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PHYSICO-CHEMICAL EVALUATION AND KINETIC STUDY OF COLOURED PRINTING WASTEWATER PRIOR AND POST- FENTON TREATMENT

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Abstract: *The paper reports removal of organic Black (Key) dye from real printing wastewater using nano zero valent iron particles as a catalyst in Fenton-like treatment. The degradation efficiency of Black diazo dye via Fenton-like treatment is reported to be 61% under established optimal process conditions: $[Fe^{2+}] = 0.75\ mgL^{-1}$, pH = 2, $[H_2O_2] = 1$ mM, within a reaction time of 75 min. The absorption spectra of Black dye clearly indicate that dye degradation is a slow process with difficult decomposition of aromatic structures, due to the cleavage of diazo bonds by hydroxyl radicals. The physico-chemical characterizations (measurements of pH, electrical conductivity, temperature, turbidity, chemical oxygen demand, biochemical oxygen demand, total organic carbon, anionic surface-active substances and phosphorus content) as well as toxicity study (Vibrio fischeri bacteria) revealed the complex nature of printing effluent. Increased conductivity and biochemical oxygen demand content after Fenton treatment imply the formation of various byproducts and intermediates, formed in a solution during dye degradation. The mineralization percentage of Black dye of 58% is followed with 47% of chemical oxygen demand reduction. Results of toxicity test on Vibrio fischeri bacteria indicate that both untreated and treated printing effluents belong to moderate toxic samples with 58% and 67% of toxicity inhibition, respectively. Among three evaluated kinetic models (the first-order, the second-order, and Behnajady–Modirshahla–Ghanbary), experimental results fitted very well to the Behnajady - Modirshahla - Ghanbary model, indicating high initial rate of Black dye degradation.*

Key words: Fenton-like treatment, Black dye removal, physico-chemical characterization, kinetic models, toxicity evaluation

1. INTRODUCTION

The printing industry is considered one of the largest consumers of synthetic dyes and wastewaters from this industry might be overloading water systems with organic and inorganic pollution if not adequately treated (Natarajan, Bajaj & Tayade, 2018; Zhu et al., 2018). Due to extremely complex structure, their removal represents a major challenge in the field of wastewater treatments. Synthetic printing dyes (azo and phthalocyanine), belong to the group of aromatic and heterocyclic compounds which are hardly biodegradable, with a tendency to show carcinogenic and toxic effect (Kale & Kane, 2019; Namgoong et al., 2018). The high consumption of dyes leads to the creation of a large amount of colored effluents that are discharged into water bodies (Karimifard & Moghaddam, 2018; Katheresan, Kasedo & Lau, 2018). The presence of these dyes in effluents, even in very low concentrations, represents a potential problem for ecological systems (Bulgariu et al., 2019). Dyes, in addition to affecting the aesthetic properties and transparency of water bodies, also affect the absorption and solubility of gases, creating very unfavourable anaerobic conditions for photosynthesis and biological activity (Bulgariu et al., 2019; Dojčinović, 2011; Karimifard & Moghaddam, 2018; Natarajan, Bajaj & Tayade, 2018). And to emphasize, the creation of by-products with pronounced negative effects is very much possible during the degradation of dyes (Natarajan, Bajaj & Tayade, 2018).

Achieving complete mineralization and degradation of printing dyes to carbon(IV)-oxide, water and inorganics is very difficult (Karimifard & Moghaddam, 2018; Pavithra et al., 2019). Application of conventional biological treatments is not efficient due to diazo groups in the form of chromophores (Collivignarelli et al., 2019; Xu et al., 2018) Possible solution to treatment of this wastewaters might be advanced oxidation processes (AOPs), i.e. Fenton-like process, which are based on *in-situ* production of highly reactive hydroxyl radicals in the presence of peroxides and ferrous ions (Mirzaei et al., 2017), which have the ability to degrade difficult biodegradable compounds, such as printing dyes are.

Nanomaterials have attracted the attention of many researchers primarily due to their large specific surface area, which makes nanoparticles achieve numerous advantages in the field of chemical catalysis, such as low resistance to diffusion, easy access to reactants, a large number of free active sites and fast development of chemical reactions (Wang et al., 2016). The use of nano zero valent iron (nZVI) particles in AOPs processes achieved certain advantages compared to conventional methods and solved their practical disadvantages, such as the need for the application of a high concentration of iron, the generation of sludge from metal hydroxides after the treatment and, at the same time, the formation of secondary pollution, operation in a narrow pH range, as well as regeneration of the catalyst and the impossibility of its reuse. Thanks to the properties and surface of nanomaterials, numerous studies have proven the success of using nZVI particles as Fenton catalysts (Mukherjee et al., 2016; Pirsaheb et al., 2019). The high efficiency of dye degradation in the presence of nZVI particles is based on electron exchange, since nZVI particles are good electron donors and dye molecules are excellent electron acceptors. The mechanism of dye degradation using the nZVI/H_2O_2 system is based on the generation of hydroxyl radicals through typical Fenton reactions that will attack the chromophore of the dye molecule and cause the cleavage of the bond in the chromophore group. The whole process is accompanied by the decomposition of the auxochromic group, and in the ideal case, complete degradation and mineralization (Raman & Kanmani, 2016).

The current investigation describes the efficiency of Black printing dye removal from real effluent using a Fenton-like treatment under previously established optimal process conditions (iron concentration, pH value and hydrogen peroxide concentration). In order to consider mineralization degree of treated effluents, physico-chemical characterization was carried out by determining the following parameters: pH, electrical conductivity, temperature, turbidity, chemical oxygen demand, biochemical oxygen demand, total organic carbon, anionic surface-active substances and phosphorus content. Three relevant kinetic models were studied to demonstrate the improved performance of the Fenton-like process for dye removal.

2. MATERIALS AND METHODS

2.1 Experimental procedure

Sample of printing wastewater was obtained from one flexographic printing facility in Novi Sad. In the present study, Fenton-like treatment of real printing effluent was carried out according to the procedure described in our previous work (Gvoić et al., 2020), under determined optimal process conditions (iron concentration, pH and H_2O_2 concentration). To assess the Fenton-like efficiency, nZVI (0.75 mgL^{-1}) and H_2O_2 (1 mM) were added to an aqueous solution containing 250 mL printing wastewater, whereby pH value (2) was adjusted using 0.1 M ccH_2SO_4. Reaction system was mixed on a JAR apparatus (FC6S Velp Scientific, Italy) at 120 rpm and constant temperature of 23 °C. Thereafter, aliquots of supernatant were analysed at different time intervals (0 - 180 min) using UV/VIS spectrophotometry (UV-1800 PG Instruments Ltd T80+ UV/VIS, Japan). The residual dye concentration was established immediately by measuring the absorbance of the aqueous solutions at 613 nm and decolourization efficiency of printing wastewater was calculated according to Equation (1):

$$E(\%) = A_0 - A/A_0 * 100 \qquad (1)$$

where: A_0 is the initial absorbance of the aqueous solution sample before Fenton treatment and A is the absorbance of the aqueous solution sample after Fenton treatment.

2.2 Physico-chemical characterization of printing effluent

The physico-chemical characterization of printing effluent before and after Fenton-like treatment included measurement of pH, electrical conductivity, temperature, turbidity, determination of chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon content (TOC), anionic surface-active substances (dodecylbenzene sulfonate - DBS) and phosphorus content. pH value, electrical conductivity and temperature were measured with AD110 Adwa instrument. Turbidity was determined by using the instrument Turb 430 IR WTW. The concentration of organic matter in printing wastewater is determined by measuring COD quantification and TOC according to the standard potassium dichromate volumetric method - SRPS ISO 6060: 1994 and SRPS ISO 8245:2007 method, respectively. Determination of BOD after 5 days at 20 °C was performed with manometric method - H1.002, by using the instrument

Velp Scientifica Italia, Lowibond and WTW. Determination of DBS was measured by the index of methylene blue MBAS spectrophotometric method based on SRPS EN 903:2009. The phosphorus content was determined with spectrophotometric method with ammonium- molybdate according to the SRPS EN ISO 6878:2008. In order to investigate the toxicity of printing effluent and to establish the negative impact on living organisms, standard ISO 11348 method (Water quality - determination of the inhibition effect of water samples on the *Vibrio fischeri* light emission (luminescent bacterial testing)) was applied. Inhibition of *Vibrio fischeri* luminescence is determined by a series of tests, combining the specific volume of the test sample or dilution sample with luminescent bacteria suspension, by using a LUMIStox 300 instrument (Dr Lange GmbH, Germany) and LUMISsoft IV software. The inhibitory effect was measured in water samples, during 30-minute exposure to bacteria at 15 °C, and expressed in %.

2.3 Kinetic experiments

The first-order, second-order and Behnajady - Modirshahla - Ghanbary (BMG) kinetic models were applied to fit the dynamic process of the Fenton-like treatment, which were expressed as Equations (2-4), respectively:

$$\frac{dA_t}{dt} = -k_1 A_t \qquad (2)$$

$$\frac{dA_t}{dt} = -k_2 (A_t)^2 \qquad (3)$$

$$\frac{A_t}{A_0} = 1 - \left(\frac{t}{m+bt}\right) \qquad (4)$$

where: A_0 and A_t are the initial dye absorbance, i.e. the dye absorbance in a certain time period t, k_1 and k_2 are the rate constants of the first- and second-order, whereas b and m are the BMG model constants related to the reaction kinetics and oxidation capacity, respectively.

The parameters of the kinetic models for the removal of Black dye under optimal process conditions were calculated using the linear forms of the first- and second-order kinetic models, as well as the BMG model (Equations 5 - 7):

$$A_t = A_0 * e^{-k_1 t} \qquad (5)$$

$$\frac{1}{A_t} = \frac{1}{A_0} + k_2 t \qquad (6)$$

$$\frac{t}{1-\frac{A_t}{A_0}} = m + bt \qquad (7)$$

Calculated kinetic parameters were further used to interpret the kinetics of the observed reactions by plotting the linear graph of ln (A_0/A_t) versus time for the first-order model, ($1/A_t$) versus time for the second-order model and t/1 - (A_t/A_0) versus of time for the BMG model.

3. RESULTS AND DISCUSSIONS

3.1. Optimized Fenton-like treatment of printing wastewater

Decolourization efficiency of Black dye from printing wastewater by the applied Fenton-like process under optimal process conditions is presented in Figure 1a. The maximum treatment efficiency of 60.63% was achieved after 75 minutes. Figure 1b presents the UV/VIS spectrum of printing effluent, as a change of peak intensity, in a function of applied Fenton treatment under optimized process conditions.

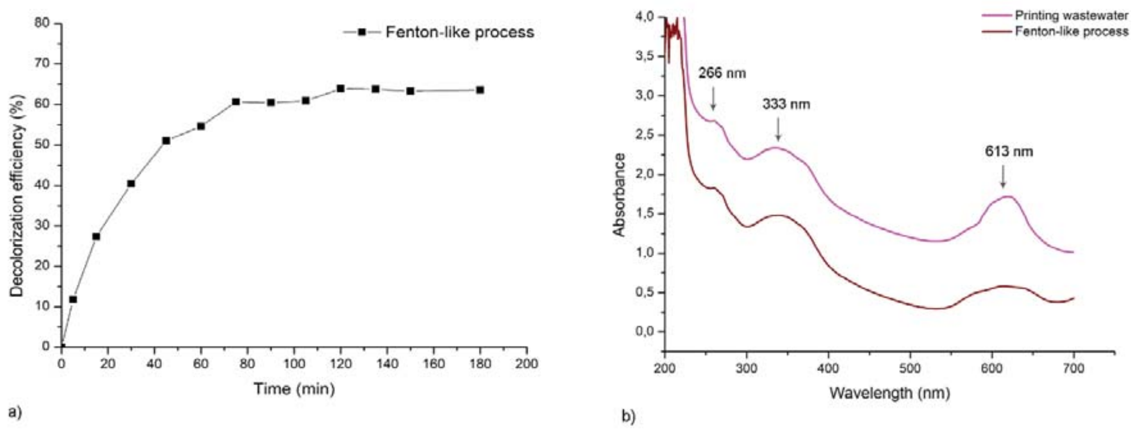

Figure 1: a) Decolorization efficiency of treated printing wastewater; b) UV/VIS spectrum of printing wastewater before and after Fenton-like process

Different structural units and functional groups in the molecule of Black dye have different absorption peaks. Three peaks are observed on the absorption spectrum of printing effluent: one main peak at 613 nm in the visible region and two smaller peaks in the ultraviolet region at 333 nm and 266 nm. It is assumed that the absorption peak at 613 nm corresponds to a conjugated functional azo group connected to aromatic substituents due to the n → π* transition, while the remaining two peaks in the UV region correspond to the benzene and naphthalene rings due to the π → π* transition, whereby the naphthalene ring occurs at a longer wavelength. It is observed that the absorption peak at 613 nm decreases, but does not disappear completely, which means that a slow degradation of Black dye has been achieved, which is in accordance with the results of the decolourization efficiency shown in Figure 1a. The intensity of the absorption peaks in the UV region also decreases, indicating the decomposition of the benzene and naphthalene rings to simpler aliphatic structures. Based on the obtained results, it can be concluded that degradation of Black printing dye is a slow process with a difficult decomposition of aromatic structures. This behaviour occurs most likely as a consequence of the n → π* electronic transition within the azo group, where the hydroxyl radicals first attack the azo group and cleave the -N=N- bonds, destroying the long conjugated π-systems, causing degradation and removal of the Black dye from of the treated sample.

3.2. Characterization of printing wastewater

Physico-chemical characterization of treated effluent was performed in order to determine the mineralization degree of printing dye, and the results are presented in Table 1. The obtained values of physico-chemical parameters for the printing effluent indicate that only tap water is used for the cleaning process of dye chambers and rotating cylinders with flexible rubber relief plates, since the content of detergents and phosphates is low. Therefore, the cleaning process of water-based dyes does not require additional application of solvents or abrasives, which makes them environmentally friendly and easy to use, unlike easily volatile, quick-drying solvent-based dyes. Furthermore, results of physico-chemical characterization indicated a conductivity increment after applied Fenton-like treatment, which may be in accordance with the formation of numerous degradation products and the release of certain inorganic ions. The increase of BOD value after Fenton process pointed out to the formation of degradation products, confirming the assumption that dye degradation does not necessarily imply its complete oxidation to CO_2 and H_2O. Also, a fragmentation of highly complex structure of dye molecule into smaller compounds and mineralization of treated effluent was confirmed with TOC and COD reduction. The mineralization degree resulted with 58% TOC and 47% COD reduction. Based on the obtained results, it is assumed that the formation of large number of aliphatic compounds is achieved.

Table 1: Physico-chemical characterization of printing wastewater

Parameter	Before Fenton-like treatment	After Fenton-like treatment
pH	7.87	1.98
Conductivity (μS cm^{-1})	590	1158
Temperature (°C)	22.60	22.50
Turbidity (NTU)	57.10	32.90
COD (mgO_2 L^{-1})	466.50	249.30
BOD (mgO_2 L^{-1})	0	18
TOC (mgC L^{-1})	106.55	45.25
DBS (mg L^{-1})	0.31	<0.10
Total phosphorous (mgP L^{-1})	<0.011	<0.011
Toxicity inhibition (%)	57.92	66.58

Based on the results of toxicity test on *Vibrio Fischeri* bacteria, it was established that printing effluent belongs to the group of moderate toxic samples, due to the toxicity inhibition of 58%. A slight toxicity increase of 66.58% is observed after the implemented Fenton-like treatment, probably due to the formation of degradation products that are more toxic than the dye molecule, classifying the treated effluent in moderately toxic samples, but again with the impossibility of safe discharge into the recipient. Based on the obtained results, it is concluded that the Fenton-like catalyst, nZVI, achieved a high catalytic activity from the aspect of Black dye removal, but entails solving the problem of the toxic and acidic effluent in the recipient.

3.3. Kinetic studies

To determine the degradation kinetic of Black dye using nZVI in Fenton-like process, the first-order, the second-order and BMG kinetic models were evaluated. Obtained kinetic parameters and correlation coefficients for all three models are presented in Table 2.

Table 2: First-order, second-order and Behnajady–Modirshahla–Ghanbary kinetic model constants and regression coefficients for decolourization of Black dye

Model	First-order		Second-order		[a]BMG model			
	K_1 (min^{-1})	R^2	K_2 (L $mg^{-1}min^{-1}$)	R^2	b	m	1/m	R^2
Fenton-like process	0.0127	0.755	0.0127	0.815	1.359	30.111	0.0332	0.996

[a]Behnajady - Modirshahla - Ghanbary model

The kinetic data of Black degradation showed that correlation coefficient values of BMG model are generally greater than those of the first-order and the second-order models. Thus, all experimental data are fitted well by BMG model (Figure 2).

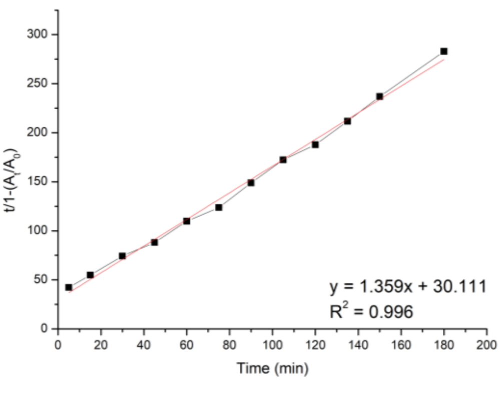

Figure 2: Decolourization kinetic of printing effluent under optimal process conditions (BMG model): $[Fe^{2+}]$ = 0.75 mgL^{-1}, $[H_2O_2]$ = 1 mM, pH = 2

Low values of the parameter 1/m indicate that the effective removal of Black dye from the printing wastewater requires a longer reaction time to achieve high efficiency primarily due to the complexity of the treated matrix.

4. CONCLUSIONS

A highly efficient Fenton-like catalyst, nano zero valent iron, was applied to remove Black dye form printing wastewater. Efficient treatment of real printing effluent under previously optimized experimental conditions ($[Fe^{2+}]$ = 0.75 mgL^{-1}, $[H_2O_2]$ = 1 mM, pH = 2) was obtained: 61% of dye removal was achieved after 75 min of reaction. Decreased intensity of three absorption peaks on UV/VIS spectrum (wavelength: 613 nm, 333 nm and 266 nm) of treated sample indicated $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electron transition within the azo group, as well as decomposition of the benzene and naphthalene rings to simpler aliphatic structures. Under the optimal operating conditions, 58% TOC and 47% COD removals were attained by the Fenton-like process. The enhanced removals of TOC and COD contributed to the fragmentation of highly complex dye molecule structure into a large number of simpler aliphatic and aromatic fragments. The results are confirmed within BOD and toxicity increase, assuming that dye degradation does not necessarily imply its complete oxidation to CO_2 and H_2O, but forming smaller compounds that could be even toxic than original dye molecule. Three kinetic models (the first-order, the second-order, and Behnajady–Modirshahla–Ghanbary) were evaluated and the Behnajady–Modirshahla–Ghanbary kinetic model was found to be the best model representing the experimental kinetic data of Black dye removal. The obtained results implied that Fenton-like process, as environmentally friendly treatment, can be used for printing dye removal from real printing wastewater. However, this study can be extended by considering various options how to overcome the well-known challenges of Fenton process, such as the acidic pH as an optimal reaction condition and high toxicity of treated printing wastewater.

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