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Iron Nanocompounds Applied in the Treatment of Screen Printing Wastewater

Abstract
The aim of the study was to determine the efficiency of wastewater treatment by the Fenton method with the use of iron nanocompounds and to compare it with the classical Fenton method. The object of the study was wastewater generated during the washing of stencils used in screen printing processes. The wastewater was purified by the classical method with the use of ferrous sulfate by means of iron nanocompounds and using ferrous sulfate with the addition of iron nanocompounds. Iron(II,III) oxide nanopowder was used as an iron nanocompound. The Fenton process was optimised while investigating the effect of the type of compound applied in the treatment process, the doses of iron, hydrogen peroxide and pH of the solution on pollutant decomposition efficiency. The use of iron nanocompounds in the classical process in the presence of ferrous sulfate made it possible to increase the degree of the reduction in organic pollutants. The effect of treatment depended on the proportion of the amount of nanocompounds and the quantity of ferrous sulfate.

Key words: *screen printing wastewater, Fenton reaction, iron nanocompounds, pollutant decomposition.*

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Introduction

Textile wastewater is difficult to treat. Its troublesome and hazardous environmental impact follows from the intensive colour, high content of chemical substances, the presence of suspensions, poor biodegradability and diversified pH. Depending on the technology of washing, dyeing and finishing applied, the composition of products varies significantly.

The problem of textile wastewater treatment in our country has not been solved completely and is gaining growing importance because of the necessity of complying with EU requirements and the ending of transient periods for the application of EU directives. In industry, there is a big number of small and medium private firms dealing with dyeing and finishing of textile products in which problems with wastewater treatment have not yet been solved satisfactorily. The development of the textile industry, the introduction of new technologies, raw materials and products and stringent environmental requirements make it necessary to carry out novel investigations and to introduce innovative, more efficient treatment methods. There is a great number of solutions which can be applied, but the main criterion is to ensure high treatment efficiency at a possible low cost.

Methods of decreasing the concentration of pollutants in textile wastewater comprise oxidation/precipitation in the Fenton process [1 - 11]. During the Fenton reaction, organic compounds are oxidised by means of hydroxyl radicals produced in the chain process of hydrogen peroxide decomposition in the presence of bivalent iron salts. The process is a radical reaction in which HO• hydroxyl radicals are generated in big amounts. They are characterised by a high oxidising potential and decompose even those pollutants present in the wastewater which are most difficult to degrade. Advantages of the method include high efficiency of the oxidation reaction, inexpensive and easily available substrates and a simple procedure. A novelty of waste oxidation by the Fenton method is that it can be carried out with the use of iron nanocompounds.

Nanotechnologies are modern, innovative technologies which consist in using materials of very small sizes. The size of particles used in nanotechnologies ranges from 1 to 100 nanometers. The presence of nanoparticles has an influence, among others, on the oxidation of many compounds present in water.

Researches on iron nanocompounds in the form of Fe-Fe_2O_3 and Fe_3O_4 nanopowder used in the Fenton process are carried out worldwide. However, despite increasing interest in this topic during the last three or four years, there are still few data available in the literature [12 - 18]. To improve the catalytic properties of iron nanocompounds, they are placed on organic nano-carriers (e.g. poly 3,4-ethylene-dihydroxythiophene) or inorganic ones (e.g. hydroxyapatites) [16,17]. Additionally, some metal oxides e.g. cobalt nano-oxide, reveal a supporting action [15, 17]. The mechanism of pollutant decomposition in the Fenton process with the use of iron nanocompounds is as yet poorly recognised. Using iron nanocompounds, investigations were carried out on azo dyes and olefins, among others, showing an increase in their decomposition efficiency as compared to the Fenton process performed in a classical way [16]. In Poland, no researches have been done so far on textile wastewater treatment by the Fenton method using iron nanocompounds.

The aim of this study was to investigate the efficiency of textile wastewater treatment by the Fenton method using iron nanocompounds and to compare it with the classical Fenton method.

Methods

The object of the studies was wastewater generated during the washing of stencils used in screen printing. They contained water solutions of dispersed dyes, extraction naphtha, a binder, polyvinyl alcohol and a thickener. They were characterised by intensive red color and a high initial COD value amounting to 1515 mg O_2/dm^3.

The pH values of the wastewater samples were reduced to 3.5 by means of a 5N solution of sulfuric acid. Next the wastewater samples were completed either exclusively with ferrous sulfate or iron(II, III) oxide nanopowder, or jointly with ferrous sulfate and iron (II, III) oxide nanopowder in a solid state, and then the solution was stirred until complete dissolution. Then a 32% solution of hydrogen peroxide was added drop-wise to the wastewater. Once the H_2O_2 had been added, the wastewater was stirred vigorously for 2 minutes, and then slowly for the next 10 minutes. The solution was left for 24 hours. Next the wastewater was neutralised with a 10% solution of NaOH to a pH of about 11. After 24 hours, the purified wastewater was decanted and filtered.

After the treatment, the color of the samples was determined by the DFZ and COD methods.

The spectral absorption coefficient (DFZ, *Durchsichtsfarbzahl* in German) was determined on the basis of absorbance measurements by the spectrophotometric method at three wavelengths (λ = 436, 525 and 620 nm), according to the DIN-38404/1 standard, using the formula

$$DFZ = \frac{1000 \cdot E(\lambda)}{d}, \text{ l/m}$$

Where *E(λ)* is the absorbance at a given wavelength λ, and *d* is the measuring cuvette thickness in mm.

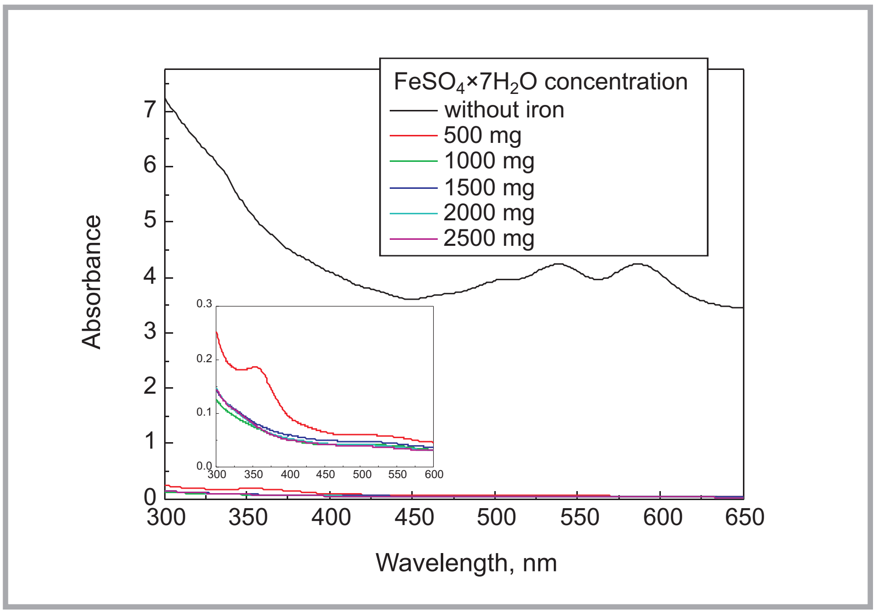

Figure 1. *Changes in the spectra of wastewater subjected to the Fenton process vs. initial wastewater.*

The chemical oxygen demand (COD) was obtained by the dichromate method according to Polish Standard No. PN-74/C-04578, corresponding to German Standard DIN EN 1899-1 and DIN 38409-H 41.

Results

The studies were commenced with the optimisation of the treatment process by the classical Fenton method to determine the effect of ferrous sulfate and hydrogen peroxide doses on pollutant decomposition efficiency in particular types of wastewater. A ferrous sulfate dose from 0.5 to 2.5 g/dm^3 and hydrogen peroxide from 10 to 50 ml/dm^3 were used.

While investigating the effect of the ferrous sulfate dose on colour and COD reduction in the screen printing wastewater, it was found that with an increase in the iron dose, there was a growth from 98.8% to 99.2% in the case of colour and from 68 to 81% in the case of COD. It

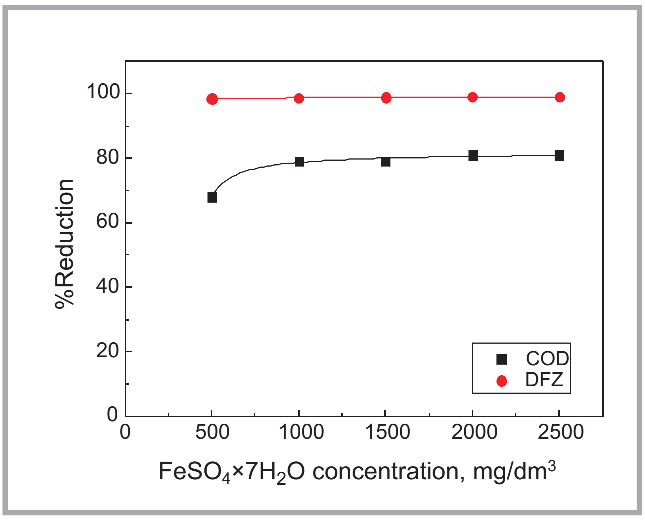

Figure 2. *Changes in the DFZ and COD of screen printing wastewater depending on the ferrous sulfate dose.*

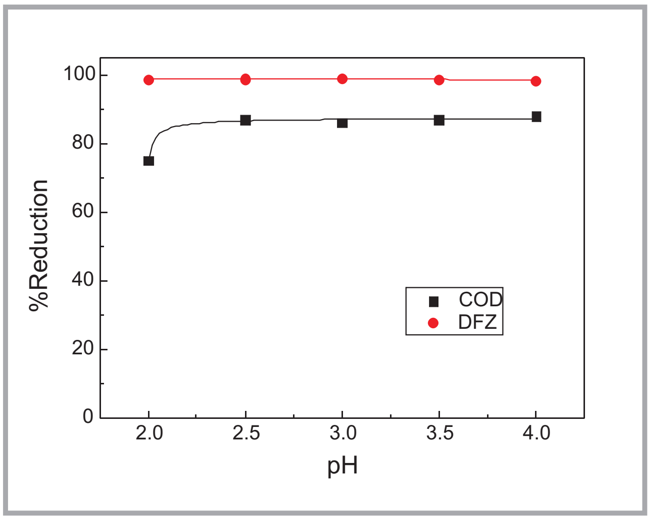

Figure 3. *Changes in the DFZ and COD of screen printing wastewater depending on the initial pH.*

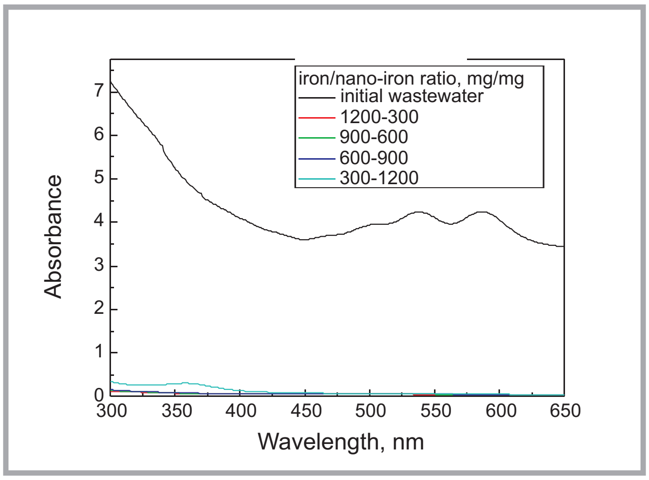

***Figure 4.** Changes in the spectra of wastewater subjected to the Fenton process vs. the initial wastewater.*

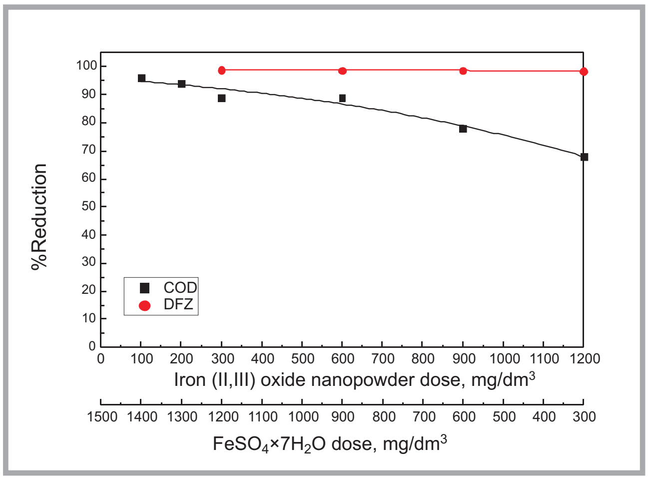

***Figure 5.** Changes in the DFZ and COD of screen printing wastewater depending on the dose of ferrous sulfate and iron(II, III) nano-oxide.*

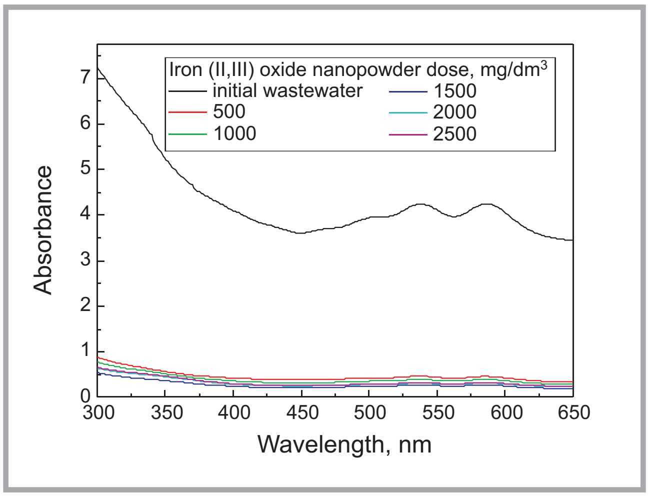

***Figure 6.** Changes in the spectra of wastewater subjected to the Fenton process as compared to the initial wastewater.*

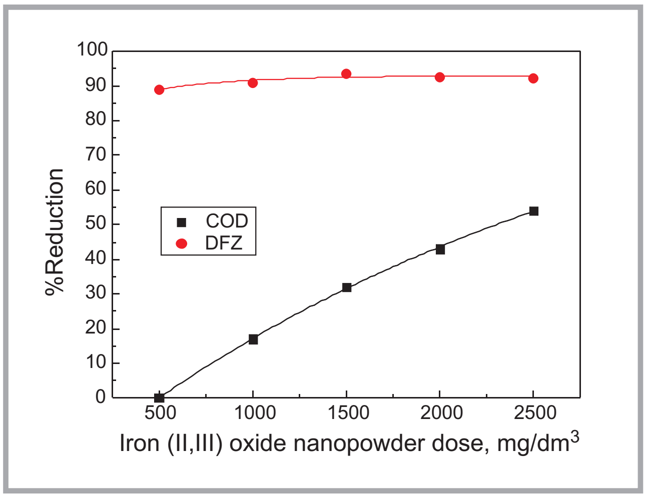

***Figure 7.** Changes in the DFZ and COD of the screen printing wastewater depending on the dose of iron(II,III) nano-oxide.*

follows from the results that the DFZ reduction in wastewater at every wavelength increased only slightly. In general, even at the lowest dose applied the wastewater was very well decolorised. In the case of COD a significant increase in this parameter reduction was observed. ***Figure 1*** shows changes in the spectra of wastewater samples depending on the ferrous sulfate dose, and ***Figure 2*** illustrates changes in the DFZ and COD.

When investigating the effect hydrogen peroxide concentration on wastewater treatment efficiency it was found that the colour reduction increased from 98.5 to 99.1%. The reduction in COD ranged from 80 to 83%, which was high. Optimum doses for the treatment process were assumed to be 1.5 g/dm^3 for ferrous sulfate and 30 ml/dm^3 for hydrogen peroxide.

The effect of pH on the treatment process was studied in the pH range of 2 to 4. The COD reduction ranged from 75% at pH = 2 to 88% at pH = 4. An optimum pH was assumed to be 3.5. Changes in the DFZ and COD of the screen printing wastewater depending on the initial pH are shown in ***Figure 3***.

Subsequent experiments covered wastewater treatment with joint use of ferrous sulfate and iron nanocompounds. The treatment was carried out using a total dose of iron compounds equal to 1.5 g/dm^3 and changing the proportions between the ferrous sulfate and iron nano-oxide at a constant dose of hydrogen peroxide of 30 ml/dm^3. The decolorisation degree and COD reduction in wastewater were examined.

It was reported that different proportions of iron compounds and nanocompounds had no significant effect on colour reduction. The wastewater samples were very well decolorised in each case. The colour reduction was very high, reaching 99%, which is illustrated in ***Figures 4*** and ***5.***

Interesting results were obtained in the case of COD (***Figure 5***). The COD decreased very much with a decrease in the amount of iron nanocompounds in the total dose. For instance, with 1.2 g/dm^3 of iron nano-oxide and 0.3 g/dm^3 of ferrous sulfate the reduction was 68%, while at 0.1 g/dm^3 of iron nano-oxide and 1.4 g/dm^3 of ferrous sulfate it was even 96%. The COD reduction was very high taking into account the high initial COD, amounting to 1515 mg O_2/dm^3. After the treatment it decreased to 62 mg O_2/dm^3 only. It seems that iron nanocompounds catalysed the process of pollutant decomposition in the classical Fenton process with the use of ferrous sulfate.

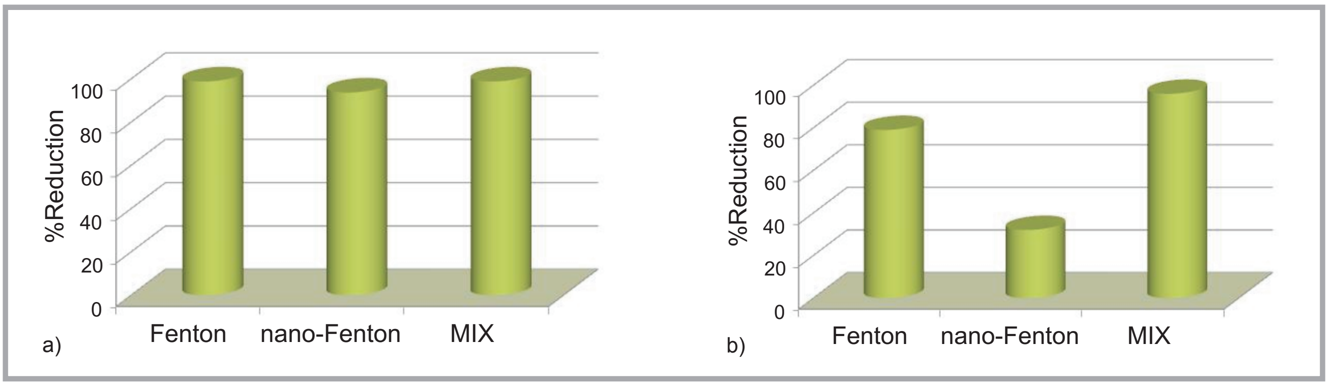

Figure 8. *Changes in the: a) DFZ (525 nm) and b) COD of screen printing wastewater depending on treatment type; Fenton: 1.5 g/dm³ ferrous sulfate, 30 ml/dm³ hydrogen peroxide. Nano-Fenton: 1.5 g/dm³ iron(II,III) nano-oxide, 30 ml/dm³ hydrogen peroxide. Mix: 1.2 g/dm³ ferrous sulfate, 0.3 g/dm³ iron(II,III) nano-oxide, 30 ml/dm³ hydrogen peroxide.*

For comparison, investigations were carried out with wastewater treated in the same conditions with the use of iron nanocompounds only. The results of decolorisation were poorer, with only 89-94% colour reduction (***Figures 6*** and *7*) and much worse reduction of COD from 0 to 54% (***Figure*** *7*).

Figure 8.a shows changes in the DFZ of the screen printing wastewater depending on the type of treatment, and ***Figure 8.b*** illustrates changes in COD.

The color reduction was the highest in samples subjected to the classical Fenton process and to the Fenton process with the use of iron nanocompounds. In the case of COD the worst results were obtained when only iron nanocompounds were used, and the best occurred when mixed treatment was applied.

Conclusions

The addition of iron nanocompounds to the classical process in the presence of ferrous sulfate made it possible to increase the degree of organic pollutant reduction demonstrated by COD. This also guaranteed a high degree of wastewater decolorisation. The treatment effects depended on the proportion between the amount of nanocompounds and the dose of ferrous sulfate. It was observed that the process of pollutant oxidation was more efficient when fewer iron nanocompounds were introduced to the reaction system. The iron nanocompounds catalysed the process of pollutant decomposition, which was demonstrated by the higher efficiency of pollutant reduction than in the classical process. Further studies on this topic covering, among others, the reaction kinetics, which we are going to carry out in the future, should contribute to the explanation of the mechanisms of oxidation processes.

Acknowledgements

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