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Treatment of spent offset-printing developer with Fenton's reagent

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Treatment of a spent HD-P1 type offset-printing developer using an advanced oxidation method has been carried out. The analysis of GC/MS and UV-visible spectra showed the presence of phenol derivatives and triphenylmethane dyes in the photoprocessed developer. The successive treatment with the Fenton's reagent led to practically complete decomposition of organics and to ~99% COD reduction. 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} Fenton's reagent concentration was estimated as optimal for the spent developer treatment. The ecotoxicity results based on the integrated assessment from the test-battery confirmed a moderation of harmfulness of the spent developer exposed to the successive treatments with the Fenton's reagent; however, the toxicity pattern did not follow the alterations of the COD at each step of decontamination. This suggests a concomitant application of chemical and biological approaches in evaluating the impact of spent developers on the environment.

Key words: offset-printing developer, Fenton's reagent, decontamination, ecotoxicity

INTRODUCTION

The growing scale of the offset printed production causes ecological problems related to the developers waste. Some components present in the initial developer solution (e. g., Polychrome 4003, Polychrome 2000 K, HD-P1), such as potassium silicate, sodium silicate, potassium hydroxide, D-sorbitol are not very harmful to the environment or are easy to decontaminate. However, after the treatment of printing plates, the developers are enriched by plate surface compounds: novolak, organic polymeric binders, photosensitive compounds, dyes and some others. Cumulative organics considerably increase the chemical oxygen demand (COD) and the toxicity of the waste developer [1]. Since most of developers contain potassium hydroxide (up to 20%) and silicates, in praxis, the photoeffluent problems often are solved by their neutralization using inorganic acids and a subsequent dilution by water. This method is effective only partially, because a large part of organics is sorbed by silicic acid gel sediments formed during the acidification, and its dump causes further problems. Many other methods for photowaste decontamination have been proposed, for instance, water evaporation and solid residue incineration, wet oxidation [2], sulfur-oxidizing bacteria/granular-activated carbon system [3, 4], biodegradation [5–8] and combined methods. Some of them – wet oxidation, evaporation and incineration – are rather costly due to large initial investments, and usually even using all the named methods, the purification cannot be performed at a satisfactory level, when applied alone. For instance, the wet oxidation method [2] performed at a temperature range from 140 °C to 370 °C under elevated pressure requires further biological treatment. The sulfur-oxidizing bacteria/granular-activated carbon system [3] should be combined with additional hydrogen peroxide processing to obtain 95% removal rate of the dissolved organic carbon in photo-processing waste. The variety of the compositions of photo-processing waste solutions makes it difficult to evaluate the effectiveness of the discussed methods for the particular photowaste. There is scarcely any special procedure designed for the decontamination of spent offset-printing developers.

One of widely known wastewater treatment methods is an advanced oxidation process employing the Fenton's reaction. The Fenton's system is a mixture of ferrous salts with hydrogen peroxide in acidic medium, which, under proper conditions, results in the generation of highly reactive hydroxyl radicals. The Fenton's process and the chemical reactions lying behind are well described in references [9, 10]. The Fenton's reaction is rather fast; therefore, it is used when high COD removal is required. Many applications of the Fenton's reaction for the destruction of organic contaminants in waste water [11–15] and for the degradation of photographic developers [16, 17] have been reported. The latter two studies deal with the developers for traditional

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silver halide photomaterials; practically full destruction of organic compounds has been achieved. No publications were found about the employment of the advanced oxidation process for the decontamination of the spent offset-printing developers. Some references concerning the ecotoxicity of spent developer constituents, such as phenol derivatives or triphenylmethane dyes can be found, while little data are available in relation to the overall toxicity of offset-printing developers [1] or photoprocessing wastewaters [5] on aquatic biota.

The aim of this work is to use the Fenton's reaction for the destruction of organic compounds present in the spent HD-P1 type plate developer and evaluate its toxicity alterations throughout the process of treatment.

EXPERIMENTAL

Materials and procedures

The photoprocessed HD-P1 type plate developer was obtained from "MTL" enterprise printing house (Vilnius, Lithuania). Fresh HD-P1 developer concentrate was indicated by the manufacturer as 7–15% sodium silicate and 10–20% potassium hydroxide solution. 1:7 water-diluted concentrate with pH 13.5 is the working developer solution**.** Due to a very high chemical oxygen demand of the spent developer, its oxidation in the present work was carried out after a fivefold dilution with water. Generally, when not diluted, the developer turns into a thick gel after its neutralization and is difficult to process**.** This solution is thereinafter denominated as SDS (spent developer solution). The Fenton's oxidation process was performed as follows: 50 ml SDS sample was put into a 400 ml chemical beaker, pH was adjusted to 4.5 with diluted H_2SO_4 (1:5), then Fe^{2+} (in form of $FeSO_4 \cdot 7H_2O$) and H_2O_2 were added up to desirable concentrations. A typical ferrous ion concentration is normally one tenth of hydrogen peroxide concentration [18]. During the treatment of the photowaste with the Fenton's reagent, the most suitable pH range was proposed by investigators to be in the range of 3 to 5 [16, 19]**.** During the Fenton's reaction (15 min), the mixture was agitated by a magnetic stirrer. A fifteen-minute reaction was selected as optimal on the ground of similar works [19, 20]. After the reaction, pH was adjusted to 8–9 using 10% NaOH solution, and gel-type precipitate separated from the supernatant solution by filtration through a paper filter. Then distilled water was added to the precipitate up to 50 ml volume and thoroughly mixed until a homogeneous suspension was achieved. The pattern of sediments prepared in such way and denominated as PS (precipitate suspension), as well as the supernatant separated earlier were analyzed for COD and organic compounds by underwritten methods, and used for the repeated treatment by the Fenton's reagent (FR). COD assays were carried out after 2 hours on the morrow of each treatment to remove the rest of hydrogen peroxide. During this time, hydrogen peroxide did decompose in a weak alkaline media. No hydrogen peroxide was detected by a permanganatometric method in the patterns prior to COD analysis. The difference in COD found in acidic and neutralized (pH 8) solutions accounted for 1.5–2%. It should be mentioned, that the volumes of H_2SO_4 and NaOH solutions, used for the pH correction was very small (less than 1 ml) and did not markedly dilute the investigated solutions.

Analytical methods

The COD values were established by the potassium dichromate method using a Spectroquant TR 320 reactor and Spectroquant Colorimeter Picco (Merk) devices. COD evaluation accuracy was ±3.5%. Organic compounds present in the waste solution were analyzed by the gas chromatography method (GC/MS). Diethyl ether was used as an extrahent for the recovery of the organic compounds. Solution pH before the extraction was adjusted to 2.0. GC/MS analysis was carried out on an HP 5890 (Hewlett Packard) gas chromatograph with an HP 5971 mass selective detector and an HP 7673 split/splitless injector. The separation was performed on a capillary column, CP-Sil 8 CB (50 m × 0.32 mm, film thickness 0.25 μm). Mass spectra in electron mode were generated at 70 eV.

The UV/VIS spectra were recorded using a Perkin Elmer Lambda 35 UV/VIS spectrometer in 1 cm path length quartz cells. The investigation was carried out at 20 °C. Before the UV/VIS analysis, PS patterns were diluted 12.5 times, and a transparent solution was obtained. The optical blank solution was pure water.

The Oxidation tests were performed using pure reagents obtained from a company "Reachim".

Ferrous ion concentration was determined by the photocolorimetric method with 1,10-phenanthroline [21] using a photoelectrocolorimeter KFK-2MP (Russia).

Electrophysiological algal test (Charatox)

Freshwater charophyte algae, *Nitellopsis obtusa* (Desv.) J. Groves, were collected in Lake Švenčius (southern Lithuania) during the vegetation period in 2005. Single internodal cells were kept at room temperature in glass vessels with equal parts of tap and lake water. Tests were carried out at room temperature (18–24 °C) in dim light.

The electrophysiological biotest employs a 90-min IC_{50} cell membrane depolarisation endpoint (a concentration causing 50% inhibition of the averaged resting potential of the cells after a ninety-minute exposure). The details of the computer-assisted experimental setup, testing procedures and the methods for measuring the cell resting potential (RP) have been published previously [22, 23]. Bioelectrical activity of up to 64 living internodal cells was measured simultaneously according to K^+-anaesthesia method [24], modified for a multichannel recording with extra-cellular chlorinated silver wire electrodes. Discrete RP values from distinct cells were taken every second. For the determination of IC_{50}, the percentage of the decrease in the average RP value of the cell group at the end of ninety-minute exposure period**,** in relation to that of the untreated cells**,** was calculated for each concentration. The IC_{50} value was estimated using a non-linear (logistic) regression of the averaged decrease in RP with the logarithms of exposure concentration.

96-h algae cell mortality test (Niteltox)

Mortality test with charophyte cells of *Nitellopsis obtusa* was mainly performed as described previously [23]. Single internodal cells (each 4–10 cm in length) were placed into Petri dishes (10 cells per dish) and kept for 1–2 days in artificial pond water (APW) containing 0.1 mM KH_2PO_4, 1.0 mM $NaHCO_3$, 0.4 mM $CaCl_2$, 0.1 mM $Mg(NO_3)_2$ and 0.1 mM $MgSO_4$ (pH 7–7.4,

unbuffered). The preadaptation in APW before the toxicity tests allowed to discard occasionally dead cells, which had been injured during the transfer to the Petri dishes. Algal cells in the Petri dishes were kept at room temperature (18–24 °C) for 96 hours in the dark. The APW and treatments in each Petri dish was changed in two days after beginning of the exposure.

For the tests, 7 concentrations and 30 cells, i. e. 3 replicates were used for each dilution. In all tests, the survival of the cells was checked daily by gently picking up each cell with a spatula. A cell was judged to be dead if there was no turgor pressure, a state in which a cell bent on the spatula and lost its cylindrical shape. The ninety-six-hour LC_{50} value (a concentration causing 50% mortality of the cells after ninety six hours of exposure) was estimated using a non-linear (logistic) regression of the averaged mortality with the logarithms of exposure concentration.

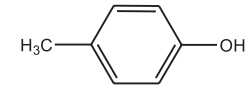
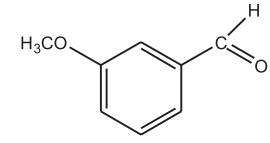
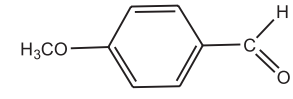
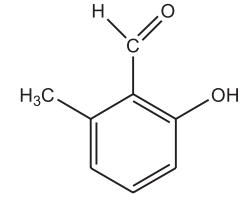
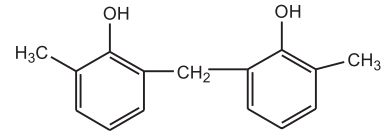
Crustacean test (Thamnotoxkit F™)

The mortality test of freshwater invertebrates *Thamnocephalus platyurus* was performed following the Standard Operational Procedure of Thamnotoxkit F™ [24]. All the materials required to perform the tests with larvae of the fairy shrimps were purchased from Microbiotests Inc., Belgium. Test organisms included in the kit in form of cysts, were started to hatch 24 h prior to testing. A twenty-four-hour LC_{50} (lethal concentration causing 50% mortality of the organisms tested) bioassay was performed in a multi-well plate in the dark.

RESULTS AND DISCUSSION

The initial colorless HD-P1 developer turns to dark blue after photoprocessing, being enriched by chemicals present on the plate surface. The GC/MS chromatogramm of the spent developer (Fig. 1) revealed the presence of several organic compounds, the most abundant of which was 2,2'-methylenebis-[3-dimethyl] phenol with $[M]^+$ 228, and retention time 30.7. The identity of the compounds found was confirmed with MS spectra and (or) using corresponding standards: 4-methylphenol (CAS 106-44-5, Fluka); 4-methoxybenzaldehyde (CAS 123-11-5, Fluka); 3-methoxybenzaldehyde (CAS 591-31-1, Fluka); 6-methyl-2-hydroxybenzaldehyde and 2,2'-methylenebis-[3-dimethyl] phenol

Table 1. **GC/MS data of etheral extract of the initial spent HD-P1 type offset-printing developer**

Nr	Retention time (min.), chemical name	Mass spectrometric fragmentation peaks	Formula of compounds
1	8.5 4-methylphenol	108 [M]+(91), 107(100), 79(21), 77(28), 53(15), 52(10), 51(19), 50(12), 39(17)	
2	10.0 3-methoxybenzaldehyde	136 [M]+(100), 135(87), 107(44), 92(25), 77(62), 65(38), 64(22), 63(26), 51(27), 39(46)	
3	10.1 4-methoxybenzaldehyde	136[M]+(67), 135(100), 107(17), 92(18), 77(35), 65(12), 64(11), 63(14), 50(11), 39(14)	
4	11.2 6-methyl-2-hydroxybenzaldehyde	136[M]+(91), 135(100), 107(22), 90(44), 89(20), 79(34), 78(11), 77(43), 51(13), 39(12)	
5	15.7 unknown	124 [M]+(40), 123(6), 80(40), 79(100), 65(3), 52(5), 51(7), 50(5), 40(3), 39(8)	
6	30.7 2,2'-methylenebis-[3-dimethyl] phenol	228[M]+(48), 195(6) 166(4), 165(7), 152(3), 122(10), 121(100), 108(36), 77(11), 51(2)	
7	31.1 unknown	284 [M]+(1), 228(35), 195(5), 166(3), 165(6), 121(100), 120(6), 108(4), 92(5), 91(11), 51(3), 39(2)	
8	31.4 unknown	229 [M]+(5), 228(32), 165(5), 122(10), 121(100), 108(40), 107(6), 92(6), 91(12), 77(11)	
9	32.6 unknown	256 [M]+(8), 228(42), 165(8), 136(6), 135(6), 121(100), 120(67), 91(21), 77(17), 40(33)	

(the latter was identified using MS spectra only). The identification was based on the retention times of known compounds and on the mass spectra comparison with the data in the mass spectral library NBS 54K.1. The results of the chromatogramm analysis are presented in Table 1. All the identified compounds are phenol derivatives, including noxious p-cresol and aromatic aldehydes.

COD value of the initial SDS amounts is 13500 mgO_2/l. COD alterations by the treatment with FR of various concentrations are presented in Table 2. After the first treatment with FR, COD values of the supernatant and the sediment suspension differ considerably being much major for PS. Evidently, the sediments

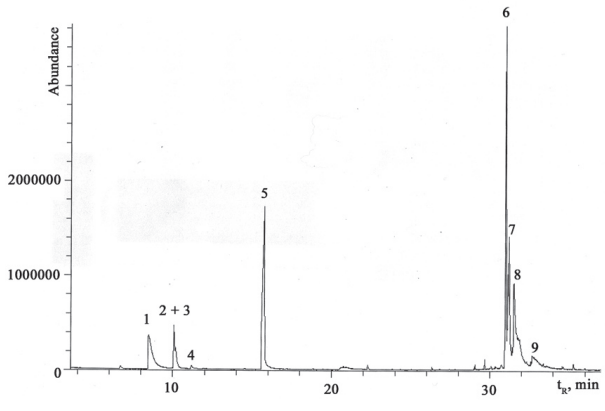


Fig. 1. GC/MS chromatogram of the spent developer etheral extract: 1 – 4-methylphenol; 2 – 4-methoxybenzaldehyde, 3 – 3-methoxybenzaldehyde; 4 – 6-methyl-2-hydroxybenzaldehyde; 5 – unknown; 6 – 2,2'-methylenebis-[3-dimethyl] phenol; 7 – unknown; 8 – unknown; 9 – unknown

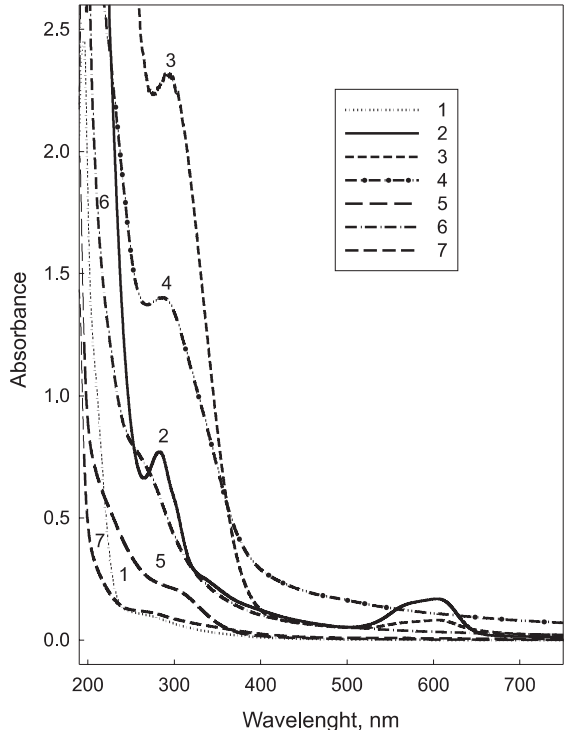


Fig. 2. UV spectra of aqueous solutions: 1 – distilled water, treated with 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} FR (blank pattern), 2 – spent developer solution (SDS, diluted 500 times), 3 – SDS treated with 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} FR, 4 – precipitate suspension (PS) after the first treatment with 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} FR, 5 – PS after the second treatment with 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} FR, 6 – PS after the first treatment with 3.0 mol/l H_2O_2 + 0.3 mol/l Fe^{2+} FR. 7 – supernatant (filtrate) after the first treatment with 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} FR. 3 – 6 patterns diluted 12.5 times

Table 2. **COD (mgO_2/l) alteration in precipitate suspension (PS) and in supernatant (SN) of the spent developer solution during the successive treatments with various concentrations of the Fenton's reagent. Initial COD – 13.500 mgO_2/l**

Treatment number	Fenton's reagent concentration							
	0.5 mol/l H_2O_2 0.05 mol/l Fe^{2+}		1.0 mol/l H_2O_2 0.1 mol/l Fe^{2+}		1.5 mol/l H_2O_2 0.15 mol/l Fe^{2+}		3.0 mol/l H_2O_2 0.15 mol/l Fe^{2+}	
	PS	SN	PS	SN	PS	SN	PS	SN
1	9350	510	5400	290	5700	465	4250	230
2	5310	400	2250	120	3400	125	2700	120
3	3540	250	140	–	200	–	–	–

Table 3. **COD and toxicity data of the initial spent developer solution (SDS), supernatant of SDS and precipitate suspension (PS) after successive treatment with the Fenton's reagent**

Sample	Chemical parameters		Biotesting results							
	COD mgO_2/l	COD reduction times	Charatox		Niteltox		Thamnotoxkit		Average toxicity[b]	Toxicity reduction
			IC_{50}, %	T.U.[a]	LC_{50}, %	T.U.	LC_{50}, %	T.U.	T.U.	times
Initial spent developer solution (SDS)	13500	–	5.7	18	2.2	46	1.0	100	54	–
Supernatant after 1st treatment of SDS with Fenton reagent (FR)	290	46	5.6	18	6.6	15	8.5	12	15	4
PS after 2nd treatment with FR	2250	6	21	4.8	33	3.0	6.4	16	8	7
PS after 3rd treatment with FR	140	96	51	1.9	80	1.3	na[c]	na	2	27

[a] The toxicity evaluation obtained as 50% effect endpoint values (in percent of dilution) was converted into toxic units (T.U.) by the formula: $T.U. = (1/l(L)C_{50}) \times 100$ [29].

[b] Mean of the end-point values of the tests used in the battery expressed in T.U.

[c] Not analyzed.

consisting of ferric hydroxide and silicic acid gel adsorbs the best part of organic compounds, residual after oxidation. The mass of dry deposit precipitated from 1 liter of SDS treated with 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} FR was 33 g, thus, about 3.3% of the deposit had sorbed the organic substances, accountable for ~95% of COD. The second treatment with FR enabled to reduce the PS COD to the largest extent when FR concentration was 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+}. COD values of the supernatant after the treatment with 1.0–3.0 mol/ H_2O_2, 0.1–0.3 mol/l Fe^{2+} FR were negligible and within the range of sewer code limits [26]. Therefore, the subsequent oxidation treatments were performed with the PS patterns only. In order to establish a possible contribution of Fe^{2+} ions to the COD value, its concentration after each treatment with FR was determined. The average Fe^{2+} concentration after each of the three treatments amounted to 0.1 mg/l, so its part in the COD value was negligible. The second and the third treatments with 1 mol/l H_2O_2 and 0.1 mol/l Fe^{2+} reagents enabled to reduce COD by 83 and 99%, respectively. The second oxidation step with the triple reagent concentration resulted in a less effective COD reduction (80%). The treatment with the lowest FR concentration, 0.5 mol/l H_2O_2 + 0.05 mol/l Fe^{2+}, resulted in a moderate COD reduction. Considering the amounts of FR used and the final COD values obtained, the concentration set of 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} can be indicated as optimal. Besides, using 3.0 mol/l H_2O_2 + 0.3 mol/l concentration set, the temperature was risen over 50 °C, and the self-decomposition and idle dissipation of hydrogen peroxide began. The diminished COD reduction by the elevated FR concentrations can also be explained by the fact that at a certain oxidation stage, the Fenton's reaction consumes the produced hydroxyl radicals faster than the organic components [17], according to the following chemical reactions:

$$H_2O_2 + HO \rightarrow H_2O + HO_2^{\cdot},$$
$$k \sim 2\text{–}3 \times 10^7\ M^{-1}s^{-1},$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+$$
$$k \sim 0.01\text{–}0.02\ M^{-1}s^{-1},$$

$$Fe^3 + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+$$
$$k \sim 1 \times 10^4\ M^{-1}s^{-1}$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^-$$
$$k \sim 1.4\text{–}4.3 \times 10^8\ M^{-1}s^{-1}.$$

These reactions are favoured in the presence of high H_2O_2 excess.

SDS treated with FR concentrations sets such as 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} and 3.0 mol/l H_2O_2 + 0.3 mol/l Fe^{2+} were investigated by GC/MS and UV spectroscopy methods. No peaks were detected in the GC/MS chromatograms of etheral extracts of the second and third time treated PS and the filtrate, despite a fair amount of COD implying the presence of residual organic compounds. UV spectroscopy appeared to be a more sensitive method to evaluate the cumulative organics. UV spectra are depicted in Fig. 2. The absorption band around 280 nm is characteristic for phenols and conjugated carboxyl groups [27], while 604 nm adsorbance peak belongs to the blue triphenylmethane dye [28], which was present at the initial waste solution and at the one that was first time treated with FR. After the subsequent treatments, this peak disappears. The decline of 284 nm peaks in the treatment course (curves 3–5) shows the decrease of the organics and corresponds to the COD change. So, the 1:5 diluted spent HD-P1 developer treated repeatedly with FR in a concentration set of 1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+} enables to destroy the main part of organics and reduce COD by ~99%.

The initial spent developer solution (1:5 dilution) and its 3 derivatives obtained by the treatments with FR of an optimal concentration set (1.0 mol/l H_2O_2 + 0.1 mol/l Fe^{2+}) were used for the ecotoxicological investigations (Table 3). The battery of tests consisted of two algal tests based on a rapid ninety-minute electrophysiological reaction of the cell membrane (Charatox) and mortality response of the cells after ninety six minute of exposure (Niteltox), and one microinvertebrate test employing a twenty four-hour lethality response of fairy shrimps (Thamnotoxkit F™). All the tests confirmed a very high toxicity of the initial SDS that could have been predicted from the considerable COD value (Table 3). The supernatant obtained after the first treatment with FR, while in lesser extent, was still very toxic to all test-organisms. As can be seen from the comparative evaluation of these two solutions in terms of general characterizations, i. e. chemical (COD) and ecotoxicological (average toxicity) ones, the COD of the supernatant has been diminished to a greater extent (forty six-fold) than the average toxicity (four-fold), both in relation to the respective initial values. As for the sediment suspension obtained after the second treatment with FR, both parameters – COD and average toxicity – showed quite a similar decrease from the initial values. Finally, the toxicity of PS was further decreased during the third successive treatment with FR, however, some acute toxicity still remained (Table 3), and this could not be envisaged from the very low COD value (140 mgO_2/l).

CONCLUSIONS

After photoprocessing, the HD-P1 developer underwent the contamination by phenol derivatives and triphenylmethane dyes. The main part of the organic compounds present in the spent HD-P1 developer was adsorbed by the sediments formed during the treatment with the Fenton's reagent. The subsequent treatment with the Fenton's reagent led to an almost complete decomposition of organics and to 99% reduction of the COD. Ecotoxicity results based on the integrated assessment from the test-battery confirmed a moderation of harmfulness of the spent developer exposed to successive treatments with the Fenton's reagent; however, the toxicity pattern did not follow the alterations of the COD at each step of decontamination. This suggests a concomitant application of chemical and biological approaches in evaluating the environmental impact of spent developers.

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PANAUDOTŲ OFSETO PLOKŠČIŲ RYŠKALŲ APDOROJIMAS FENTONO REAGENTU

S a n t r a u k a

Tirtas panaudoto ofseto plokščių ryškalo HD-P1 nukenksminimo procesas, oksiduojant jį Fentono reagentu. Dujų chromatografijos ir UV spektroskopijos metodais nustatyta, kad ryškinimo proceso metu tirpale atsiranda fenolo darinių ir trifenilmetano dažų. Tirpalą rūgštinant susidariusios nuosėdos sugeria daugumą jame esančių organinių junginių. Palaipsniui oksiduojant šį tirpalą ir nuosėdų suspensiją Fentono reagentu pasiektas cheminio deguonies sunaudojimo (ChDS) sumažėjimas ~99%. Nustatyta optimali Fentono reagento koncentracija (1,0 mol/l H_2O_2 +0,1 mol/l Fe^{2+}). Palaipsniui oksiduojant ryškalą taip pat mažėja jo toksiškumas, tačiau neproporcingai ChDS mažėjimui.