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Measurement of copper deposition by electrocoagulation/flotation from waste printing developer

Savka Adamović [a], Miljana Prica [a,*], Božo Dalmacija [b], Marijana Kragulj Isakovski [b], Đurđa Kerkez [b], Sanja Rapajić [c], Dragan Adamović [d]

[a] University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia
[b] University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia
[c] University of Novi Sad, Faculty of Sciences, Department of Mathematics and Informatics, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia
[d] University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering and Occupational Safety and Health, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia

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ABSTRACT

The electrocoagulation/flotation treatment (ECF) was employed for the reduction of copper from the waste printing developer in a batch study by using four different aluminum and iron electrode combinations with independent ECF parameters such as current density, interelectrode distance and operating time. The individual and interactive effects of the three main independent ECF parameters were studied by using the response surface methodology. Based on the results, parameters for high copper removal efficiency (95.5%) from the waste printing developer by the ECF were: Al(−)/Al(+) electrode combination with an interelectrode distance of 1.0 cm, operating time of 10 min and a current density of 4 mA cm^{-2}. Moreover, the kinetic study of the ECF treatment of waste printing developer demonstrated that the removal of copper follows the pseudo second-order model with current dependent parameters. For immobilization process of copper in waste ECF sludge, the solidification/stabilization (S/S) treatment was conducted with Portland cement, lime, bentonite, and local clay as immobilization agents. The efficiency of the S/S treatment was monitored by applying leaching tests with one extraction fluid during a certain time. Therefore, using ECF and S/S treatments, copper from the printing effluent can be safely disposed into the environment.

1. Introduction

Industrial wastewater pollution has become one of the most serious environmental problems today [1]. The offset printing process generates waste chemicals such as printing developer, fountain solution, solvents, inks, fixer or ink residues, and polluted water from washing. As hazardous waste producers, the offset printing sites should install measures that would primarily be focused on monitoring and prevention of pollutants, and then on the preparation of waste chemicals for re-use [2]. In the plate development process, the offset printing developer changes and becomes enriched by the chemicals that are present on the plate surface, i.e. various organic binders, photosensitive compounds [3] and heavy metals, which are part of the offset plate and it is transformed into the complex printing effluent.

Heavy metals (chromium, cadmium, copper, zinc, and nickel) are contained in industrial waste, which pollutes the environment and strongly affects human health. According to USEPA, copper is a priority pollutant which finds its way to aquatic ecosystems through wet or dry deposition, mining activities, land runoff, and industrial, domestic and agricultural waste disposal [4]. The separation techniques of heavy metals from the industrial wastewater include precipitation, ion exchange, adsorption, electro-dialysis, and filtration [5,6]. The ECF treatment has often been taken into consideration for the removal of heavy metals (chromium, copper, nickel, and zinc) from liquid wastes by using sacrificial electrodes of aluminum or iron [7–12]. Copper has been removed with high efficiency from a dilute industrial effluent in an electrochemical reactor with plate electrodes [8,13–15].

The characteristics of the ECF process are: (i) simple equipment and easy operation, (ii) brief reactive retention period, (iii) decreased or negligible equipment for adding chemicals, (iv) the decreased amount of sludge [9,16,17], (v) versatility, (vi) safety, (vii) selectivity, (vii) amenability to automation, (ix) environmental

* Corresponding author.
E-mail address: miljana@uns.ac.rs (M. Prica).

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compatibility, and (x) low operational and investment costs [14,17]. All of these advantages of the ECF when compared to the conventional methods have determined our application of the ECF treatment for the removal of copper from the waste printing developer. On the other side, the review of scientific literature data points to the fact that insufficient attention has been paid to the treatment of offset effluents, such as waste printing developer, or effluents of other printing techniques. In compliance with current environmental standards and to avoid or reduce offset printing pollution of the environment, the offset effluent must be treated appropriately before being discharged into the sewage system or the recipient in nature (water, land, etc.). Therefore, the ECF treatment was for the first time applied to remove copper from the waste printing developer and to obtain a waste offset product with a minimised environmental impact. The innovation point of the ECF treatment used for copper purification of waste printing developer has not been evaluated solely by the efficiency of the method, but also the mechanism of copper removal has been defined as well as the optimisation of the operational variables of the process itself.

In the ECF process, electro-dissolution of the sacrificial anode (aluminum or iron) into the wastewater leads to the formation of hydrolysis products (hydroxo-metal species) that are effective in the destabilization of pollutants and/or in the formation of particles with reduced solubility that entrap the pollutants. Also, the electrochemical reduction of water in the cathode produces the formation of hydrogen bubbles that promote a turbulence in the system, bond with the pollutants decreasing their relative specific weight and float together with them to the upper surface of the solution [18,19]. In summation, the ECF process involves three main mechanisms for pollutant removal, i.e. electrode oxidation, gas bubble generation, and flotation and sedimentation of formed flocs [20].

Some publications have shown the effectiveness of response surface analysis modeling for metal (copper, mercury and chromium) removal [4,21–25]. The response surface methodology (RSM) is a collection of mathematical and statistical techniques for designing experiments, building models, evaluating the effects of several factors, searching the optimum conditions for specified responses [18,26] and performing the minimum number of experiments. This technique confirms the closeness of the practical results when compared to theoretical models as it arises from an experimental methodology [1].

The amount and the composition of printing wastes depend on raw materials used, process techniques applied and properties to be achieved [27]. Waste printing materials are most often not geochemically stable and safe to the environment and need to be treated before their disposal. One of the most often used treatments for the heavy metal waste is solidification/stabilization (S/S). That is why an assessment of potential risk of waste pollutants released during the different phases of their exposure to environmental conditions is necessary. In order to evaluate the efficiency of the treatment and potential risks of waste to human health and the environment, it is necessary to conduct leaching tests. The main goals of the leaching tests are [28,29]: (i) classification of hazardous and non-hazardous waste, (ii) assessment of the leaching potential of waste pollutants in environmental conditions, (iii) simulation of conditions which facilitate leaching, (iv) getting samples that represent the quality of leaching water originating on landfills, (v) assessment of the waste treatment efficacy, (vi) identification of a suitable scenario of waste management, and (vii) determining the kinetic parameters for pollutant transport modeling.

The offset printing process is arguably the most common of all printing processes and produces large amounts of waste printing developer during the plate developing process. As the waste printing developer contains significant amounts of copper, it needs to be suitably treated before being discharged into water and soil recipients or sewerage system. The main objective of this study was deposition of copper from the offset effluent and its translation into a non-hazardous form that is safe for disposal in the environment by using for the first time the ECF and S/S treatments. The additional objective of this research is to investigate and optimize the individual and interactive effects of process parameters, such as electrode combinations, current density, interelectrode distance, and operating time, on the removal efficiency of copper from the waste printing developer by the ECF treatment while also utilizing the RSM. Also, a kinetic study of the ECF treatment has been performed to define the rate of copper removal and research the correlation between the reaction rate constant and operational variables (electrode combination, interelectrode distance and current density). Additionally, during the ECF treatment of the waste printing developer, the sludge with removed copper is formed as a byproduct. To solve the problem of the disposal of sludge formed after the ECF treatment of the waste printing developer, the S/S treatment with Portland cement, lime, bentonite, and local clay as immobilization agents were applied. The efficiency of the S/S treatment of the waste printing developer sludge were defined by the application of single-extraction leaching tests (standard German (DIN 38414–4) and Toxicity Characteristic Leaching Procedure (TCLP)) to ensure that the results obtained are in accordance with the maximum permissible concentrations according to current regulations.

2. Methods and materials

2.1. The waste printing developer

The waste printing developer was taken from the offset printing facility in Novi Sad, Republic of Serbia. In the plate development process, the fresh developer (FUJI FILM LP-DS) was dispensed in quantities of 100 mL per m^2 of the plate (Brillia LP-NV). After the development process, the obtained waste printing developer was cumulatively collected in containers of 20 L. The initial concentration of copper (23.95 mg L^{-1}), pH value (11.8), temperature (25.4 °C), and electrical conductivity (16.31 mS cm^{-1}) of the waste printing developer were measured before the ECF process. Heavy metal analyses were carried out by the Atomic Absorption Spectroscopy (PerkinElmer Aanalyst 700, USA) according to the standard EPA 7000B method [30]. The concentration of other metals (chromium(total), nickel, cadmium, zinc, and lead) was below the method detection limit (MDL). A digital calibrated pH-meter (EC30 pH meter, USA) and a conductivity-meter (Cond 3210 conductometer, Germany) were used to measure the pH value and the electrical conductivity of the waste printing developer.

2.2. The ECF treatment of the waste printing developer

The ECF unit is made of borosilicate glass with the volume of 250 mL. Four plate aluminum or iron electrodes with the same dimensions of 10 cm × 5 cm × 0.1 cm and with a total area of 100 cm^2 were used. In each batch treatment, the electrode surface was first mechanically polished with abrasive paper [31] in order to ensure surface reproducibility, rinsed with distilled water, and dried before the immersion in the electrolyte. The oxide and passive layers on the surfaces of aluminum were removed by dipping the electrodes for 10 min in a 5 M solution of hydrochloric acid [32].

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