Effect of Formic Acid on Pollutant Decomposition in Textile Wastewater Subjected to Treatment by the Fenton Method

Abstract
The aim of this research was to determine the effect of formic acid on pollutant decomposition in textile wastewater subjected to treatment by the Fenton method. To estimate the effect of formic acid on treatment efficiency for different types of textile wastewater tested, COD reduction in mixtures of wastewater and formic acid was calculated. The values of COD calculated were then compared with COD values obtained experimentally during the oxidation of samples of wastewater-formic acid mixtures in the Fenton process. It was found that the presence of formic acid did not deteriorate the conditions of wastewater treatment in the Fenton process. Thus the presence of formic acid in textile wastewater is more advantageous than that of acetic acid.

Key words: formic acid, textile wastewater, chemical oxidation, Fenton method.

Introduction
The Fenton process is one of the simplest and cheapest methods to significantly reduce the concentration of pollutants in textile wastewater. It consists in non-selective and highly efficient oxidation of organic compounds by means of hydroxyl radicals produced in the chain process of hydrogen peroxide degradation in the presence of bivalent iron salts. The HO• hydroxyl radicals with high oxidizing potential are able to oxidise even the most resistant pollutants [1 - 9]. The run and efficiency of oxidation is determined by specific types of chemical compounds present in the textile wastewater. This refers, among others, to low-molecular compounds which on the one hand are a natural result of textile dyeing and finishing technology, but on the other one are intermediate or final products formed as a result of the oxidation of high-molecular compounds. The latter ones can be produced in quantities which may affect the run and mechanism of the oxidation reaction [10 - 12]. One such compound occurring in textile wastewater is formic acid.

While studying the results of pollutant oxidation in wastewater with the use of hydroxyl radicals, a significant decrease in the concentration of total organic carbon in the wastewater with a simultaneous increase in the concentration of carboxylic acids was observed [13]. One of the main products was formic acid. The total organic carbon content in the oxidised wastewater generated by carboxylic acids being formed reached even 50% of the total value of TOC (Total Organic Carbon). During the oxidation processes 70% of organic compounds present in the wastewater was mineralised to CO₂, while 30% was transformed into carboxylic acids. Hence the presence of formic acid can affect significantly the oxidation processes which proceed in the wastewater. Our earlier studies on the effect of acetic acid on pollutant oxidation in textile wastewater by the Fenton method showed that this acid had a negative effect on pollutant decomposition [14]. In literature there are scarce and ambiguous data on the effect of low-molecular compounds on pollutant decomposition in wastewater in the Fenton process.

Japanese researchers [15] achieved 92% decomposition of formic acid in a Fenton reaction at an initial acid concentration of 1.1×10⁻² mol/dm³. The dose of Fe²⁺ ions applied was 2.8×10⁻⁴ mol/dm³, that of hydrogen peroxide 2.5×10⁻² mol/dm³, pH 2, and the time of reaction was 30 minutes. Formic acid decomposition in water solutions was also investigated by Rossetti et al. [16]. The initial concentration of formic acid was 2×10⁻³ mol/dm³, and the ferrous sulfate doses were 1×10⁻³ mol/dm³ and 2.2×10⁻³ mol/dm³. The ratio of hydrogen peroxide to formic acid concentration was 3 : 1 and 6 : 7. The authors obtained 31% decomposition of formic acid at the ratio 3 : 1 and 43% decomposition at the ratio 6 : 7. The increase in hydrogen peroxide dosage was advantageous from the point of view of acid decomposition efficiency.

The aim of the research was to verify the Fenton process efficiency in relation to water solutions of formic acid and real textile wastewater with different concentrations and compositions which contain formic acid.

Experimental methods
The objects of the studies were water solutions of formic acid and textile wastewater of different concentrations and compositions, including dyeing and laundry wastewater and concentrate from the nanofiltration process. Laundry wastewater was generated in the initial washing of polyester knitwear. In the washing process anionic detergent was applied. The pH of the wastewater was 7.2, COD (Chemical Oxygen Demand) 350 mg O₂/dm³ and the content of anionic detergents was 30 mg/dm³. The dyeing wastewater tested came from the dyeing of cotton knitwear with reactive dyes. The pH of this wastewater was 10.3, COD = 4170 mg O₂/dm³ and the content of chlorides was 2100 mg/dm³. The concentrate examined came from the process of nanofiltration of wastewater after cotton knitwear dyeing. The concentrate had pH = 10.3 and COD = 4930 mg O₂/dm³.

Concentrated formic acid (PPH POC, Gliwice, Poland) at a concentration of 91.3% was used in the experiments. Fenton’s reagent consisted of about 30% solution of hydrogen peroxide (PPH POC, Gliwice, Poland) and FeSO₄·7H₂O as iron (II) salt.
In the case of water solutions, experiments were carried out at assumed formic acid concentrations without correcting the pH value. For instance, in a solution with acid concentration 3 g/dm³ the pH was 2.5. Next ferrous sulfate in a solid state was added to the solution, which was stirred until complete sulfate dissolution. Hydrogen peroxide was added drop-wise to the wastewater. Once H₂O₂ was instilled, the wastewater was stirred vigorously for 2 minutes and next slowly for 10 minutes. The solution was allowed to rest for 24 hours. Then the wastewater was neutralised with 10% solution of NaOH to a pH of around 11. After 24 hours the purified wastewater was decanted from the precipitate and filtered. COD was determined in the samples of water solutions of formic acid after treatment.

In the case of textile wastewater, its pH was reduced to 2.5 by means of 1 M solution of sulfuric acid. The procedure with the Fenton process was the same as in the case of water solutions of formic acid. COD was determined by Hach-Lange tests in the wastewater samples after treatment. The COD determination included the correction factor for chloride content in the wastewater.

Results and discussion

Co-precipitation of formic acid

In the Fenton process, besides the oxidation of formic acid by means of hydroxyl radicals, the process of co-precipitation induced by iron (II) hydroxide can also have an influence on the final COD reduction. To identify the contribution of this phenomenon in the Fenton process, experiments with the co-precipitation of formic acid in the range of concentrations from 0.4 to 8.3 g/dm³ were carried out with two iron doses: 1.6 and 4.0 g FeSO₄·7H₂O/dm³ solution, the results of which are shown in Figure 1. The point of reference were COD values for different initial formic acid concentrations.

The results obtained show that there is no adsorption of formic acid particles on the flocules of iron (III) hydroxide formed during co-precipitation. In the whole range of acid concentrations the values of COD of the initial solutions overlap those obtained after co-precipitation at two different doses of iron (II) sulfate.

Oxidation of formic acid solutions in the Fenton reaction

Studies on the decomposition of formic acid by means of its oxidation in the Fenton process covered the determination of the effect of acid concentration, the concentration of iron (II) ions used, the quantity of hydrogen peroxide and pH on the efficiency of oxidation processes.

When investigating the effect of the concentration of Fe²⁺ ions on the efficiency of formic acid decomposition, FeSO₄·7H₂O was used in the amounts of 0.32, 0.6, 1.0, 2.0, 4.0 and 6.0 g/dm³ in the solution. The quantity of hydrogen peroxide applied was constant and amounted to 13.2 cm³/dm³ solution. The molar ratios of hydrogen peroxide to ferrous sulfate calculated were 4.5 : 1, 5.4 : 1, 8 : 1, 11 : 1, 16 : 1, 32 : 1 and 53 : 1, respectively. The formic acid concentration applied was 3 g/dm³. The initial COD of the solution was 990 mg O₂/dm³. The values of COD obtained after the Fenton process before and after coagulation are shown in Figure 2.

As seen in Figure 2, the efficiency of formic acid decomposition measured by COD reduction at the applied doses of ferrous sulfate was constant within the measurement error. It was approximately 97%, so it was high.

The next stage of experiments involved testing the effect of the addition of hydrogen peroxide on the efficiency of formic acid oxidation in the Fenton process. The experiments were carried out with the use of hydrogen peroxide in the doses 13.2, 20, 30, 40, 50 and 60 cm³/dm³ solution. The ferrous sulfate dose applied was constant, amounting to 1 g/dm³ solution. The formic acid concentration was 3 g/dm³. The initial value of COD of the solution was 990 mg O₂/dm³. Values of COD obtained after the Fenton process prior to and after coagulation are shown in Figure 3.

The highest COD reduction, equal to ca. 98%, was achieved for hydrogen peroxide doses ranging from 20 to 60 cm³/dm³ solution. With an increase in the dose of H₂O₂ the COD reduction was maintained at a similar level.

A very important parameter which has an influence on the Fenton process is the pH of the solution. The efficiency of formic acid oxidation was investigated for the following pH values of the solution: 1.7, 2.5, 3.1, 3.6, 4.1 and 4.5. The pH of

![Figure 1. Dependence of COD on the concentrations of water solutions of formic acid co-precipitated by means of ferrous sulfate at concentrations 1.6 and 4.0 g/dm³ and not subjected to co-precipitation (initial solutions).](image1)

![Figure 2. Value of COD in formic acid water solutions at the initial concentration - 3 g/dm³ after the Fenton process before and after coagulation depending on the dose of FeSO₄·7H₂O. The dose of hydrogen peroxide applied – 13.2 cm³/dm³ solution. Initial COD – 990 mg O₂/dm³.](image2)
The results confirm that the Fenton process can be efficient only in a highly acidic environment [1, 2]. In the case of formic acid, in the reaction system applied the process should not be carried out at a pH exceeding 3 because then the oxidation efficiency decreases abruptly. The best results of COD reduction were obtained for a pH of around 2.

The next stage of experiments were investigations of the Fenton process efficiency for formic acid solutions at different initial concentrations ranging from 0.8 g/dm$^3$ to 8.3 g/dm$^3$. Experiments were made for two different doses of the reagents, namely ferrous sulfate dose 1.6 g/dm$^3$ and $H_2O_2$ = 20 cm$^3$/dm$^3$, and ferrous sulfate dose 4.0 g/dm$^3$ and $H_2O_2$ = 80 cm$^3$/dm$^3$. Figure 5 shows the results obtained. Additionally the diagram shows initial values of COD for formic acid solutions, which facilitates estimation of the process efficiency.

Formic acid decomposition in the Fenton process was very efficient in the whole range of concentrations tested, from 0.8 to 8.3 g/dm$^3$. The final values of COD were in the range from 30 to 50 mg $O_2$/dm$^3$, with the initial value being 2850 mg $O_2$/dm$^3$ for the most concentrated solution. With such good results of the decomposition it was unnecessary to use a double dose of ferrous sulfate and to increase the amount of hydrogen peroxide four times. The process is very efficient in a broad range of formic acid concentrations, as well as being fast and not requiring big initial doses of the reagents.

In the Fenton process 97% COD reduction was obtained at the initial formic acid concentration - $6.5\times10^{-2}$ mol/dm$^3$, dose of $Fe^{2+}$ ions $1.2\times10^{-2}$ mol/dm$^3$ and hydrogen peroxide - $3.55\times10^{-4}$ mol/dm$^3$. For comparison, Japanese researchers [15] achieved 92% decomposition of formic acid in the Fenton process at an initial acid concentration of $1.1\times10^{-2}$ mol/dm$^3$, dose of $Fe^{2+}$ ions $2.8\times10^{-4}$ mol/dm$^3$ and hydrogen peroxide $2.5\times10^{-2}$ mol/dm$^3$. Italian researchers [16] obtained 31% decomposition of formic acid at an initial concentration of $2\times10^{-3}$ mol/dm$^3$, and in the Fenton process with the use of a dose of $Fe^{2+}$ ions of $5\times10^{-4}$ mol/dm$^3$ and hydrogen peroxide $6\times10^{-3}$ mol/dm$^3$.

**Effect of formic acid on pollutant decomposition in textile wastewater**

The effect of formic acid on pollutant decomposition was investigated for three types of real textile wastewater with different initial COD, ranging from 350 to 4930 mg $O_2$/dm$^3$.

To the least concentrated laundry wastewater with an initial COD of 350 mg $O_2$/dm$^3$ formic acid was added in doses of 0.5, 1.0, 1.2 and 3.9 g/dm$^3$ wastewater. The dose of Fe$SO_4\cdot7H_2O$ applied was constant and amounted to 1.6 g/dm$^3$ wastewater. The hydrogen peroxide dose was also constant and equal to 20 cm$^3$/dm$^3$ wastewater. Figure 6 shows values of...
COD of the wastewater prior to and after treatment by the Fenton method.

It follows from the diagrams that the initial COD of laundry wastewater mixed with formic acid changed linearly with an increase in acid concentration. The values of COD after treatment by the Fenton method were practically constant. The degrees of COD reduction ranged from 93 to 97%. For comparison, the diagram shows calculated theoretical values of COD in the wastewater after the Fenton process. The calculations are based on the results of COD reduction obtained in the Fenton process for single components, i.e. wastewater and formic acid solutions of specified concentration under the assumption of additivity. Practically ideal overlapping of the theoretically and experimentally determined curves provides evidence of the lack of any effect of formic acid on the efficiency of pollutant decomposition in laundry wastewater in the range of concentrations tested.

In the case of dyeing wastewater with an initial COD of 4170 mg O₂/dm³, formic acid was added in the doses 0.8, 2.1, 4.2, 6.2 and 8.3 cm³/dm³ wastewater. Constant doses of ferrous sulfate – 1.6 g/dm³ and hydrogen peroxide – 20 cm³/dm³ wastewater were used. Figure 7 shows the values of COD obtained in the wastewater before and after treatment.

With an increase of formic acid concentration in the wastewater, a significant linear increase in COD occurred. After treatment by the Fenton method the values of COD were remarkably reduced in the range from 47% to 82%. Purification of the wastewater was worse at a lower formic acid concentration, i.e. at concentrations of 0.8 and 2.1 g/dm³ COD decreased by 47 and 60%, respectively. At higher acid concentrations the percent of COD reduction was approximately constant and equal to about 72%.

Additionally, for comparison, Figure 7 shows calculated theoretical values of COD in wastewater subjected to the Fenton process. The calculations are based on the results of COD reduction obtained in the Fenton process for single components, i.e. wastewater and formic acid solutions of specified concentration under the assumption of additivity. The theoretical COD values calculated after the Fenton process for the dyeing wastewater – formic acid mixture are practically constant and only slightly lower, up to 6%, than the experimental values. An exception is the sample in which the initial acid concentration was 0.8 g/dm³, where the difference was higher, amounting to 18%. These relations may suggest a slightly negative effect of formic acid on pollutant decomposition in the dyeing wastewater.

The last sample tested was a concentrate produced during the nanofiltration of wastewater coming from the process of cotton knitwear dyeing. Its initial COD was 4930 mg O₂/dm³. In this case formic acid was added in the amounts of 0.4, 1, 2 and 4 cm³/dm³ wastewater. The dose of FeSO₄·7H₂O applied was constant and equal to 4 g/dm³ wastewater. Similarly the hydrogen peroxide dose was also constant, amounting to 80 cm³/dm³ wastewater. The values of COD obtained in the wastewater before and after treatment by the Fenton method are shown in Figure 8. In the case of the concentrate the value of COD decreased after the Fenton process to about 2000 mg O₂/dm³ in the entire range of formic acid concentrations. For comparison, Figure 8 shows that the theoretically calculated COD assuming additivity, after the Fenton process to about 2000 mg O₂/dm³ wastewater. For comparison, theoretical COD reduction was presented assuming the additivity of the decomposition of the formic acid – dyeing wastewater mixture.
ton process, under the assumption that the independence of the concentrate and formic acid decomposition is bigger than the experimental data. The relations obtained suggest a slightly positive effect of formic acid on the concentrate decomposition.

Conclusions

Formic acid was very well decomposed in the Fenton process. No effect of the acid concentration on final COD reduction in the wastewater was found in the range of formic acid concentrations tested. A similar relation was observed while testing the effect of the amount of iron (II) dose on formic acid decomposition. In the case of hydrogen peroxide it was reported that this dose had an influence on COD reduction. Hydrogen peroxide should be added in the amount sufficient to carry out the process. An increase in the amount of H$_2$O$_2$ above the optimum dose did not enhance the decomposition. The Fenton process should be carried out in an acidic environment at a pH of around 2. The presence of formic acid in the textile wastewater tested had no significant effect on pollutant decomposition. Depending on the wastewater type, either a slight increase or decrease in oxidation efficiency or a similar reduction in pollutant concentration was observed in the case of the presence and absence of formic acid in the wastewater. Thus the presence of formic acid in the wastewater is more advantageous than that of acetic acid. In the latter case our investigations revealed a clearly negative effect of the presence of acetic acid on the decomposition of pollutants contained in textile wastewater [14]. From an ecological point of view it is recommended to replace acetic acid by formic in all technological processes wherever possible.

References


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