The Combined Electrocoagulation/Flotation and Adsorption Processes for Organic Substances Regeneration of Waste Printing Developer

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Abstract
This paper investigates the possibility of reducing the content of organic substances in waste printing developer using a combination of electrocoagulation/flotation (ECF) and adsorption (AD) processes. The content of organic substances in waste printing developer was monitored by analysis of total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD_5) before and after the ECF and AD processes, respectively. When combining the two processes, a removal of 99.4, 92.9 and 96.0% of the TOC, COD and BOD_5 was achieved, respectively. Obtained results confirm the improvement in the printing industrial effluent quality and height removal of organic substances by the combined ECF and AD treatments.

Keywords: electrocoagulation/flotation, adsorption, treatment, organic substances

Introduction
The ECF process involves the passage of an electric current into the reaction cell using sacrificial aluminum or iron electrodes. The generation of the metal ions takes place at the anode by dissolving electrically metal electrodes. These ions, at an appropriate pH, can form wide ranges of coagulated species such as corresponding aluminum or iron hydroxides and/or polyhydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Also, electrooxidation, surface complexation, electrostatic attraction, and chemical modification occur in the ECF reactor. The flocks generated of coagulated species and the pollutants then can be removed using liquid-solid separation methods, such as, settling, flotation, or filtration [1, 2, 3]. The typical benefits of the ECF process are: no liquid chemical is added; alkalinity is not consumed, pH adjustment is not needed, requires less dosage and produces less sludge, the space required for apparatus is smole because ECF does not require chemical storage, dilution, and rapid mixing, short reaction time (few minutes), oxidation or reduction of much pollutant, coagulation and flocculation of finest colloids and economic advantages [1, 2].
Research has shown that ECF is an effective treatment for removing pollutants from lowland surface water, urban wastewaters, synthetic colloid-polluted wastes, restaurant effluents, metal plating wastes, actual industrial discharges, cardboard paper mill effluents, etc. [3, 4]. Also, ECF was not used for treatment of waste offset printing effluent such as waste printing developer (WPD). As can be see, ECF has a wide application field and it can also be effective for complicated wastewater which contains: heavy metals, oils, turbidity, color, bacteria, algae and microorganisms, tannin, dyes, organic matter (BOD and COD), suspended solids, and colloids [3, 5].
Also, the AD is a very well known, effective and commercially applicable water and wastewater treatment process, which is gaining prominence as a means of reducing inorganic

and organic concentrations in industrial effluents [2, 3, 6, 7]. Adsorption has been found to be superior to other techniques for water and wastewater re-use in terms of the initial cost, simplicity of design, ease of operation and insensibility to toxic substances [8]. Activated carbon is one of the commercially applicable and most effective adsorbent, which are remove different types of dyes, organic and inorganic pollutants such as metal ions, phenols, pesticides, chlorinated hydrocarbons, humic substances, PCBs, detergents, organic compounds which cause taste and odor, and many other chemicals and organisms [7]. Nevertheless, as an individual process for treating effluents, AD requires overdoses of the adsorbent. In addition, the regeneration of the activated carbon is very complicated and expensive [3].

In the recent years, the potential of ECF technology for the treatment of industrial effluents is tried to be even further increased by the synergistic combination with other treatment technologies, such as ozonation, adsorption, ultrasound irradiation, and pulses [6]. Barrera-Díaz et al. [6] reported that the use of an ECF treatment in combination with AD take place within the two systems. In the first system ECF treatment was combined with AD as a pre-treatment step to enhance AD capability of adsorbents. Also, this coupling technology has been studied in systems in which an adsorbent used for the fast removal of pollution from wastewater is continuously regenerated using electrolysis.

Materials being used in the printing industry are very diverse and complex and they influence the quality of printing products to a great extent. The knowing of the structure and characteristics of the materials and their exploitative properties conditions the choice of the optimal technological procedure in the printing industry [9]. Also, the characteristics of the waste printing materials have a major impact on the environment. The WPD is expected to contain residual ingredients and products present in the offset plate surface such as organic binders and photo-sensitive compounds. Also, in the preservation process, plate is covered with a thin solution of "*gum arabic*" or similar chemical. These processes resulted in high amount of organic substances witch were originated from plate surfaces and chemicals [10].

The objective of this paper is to investigate the maximum TOC, COD and BOD_5 removal from WPD by combining ECF and AD treatments. The ECF treatment with iron electrodes, as a pre-treatment, was followed by AD of residual organic substances on commercially powder activated carbon (Norit W35).

Experimental

The waste printing developer

In the plate development process, initial printing developer was dispensed in quantities of 100 mL per m^2 of plate. After the development process, the obtained WPD cumulatively was collected in containers of 20 L. The WPD was collected from the offset printing facility in Novi Sad, Republic of Serbia.

The electrocoagulation/flotation treatment of the WPD

The ECF experiments was performed in a batch cell (borsilicate glass of 250 mL) with four plate iron electrodes (dimensions of 10 cm × 5 cm × 0.1 cm) connected in a parallel (bipolar) mode. Only the outer electrodes have been connected to the DC power supply (DF 1730LCD). The current density of 8 mA cm^{-2} was applied for the interelectrode distance of 0.5 cm and operating time of 60 minutes. The ECF treatment was carried out at the ambient temperature (25±1°C), with 220 mL aliquots of the WPD which has been mixed with the 0.5 g of sodium chloride as a conductor. Then the ECF treated WPD was filtered through a set of membrane filtration with Millipore vacuum pump and cellulose nitrate filter (pore size of 0.45μm). Supernatant has then been used for the analyses of TOC, COD and BOD_5. Before each run, iron electrodes have been mechanically polished with abrasive paper, rinsed with distilled water, dried, dipped for 10 min in a 5 M solution of hydrochloric acid, rinsed with distilled water, and placed vertically in the ECF cell [10].

Adsorption treatment of the WPD

The adsorption (AD) treatment were run in duplicate at room temperature (25±1°C)) in 1100 mL plastic bottle. The amount (10 g L^{-1}) of powder activated carbon (Norit W35) was added to 1L of ECF treated WPD. The head space in bottle was kept at a minimum in order to minimize the loss of compounds during the experiment due to evaporation. The amount of adsorbent (10 g) and the equilibration period of 30 minutes were selected based on a preliminary kinetics experiment which was performed with amount of 5, 10, 15 g L^{-1}, respectively, and operating times over 6h. The ECF treated WPD was filtered through a set of membrane filtration with Millipore vacuum pump and cellulose nitrate filter (pore size of 0.45 μm). Supernatant has then been used for the analyses of TOC, COD and BOD_5.

Analytical procedure and calculation

Measurements of TOC were performed after sample acidification with concentrated hydrochloric acid to pH = 2 and membrane filtration with cellulose nitrate filter (pore size of 0.45 μm). The TOC was measured using an Elementar Germany Liqui TocII analyzer, according to SRPS ISO 8245 (2007) method [11]. For COD determination, calculated from the consumption of $Cr_2O_7^{2-}$, SRPS P-IV-10 method was used [12]. The BOD_5 was determined by SRPS EN 1899-1:2009 [13].

The removal efficiencies of investigated parameters (TOC, COD and BOD_5) by ECF or AD treatments were evaluated by the following universal equation [5, 10]:

$$E_X\ (\%) = \frac{X_o - X_t}{X_o} \times 100 \qquad (1)$$

where X_o – the initial values of investigated parameters in the WPD before of certain treatment (ECF or AD), and X_t – the final values of investigated parameters in the WPD after of certain treatment.

Results and discussion

The initial values of TOC, COD and BOD_5 in the WPD and values of investigated parameters after ECF and AD treatments of WPD are presented in Table 1.

Table 1. The values of TOC, COD and BOD_5 in the WPD and before and after ECF and AD treatments

Parameter	WPD	ECF treated WPD	AD treated WPD	Efficiency (%)		
				ECF treatment	AD treatment	ECF + AD treatment
TOC (mg L^{-1})	60800	1740	391	97.1	77.5	99.4
COD (mg L^{-1})	21100	11300	1499	46.5	86.7	92.9
BOD_5 (mg L^{-1})	9400	5350	372	43.1	93.0	96.0

The results indicate that the ECF treatment reduces TOC, COD and BOD_5 values by 97, 46.5 and 43.1%, respectively, which still does not comply with environmental discharge standards. In relation to ECF process, AD process removes almost twice more COD and BOD_5 values. Thus, additional techniques such as AD are needed to improve the quality of the wastewater.

AD process used as a secondary treatment is effective and requires limited amounts of activated carbon. According to Linares-Hernández et al. [4] the use of an ECF treatment as a pre-treatment step to enhance AD capability of adsorbents can be justified if the resulting industrial wastewater quality expressed as color and COD removal is good. Thus, the coupling of electrochemical and adsorption processes might prove a judicious choice for treating industrial wastewater with mixtures of different types of pollutants [4].
The combined ECF and AD processes are able to eliminate TOC, COD and BOD_5 from printing industry effluent, respectively. The overall elimination reaches of TOC, COD and BOD_5 are 99.4, 92.9 and 96.0%, respectively.

Conclusion
The proposed combined ECF (with iron electrodes) and AD (with activated carbon Norit W35) treatmnents used in this study excellent reduces the concentration of organic substances in waste printing effluent. The removal efficiency of TOC, COD and BOD_5 from WPD by combined ECF and AD processes are 99.4, 92.9 and 96.0%, respectively. In the future, the combined effect of ECF and AD treatments could be applied to other effluents of printing industry.

Acknowledgements
The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development, Republic of Serbia (Project No. III43005).

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