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Physico-chemical evaluation and kinetic study of coloured printing wastewater prior and post- Fenton treatment

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Introduction

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. The high consumption of dyes leads to the creation of a large amount of colored effluents that are discharged into water bodies.

Possible solution to treatment of printing 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, which have the ability to degrade difficult biodegradable compounds, such as printing dyes.

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 iron concentration, 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.

Problem Description

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 and H_2O_2 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 (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), anionic surface-active substances and phosphorus content.

Methods

Sample of printing wastewater was obtained from one flexographic printing facility in Novi Sad. Fenton-like treatment of real printing effluent was carried out under determined optimal process conditions ($[H_2O_2]$ = 1 mM, pH = 2, $[Fe^{2+}]$ = 0.75 mg L^{-1}). To assess the Fenton-like efficiency, nZVI and H_2O_2 were added to an aqueous solution containing printing wastewater, whereby pH value was adjusted using 0.1 M ccH_2SO_4. Reaction system was mixed on a JAR apparatus at 120 rpm and constant temperature of 23 °C. Aliquots of supernatant were analyzed at different time intervals (0 - 180 min) using UV/VIS spectrophotometry. The residual dye concentration was established immediately by measuring the absorbance of the aqueous solutions at 613 nm and decolorization efficiency of printing wastewater was calculated according to Equation:

$$E(\%) = A_0 – A/A_0 * 100$$

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.

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. 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.

Results and Discussion

Maximum Black dye decolorization efficiency of 61% from printing wastewater was obtained by the applied Fenton-like process under optimal process conditions (Figure 1).

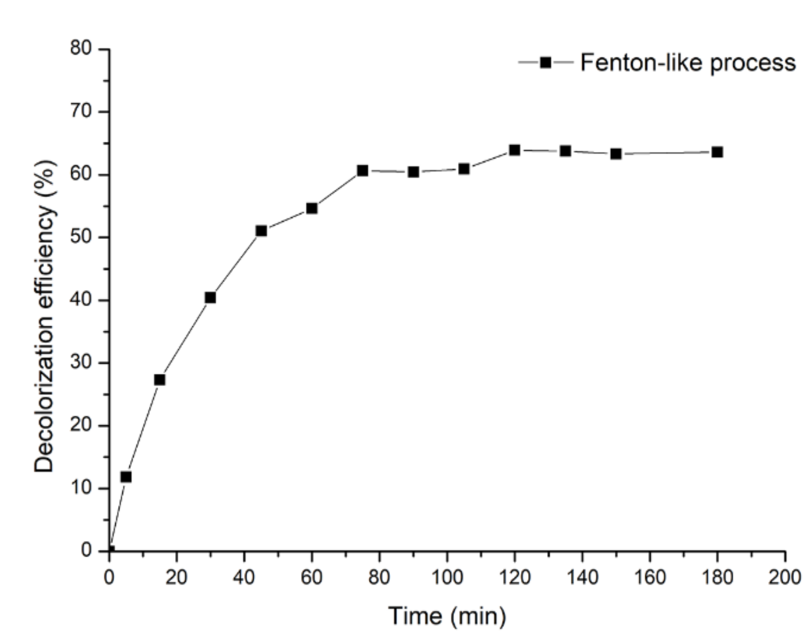

Figure 1

Decolorization efficiency of treated printing wastewater

Three peaks are observed on the absorption spectrum of printing effluent (Figure 2): 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. Based on the absorption peak decreasing, it can be concluded that degradation of Black printing dye is a slow process with a difficult decomposition of aromatic structures.

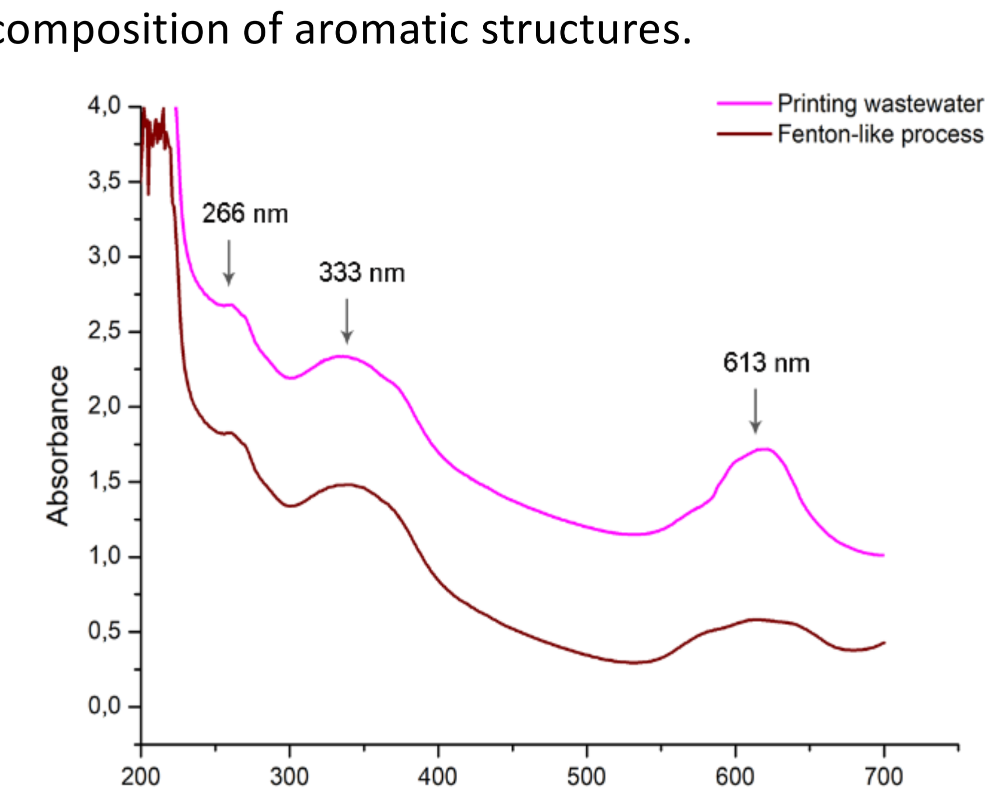

Figure 2

UV/VIS spectrum of printing wastewater before and after Fenton-like process

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.

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)	22.6	22.5
Turbidity (NTU)	57.1	32.9
COD (mgO_2 L^{-1})	466.5	249.3
BOD (mgO_2 L^{-1})	0	18
TOC (mgC L^{-1})	106.55	45.25
DBS (mg L^{-1})	0.31	<0.1
Total phosphorous (mgP L^{-1})	<0.011	<0.011
Toxicity inhibition (%)	57.92	66.58

A conductivity increment after applied Fenton-like treatment 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.

Conclusion

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 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 → π* and π → π* 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.

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