm^2)	Parameter of removal	Operating time (min)					
		1	5	10	20	40	60
2	C(copper ions), mg/L	21.12	14.89	11.74	2.35	1.95	1.83
	E, %	11.82	37.82	50.98	90.18	91.86	92.36
4	C(copper ions), mg/L	20.12	13.90	1.81	1.76	1.58	1.43
	E, %	15.99	41.96	92.44	92.65	93.40	94.03
8	C(copper ions), mg/L	18.99	1.91	1.53	1.44	1.40	1.29
	E, %	20.71	92.02	93.61	93.99	94.15	94.61

These results can be attributed to the fact that, according to Faraday's law, increasing the current density increases the dissolution rate of aluminum electrode with the formation of Al^{+3} and hence also with the formation of $Al(OH)_3$ coagulant according to the following reactions:

$2Al \longrightarrow 2Al^{3+} + 6e$ (anode at alkaline conditions) (2)

$6H_2O + 6e \longrightarrow 3H_2 + 6OH^-$ (cathode) (3)

$2Al^{3+} + 6OH^- \longrightarrow 2Al(OH)_3$ (4)

The overall:

$Al + 3H_2O \longrightarrow Al(OH)_3 + 3/2H_2$ (5)

A higher rate of freshly formed amorphous $Al(OH)_3$ have a large surface area on which rapid adsorption of copper ions and trapping of colloidal particles take place with a consequent removal of copper ions from wastewater. The cathodically evolved H_2 bubbles make the $Al(OH)_3$ along with the adsorbed copper ions float to the upper surface of the solution [4, 8].

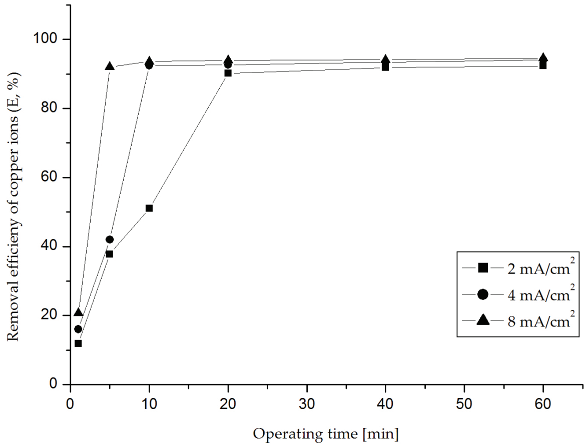

Figure 1: Effect of current density on the percentage of copper ions removal

Figure 1 shows that the current density of 2 mA/cm^2 produces the slowest treatment with 90.18% of copper ions reduction which occurs after only 20 minutes. The removal efficiency of copper ions at a current density of 4 mA/cm^2 was 92.44% after 10 minutes. The kinetics of electrocoagulation–electroflotation process at a current density of 8 mA/cm^2 is very fast (5 minutes), and the removal rate reached 92.02%.

The regulation of emission limit values of pollutants into water and deadlines for their achievement [9] proscribes the maximum allowed concentrations (MAC) for copper ions (1 mg/L). It is evident that the concentrations of copper ions in the waste offset printing developer before the electrocoagulation–electroflotation treatment are almost 24 times higher than the MAC values. At the end of the electrocoagulation–electroflotation process (60 minutes) at current densities of 2, 4 and 8 mA/cm^2 the values of copper ions concentration are almost 1.83, 1.43 and 1.29 times higher than the MAC values, respectively.

It is necessary that the efficiency of the electrocoagulation–electroflotation process for copper removal is higher than 96% for concentration values of copper ions below the MAC. This can be achieved by increasing the operating time of the electrocoagulation–electroflotation or the current density. The downside of the increase of the operational parameters was the increased loss of electricity and heating of waste offset printing developer. Perhaps a combination of electrocoagulation–electroflotation treatment increased the adsorption efficiency of removal of copper below 1 mg/L.

4. Conclusion

The results of this study have shown the applicability of electrocoagulation–electroflotation in the treatment of waste offset printing developer containing copper ions with initial concentration of 23.95 mg/L. The electrocoagulation–electroflotation process was successfully applied to the purification treatment of waste offset printing developer where an effective reduction of copper concentration (92.36, 94.03 and 94.61% at current densities 2, 4 and 8 mA/cm^2, respectively) close to MAC values has been obtained.

The waste offset printing developer must not be directly discharged into the sewage system or the environment, and it can be prepared for re-use in the development process application by electrocoagulation–electroflotation process. In the future, a combination of electrocoagulation–

electroflotation process for treatment of waste offset printing developer with other purification techniques such as adsorption could achieve removal efficiency of copper ions higher than 96%.

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5. References

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