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Treatment of Textile Dyeing Wastewater by Hydrogen Peroxide and Ferrous Ions

Abstract

The results of investigations on the applicability of Fenton reagent in the treatment of textile dyeing wastewater were discussed. The optimum conditions and efficiency of the method were determined, taking as an example three types of wastewater produced while dyeing cotton, polyacrylonitrile and polyester. The effect of the type and dose of coagulant was investigated. Two types of iron (II) salt were used: sulphate ($FeSO_4$ x 7 H_2O) and chloride ($FeCl_2$ x 4 H_2O); to adjust the pH of the wastewater, a 1% solution of calcium oxide (CaO) was used. The process of pollutant decomposition which took place in the wastewater under the influence of hydrogen peroxide alone at different concentrations was investigated. When the Fenton reagent was used both for sulphate and iron (II) chloride, the optimum doses of the two salts and hydrogen peroxide were determined. It was found that the tested dyeing wastewater revealed high susceptibility to treatment using a combined action of ferrous salts and hydrogen peroxide. The main parameters of wastewater, i.e. the colour threshold number, chemical oxygen demand and anionic surfactants, were reduced by dozens of percent. Investigations of the wastewater after treatment showed a remarkable increase in susceptibility to biodegradation.

Key words: *textile wastewater, wastewater treatment, hydrogen peroxide, iron salts, Fenton reagent.*

Introduction

The most frequently used physico-chemical method of textile wastewater treatment is coagulation. It is used mainly in wastewater decolorisation and reduction of the total load of suspensions and organic pollutants. The most popular is the coagulation with iron salts. The applied coagulant doses depend mainly on the type of wastewater and its reaction. They usually range from 300 to 5000 g/m^3 wastewater. Using the processes of coagulation, a 40-70% reduction of COD and 40-60% colour reduction was obtained in the wastewater [1].

The oxidation of organic compounds is much faster in the solutions which contain hydrogen peroxide and iron (II) salts that form hydroxyl radicals during the reaction:

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

This system is known as the Fenton reagent, and is used for wastewater treatment [2-4]. The oxidising efficiency of the Fenton reagent is the highest for pH ranging from 2 to 5, and for molar H_2O_2 to Fe^{2+} ratio, about 1:1. The mechanism of this reagent was tested in detail for many reactions of organic compounds [5 -12] and enzymatic reactions [13]; however it has not been fully explained because of the variety of iron (II) and iron (III) complexes, numerous radical intermediate products and their consecutive reactions. A significant role is played here by the formation of Fe^{3+} ions, which decompose H_2O_2 and produce $HO_2^\bullet$ radicals:

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+H^++HO_2^\bullet \quad (2)$$

In the solutions of H_2O_2 and iron (II) salts, organics (RH) are oxidised during radical chain reactions. The main agents oxidising and propagating the reactions are $HO^\bullet$ radicals:

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \quad (3)$$

$$R^\bullet + H_2O_2 \rightarrow ROH + HO^\bullet \quad (4)$$

$HO^\bullet$ radicals also decompose H_2O_2, producing $HO_2^\bullet$ radicals.

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (5)$$

In the reactions of $R^\bullet$ radicals with Fe^{3+} ions, carbo-cations R^+ may be formed, while in these involving Fe^{2+} ions, carbanions R^- may occur. The kinetic chain is terminated in the reactions between radicals:

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \quad (6)$$

$$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2 \quad (7)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (8)$$

Radicals $R^\bullet$ and $RO_2^\bullet$ also recombine, contributing in this way to the termination of the chain reaction:

$$R^\bullet + RO_2^\bullet \rightarrow ROOR \quad (9)$$

$$RO_2^\bullet + RO_2^\bullet \rightarrow ROOR + O_2 \quad (10)$$

These short characteristics of reactions (1) to (10) shows the complex mechanism of the Fenton reagent's oxidation. The most significant are $HO^\bullet$ radicals, because they propagate the chain reaction of oxidation, and in parallel, in reaction (5), they produce HO_2 radicals which also take part in the propagation.

In our previous study [10,11], the results of investigations of the applicability of the Fenton reagent in the treatment of model dyeing and laundry wastewater were discussed. They showed that the addition of hydrogen peroxide greatly increased the efficiency of pollutant removal during coagulation. Real textile wastewater is a much more complicated system. It contains at least a dozen different components, including pollutants

Table 1. Physico-chemical characteristics of real textile wastewater used in the experiments

Determination	Unit	Wastewater type		
		from cotton dyeing	from polyacrylonitrile dyeing	from polyester dyeing
Specific colour	description	bright green	orange	brown
Colour threshold number (CT)	–	100	1000	170
pH	pH	8.5	9.3	6.9
Chemical oxygen demand (COD)	mg O_2/dm^3	570	1290	450
Biochemical oxygen demand (BOD_5)	mg O_2/dm^3	<10	<10	50
Anionic detergents (AD)	mg/dm^3	4.6	14.8	11.6
Chlorides (Cl^-)	mg/dm^3	1205	124	11
Dry residue (DR)	mg/dm^3	2550	1430	580
Soluble substances (SS)	mg/dm^3	2500	1190	560
Suspension (S)	mg/dm^3	50	240	20

coming from the processed raw materials, residues of a variety of dyes [7,8,10], dyeing assistants [9] and chemicals [6] used in finishing processes. Hence the aim of the investigations presented in this article was to verify the efficiency of the Fenton reagent as used in real wastewater treatment [9,11,14].

Methodology

The aim of this study was to investigate the wastewater from the dyeing of cotton, polyacrylonitrile and polyester, taken from textile plants in Łódź. It was characterised by strong or very strong colour (CT from 100 to 1000). The chemical oxygen demand varied and ranged from 450 to 1290 mg O_2/dm^3 at a low value of biochemical oxygen demand (maximum 50 mg O_2/dm^3), which provides evidence of low susceptibility to biodegradation. The content of anionic detergents ranged from 4.6 to 14.8 mg/dm^3. The concentration of soluble substances and chlorides also varied widely - from 560 to 2500 mg/dm^3, and from 11 to 1205 mg/dm^3 respectively. The physico-chemical characteristics of the dyeing wastewater used in the study are given in Table 1.

Wastewater was treated by means of coagulation with the use of ferrous salts. The process of coagulation was carried out in Imhoff funnels of 1 dm^3 capacity using 10% water solutions of ferrous sulphate ($FeSO_4 \times 7H_2O$) and ferrous chloride ($FeCl_2 \times 4H_2O$). To adjust pH to the level of pH=7-8 after treatment of the wastewater, a 1% solution of calcium oxide (CaO) was used. The applied doses of coagulants ranged from 100 to 1600 mg/dm^3 wastewater in the case of ferrous sulphate and ferrous chloride. Lime milk was used in the amount of 35 to 530 mg/dm^3 wastewater. In the experiments covering investigations with use of the Fenton reagent, firstly analar 30% hydrogen peroxide solution in the amount from 5 to 25 cm^3/dm^3 of wastewater, and then ferrous salts, were added to the wastewater.

The crude and treated wastewater was subjected to analytical control which covered the following determinations:
- specific colour
- colour threshold number - CT,
- pH,
- chemical oxygen demand - COD,
- biochemical oxygen demand - BOD_5,
- anionic detergents - AD,
- chlorides - Cl^-,
- dry residue - DR,
- soluble substances - SS,
- suspensions - S.

All analytical determinations were made according to the methods covered in the Polish Standards.

Results

The studies were started with the determination of the effect of coagulant dose on the efficiency of the wastewater treatment measured by the value of COD of the wastewater. Two types of iron (II) salt were used, namely ferrous sulphate
$FeSO_4 \times 7H_2O$
and ferrous chloride
$FeCl_2 \times 4H_2O$.
The addition of lime milk (in the amount of 1/3 in relation to ferrous (II) salt) ensured the solution's proper pH and coagulation conditions. Changes in the chemical oxygen demand of the wastewater after coagulation, depending on the coagulant dose, are shown in Figures 1 and 2.

On the basis of the results obtained, the optimum doses of coagulants, i.e. ferrous phosphate $FeSO_4 \times 7H_2O$ and ferrous chloride $FeCl_2 \times 4H_2O$ were specified for each of the three types of wastewater tested. The optimum doses of coagulants for a given wastewater type were as follows:
- wastewater from cotton dyeing; 200 mg/dm^3 $FeSO_4 \times 7H_2O$ and 200 mg/dm^3 $FeCl_2 \times 4H_2O$,
- wastewater from polynitroacrile dyeing; 800 mg/dm^3 $FeSO_4 \times 7H_2O$ and 800 mg/dm^3 $FeCl_2 \times 4H_2O$,
- wastewater from polyester dyeing; 200 mg/dm^3 $FeSO_4 \times 7H_2O$ and 200 mg/dm^3 $FeCl_2 \times 4H_2O$.

The next stage included investigations of wastewater treatment using the Fenton reagent, and covered the process of optimisation by determining the effect of the amount of hydrogen peroxide used for pollutant reduction which took place in the process of oxidation and coagulation. The effect of hydrogen peroxide concentration on the reduction of chemical oxygen demand (COD) was investigated for the three types of wastewater and two kinds of coagulants (ferrous chloride and sulphate) used in the determined optimum quantities. The amount of hydrogen peroxide added in the form of a 30% solution ranged from 5 to 25 cm^3/dm^3 wastewater. The diagrams in Figures 3 and 4 show the results obtained. A zero result was the COD value obtained by means of coagulation in the same conditions without hydrogen peroxide added. As can be seen in the graphs, the obtained curves do not have clear maxima, therefore the choice of an optimum hydrogen peroxide concentration is not always obvious. Most advantageous seems to be the application of low concentrations of hydrogen peroxide in the range from 5 to 10 cm^3/dm^3 wastewater.

The optimum composition of coagulating-oxidising mixtures for both ferrous salts and three types of wastewater was as follows:
- wastewater from cotton dyeing; 10 cm^3/dm^3 H_2O_2 + 200 mg/dm^3 $FeSO_4 \times 7H_2O$ and 5 cm^3/dm^3 H_2O_2 + 200 mg/dm^3 $FeCl_2 \times 4H_2O$,
- wastewater from polyacrylonitrile dyeing; 20 cm^3/dm^3 H_2O_2 + 800 mg/dm^3 $FeSO_4 \times 7H_2O$ and 15 cm^3/dm^3 H_2O_2 + 800 mg/dm^3 $FeCl_2 \times 4H_2O$,
- wastewater from polyester dyeing; 5 cm^3/dm^3 H_2O_2 + 200 mg/dm^3 $FeSO_4 \times 7H_2O$ and 5 cm^3/dm^3 H_2O_2 + 200 mg/dm^3 $FeCl_2 \times 4H_2O$.

For comparison, the wastewater was treated using the Fenton reagent based on $FeSO_4$ and $FeCl_2$ (in optimum doses), and then was subjected only to coagulation and oxidation with hydrogen peroxide. From the complete physico-chemical analysis, the changes of the most important physico-chemical parameters of the wastewater, i.e. COD, CT and AD, were selected. These are shown in the diagrams in Figure 5 and 6.

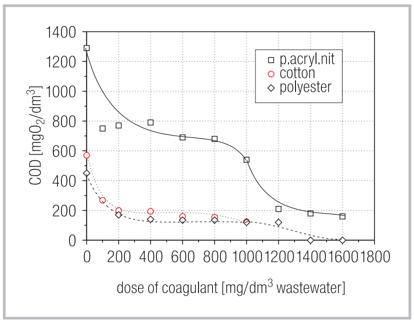

Figure 1. Changes in COD of dyeing wastewater after coagulation using ferrous phosphate ($FeSO_4$ x 7 H_2O).

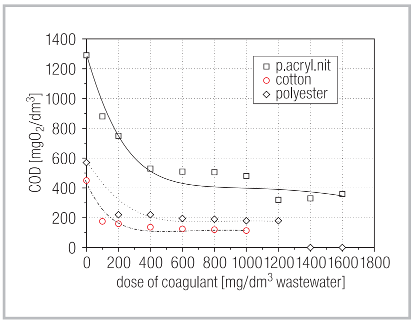

Figure 2. Changes in COD of dyeing wastewater after coagulation using ferrous chloride ($FeCl_2$ x $4H_2O$).

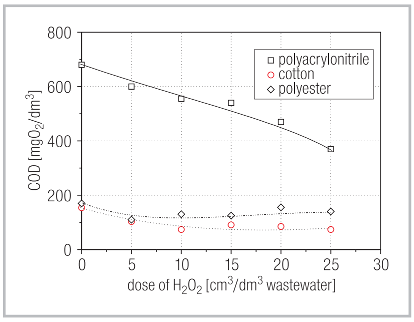

Figure 3. The effect of the amount of hydrogen peroxide on wastewater treatment efficiency measured by changes of COD in the Fenton process, using ferrous sulphate (FeSO$_4$ × 7 H$_2$O).

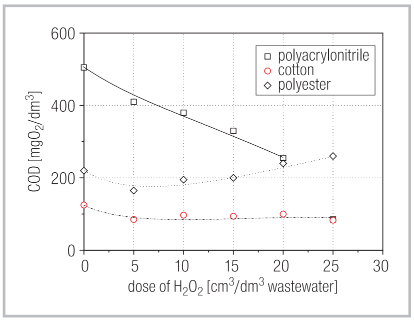

Figure 4. The effect of the amount of hydrogen peroxide on wastewater treatment efficiency measured by changes of COD in the Fenton process, using ferrous sulphate (FeCl$_2$ × 4 H$_2$O)

Discussion

The investigations showed that the tested real wastewater coming from the processes of dyeing of cotton, polyacrylonitrile and polyester revealed high susceptibility to coagulation by means of iron (II) salt. The obtained degrees of wastewater treatment depended on the initial composition of the wastewater and the concentration of pollutants contained in it. The main effect on the treatment result was imposed by the dose and type of coagulant used. Thus, in the case of the wastewater from polyester dyeing at the same doses of coagulants, better results were obtained using ferrous sulphate (maximum COD reduction 73%) than ferrous chloride (reduction 60%). In the case of the wastewater produced from polyacrylonitrile dyeing with the same doses of applied coagulants, better results were also obtained using ferrous sulphate (maximum reduction 88%) than ferrous chloride (reduction 75%). The COD reduction obtained in the wastewater from cotton dyeing using both types of coagulants was similar: 78% for ferrous sulphate and 80% for ferrous chloride.

The optimum doses of coagulants depended first of all on the initial concentration of pollutants. In the case of less concentrated wastewater from cotton and polyester dyeing, the optimum doses did not exceed 800-1000 mg/dm^3 wastewater without use of H$_2$O$_2$, while in the case of more concentrated wastewater from polyacrylonitrile dyeing, the optimum dose of coagulants was higher, amounting to 1400-1600 mg/dm^3 also without use of H$_2$O$_2$. The highest COD reduction was achieved for the most concentrated wastewater from polyacrylonitrile dyeing (75-80%) and from cotton dyeing (78-80%), while the lowest was in the case of the least concentrated wastewater from polyester dyeing (60-73%).

Additional application of hydrogen peroxide solution beside ferrous salt in the treatment increased process efficiency. The degree of COD reduction depended principally on hydrogen peroxide concentration, and also on the type and concentration of pollutants in the wastewater. With an increase of the amount of added hydrogen peroxide solution, COD reduction increased, except for the wastewater from polyester dyeing, where the most advantageous results of reduction were obtained at lower hydrogen peroxide concentration. The best results of coagulation with the addition of hydrogen peroxide solution were achieved for the wastewater from polyacrylonitrile dyeing; this was more advantageous, because this was the most concentrated wastewater.

The application of a coagulant system with hydrogen peroxide had a positive influence on the reduction of other wastewater parameters. For instance, in the wastewater from cotton dyeing after coagulation with ferrous sulphate, the colour reduction was 75%, whereas when hydrogen peroxide solution was applied additionally, the wastewater was decolourised completely. For comparison, the COD reduction increased from 65% to 88%. In the same wastewater after coagulation with ferrous chloride, the colour reduction increased from 50% to 100% when hydrogen peroxide solution was added. The reduction of AD increased from 30% to 52%, and of COD from 72% to 85%. In wastewater from polyacrylonitrile dyeing after coagulation with ferrous phosphate, the colour reduction increased from 50% to 82% after addition of hydrogen peroxide, the reduction of anionic detergents AD grew from 49% to 74%, while COD from 47% to 78%. In the same wastewater coagulated with ferrous chlo-

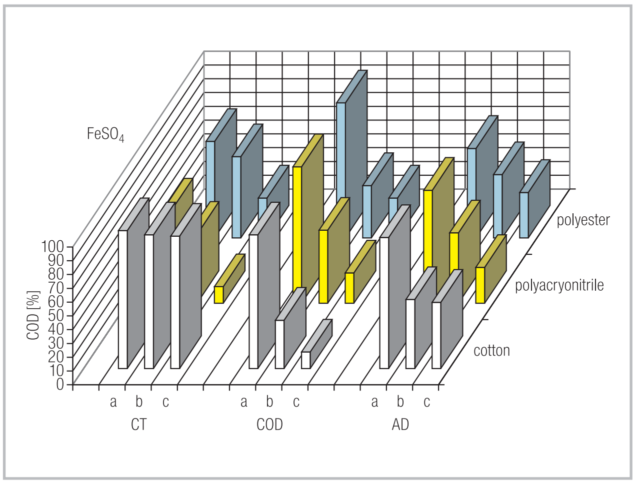

Figure 5. Changes in main physico-chemical parameters (CT, COD and AD) of three types of dyeing wastewater treated with: a) hydrogen peroxide only, b) ferrous sulphate only, c) Fenton reagent. The experiments were carried out under optimum conditions.

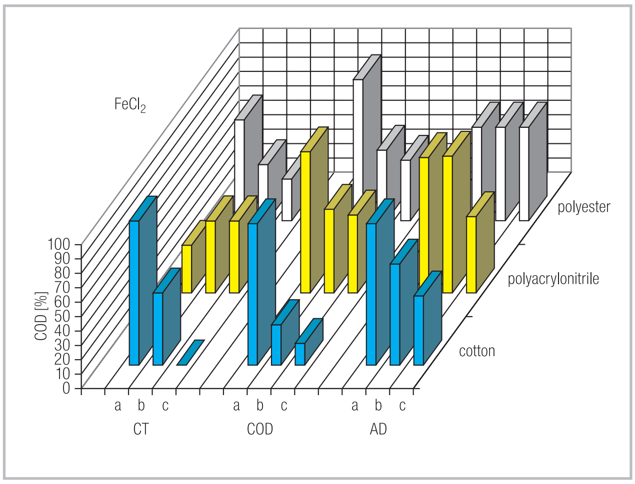

Figure 6. Changes in main physico-chemical parameters (CT, COD and AD) of three types of dyeing wastewater treated with: a) hydrogen peroxide only, b) ferrous sulphate only, c) Fenton reagent. The experiments were carried out under optimum conditions.

ride, the increase of efficiency of pollutant decomposition as a result of adding hydrogen peroxide was as follows: for CT from 90% to 95%, AD from 49% to 74%, and COD from 60% to 80%.

In wastewater coming from polyester dyeing coagulated with $FeSO_4$, the colour reduction increased from 59% to 71%, AD from 53% to 80% and COD from 62% to 76%. In the same wastewater coagulated with $FeCl_2$, the colour reduction due to the application of hydrogen peroxide increased from 61 to 71%, AD from 34% to 68%, and COD from 51% to 63%.

The application of hydrogen peroxide solution only brought about very poor results of wastewater treatment. The concentration of pollutants was maintained at practically the same level as in the untreated wastewater. There was only the wastewater decolourisation, the highest in the strongly coloured wastewater from polyacrylonitrile dyeing.

As far as the other parameters, i.e. dry residue and soluble substances, are concerned, no significant changes within the range of determination error were observed. The pH of wastewater decreased. The most significant decrease was reported when coagulation and hydrogen peroxide were used jointly.

A very interesting and positive result is the increase of the treated wastewater susceptibility to biodegradation. At very low input values of BOD_5 it is difficult to estimate its percentage increment. However, it can be stated that biodegradability increases by several times at least.

Conclusions

Additional application of hydrogen peroxide solution has a significant effect on the increase in efficiency of organic pollutant removal during coagulation in the presence of ferrous salts. Experiments carried out on real wastewater at different concentrations and compositions confirmed the relations obtained earlier for model wastewater. The results of the coagulation are enriched by pollutant oxidation. Hydroxyl radical is an oxidising agent formed as a result of the reaction of hydrogen peroxide with iron (II) ions. Undoubtedly, the process efficiency can be much improved and intensified. The presented investigations are preliminary, and their aim was to establish whether this version of the physico-chemical process is suitable for the technology of textile wastewater treatment [14] in our country.

The significant increase of susceptibility of the wastewater to biodegradation after treatment with coagulation assisted with hydrogen peroxide is especially interesting. This is of special importance for further treatment of wastewater by biological methods.

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