BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LXVII No. 1/2015	1 – 9	Seria Tehnică

The Effect of Fenton Process on the Inert Chemical Oxygen Demand (COD) Fractions of Printing-Dyeing Textile Wastewater

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Abstract

Textile industry produces large volumes of effluents that contain appreciable quantities of organic compounds that are not easily amenable to chemical or biological treatment. The main pollution source of textile wastewater comes from the dyeing and finishing process. The COD of the wastewater is 1045 mg/l. Optimum Fenton experiment conditions were obtained as pH=4.0, 750 mg/l for $FeSO_4$*, 400 mg/l for* H_2O_2 *and 20 min oxidation time. To determine inert COD components, the initial inert particulate* $COD(X_I)$ *and the initial inert soluble* $COD(S_I)$ *of the wastewater, the Fenton process of which was applied, have been obtained as 10 mg/l and 128 mg/l, respectively.*

Key words: *Fenton process, inert particulate COD, inert soluble COD, textile wastewater.*

Introduction

The textile industry is known to be one of the major sources of water pollution. The quantity of wastewater from the textile industries has been increasing together with the growing demand for textile products [20]. The impact of textile industry effluents on aquatic medium has been traditionally of great concern, because they contain a large variety of raw materials and reagents such as synthetic dyes, pigments, biocides, heavy metals, oils, salts, nutrients and organic compounds [2]. The dyes and polyvinyl alcohol (PVA) contained in textile wastewaters are the main refractory organics of concern, in terms of meeting more stringent effluent standards of COD (chemical oxygen demand) and color [6]. The physical, chemical and mostly biological technologies have been widely used to treat textile effluents [2]. Methods commonly applied in textile wastewater, such as chemical precipitation, coagulation- flocculation, membrane separation or elimination by activated carbon adsorption, only transfer the pollutant from one phase to another, and biological treatment is not a complete solution to the problem due to biological resistance of some dyes [13]. Therefore, a method of treating textile wastewater like Fenton oxidation process is required to reduce COD and color.

Most textile wastewater treatment plants use biological treatment processes to remove most part of BOD (biochemical oxygen demand) and some part of COD, but a significant part of dyes cannot be biodegradable in conventional biological wastewater treatment processes [4].

Alternative technologies employed for textile wastewater treatment and/or reuse grouped into physicochemical, biological and combined processes have been recently reviewed [16, 18]). Recently, Fenton process has been used for different treatment processes due to its ease to operation, the simplicity of its technology, and the possibility to work in a wide range of temperatures [17, 18, 19]. Fenton process employs ferrous ions and hydrogen peroxide under acidic pH conditions [14, 24]. The high removal efficiencies of this technique can be explained by the formation of strong hydroxyl radical ($HO^{\bullet}$) and oxidation of Fe^{2+} to Fe^{3+}. The Fenton process is significantly affected by changes in pH values. At pH values ≤4.0, ferrous ions decompose H_2O_2 catalytically yielding hydroxyl radicals most directly [12, 14, 21]. The application of Fenton's reagent to destroy partially or completely the organic compounds is promising [23]. In fact, Fenton oxidation process produced a strong degradation of the organic molecules present in the original wastewaters, allowing a more efficient bio-degradation by the microorganisms present in the biological treatment stage [1].

The determination of COD fractions of the textile industry wastewater provides more information on biological treatment of textile industry effluents, because the type of the dyes and textile additives change continuously in the process as well as for complying with the stringent discharge standards [8]. The inert COD fractions considered in modelling and design of activated sludge systems are not only inert COD components in wastewater. It must also determined the soluble microbial product (S_P) and particulate microbial product (X_P) occurred with biological growth processes [5, 15].

The inert COD fractions in wastewaters are defined as initially inert particulate COD (X_I), initially inert soluble COD (S_I), particulate residual metabolic products (X_P), and soluble residual metabolic products (S_P). S_I and X_I leave the treatment system unchanged, however, X_I is entrapped and accumulated in the sludge line [8].

The objective of this study is to determine the effect of Fenton process, one of the advanced oxidation process (AOPs), thought to be applied before biological treatment, upon the treatability of printing-dyeing textile wastewater and upon inert COD fractions. In addition, operational conditions which have importance effect on Fenton process performance were investigated. The inert COD content of the wastewater was assessed according to an experimental procedure suggested by Orhon et al. [15].

Materials and Methods

Characterization of the wastewater

The wastewater was obtained from printing-dyeing process on cotton fabric from a textile factory in Tokat, Turkey. The raw wastewater samples were drawn from different processes separately in two different channels in the 2-hours composite samples taken from the wastewater were characterized. The characterization of the wastewater are depicted in Table 1.

Fenton process

The Fenton process experiments were performed in beakers by using a standard jar test apparatus (FC6S Velp Scientifica). Every beaker was first filled with 250 ml of wastewater sample, and the pH was adjusted in optimum amount of 4.0 with 1N NaOH and H_2SO_4 solutions. Then $FeSO_4$ and H_2O_2 were added and mixed for 2 min rapid mixing at 200 rpm, then 20 min slow mixing at 30 rpm, and then maintaining standstill for 30 min. After the settling time, supernatant pH readjust to 7.5 in order to stop oxidation and subsequently settling for an half hour. The supernatant was filtered 0.45 µm filter paper for COD and color analyses. All experiments were carried out at room temperature.

Table 1. The raw textile wastewater characteristics

Parameters	**Wastewater samples**	
	Washing, bleaching, desizing	Printing, dyeing, palet washing
pH	6.81	8.21
COD (mg/l)	1756	239
Color λ_{max} = 518 nm (1/cm)	0.304	0.439
EC (µs/cm)	2510	1009
SS (mg/l)	40	30
Turbidity (NTU)	72,6	103,1
Alkalinity (mg/l)	480	487

The experimental procedure of inert COD

Three batch aerobic reactors were experimentally studied in order to determine inert COD fractions based on suggested method by Orhon et al. [15, 25]. The experimental assessment of the particulate inert COD involved using three 2 L batch reactors, constantly aerated to maintain a dissolved oxygen concentration of more than 6 mg/L. The first one fed with the raw wastewater (C_{T1}) sample, the second one with the soluble (filtered) wastewater (S_{T1}) sample and the third reactor with a glucose solution approximately having the same COD content as the soluble wastewater reactor in accordance with the procedure defined by Germirli et al. [9] for the determination of soluble inert COD. All reactors were initially seeded with 30-40 mg VSS/L of acclimated biomass. The acclimated biomass was obtained from a lab-scale fill and draw aerobic reactor operated under steady-state with the same wastewater for sludge ages of 10 days. A mixture of 50% glucose and 50% raw (treated by Fenton process) sample was applied as the feed for this fill and draw reactor. Aliquots were removed periodically from the mixed liquor and analyzed for total and soluble COD. Experiments were continued and data were collected until the COD profiles were reached a plateau. Any wastewater loss from the reactors by evaporation was replaced by adding distilled water before measuring COD. The samples were adjusted to a pH of 7-8 that was a range suitable for biological activity in the batch experiments.

Analytical procedures

The soluble (filtrated) COD was defined as the filtrate through Millipore membrane filters (pore size: 0.45 µm) using closed reflux method. AP40 glass fiber filters were used in determination of suspended solids (SS) and volatile suspended solids(VSS) concentration. All analyses were measured according to Standard Methods [26]. The color of wastewater was determined by the measure of the absorbance at maximum wavelength (λ_{max}=518 nm) using a Pharmacia Biotech Novaspec II model spectrophotometer.

Results and Discussions

Fenton process

To determine the desired conditions of Fenton process for the COD and color removal of printing-dyeing textile wastewater, important variables such as effect dosage of H_2O_2 and $FeSO_4$ concentration on color and COD removal efficiencies were investigated.

The pH of the textile wastewater discharge is a very important parameter in the Fenton's process [3]. The optimal pH values obtained are within the range commonly found for the Fenton process, which usually falls in acidic values of pH 3 and 4 [13, 16]. Therefore, in the experimental design a pH of 4 was considered [7] because in industrial practice this would require less acid in the previous acidification step of textile dyeing wastewaters, which are generally alkaline [16].

Oxidation of dyes and COD by the Fenton process is carried out by OH radicals that are directly produced from the reaction between H_2O_2 and Fe^{+2} [3]. In order to investigate the effect of $FeSO_4$ concentration on the color and COD removal efficiencies, experiments were conducted, when the H_2O_2 dosages were raised up to 200-500 mg/l, and results obtained are represented in Figures 1 and 2, respectively. The color and COD removal efficiencies with $FeSO_4$ concentration at different dosages of H_2O_2 show that the color and COD removal increase with increasing dosage of H_2O_2. In general, the results show that the maximum color and COD removal levels are reached for a $FeSO_4$ dosage of 750 mg/l, the performance being not changed for higher dosages.

From Figure 1, it can be seen that the color removal efficiency varied between 51% and 61% as a consequence of increasing H_2O_2 dosage from 200 to 500 mg/l at 750 mg/l of $FeSO_4$ concentration. When the dosage of H_2O_2 increased from 200 to 500 mg/l at 750 mg/l of $FeSO_4$ concentration, the COD removal efficiency varied between 49% and 63% (fig. 2).

In Figures 1 and 2, the optimum color and COD removal levels are reached for a H_2O_2 dosage of 400 mg/l. In this study, the results show that the addition of higher concentration of H_2O_2 did not improve the removal efficiencies [7]. This could be due to the fact that hydroperoxyl radicals ($H_2O^{\cdot}$) was generated in the presence of excess H_2O_2 [11, 22].

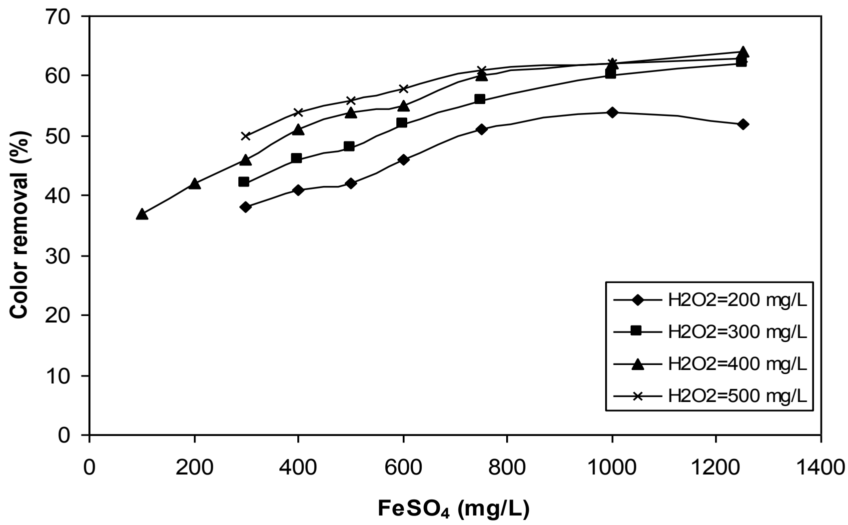

Fig. 1. Effect of $FeSO_4$ concentration on color removal in the presence of different H_2O_2 dosages (pH = 4, COD_i = 1045 mg/l, oxidation time = 20 min, λ_{518} = 0.231 1/cm).

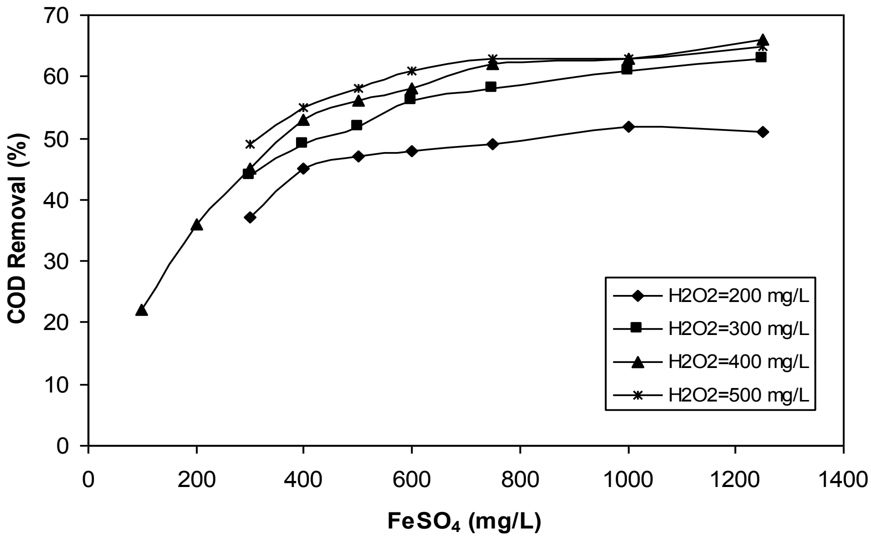

Fig. 2. Effect of $FeSO_4$ concentration on COD removal in the presence of different H_2O_2 dosages (pH = 4, COD_i = 1045 mg/l, oxidation time = 20 min, λ_{518} = 0.231 1/cm).

Determination of inert COD fractions

The results of the experiments conducted on three parallel batch reactors operated with the printing-dyeing textile wastewater which were treated by Fenton process are summarized in Table 2.

Table 2. Experimental results related to the inert COD fractions of printing-dyeing textile wastewater treated by Fenton process

	Reactor I fed with raw wastewater (COD, mg/l)		Reactor II fed with filtrated/soluble wastewater (COD, mg/l)		Reactor III fed with glucose (COD, mg/l)
	C_T (Total COD)	S_T (Total soluble COD)	C_T (Total COD)	S_T (Total soluble COD)	S_T (Total soluble COD)
Start of the experiment	415 (C_{T1})	351 (S_{T1})	-	350 (S_{T1})	355 (S_{G1})
End of the experiment	234 $(C_T)_1$	178 $(S_T)_1$	174 $(C_T)_2$	137 $(S_T)_2$	14 $(S_P)_G$
Duration (hours)	600	600	600	600	600

The experimental procedure is structured as a unified approach for the calculation of the inert COD fraction in wastewaters, by providing first the necessary data for the assessment of S_{I1}, f_{ES} and f_{EX} from simultaneously but independently run experiments. The procedure involves three aerated batch reactors, the first one fed with the raw wastewater, the second with soluble/filtered wastewater and the last with glucose. S_{I1} and f_{ES} are first calculated with the results from the soluble wastewater and glucose reactors; f_{EX} is computed on the basis of soluble wastewater reactor and X_{I1} is then calculated from raw wastewater reactor using the S_{I1}, f_{EX} and Y_H values specific for the wastewater tested. The heterotrophic yield coefficient, Y_H, was taken as 0,64 g cell COD (g COD)$^{-1}$ in order to calculate X_{I1}. The results of the COD experiments are shown in Table 3.

Table 3. Evaluation of the inert COD experiments

Equations	Example calculations for printing-dyeing textile wastewater by using notations and values given in Table 2
$Y_{SP} = f_{ES}.Y_H = \frac{(S_P)_G}{S_{G1}} = \frac{14}{355} = 0{,}039$	$Y_{SP} = \frac{14}{355} = 0{,}039$
$f_{ES} = \frac{1}{Y_H}.\frac{(S_P)_G}{S_{G1}}$	$f_{ES} = \frac{1}{0.64}.\frac{14}{355} = 0{,}060$
$(S_P)_2 = (S_T)_2 - S_{I1} = f_{ES}.Y_H.(S_{T1} - S_{I1})$	137-128=9 mg COD/l
$S_{I1} = \frac{(S_T)_2 - f_{ES}.Y_H.S_{T1}}{(1 - f_{ES}.Y_H)}$	$\frac{137 - 0{,}06.0{,}64.350}{(1 - 0{,}06.0{,}64)} = 128$ mg COD/l
$X_{P2} = (C_T)_2 - (S_T)_2$	174-137=37 mg COD/l
$S_{S1} = S_{T1} - S_{I1}$	350-128=222 mg COD/l
$Y_{XP} = f_{EX}.Y_H = \frac{(X_P)_2}{S_{S1}}$	$\frac{37}{222} = 0{,}167$
$f_{EX} = \frac{1}{Y_H}\frac{[(C_T)_2 - (S_T)_2]}{(S_{T1} - S_{I1})}$	$\frac{1}{0{,}64}\frac{(174 - 137)}{(30 - 128)} = 0{,}26$
$(X_T)_1 = (C_T)_1 - (S_T)_1 = X_{I1} + (X_P)_1$	234-178=56 mg COD/l
$(X_P)_1 = (X_T)_1 - X_{I1} = f_{EX}.Y_H(C_{T1} - X_{I1} - S_{I1})$	56-10=46 mg COD/l
$X_{I1} = \frac{(X_T)_1 - f_{EX}.Y_H.(C_{T1} - S_{I1})}{(1 - f_{EX}.Y_H)}$	$\frac{56 - 0{,}26.0{,}64(415 - 128)}{(1 - 0{,}26.0{,}64)} = 10$ mg COD/l

Using corresponding values of Y_{SP} or f_{ES} parameters in conjunction with the experimental results of the soluble wastewater reactor, the initial soluble inert COD concentration of the printing-dyeing textile wastewater (treated by Fenton process) sample was calculated 128 mg/l, corresponding to 31% of the initial total COD value at the start of the experiment. The particulate inert COD fraction, X_{I1} of printing-dyeing textile wastewater was evaluated, on the basis of the f_{EX} value derived from each experimental setup and related data of the raw wastewater reactor. The X_{I1} was calculated 10 mg/l, corresponding to 2.4% of the initial total COD content of textile wastewater samples, as shown in Table 4.

Table 4. Inert COD fractions of printing-dyeing textile wastewater and its stoichiometric coefficients

f_{ES}	S_{I1}	S_{I1}/C_{T1} (%)	S_{I1}/S_{T1} (%)	f_{EX}	X_{I1}	X_{I1}/C_{T1} (%)
0.06	128	31	36	0.26	10	2.4

As X_P is defined as residual products of metabolic activities, it is expected to be as a constant fraction of the amount of biodegradable COD in batch reactors. The observed X_P level should be higher in reactor started with raw wastewater as compared to their counterparts resulting from reactor initially fed with filtered wastewater with slightly higher biodegradable COD content. The results were given in Table 5.

Table 5. The amount of particulate and soluble microbial products generated from reactors fed with raw and filtered printing-dyeing textile wastewater samples and its stoichiometric coefficients

Raw wastewater reactor		**Filtered/soluble wastewater reactor**				
C_{T1} (mg/l)	**X_{P1} (mg/l)**	**S_{T1} (mg/l)**	**X_{P2} (mg/l)**	**S_{P2} (mg/l)**	**Y_{XP}**	**Y_{SP}**
415	46	350	37	9	0.167	0.039

Conclusions

In this study, it is investigated the effect of Fenton processes on inert COD of printing-dyeing textile wastewater. Optimum Fenton experiment conditions were obtained as pH = 4.0, 750 mg/l for $FeSO_4$, 400 mg/l for H_2O_2 and 20 min oxidation time. To determine inert COD components, the initial inert particulate COD(X_I) and the initial inert soluble COD(S_I) of the wastewater, the Fenton process of which was applied, have been obtained as 10 mg/l and 128 mg/l, respectively. Inert COD components, particularly in influent of high-strength wastewater, may seriously affect treatability of the system or may prevent to reach to discharge standards developed for different industrial categories. It is impossible to obtain the discharge standards that are put forward, using existing treatment technologies because textile wastewater has high-strength characteristic and its degradability is low.

It is though that obtained results in this study may be useful for the planned future investments such as changing characteristics of the wastewater facility, variable washing volumes and rinsing time depending on the color of dye, and lack of a treatment plant. The obtained experimental results were showed that the inert COD fractions of wastewater vary depending on the wastewater structure and must be determined by experimental studies. The results of the studies revealed that Fenton process which is one of the advanced oxidation method is useful for the established discharge standards in which removal soluble inert COD which constituents one of the component of the COD parameters. Consequently, this study will contribute to literature by presenting on efficient process for treating this kind of real wastewater.

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Efectul procesului Fenton la inertizarea consumului chimic de oxigen (CCO) al apelor reziduale de la fracțiile de imprimare – vopsire din industria textilă

Rezumat

Industria textilă produce volume mari de efluenți care conţin cantităţi apreciabile de compuși organici care nu sunt ușor îndepărtaţi în tratamentul chimic sau biologic. Principala sursă de poluare a apelor uzate din industria textilă provine din procesul de vopsire și finisare. CCO al apei uzate este de 1045 mg/l. S-au obținut condiții optime pentru experimentul Fenton la pH = 4,0, 750 mg/l pentru $FeSO_4$, 400 mg/l pentru H_2O_2 și timpi de oxidare de 20 min. In urma procesului Fenton aplicat, au fost determinate componentele inerte ale CCO, CCO(XI) inițial inert, și inert solubil CCO (S_I) ale apei de spălare, obţinând valorile de 10 mg/l și, respectiv, 128 mg/l.