THE FULL-SCALE TREATMENT PLANT FOR DECOLOURISATION OF DYE WASTEWATER

Krzysztof BARBUSIŃSKI [a]

[a] Prof., Faculty of Energy and Environmental Engineering, The Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland
E-mail address: *krzysztof.barbusinski@polsl.pl*

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Abstract
The paper presents a short description of full-scale chemical treatment plant, based on the Fenton reagent, designed for decolourisation and purification of dye wastewater from production of matches. This treatment plant has been working since December 2000 in a chemical factory located in southern Poland. It is the first chemical plant in Poland, with Fenton reagent, intended for treatment of this type wastewater. It has been shown that the Fenton reagent process is a highly effective treatment technology for decolourisation and degradation of dye wastewater from production of matches. The Fenton reagent can achieve high removal efficiency for various parameters, such as COD, colour, and toxicity. After the Fenton oxidation, complete elimination of specific colour and toxicity (in relation to bacteria *Vibrio Fischeri*) is observed. This technology is fully professional, highly efficient, safe and flexible. The long-term experiences on a technical scale, suggest that Fenton reagent can be also applied successfully in other industries, which produce wastewater resistant to biodegradation.

Streszczenie
Przedstawiono krótki opis chemicznej oczyszczalni ścieków w skali technicznej przystosowanej do odbarwiania i oczyszczania ścieków z produkcji zapałek. Oczyszczalnia pracuje od grudnia 2000 w jednym z zakładów chemicznych zlokalizowanych w południowej Polsce. Jest to pierwsza oczyszczalnia w Polsce zaprojektowana do oczyszczania tego typu ścieków z wykorzystaniem odczynnika Fentona. Na podstawie kilkuletnich doświadczeń można stwierdzić, że technologia bazująca na odczynniku Fentona jest efektywna w odniesieniu do usuwania barwy i zanieczyszczeń organicznych ze ścieków z produkcji zapałek. Zastosowanie odczynnika Fentona pozwala uzyskać wysokie efekty obniżenia ChZT, usunięcia barwy oraz detoksykacji ścieków. W ściekach oczyszczonych następuje całkowite usunięcie specyficznej barwy oraz toksyczności (w stosunku do bakterii *Vibrio Fischeri*). Jest to w pełni profesjonalna, wysoko efektywna, bezpieczna i elastyczna technologia. Dotychczasowe obserwacje w skali technicznej pozwalają stwierdzić, że odczynnik Fentona może również być z powodzeniem stosowany do oczyszczania niepodatnych na biodegradację ścieków z innych gałęzi przemysłu.

Keywords: **Fenton reagent; Fenton reaction; Dye wastewater; Decolourisation; Wastewater from production of matches.**

1. INTRODUCTION

Many industrial processes generate hazardous and/or toxic wastewaters that are hardly biodegradable and require a chemical or physico-chemical pretreatment [1]. Biological degradation and elimination from water are important factors to characterize the ecological behaviour of chemical substances and wastewater streams. Some chemicals are designed to be resistant to environmental conditions like light, effects of pH and microbial attack. Most dyestuffs belong to this class [2]. Residual dyestuffs in dye wastewater absorb sunlight, thus they can inhibit photosynthesis process in surface water. Generally, a strong colour of the wastewater effluent, if not removed, would cause disturbance to the ecological system of the receiving waters.

The dyestuffs are very difficult to decompose biologically because most commercial dyestuffs are toxic to organisms used in the process and can disturb the function of biological wastewater plants [3]. Hence there is relatively little change of these dyestuff molecules in an activated sludge process [4]. It is assumed that main abiotic elimination mechanism for dyestuffs in biological treatment plants is adsorption onto activated sludge flocs [2]. Thus, after some time, desorption from the sludge flocs into the wastewater may occur.

Generally, dyes are released into the environment in effluents mainly from textile and dyestuff industries. However, dye wastewater is also generated during production of matches. In this case dyes are used in the dyeing processes of match-heads. Similarly to effluents from textile and dyestuff industries, wastewater from production of matches is very difficult to purification. Most of traditional methods are becoming inadequate. Therefore, it was necessary to find an effective method capable of removing colour and toxicity from this wastewater. One of the possible methods is advanced oxidation process (AOPs) using e.g. Fenton reagent.

In this paper, short description of full-scale chemical treatment plant designed for decolourisation of dye wastewater from production of matches is given. This plant, based on the Fenton reagent, is designed according to the concept of the author of this article, and is working since December 2000 in a chemical factory located in southern Poland. It is the first chemical plant in Poland, with Fenton process, intended for treatment of this type of wastewater.

2. FENTON REAGENT

The Fenton reagent (or reaction) is defined as a mixture of hydrogen peroxide and ferrous iron (H_2O_2 + Fe^{2+}). The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream but the nature of these species is still under discussion and its formulation is a subject of controversy in the past and recent Fenton oxidation related literature [5-9]. Two reaction pathways for the first step of Fenton chemistry have been advanced: a radical pathway, which considers an OH radical production (reaction 1) and a non-radical pathway considering ferryl ion (FeO^{2+}, an oxidizing Fe^{IV} species), production (reaction 2) [10].

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

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \qquad (2)$$

Although the Fenton reagent has been known for more than a century, its application as an oxidizing process for destroying hazardous organics was not applied until the late 1960s [11-12]. At present (independently from this controversy) we know that the Fenton reagent is one of the most effective methods of the oxidation of organic pollutants. The efficiency of the Fenton reaction depends mainly on H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, pH and reaction time. Also, initial concentration of the pollutant and its character as well as temperature, have a substantial influence on final efficiency.

The Fenton reagent destroys a wide variety of organic compounds without the formation of toxic by-products. Among the different technologies reported in literature for the treatment of highly contaminated effluents, Fenton's reagent is characterized by its cost effectiveness, simplicity and suitability to treat aqueous wastes showing a variable composition [13, 14]. This method offers a cost-effective source of highly oxidizing species, using easy-to-handle reagents. The important advantage of the Fenton process is that oxidation and coagulation take place simultaneously. The comprehensive investigations showed that Fenton reagent is effective in treating various industrial wastewater components including aromatic amines [15], a wide variety of dyes [16-18], pesticides [19-21], surfactants [22-24], explosives [25] as well as many other substances. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile industry, chemical manufactures, refinery and fuel terminals, engine and metal cleaning etc. [13, 18]. Also, the Fenton reagent can be effectively used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for a secondary biological treatment [26].

3. WASTEWATER TREATMENT PLANT BASED ON FENTON REAGENT

3.1. Characteristic of dye wastewater from production of matches

Dye wastewater from production of matches contains strong specific colour, a large amount of suspended solids, and a high COD concentration. The combination of strong colour and a large amount of tiny suspended solids results in high turbidity of the wastewater. Depending on the type of dyestuff used, the specific colour of the wastewater varies between red, yellow, blue, green, or purple, due to their intensified and dark varietes. This wastewater can change colour from day to day, because the dyestuff used in the dyeing process (Table 1) changes frequently due to customers' requirements. Frequent changes of dyestuff

Table 1.
The main dyes used in production of matches

Dye	Colour index, C.I.
Acid Green 16	44025
Acid Yellow 36	13065
Acid Red 18	16255
Acid Orange 7	15510
Direct Blue 86	74180

Table 2.
Characteristics of raw wastewater for the years 2000-2008

Parameter	Value
COD	960–3150 (mg O_2/dm^3)
$N\text{-}NH_4$	0.4–0.7 (mg/dm^3)
$N\text{-}NO_3$	10.2–18.7 (mg/dm^3)
Total phosphorus	20.5–30.0 (mg/dm^3)
pH	6.0-7.0
Toxicity to *Vibrio Fischeri*	100%

cause considerable variation in the wastewater colour, turbidity, and COD concentrations.

An evaluation of the wastewater characteristics was performed in 2000 before the design of the plant. The actual values for parameters characterising the raw wastewater are in the same range as those initially determined as the design parameters (Table 2).

It is very important that during treatment of industrial wastewater, persistent and toxic constituents should be reduced to acceptable levels. Unfortunately, in technical scale, in most cases the treatment methods are optimised 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, it should be noted that in some cases chemical oxidation may even lead to increased toxicity due to formation of more toxic oxidation by-products. Therefore, there is a real danger that different hazardous industrial wastewater can still be toxic to biocenose of the receiving waters. In order to optimise the chemical treatment methods special care should be taken not only to remove organic constituents but also to reduce toxicity [27]. Toxicity of wastewater from production of matches was measured using bioluminescent bacteria *Vibrio Fischeri* NRRL B-11177 (with ToxAlert® 10 instrument). It has been found that the toxicity of raw wastewater is very high (100% inhibition of vital functions of bacteria *Vibrio Fischeri*). The ToxAlert® 10 system is a screening tool designed to provide a rapid and simple test for determining acute biological toxicity.

3.2. Operating parameters

In order to estimate the operating parameters of Fenton reagent, the laboratory scale experiments were performed before the design of the plant. The effects of several process conditions such as H_2O_2 concentrations, $FeSO_4$ dosage, pH, and oxidation as well as neutralisation time on the treatment efficiency were examined and optimised. On the basis of these investigations the following values of operating parameters were established:

- acidification to pH 3.5
- H_2O_2 dose (depending on COD concentration): 0.4 – 0.6 or 1.0 – 1.5 g H_2O_2/dm^3
- Fe^{2+}/H_2O_2 ratio = 1:3 (weight)
- reaction (oxidation) time: 2.5 – 3.0 hour
- neutralisation with 5% solution of $Ca(OH)_2$ to pH 7 (minimum 30 minutes)
- sedimentation time: from 2 to 3 hour.

Doses of hydrogen peroxide were established depending on concentration of COD in wastewater. When COD > 2000 mg O_2/dm^3, the higher initial dosage of H_2O_2 (1.0-1.5 g/dm^3) is necessary. When COD < 2000 mg O_2/dm^3, amount of 0.4-0.6 g H_2O_2/dm^3 is sufficient.

Moreover, it was found that a stepwise or slow addition of Fenton reagent (particularly H_2O_2) was more effective than a large single dose of reagents. This remains in agreement with the observations by Bowlers et al. [28]. This could be due to scavenging of hydroxyl radicals by hydrogen peroxide, when applying a large initial dose of H_2O_2. Stepwise or slow addition keeps H_2O_2 concentration at relatively low levels, reducing the detrimental effect of hydroxyl radical scavenging [29, 30].

3.3. Wastewater treatment plant

The technological scheme of wastewater treatment plant is presented in Figure 1. The technology of wastewater treatment is based on the Fenton reagent. The plant is designed for 50 m^3/day. The industrial wastewater is coming from matches industry.

Dye wastewater incoming to the wastewater treatment plant is screened and introduced to an equalising tank and then pumped into the two batch Fenton reactors consisting of two nonpressured stirred tanks (each one with a net volume of 25 m^3) with metering pumps for hydrogen peroxide (35%), ferrous sulphate solution (5%), acid (H_2SO_4) and base ($Ca(OH)_2$). Two reactors enable a significant operation flexibility of purification system. The reactor vessel interior is coated with an acid-resistant material because the Fenton reagent is very aggressive. The Fenton reactors are also equipped with on-line sensors to control pH, temperature and level sensor to prevent overflow.

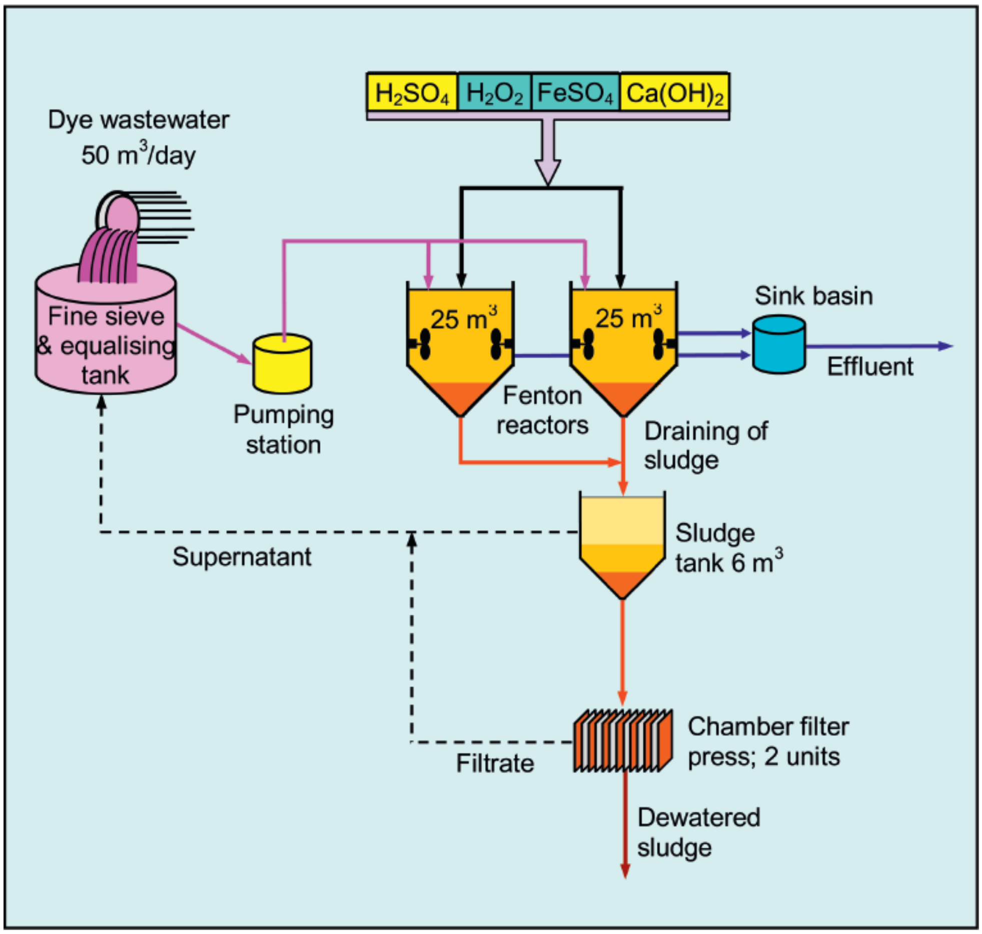

Figure 1.
Process scheme of the Fenton treatment plant

Table 3.
Characteristics of treated wastewater for the years 2000-2008

Parameter	Value	Comment
COD (mg O_2/dm^3)	40 – 120	Removal efficiency 91% – 96%
N-NH_4 (mg/dm3)	6.4 – 13.0	Values > 10 mg/dm^3 only when COD > 2000 mg O_2/dm^3
N-NO_3 (mg/dm^3)	25.5 – 29.0	
Total phosphorus (mg/dm^3)	5.5 – 9.0	
SO_4^{2-} (mg/dm^3)	60 – 250	Above 250 mg/dm^3 only when COD > 2000 mg O_2/dm^3
pH	6.8 – 7.0	
Toxicity to *Vibrio Fischeri*	0 – 5%	The wastewater that causes inhibition of vital function of bacteria *Vibrio Fischeri* below 20% is considered as non-toxic when ToxAlert® 10 system is used

The Fenton reactors are operating alternately with 8 hour cycles divided in six phases: fill, adding of reagents, oxidation reaction, neutralisation, settling of chemical sludge, and draw. Each Fenton reactor is first filled with the dye wastewater and then pH is adjusted (with H_2SO_4) to value of 3.5. The next step is the addition of part of the ferrous sulphate solution (catalyst). After some catalyst is mixed into the solution, hydrogen peroxide is slowly introduced, along with continuous catalyst supplements. To prevent excessive heating, the hydrogen peroxide must be added slowly because the Fenton reaction is exothermic. When the proper amount of H_2O_2 and $FeSO_4$ is added, the pumps are shut off and Fenton reaction occurs. All the time the wastewater is mixed by means of paddle agitator.

After the required reaction time is complete, the wastewater is adjusted to pH 7 using 5% solution of $Ca(OH)_2$. In this neutralisation step, precipitate of iron hydroxide also occurs. The final step is sedimentation of chemical sludge and draining of treated wastewater. Chemical sludge from Fenton reactors is periodically withdrawn and directed to a sludge tank and next is dewatering (without the use of chemicals, e.g. polymer) on two chamber filter presses. A supernatant from sludge tank and filtrate from filter press are directed to the equalising tank and in consequence again to the treatment process.

3.4. Effectiveness of wastewater treatment

This wastewater treatment plant has to guarantee an appropriate degree of organic compounds, colour and toxicity removal. Due to a small amount of wastewater there is no necessity of nutrient (nitrogen and phosphorus) removal. Moreover, the treated wastewater is discharged into sewerage system and next to municipal treatment plant with biological nutrient removal.

The efficiency of wastewater treatment process occurring in Fenton reactors practically does not depend on temperature. Characteristics of treated wastewater in described treatment plant are presented in Table 3. As it may be seen from the data in Table 3, in the Fenton reactors not only organic pollutions are effectively removed, but also complete decolourisation of wastewater takes place. High toxicity of wastewater in relation to bacteria *Vibrio Fischeri* is also eliminated to the non-toxic level.

The values of SO_4^{2-} exceed the Polish Standards regulations only when COD > 2000 mg O_2/dm^3. It is due to required large amounts of H_2O_2 and in consequence $FeSO_4$ for maintain the Fe^{2+}/H_2O_2 ratio = 1:3. Similarly, when COD > 2000 mg O_2/dm^3, high values of N-NH_4 (exceed 10 mg/dm^3) are observed because during the oxidation process nitrogen compounds are released from degraded dyes. Next N-NH_4 is oxidising to N-NO_3.

The phosphorus compounds (mainly phosphates) are precipitated under neutralisation step. However, because the neutralisation is leading only to pH 7, effectiveness of precipitation process is not very high. As a result, total phosphorus in purified wastewater is in the range 5.5-9.0 mg/dm^3. In order to improve precipitation effectiveness, neutralisation process should be realised for higher value of pH. However, because the treated wastewater is next discharged to municipal treatment plant with biological nutrient removal, there is no needs for increase of phosphorus removal.

4. SUMMARY

Since December 2000, the full-scale chemical treatment plant, based on the Fenton reagent, has been operated for eight years with very good performance. It has been shown that the Fenton reagent process is a highly effective treatment technology for decolourisation and degradation of dye wastewater from production of matches. The Fenton reagent can achieve high removal efficiency for various parameters, such as COD, colour, and toxicity. After Fenton oxidation in all cases the complete elimination of colour is observed and toxicity is eliminated to a non-toxic level. Because of the treated wastewater is next discharged to municipal treatment plant with activated sludge system, detoxification of wastewater is a critical measure of the success of used methods.

The treatment technology based on the Fenton reagent, proposed for the dye wastewater from production of matches, is fully professional, highly efficient, safe and flexible. The presented chemical treatment plant consists of a combination of level sensors, timers, and microprocessors. Programmable logic controllers was configured in this manner, that the plant does not require continuous monitoring and its maintenance is limited to periodic control device (one hour per day). The long-term experiences on a technical scale, suggest that Fenton reagent can be also applied successfully in other industries, which produce resistant to biodegradation, toxic and/or coloured wastewater.

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