CHEMIJA. 2012. Vol. 23. No. 4. P. 263–268

Treatment of water-based wood paint wastewater with Fenton process

Tomas Vengris[1]*,

Rima Binkienė[1],

Rita Butkienė[1],

Romas Ragauskas[1],

Arvydas Stončius[1],

Levonas Manusadžianas[2]

[1] *Institute of Chemistry of Center for Physical Sciences and Technology, A. Goštauto 9, LT-01108 Vilnius, Lithuania*

[2] *Institute of Botany of NRC, Žaliųjų Ežerų 49, LT-08406 Vilnius, Lithuania*

Fenton oxidation process for decontamination of water-based wood paint effluent was performed. The amounts of identified organic compounds present in the effluent, such as 1-butoxy-2-propanol, dipropylene glycol monomethyl ether (mixture of isomers), 2-hydroxy-2-methylpropiophenone and 2-butoxyethanol, were reduced by 96% and the total chemical oxygen demand (COD) by ~80%, whereas the initial COD was ~16,000 mgO_2/l. Considering oxidation kinetics, ultimate COD removal and peroxide consumption, 1.0 M H_2O_2 and 0.01 M Fe(II) Fenton concentrations at 50 °C were admitted as optimal. To evaluate the effluent toxicity, the following three toxicity tests were performed: Charatox (electrophysiological algal test), Daphtoxkit F™ magna and Thamnotoxkit F™. Toxicological data confirmed the decrease of adverse effects of water-based wood paint effluent on water biota after the treatment by the Fenton-advanced oxidation process.

Key words: Fenton's process, paint wastewater, chemical oxygen demand, toxicity

INTRODUCTION

Painting industry wastewater (WW), contaminated by organic and inorganic pigments, binders, thickeners and other additives create serious ecological problems. Water-based wood paint WW output amounts up to 500 metric tonnes in Lithuania annually. In many cases these WW, especially those including UV dyestuff, are not biodegradable, so the made-up treatment methods must be implemented. The most effective method is presumably a physical cleaning process based on ultrafiltration and reverse osmosis, though it requires quite high capital investments. Decontamination of painting wastewaters is described in scientific literature mostly related to the textile dyeing wastes. Physico-chemical and chemical methods in this field are reviewed [1]. There are few scientific reports about the chemical treatment of water-based wood paint WW. Dyeing WW is often treated with the Fenton oxidation process, which oxidizes organics and enables to reduce the chemical oxygen demand (COD). Fenton process is based on the oxidizing power of $OH^{\cdot}$ radicals and is thoroughly described in monographs [2, 3]. Beside the oxidation, part of COD can be removed by coagulation with iron hydroxide emergent during the course of the Fenton process.

* Corresponding author. E-mail: tvengris@chi.lt

Up to 80% COD removal by treatment of azo dye production WW using the photo-Fenton-like advanced oxidation process has been reported [4]. Fenton oxidation process enables to decolorize and to reduce COD of textile industry WW [5] and can also markedly increase the biodegradability of dye WW [6]. The oxidation of methylene blue in water solution was thoroughly studied [7], and it has been found out that more than 98% of the dye could be eliminated. In the study [8] about 80% of COD have been eliminated by the Fenton treatment of water-based paint WW produced in television manufacture.

Various polyferric chloride coagulants and its copolymers with Al(III) and Si(IV) were used to remove the compounds present in WW from dye manufacturing industry, but the COD removal did not exceed ~55% [9].

In most of the mentioned references the toxicity investigation of treated WW was not performed, meanwhile it is established that toxicity is not proportional to the drop of COD value and that toxicity tests are essential for the characterisation of WW decontamination [10, 11]. In the present work, the action of the Fenton reaction on water-based wood painting WW was evaluated checking the change of the organics amount (COD) and the toxicity.

EXPERIMENTAL

Materials and procedures

The object of the investigation was water-based paint WW from the Lithuanian enterprise "Universal Wood Products". This water results from the cleaning of the equipment used in wood painting productions. To separate the unsoluble components WW in the plant was primarily treated by $CaCl_2$, $FeCl_3$, $Ca(OH)_2$ and floculant. After settling the sediments, the supernatant was decanted and employed as an object for our investigation, denominated in our work as PW1. Its COD amounts to about 18,000 mgO_2/l. The concentration of chloride ions in the decanted solution reached 0.11 mol/l, which contributed to 878 mg O_2/l of COD. According to the paint production technology the main paint components, as well as those of WW are water-soluble organic compounds: 1-butoxy-2-propanol (BP), dipropylene glycol monomethyl ether (mixture of isomers) (DGE), 2-hydroxy-2-methylpropiophenone (HMP), 2-butoxyethanol (BE) and acrylates oligomers, all of them are nominated as harmful.

Fenton oxidation was performed in a beaker, adding to 200 ml of acidized WW an appropriate amount of ferrous sulfate $FeSO_4$ H_2O salt and hydrogen peroxide with continuous magnetic stirring. Peroxide-to-iron molar ratios usually employed in water treatment lie in the wide range ~10–1,000 [3, 12]. In our work iron concentrations covered 5–150 peroxide-to-iron molar ratios.

Desirable temperatures were maintained by a water thermostat. In many cases it deals with the initial temperatures only, since the temperature of solutions raises when the Fenton reaction progresses. Each assay was repeated three times. The reagents for the primary treatment ($CaCl_2$, $FeCl_3$, $Ca(OH)_2$ and floculant) were of the technical quality.

Analytical methods

COD of the tested solutions was established by the standard potassium dichromate oxidation method, using a Spectroquant TR 320 Reactor and a Spectroquant Picco Colorimeter (Germany). Accuracy of the COD analysis amounts to ~10%. Before the analysis the pH of the tested solutions was increased to 9–10 and warmed up to remove the residual hydrogen peroxide, because it would interfere with the COD analysis, and filtered to remove iron hydroxide. Residual H_2O_2 was analyzed by the permanganatometric method.

Analyses of the organic compounds were carried out by GC after extraction with diethyl ether. The separation of components was performed on the column DB-Wax (30 m × 0.25 mm, film thickness 0.25 mkm) using a gas chromatograph GC (Clarus 500, Perkin Elmer, USA) with a flame ionization detector (FID) and a split / splitless injector. For the quantitative measurements the initial solutions were analysed in the split mode, and to evaluate the reduction rate of organics after the Fenton treatment the extracts (owing to small organics concentrations) were analysed in the splitless mode (splitless for 1 min). Standard reagents were dissolved in distilled water and the following concentrations were obtained (mkg/l): BP – 1.54; BE – 2.5; DGE – 2.4; HMP – 2.5. 10 ml of the standard solution were extracted with 5 ml diethyl ether and this extract was concentrated to 1 ml by evaporation. The investigated solutions were extracted in the same way.

BP, DGE, HMP and BE reagents as analytical standards were purchased from Dr. Ehrenstorfer GmbH. Samples pH was adjusted using dilute H_2SO_4 or NaOH solutions.

Electrophysiological algal test (Charatox)

Stonewort charophyte algae, *N. obtusa* (Desv.) J. Groves, were harvested in freshwater Lake Obelija (southwest Lithuania) during the vegetation in 2011. Cell storage conditions were described previously [13]. Charatox employs a rapid 90-min 50% inhibition concentration (IC50) endpoint of cell membrane depolarization. The details of the computer-assisted experimental setup, testing procedures and the methods for measurement of the cell transmembrane resting potential (RP) have been published previously [14, 15]. In short, bioelectrical activity of up to 32 living internodal cells was measured simultaneously according to the K^+-anaesthesia method [16], modified for multichannel recording with extra cellular chlorinated silver wire electrodes. Tests were carried out at room temperature in dim light. The discrete RP values from distinct cells were taken every second and stored for analysis. For the determination of IC50, the percentage decrease in the average RP value within 90-min period, in relation to that of untreated cells, was calculated for each concentration.

Toxkit bioassays

A 24-h and 48-h *D. magna* mortality (immobilization) (Daphtoxkit F™ magna) [17] test and 24-h mortality of shrimps *Thamnocephalus platyurus* [18] bioassays were performed following the Standard Operational Procedures of the respective toxkits. Test organisms and the materials required to perform the tests were purchased from Microbiotests Inc., (Belgium). The LC50 value was estimated using a non-linear (logistic) regression of the percentage of mortality with the logarithms of exposure concentration.

RESULTS AND DISCUSSION

Fenton treatment

Before the Fenton oxidation PW1 was treated with NaOH solution till pH = 12. It determined the formation of some precipitation and COD reduction by ~12%. COD of the supernatant amounted to 16,400 mgO_2/l when that of the initial PW1 was 18,200 mgO_2/l. The chromatograms of the PW1 extract are shown in Figure. The abundance peaks of BP, DGE, HMP and BE compounds were somewhat reduced after the PW1 treatment with NaOH. Further the rest of organics in the solutions treated with NaOH (denominated as PW2) were attempted to oxidize by the Fenton reaction. Dependence of COD removal upon H_2O_2 concentration at 50 °C initial temperature is depicted in Table 1.

The increase in peroxide concentration determines the augment in COD removal. It was observed that the addition of Fenton's reagent to PW2 at 50 °C put the raise in temperature dependent on the H_2O_2 concentration with a gradual decrease up to 50 °C in approximately 1.0 hour. The maximal COD removal extent is attained roughly in 1 hour and reaches about 82% using H_2O_2 at a concentration of 1.5 M. The prolonged oxidation (4–5 days) did not govern the COD decline.

After the Fenton oxidation the wastes undergo neutralization to a slightly alkaline medium, whereupon iron hydroxide sludge is produced. To estimate herewith the contribution of coagulation effect to COD decline the following test was performed: in two aliquots of PW2 (pH 2.5) 0.1 and 0.01M $FeSO_4$ were added, then pH was increased to 9 using NaOH solution. After 10 min iron hydroxide precipitate was filtered and COD of solutions was established. Initial COD was 15,000 and those of filtered samples were 12,000 and 11,600 mgO_2/l, respectively. So the coagulation contributes to ~21% of COD reduction. This result is in a fair accord

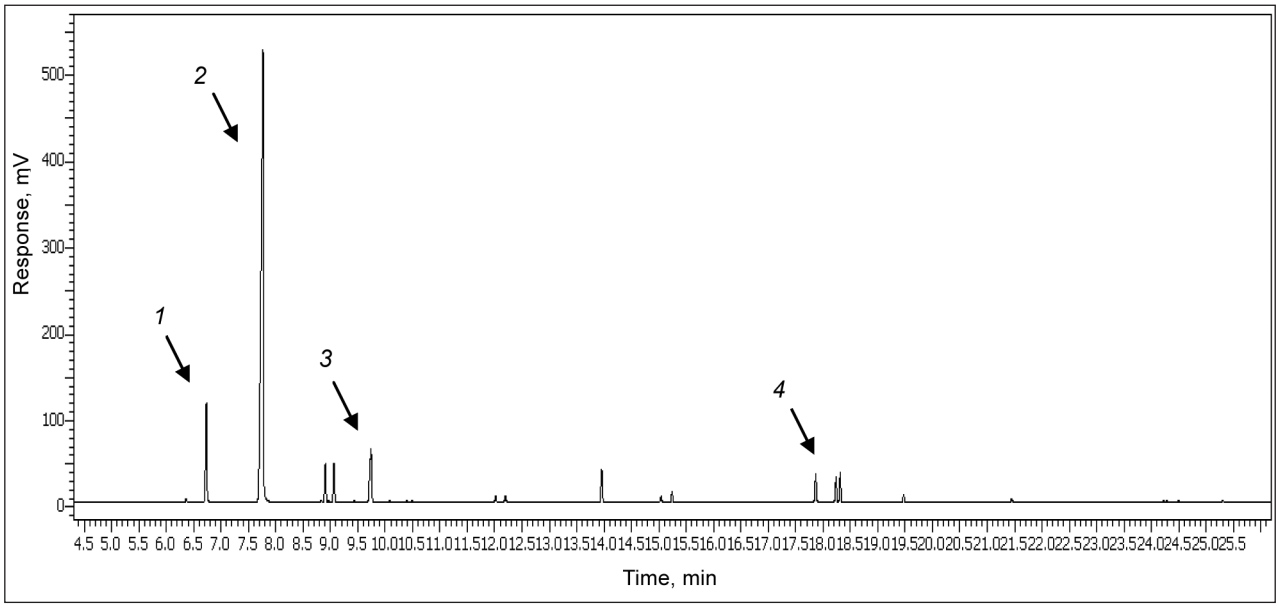

Figure. Chromatogram of diethyl ether extract of the initial (PW1) paint wastewater. *1* – 1-butoxy-2-propanol, *2* – ethylene glycol buthyl ether, *3* – dipropylene glycol monomethyl ether, *4* – 2-hydroxy-2-methylpropiophenone. Chromatographic conditions are given in *Analytical methods*

Table 1. **Dependence of COD removal kinetics on H_2O_2 concentration. Initial COD of effluent (PW2) 16,400 mgO_2/l, pH = 2.5, initial temperature 50 °C. [Fe(II)] = 0.01 M**

H_2O_2, M	Max. temp., °C	0.5 h	1 h	2 h	3 h	24 h	COD reduction after 24 h, mgO_2/l
0.25	52	11,900	11,700	11,600	11,650	11,600	4,800
0.5	55	8,200	6,600	6,700	6,600	6,600	9,800
1.0	60	4,400	4,350	4,300	4,300	4,200	12,200
1.5	68	3,200	3,000	2,900	3,000	3,000	13,400

with the data of similar work [19]. Given that every mole O_2 replaces two moles of H_2O_2, 0.25, 0.5, 1.0 and 1.5 moles H_2O_2 correspond to 4,000, 8,000, 16,000 and 24,000 mgO_2 COD, respectively. Table 1 depicts COD reduction depending on different H_2O_2 concentrations. These data, corrected according to coagulation contribution (decrease by 21 percent), show that COD removal is approximately stoichiometric to H_2O_2 content, when H_2O_2 concentrations are 0.25 and 0.5 M. At 1.0 and 1.5 M H_2O_2 concentrations the COD reduction rate is markedly lesser than stoichiometric, namely by 60% and 44%, respectively. Presumably, in this case at elevated temperatures part of H_2O_2 is wasted through self-decomposition. These data suggest the Fenton reaction performance by steps would be more preferable. In the further test PW2 with 16,000 mgO_2/l COD was treated by 0.5 M H_2O_2 + 0.01 M Fe(II) at 50 °C, and then, after 1 hour, treated repeatedly by the same Fenton's reagent concentrations. The results were as follows: 5,000 mgO_2/l and 4,200 mgO_2/l COD after the first and the second steps, respectively. Three parallel identical tests were carried out and the results differed by less than 10%. So the stepped oxidation showed practically the same ultimate results as a single-stage test, performed using 1.0 M H_2O_2. A similar result was obtained by the Fenton oxidation of pharmaceutical manufacture wastewater [20]. Evidently, organic compounds, which determine the residual COD, resist the Fenton oxidation. Considering peroxide consumption and ultimate COD removal, 1.0 M H_2O_2 and 0.01 M Fe(II) concentrations at 50 °C seem to be optimal. COD removal kinetics data at the initial 20 °C temperature are depicted in Table 2.

At the initial 20 °C temperature oxidation progress is more effective in solution with the elevated Fe(II) concentration (0.1 M). It reflects in temperature rise: after addition of Fenton's reagent to PW2 with Fe(II) concentration 0.01 M, temperature rises maximum to 24–25 °C and to 35–37 °C when 0.1 M Fe(II) was added. Oxidation with 1.0 M H_2O_2 and 0.001 M Fe(II) concentrations goes slowly, without temperature increment, and does not reach the oxidation level in 0.1 or 0.01 M Fe(II) concentration cases. COD removal dependence on the initial temperature is depicted in Table 3.

As the data of Table 3 depict, the final COD removal value is approximately equal after 24 hours in the temperature range 20–50 °C, though at lower temperatures oxidation runs slower. In summary, action of 1.0 M H_2O_2, 0.01 M Fe(II) concentrations at 50 °C seems to be optimal, considering oxidation kinetics, ultimate COD removal and peroxide consumption. COD removal dependence on pH has been further established. Test data are depicted in Table 4.

Obviously, there is no significant difference of COD removal kinetics in the pH range 2.5–6. It is in accordance with the data of other authors [21].

After the Fenton treatment (1.0 M H_2O_2, 0.01 M Fe(II), 20–50 °C), significantly reduced peaks specific to BP, DGE, HMP and BE compounds have been observed on the GC/MS spectra, as well as negligible peaks inherent to other organic compounds. Possibly, the rest of COD (~20%) was determined by the compounds not extractable by ethyl ether.

Concentrations of BP, DGE, HMP and BE compounds in the initial and treated solutions calculated by the peak area are listed in Table 5.

Table 2. **COD removal kinetics data at 20 °C initial temperature. Initial COD of wastewater 16,400 mgO_2/l, pH = 2.5**

Fenton's reagent concentration	Max. temperature, °C	0.5 h	1 h	2 h	3 h	24 h
0.5 M H_2O_2, 0.01 M Fe(II)	22	11,000	11,000	10,000	9,300	7,800
1.0 M H_2O_2, 0.01 M Fe(II)	25	12,000	9,100	9,100	8,500	4,500
0.5 M H_2O_2, 0.1 M Fe(II)	28	7,800	8,050	6,350	5,700	5,700
1.0 M H_2O_2, 0.1 M Fe(II)	37	5,000	4,700	4,500	4,500	4,600
1.0 M H_2O_2, 0.001 M Fe(II)	20	11,200	1,100	10,300	9,900	8,650

Table 3. **COD removal kinetics dependence on initial temperature. Fenton's reagent concentration: 1.0 M H_2O_2, 0.01 M Fe(II). Initial COD of wastewater 16,000 mgO_2/l, pH = 2.5**

t°C	0.5 h	1 h	2 h	3 h	24 h
20	12,100	9,100	9,100	8,500	4,500
30	12,400	10,700	6,600	6,500	4,600
40	8,650	5,800	5,010	3,800	4,100
50	4,400	4,300	4,250	4,300	4,250

Table 4. **COD removal dependence on initial pH. Fenton's reagent concentration: 1.0 M H_2O_2, 0.01 M Fe(II). Initial COD of wastewater 15,800 mgO_2/l, temperature 50 °C**

pH	0.5 h	1.0 h	3.0 h	24 h
2.5	4,500	4,400	4,300	4,300
4.0	5,150	4,000	4,200	3,900
5.0	4,400	3,900	3,950	3,900
6.0	4,550	3,900	4,020	4,000

Table 5. **Concentrations of 1-butoxy-2-propanol (BP), 2-butoxyethanol (BE), dipropylene glycol monomethyl ether (DGE) and 2-hydroxy-2-methylpropiophenone (HMP) in the initial paint WW (PW1), in the paint treated with NaOH (PW2) and in the paint next treated with Fenton's reagent**

Compound	PW1, mkg/mkl	PW2, mkg/mkl	Reduction rate,%	PW2 treated with Fenton's reagent[a], mkg/mkl	Reduction rate, %
BP	5.59	4.61	17.5	0.052	98.87
BE	42.45	34.52	18.7	1.162	96.63
DGE	5.72	5.55	3.1	0.507	90.86
HMP	0.81	0.25	69.1	0.002	99.20

[a] 1.0 M H_2O_2 + 0.01 M Fe(II).

Table 6. **Toxicity data obtained by three biotests (endpoint values are expressed in percentage of dilution, mean ± SE): 90-min electrophysiological algae test with *N. obtusa* (Charatox) and 24-h lethality tests with *D. magna* (Daphtoxkit F™) and *T. platyurus* (Thamnotoxkit F™)**

Sample	Toxicity test		
	Charatox	Daphtoxkit	Thamnotoxkit
	90-min IC50, %	24-h LC50, %	24-h LC50, %
Untreated	5.7 ± 0.5	56 ± 4.8	27 ± 0.1
Fenton-treated [1.0 M H_2O_2, 0.01 M Fe(II)]	8.5 ± 0.7	100% ⇨ 15%[a]	39 ± 0.32
Artificial salt solution[b]	98 ± 14	100% ⇨ 25%	82 ± 1.4

[a] ⇨ indicates a reaction (in %) at the respective toxicological endpoint that was observed at the maximum available effluent concentration.

[b] [Ca^{2+}] = 20 mM (0.8 g/L), [Na^+] = 80 mM (1.84 g/L).

Average reduction of the concentrations after the PW2 treatment with Fenton's reagent reaches 96.1%, so the rest of COD (3,400 mgO_2/l, Table 3) in the treated solution is mainly determined by other organic compounds.

Toxicity tests

All three biological tests showed the toxicity of untreated effluent with the Charatox being the most and Daphtoxkit F™ the least sensitive ones (Table 6).

Fenton-treated effluent was still acutely toxic to algae and shrimps, although toxicity diminished to those test-organisms by approximately 30%. Water fleas *D. magna* affected by the highest available Fenton-treated effluent sample could survive for 24-h exhibiting only negligible 15%-mortality. According to the chemical data of the untreated effluent sample, it contained relatively high concentrations of basic ions, such as $Ca^{2+}$and Na^+. These ionic concentrations had to be left after the treatment with Fenton. To have an idea to what extent the elevated ionic concentrations influence toxicity responses, test-organisms were subjected to an artificial mixture (AM) consisting of 20 mM Ca^{2+} and 80 mM Na^+, pH = 8. It was found that this AM adversely affected all three test-organisms by itself and was as much as twice more toxic to algae and shrimps than to *D. magna*. However, from the endpoint values reported in Table 6 it can be seen that AM could only have an insignificant contribution to the overall toxicity in case of charophyte algae, thus major toxicity to algae should be due to the organic compounds remaining after the Fenton-treatment. Similarly, AM in comparison to the Fenton-treated sample had no significant effect on the mortality of daphnids; however, it could have higher input to the toxic response of shrimps. Overall, the toxicological data obtained with three biological tests showed the decrease of adverse effects induced by the Fenton-treated effluent to water biota.

CONCLUSIONS

Fenton treatment of water-based wood paint wastewater enables to reduce the amounts of the main components present in effluent, such as 1-butoxy-2-propanol, dipropylene glycol monomethyl ether (mixture of isomers), 2-hydroxy-2-methylpropiophenone and 2-butoxyethanol, by ~96% and the total COD amount by ~80%. The rest of COD in the treated solution is conditioned mainly by more resistant organic compounds. Considering oxidation kinetics, ultimate COD removal and peroxide consumption, 1.0 M H_2O_2 and 0.01 M Fe(II) Fenton's reagent concentrations at 50 °C were admitted as optimal. Toxicological data obtained with three biological tests showed the decrease of adverse effects induced by the Fenton-treated effluent to water biota.

Received 2 May 2012
Accepted 15 May 2012

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Romas Ragauskas, Arvydas Stončius, Levonas Manusadžianas

VANDENINIŲ MEDIENOS DAŽŲ NUOPLOVŲ NUKENKSMINIMAS FENTONO REAKCIJA

S a n t r a u k a

Tirtas vandeninių medienos dažų nuoplovų nukenksminimas oksiduojant Fentono reagentu (vandenilio peroksidu ir dvivalente geležimi). Pradinis dažų atliekų turinčio vandens (nuoplovų) cheminis deguonies sunaudojimas (ChDS) buvo ~16 000 mgO_2/l. Fentono procesu pavyko sumažinti pagrindinių nuoplovose esančių organinių junginių – 1-butoksi-2-propanolio, dipropileno glikolio monometilo eterio, 2-hidroksi-2-metilpropiofenono ir 2-butoksietanolio koncentracijas 96 %, o bendrąjį ChDS ~80 %. Nustatyta optimali Fentono reagento koncentracija – 1,0 M H_2O_2 ir 0,01 M Fe(II) esant 50 °C temperatūrai. Buvo atlikti nuoplovų toksikologiniai tyrimai ir nustatyta, kad Fentono procesas sumažina neigiamą nuoplovų poveikį vandens organizmams.