Original Research

Toxicity of Industrial Wastewater Treated by Fenton's Reagent

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Abstract

Toxicity of four types of industrial wastewater, treated by Fenton's reagent, was analyzed. Toxicity was measured using bioluminescent bacteria *Vibrio fischeri NRRL B-11177*. Application of Fenton's reagent was a efficient method for treatment of this wastewater. Nevertheless, high efficiency of organic components degradation was not always followed by reduction of toxicity to a very low level. In all cases, in order to achieve total reduction of toxicity, it was necessary to increase both the H_2O_2 dose and reaction time. It was concluded that optimization of Fenton's reaction should be performed assuming toxicity changes in the examined wastewater. Reduction in toxicity should be a critical measure of the success of this method. Such an approach should be general practice in relation to all hazardous industrial wastewater.

Keywords: Fenton's reagent, chemical oxidation, toxicity, industrial wastewater

Introduction

Fenton's reagent (mixture of hydrogen peroxide and ferrous iron) is one of the most effective methods of the oxidation of organic pollutants [1]. Fenton's reaction is based on the catalyzed decomposition of hydrogen peroxide by iron (II) to produce very reactive hydroxyl radicals:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (1)$$

The hydroxyl radicals which are second only to fluorine among common oxidants, could react rapidly and non-selectively with nearly all‒organic pollutants [2‒4]. Indeed, the $OH^\bullet$ concentration determines the lifetimes of many compounds in the environment and, consequently, it has been called "mother nature's vacuum cleaner" [5].

The efficiency of Fenton's oxidation depends on H_2O_2 and Fe^{2+} concentrations, time and pH of the reaction. The pH value should be in the range of 2.5 to 4.0 [6]. Fenton's reagent has been found effective in treating various industrial wastewater components including aromatic amines [7] and wide variety of dyes [8], pesticides [9, 10] and surfactants, [11, 12] as well as many other substances.

Biological degradation and elimination of pollutants from water are important factors which characterize the ecological behaviour of chemical substances and wastewater streams [13]. It is very important that during treatment of industrial wastewater, persistent and toxic constituents should be reduced to acceptable levels. These goals may often be achieved by chemical oxidation. For example, Eckenfelder and Englande [14] investigated the application of Fenton's reagent to enhance biological oxidation and reduce toxicity as measured by LC_{50} for a number of organic compounds, such as nitrobenzene, aniline, o–,m–,p–cresol, o–,m–,p–chlorophenol, 2.3–,2.4–,2.5–,2.6–,3.5–dichlorophenols, 2.3–,2.4–dinitrophenols and 2,4,6–trichlorophenol. In all cases, toxicity was reduced and with most compounds to non-toxic levels. In another investigation [15] it was found that the photo-Fenton oxidation effectively reduces the concentrations of 2-and 3-ring polycyclic aromatic hydrocarbons (PAHs), heterocyclics and phenolic parent

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Table 1. Characteristics of the industrial wastewater used in this study.

Main pollutants	COD (mg/dm^3)	pH
Wastewater from the production of maleic acid anhydride (MAA)		
maleic acid, fumaric acid, phthalic acid, benzoic acid, o-xylene	13400	2.5
Wastewater from the production of 2-ethylhexyl alcohol (2−EHA)		
n-butanal, i-butanol, n-butanol, acrolein, 2-ethylhexyl alcohol, NaOH	2005	11.5
Wastewater from the production of urea-formaldehyde resin adhesive (UFRA)		
formaldehyde, methanol, ammonia nitrogen, urea	1494	9.0
Pesticide-containing wastewater (PCW)		
α−HCH (51 $\mu g/dm^3$), β−HCH (24.3 $\mu g/dm^3$), γ−HCH (57.5 $\mu g/dm^3$), DDT (16.1 $\mu g/dm^3$), DMDT (53.8 $\mu g/dm^3$), fenitrothion (158 $\mu g/dm^3$), chlorfenvinphos (139.9 $\mu g/dm^3$)	234	5.5

compounds including PCP in creosote/PCP-contaminated water. The acute toxicity (lethal dose to 50% of test population) to fathead minnows (*Pimephales promelas*) was nearly eliminated and in the case of daphnia (*Daphnia pulex*) it was reduced.

Unfortunately, in most cases the chemical oxidizing methods are optimized only on account of organic constituents removal (COD, BOD, TOC or specific pollutants). It is then presumed that considerable reduction of toxicity occurs simultaneously. However, sometimes it is impossible to reduce organic compounds completely to carbon dioxide and water by chemical oxidation. Moreover, it should be noted that in some cases chemical oxidation may even lead to increased toxicity due to the formation of even more toxic oxidation by-products [16−18]. Therefore, there is a real danger that different hazardous industrial wastewaters can still be toxic to biocenose of the receiving waters.

Thus, the objective of this study was to estimate and compare the optimum conditions of Fenton's reaction not only on account of COD removal but also of toxicity decrease. The aim was to explain whether high efficiency of organic components degradation is followed by reduction of toxicity to a non-toxic level. Fenton's reagent was used for four types of industrial wastewater.

Materials and Methods

Wastewater

Four types of industrial wastewater were collected from two chemical factories in southern Poland. It was wastewater from the production of maleic acid anhydride (MAA), 2−ethylhexyl alcohol (2−EHA) and urea-formaldehyde resin adhesive (UFRA), as well as pesticide-containing wastewater (PCW). All wastewater samples were analyzed and treated by Fenton's reagent directly after being delivered to the laboratory. Composition and characteristics of industrial wastewater used in this study are presented in Table 1.

Experimental Procedure

The following parameters of Fenton's reaction were examined and optimized: H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, pH and time. Toxicity analysis was made after prior optimization of Fenton's reaction – on account of COD removal. When toxicity was not reduced to non-toxic levels under these conditions, optimization was continued until toxicity was successfully reduced.

The procedure of Fenton's reaction was as follows: the wastewater was put into reactors of 2-litre volume, and then acidified with H_2SO_4, if necessary. Fenton's reaction is only effective in the acidic pH range. Hence, when the initial pH of wastewater was above 5.0, the samples were acidified to the selected value, in the pH range of 3.0–5.0, in order to estimate the pH effect on COD removal. After that, the various amounts of hydrogen peroxide solutions and $FeSO_4 \cdot 7H_2O$ (in a solid state) were added with continuous magnetical stirring. After appropriate time the wastewater was neutralized with 5% solution of CaO up to about pH 7. After sedimentation, the residual amount of H_2O_2 was determined in the clear solution. Toxicity tests and COD analyses were made after total removal of residual H_2O_2, using Na_2SO_3, as even very low concentrations of hydrogen peroxide resulted in the inhibition of vital activity of bioluminescent bacteria *Vibrio Fischeri NRRL B-11177* used as toxicity indicators. The residual H_2O_2 also increased the COD value since it acts as a reductant, especially in the chromate−based analysis of COD. Talinli and Anderson [19] investigated the reducing effect of H_2O_2 on $K_2Cr_2O_7$ and they showed linear relationships between concentrations of H_2O_2 and COD.

Analytical Methods

The ToxAlert® 10 instrument (Merck) was used to determine wastewater toxicity. The ToxAlert® 10 system is a screening tool designed to provide a rapid and simple test for determining acute biological toxicity. It is based upon a freeze−dried bioluminescent bacteria *Vibrio fisch-*

Table 2. Optimized parameters of Fenton's reaction and changes of wastewater toxicity.

Wastewater	H_2O_2 (g/dm³)	Fe^{2+}/H_2O_2	pH	Time (h)	COD removal (%)	Wastewater toxicity (%)	
						raw	after Fenton
MAA	5.0	0.33	3.0	1.5	87.8	100	53
2−EHA	5.0	0.50	3.5	1.5	86.3	98	47
UFRA	4.0	0.33	3.5	1.5	88.6	100	88
PCW	5.0	0.33	3.2	1.5	71.7	70	0.0

eri NRRL B-11177. These bacteria are commonly used in Microtox test [20]. Bioluminescence is linked directly to the vitality and the metabolic status of the cell. A toxic substance will cause changes in the cellular state – cell wall, cell membrane, the electron transport system, enzymes, and cytoplasmic constituents – which are rapidly reflected in a decrease in bioluminescence. Toxicity measurements were performed twice. The difference between the two results of toxicity expressed as a percentage of inhibition of vital activity of bioluminescent bacteria in no case exceeded 2 units, i.e. 2 percent. The values reported are the average of the two samples.

COD (closed reflux, titrimetric method No. 5220C) was determined in accordance with Standard Methods [21], while pH was measured using a pH-meter (pH−196, WTW Germany). Concentration of residual H_2O_2 was analyzed by the iodometric method. The main pollutants in MAA, 2−EHA and UFRA wastewater, as well as the pesticides in PCW wastewater, were determined chromatographically.

Results and Discussion

In the first part of the investigations, optimization of Fenton's reaction (on account of COD removal) was carried out for the particular types of wastewater. Different doses of H_2O_2 (from 2 to 10 g/dm³), as well as concentrations of Fe^{2+} ions ($[Fe^{2+}]$ to $[H_2O_2]$ ratio from 0.2 to 0.75), and pH (from 2 to 5) and reaction time (from 2 to 24 hour) were tried at this time. Optimized parameters, efficiency of COD removal and changes of toxicity are shown in Table 2. In all cases toxicity of raw wastewater was very high. After Fenton's reagent was used, MAA and 2−EHA wastewater indicated a twofold reduction in toxicity to bacteria *Vibrio fischeri*. However, for UFRA wastewater, a decrease in toxicity from 100% to only 88% was observed. Toxicity was completely eliminated only for pesticide-containing wastewater (PCW) – Table 2. Therefore, in the second part of the investigations, optimization of Fenton's reaction was continued on account of toxicity reduction to a non-toxic level for only three types of wastewater (i.e. MAA, 2−EHA and UFRA).

Generally, for MAA, 2−EHA and UFRA wastewater an increase of H_2O_2 doses resulted in a decrease of toxicity. The Fenton reaction time also was an important factor. However, for MAA wastewater, when reaction time was increased up to 24 hours at 2 g H_2O_2/dm³, no substantial decrease in toxicity was observed. Also, relatively little toxicity decrease was observed at 5 g H_2O_2/dm³ (Fig. 1). Beginning with an H_2O_2 dose of 6 g/dm³ the effect of reaction time was detectable. However, high toxicity reduction (down to level of 10%) was achieved only after 24 hours. Total toxicity reduction in MAA wastewater was achieved at a H_2O_2 dose of 8 g/dm³ and reaction times of 4 hours and more.

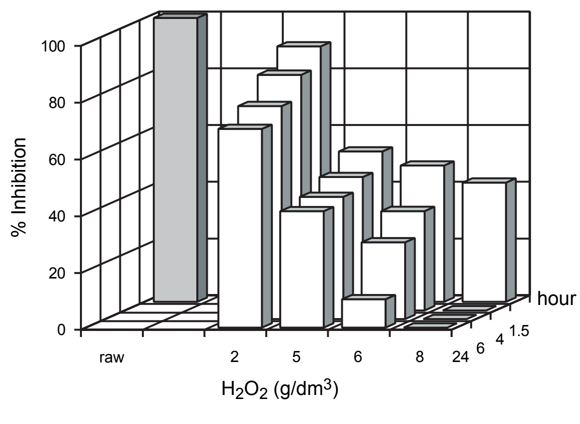

Fig. 1. Changes of toxicity during Fenton's reaction (wastewater from production of maleic acid anhydride, MAA); Fe^{2+}: H_2O_2 = 0.33, pH 3.

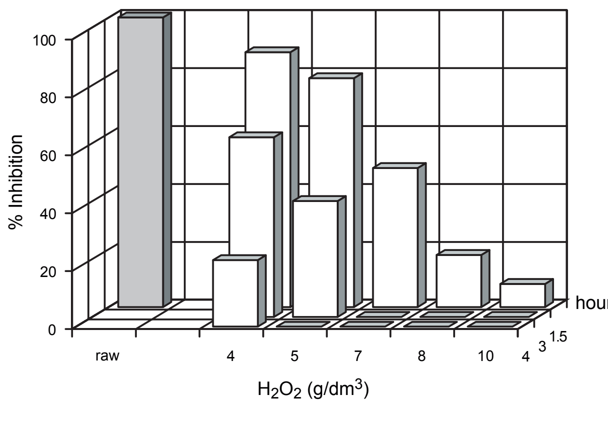

Fig. 2. Changes of toxicity during Fenton's reaction (wastewater from production of urea-formaldehyde resin adhesive, UFRA); Fe^{2+}: H_2O_2 = 0.33, pH 3.5.

Table 3. Optimized H_2O_2 concentrations and reaction time.

Wastewater	Low toxic level *		Total reduction of toxicity	
	H_2O_2 (g/dm^3)	Reaction time (h)	H_2O_2 (g/dm^3)	Reaction time (h)
MAA	6.0	24	8.0	4.0
2−EHA	5.0 or 8.0	4.0 or 3.0	8.0 or 10.0	4.0 or 3.0
UFRA	4.0	4.0	5.0 or 7.0	4.0 or 3.0

* - Low toxic level is understood by less than 25% inhibition of vital function of bioluminescent bacteria *Vibrio fischeri*.

For UFRA wastewater at 2 hours' reaction time and a H_2O_2 dose of 4 and 5 g/dm^3, relatively little toxicity decrease in relation to raw wastewater was observed. A substantial decrease in toxicity at 2 hours' reaction time was attained after increasing H_2O_2 dose up to 7 g/dm^3 (Fig. 2). Distinct toxicity reduction at 4 and 5 g H_2O_2/dm^3 occurred when reaction time was extended up to 4 hours. Other investigators have previously reported that reaction time for effective detoxication of wastewater is of particular importance [3, 18]. Total reduction in toxicity was observed both at 5 g H_2O_2/dm^3 (4 hours' reaction time) and at 7 g H_2O_2/dm^3 and more (3 hours' reaction time and more). Two hours' reaction time even at 8 and 10 g H_2O_2/dm^3 was too short to eliminate toxicity totally.

For 2−EHA wastewater at 2 hours' reaction time, similarly to UFRA wastewater, even high doses of H_2O_2, i.e. 8 and 10 g/dm^3, did not eliminate toxicity totally (Fig. 3). Prolongation of reaction time up to 4 hours caused distinct toxicity reduction. Low toxicity level in 2−EHA wastewater (25% toxicity and less) was observed at 5 g H_2O_2/dm^3 (4 hours' reaction time), at 8 g H_2O_2/dm^3 (3 hours' reaction time) as well as at 10 g H_2O_2/dm^3 (2 hours' reaction time). Total elimination of toxicity was also achieved at 8 and 10 g H_2O_2/dm^3 but this required prolonging the reaction time up to 4 and 3 hours, respectively. It can be seen, that increasing H_2O_2 doses resuls in decrease of reaction time needed to obtain low toxicity as well as non-toxic levels.

Optimum doses of H_2O_2 and reaction times, on account of toxicity removal, are presented in Table 3. Compared with the data presented in Table 2, it was observed that in order to obtain high reduction in toxicity in 2−EHA and UFRA wastewater, it is necessary to increase the reaction time from 2 to 4 hours using the same H_2O_2 doses that were applied in order to achieve optimum COD removal. For 2−EHA wastewater, even when H_2O_2 dose was increased to 8 g/dm^3, it required a longer reaction time to obtain low toxicity level, (up to 3 hours) in comparison to the reaction time needed to obtain optimum COD removal. To get similar results for MAA wastewater, the H_2O_2 dose should be increased from 5 g/dm^3 to 6 g/dm^3 and the reaction time prolonged up to 24 hours. In all cases, to reduce toxicity totally it was necessary to increase both H_2O_2 dose and reaction time. However, such extreme conditions do not have to be applied in practice since the results that show inhibition of vital functions of bacteria *Vibrio fischeri* below 20%, are considered as non-toxic when the ToxAlert® 10 system is used.

Fig. 4 demonstrates changes in COD removal during Fenton's reaction for 2−EHA wastewater. The H_2O_2 dose of 3 g/dm^3, even at 4 hours' reaction time, did not eliminate COD effectively. Only 43.2% and 58.9% efficiency of COD removal at 2 and 4 hours' reaction time was observed respectively. Considerable COD removal (by above 86%) was achieved when an H_2O_2 dose of 5 g/dm^3 was used at the beginning. However, when both H_2O_2

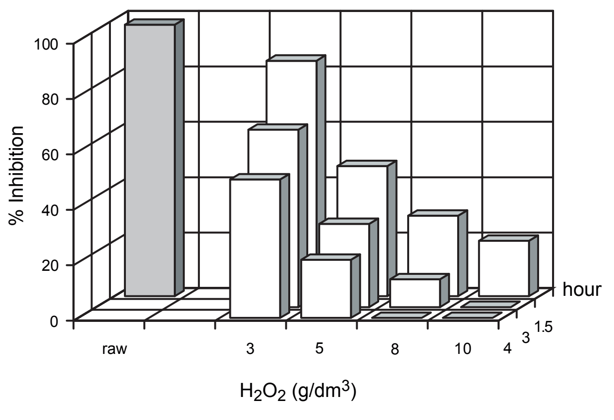

Fig. 3. Changes of toxicity during Fenton's reaction (wastewater from production of 2-ethylhexyl alcohol, 2-EHA); Fe^{2+}: H_2O_2 = 0.5, pH 3.5.

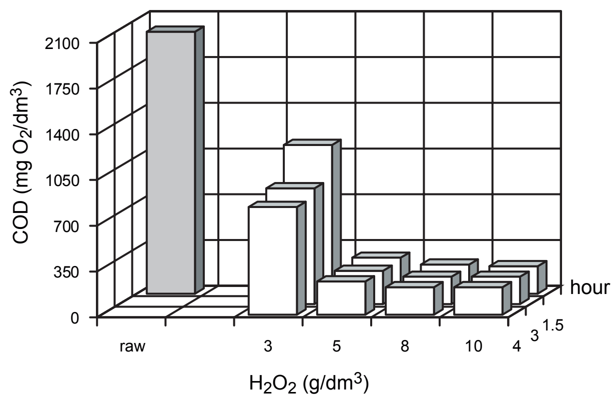

Fig. 4. Changes of COD during Fenton's reaction (wastewater from production of 2-ethylhexyl alcohol, 2-EHA); Fe^{2+}: H_2O_2 = 0.5, pH 3.5.

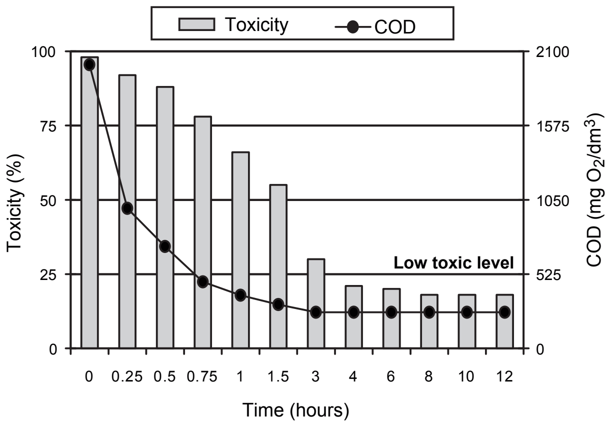

Fig. 5. COD and toxicity changes vs. Fenton's reaction time (wastewater from production of 2-ethylhexyl alcohol, 2-EHA); 5 g H_2O_2/dm^3, Fe^{2+} : H_2O_2 = 0.5, pH 3.5.

dose (up to 10 g/dm³) and reaction time (up to 4 hours) were further increased no substantial changes of COD were observed. Similar results were achieved for MAA and UFRA wastewater. Generally, when optimum COD removal was attained (see Table 2) the increase of H_2O_2 doses caused only insignificant decreases in COD values. Prolongation of reaction time produces even less effect (Fig. 4). In all cases the highest COD reduction was received within the first 2 hours of reaction time. After this time, slight or no COD reduction was observed.

An example of the COD and toxicity changes for 2−EHA wastewater are shown in Figure 5. The presented data were chosen for optimum parameters of Fenton's reaction, which made it possible to obtain low toxicity levels (see Table 3). The analysis of time characteristics clearly showed the time delay between the COD and toxicity changes. When COD values stabilized, toxicity showed further tendency to decrease. Similar observations were made for MAA and UFRA wastewater. It confirms the conclusion that the efficient optimization of Fenton's reaction requires both removal of organic constituents and reduction in wastewater toxicity.

On the basis of the above results it can be stated that the decrease of toxicity was not proportional to the drop of COD value. More rapid COD changes than in the case of changes in toxicity level, may indicate that toxicity is significantly influenced by intermediates that are formed during Fenton's reaction. This is especially visible when we look at the initial kinetics of toxicity and COD changes (Fig.5). It can be assumed that during Fenton's reaction easily degradable substrates undergo oxidation at the beginning and then more resistant compounds are oxidized. The latter substances most probably cause a slower rate of reduction of toxicity in the investigated wastewater. However, further detailed research is needed to confirm this statement.

In order to minimize treatment costs, further optimization of this system would take into consideration use of combined chemical and biological oxidation processes. In such a combined system, chemical pretreatment can destroy toxic substances to less toxic by-products and may produce intermediates that are amenable to biological degradation. Because biological treatment is generally less expensive than chemical oxidation, the total cost of this combined treatment probably may be reduced.

Conclusions

Application of Fenton's reagent is an efficient method for treatment of the four types of industrial wastewater which were tested. Nevertheless, although toxicity was generally decreased by chemical oxidation, high efficiency of organic components degradation is not always followed by reduction of toxicity to an acceptable level. Therefore, in order to optimize Fenton's reaction special care should be taken not only to remove organic constituents (COD or TOC) but also to reduce toxicity. Reduction in toxicity should be a critical measure of the success of this method. Such an approach should generally be adopted in relation to all hazardous industrial wastewater.

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