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APPLICATION OF FENTON REAGENT IN THE TEXTILE WASTEWATER TREATMENT UNDER INDUSTRIAL CONDITIONS

ZASTOSOWANIE ODCZYNNIKA FENTONA DO OCZYSZCZANIA ŚCIEKÓW WŁÓKIENNICZYCH W WARUNKACH PRZEMYSŁOWYCH

Abstract: Application of reactive dyes is very popular in textile industry as these dyestuffs are characterized by good fastness properties. Constapel et al estimated the production of this type dyes for over 140,000 Mg/year. The reactive dyes are mostly (50%) employed for coloration of cellulosic fibers, however they can be also applied on wool and nylon. Unfortunately, they possess a low degree of fixation (50÷90%), since the functional groups also bond to water, creating hydrolysis and the excess of dyes applied cause a colored pollution of aqueous environment. Moreover, dyeing process requires the use of: electrolytes in the form of aqueous solutions of NaCl or Na_2SO_4 in the concentration up to 100 g/dm^3, alkaline environment (pH > 10) and textile auxiliary agents (among others detergents). Therefore, the wastewater generated during the reactive dyeing processes are characterized by high salinity, pH value and color, and due to low value of the ratio BOD_5/COD are non-biodegradable. The successful methods of the textile wastewater treatment could be an advanced oxidation processes (AOPs), amongst which the Fenton reagent seems to be the most perspective as it is the cheapest and easy in use. Based on the newest literature survey it was found that many successful tests with Fenton reaction were performed mainly in decolorization. However, not enough attention was devoted to decolorization of real industrial wastewater containing dyes, detergents and salts NaCl, or Na_2SO_4. The experiments carried out in lab scale were focused on the impact of NaCl and textile auxiliary agent (liquid dispersing and sequestring agent) on an inhibition of decolorization process by Fenton reagent. The objects of the investigation were the synthetic mixtures simulating the composition of real textile wastewater as well as the real industrial wastewater generated in the reactive dyeing. The inhibition of the Fenton decolorization in the presence of NaCl and liquid dispersing and sequestering agent was demonstrated.

Keywords: Fenton reagent, textile wastewater, decolorization, inhibition

A full range of bright colors, stable covalence bond to the fiber, providing a good fastness of dyeing and relatively easy synthesis - these properties make reactive dyes so popular in textile industry [1]. Constapel et al [2] estimated the annual production of these type of dyestuff for over 140,000 Mg (tones), while Ahmed and El-Shishtway [3] announce, that 50% of all cellulose fibers is dyed with reactive dyes, and only 17% with vat dyes, 16% with direct dyes, 7% with sulfur dyes, also 7% with indigo dyes and 3% with glacial dyes. Reactive dyes are mostly used to dye cellulose fibers, however there are also groups of reactive dyes dedicated for wool and polyamide. Unfortunately, despite those advantages and common use, reactive dyes are marked by low degree of fixation, between 50 and 90%, depending on the assortment. It means, the excess of dye, used in industrial dyeing process, does not bound to the fibers and in the hydrolyzed form is expelled to the sewage, causing higher contamination of aqueous environment. The fact, that the process of reactive dyeing requires special technology, also has to be taken into consideration. A fixation of reactive dye onto fiber is possible, when an electrolyte NaCl or Na_2SO_4 is used in dye bath, strong alkaline pH is produced and auxiliary *surface active agents* (SAA)

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are applied. The consumption of dyestuff in process of reactive textile dyeing amounts on average 0.5÷80 g/kg textiles, organic auxiliary agents up to 30 g/kg textiles, inorganic auxiliary agents 30÷250 g/kg textiles, electrolyte 90÷1500 g/kg textiles. Therefore, the wastewater generated in reactive dyeing process is marked by high salinity and coloration, high pH value and SAA presence. Moreover, textile wastewater is characterized by high *Chemical Oxygen Demand* (COD) value and low *Biological Oxygen Demand* (BOD) value, what makes it non-biodegradable.

A way of purification of this kind of wastewater could be AOPs methods (advanced oxidation processes), amongst which the Fenton reagent is worth of consideration, as it is not expensive and easy in use. Fenton's reagent is a method of generating hydroxyl radicals ($HO^{\bullet}$) by using reaction of hydrogen peroxide decomposition catalyzed by ferrous ions Fe^{2+}. The application of oxidizer with high redox potential (for $HO^{\bullet}$ 2.81 V) generated under *in situ* conditions, with Fenton's reaction, enables decomposition of low biodegradable substances, including dyestuff used in textile industry.

According to the newest literature report a lot of successful tests were performed, mostly in discoloration of dye solution used in textile industry, not only of reactive dyes. Xu et al [4], Papić et al [5], Kusić et al [6], Tantak and Chaudhari [7] and Arslan-Alaton et al [8] worked on discoloration of reactive dye solution with use of Fenton reagent. Wang et al [9], Gulkaya et al [10], Bianco et al [11] worked on discoloration of real industrial wastewater. These studies were focused on optimization of the method regarding color reduction, reduction of *Total Organic Carbon* (TOC) and comparison of working effects of Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2/UV.

The aim of the present publication is to show the inhibition impact of NaCl and SAA, present in real industrial wastewater, on their discoloration. Similar tests have already been performed by Alnuaimi et al [12], Riga et al [13] and Arslan-Alaton et al [14] and reveled the inhibition impact of salt on Fenton's reaction. Those tests included the impact of different kinds of salts on discoloration process of dye solution with Fenton's reagent, however the impact of SAA has not been examined yet. Moreover, the highest salt concentration (NaCl) used in these tests was 15 g/dm^3, while in industrial practice of dyeing process it can reach up to 100 g/dm^3. Therefore, conducting further study on this matter, including higher salt concentration and SAA presence, concentrated on examination of both synthetic mixtures simulating the composition of real textile wastewater and real wastewater generated in reactive dyeing process, seems to be justified.

Experimental

The experiment has been carried out with the use of a black dye commonly used in industrial practice - C.I. Reactive 5 known in trade form as Setazol Black DPT supplied by Setas Kimya. Chemical formula of the dye is presented in Figure 1. Molecular weight of Reactive 5 is 991.82 g/mol and the maximum absorbance for this dye was observed for $\lambda = 596$ nm. Furthermore, $FeSO_4 \cdot 7\,H_2O$, perhydrol - H_2O_2 conc. 30%, H_2SO_4 conc. 94% - aqueous solution 1:10, NaOH, NaCl, Perigen LDR supplied by Textilchemie Dr Petry GmbH - liquid dispersing and sequestering agent based on naphthalene sulphonic acid condensate and carboxylates have been used. The aqueous solutions of dyes and auxiliary agents have been prepared by Dosorama machine provided by Technorama. The dyestuff in a hydrolyzed form has been used, since it is present in this form in textile wastewater. The hydrolysis of dye solution has been performed in water bath at temperature 80°C during 2 hours, at pH 12. Initial dye concentration in the simulated industrial wastewater mixtures has been fixed, basing on earlier experiments, on 200 mg/dm^3.

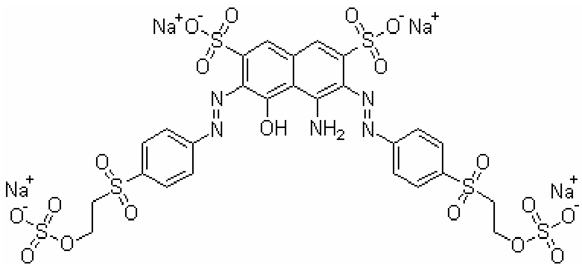

Fig. 1. C.I. Reactive 5 (trade form - Setazol Black DPT) chemical formula

The color of the dye water solution has been measured by defining the absorbance with maximum absorbance of the dye. The kinetics of discoloration of water dye solution with Fenton's reagent has been examined by measuring the absorbance with transient absorption spectrophotometer Helios, delivered by Thermo company, with constant, automatic tests collection and flow cell. Discoloration has been carried out for the three objects: aqueous solutions of BDPT dye only, simulated lab mixtures imaging the composition of real wastewater (BDPT dye solution with NaCl and Perigen LDR) and for real wastewater after dyeing process. Tests have been taken in textile testing laboratory under conditions of normal alternative climate according to ISO 139:2005, point 3.2 standards.

Results and discussion

Effect of pH

Natural pH value after discoloration process reaches 11, or even 12. However, the decomposition reaction of H_2O_2 is catalyzed most efficiently by Fe^{2+} ions in water solutions with pH value between 2 and 3. In order to verify this the discoloration of BDPT dyestuff was proceeded for pH values equal to 2 and 3. Comparatively also for two other reactive azo dyestuff (YKHL - Synozol Yellow KHL and YHB - Synozol Yellow HB) the same test was proceeded, what has been presented in Figure 2. The discoloration with Fenton's reagent for all examined dyestuff solutions proceeded the fastest with pH value equal to 3. Therefore, further tests have been performed with pH value equal to 3. In all tests the pH value of examined samples was set with H_2SO_4 1:10 solution.

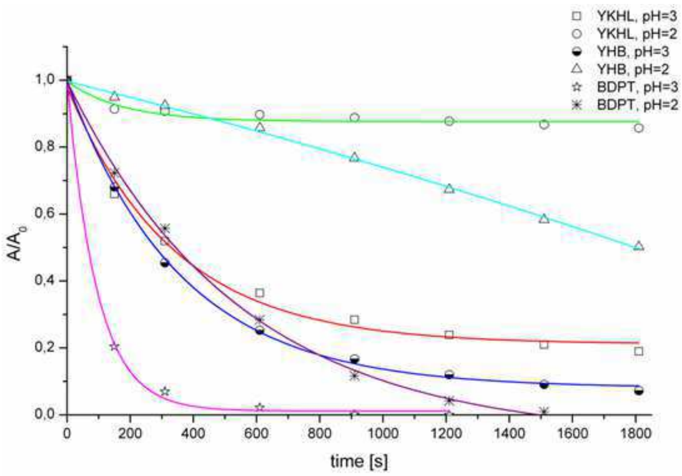

Fig. 2. Discoloration of aqueous solutions of dyestuffs: YKHL, YHB, BDPT with dyestuff concentration 200 mg/dm^3 and 75 mg Fe^{2+}/ 750 mg H_2O_2 at pH value equal to 2 and 3

Effect of ferrous dosage and Fe^{2+} : H_2O_2 ratio

In order to find an optimal dosage and reagent ratio assuring effective discoloration process tests for aqueous solution of BDPT have been performed. The concentrations of $FeSO_4$ within the range 25÷100 mg/dm^3 and reagent ratio $FeSO_4$: H_2O_2 1:5 and 1:10 have been applied. The results gained for the solutions have been presented in Figure 3. In each case higher degree of color reduction has been noticed for the reagents ratio 1:10, which has been chosen for the further tests of BDPT discoloration with $FeSO_4$ concentration amounting 75 mg/dm^3. The degree of color reduction of aqueous solution of BDPT exceeded 99%.

Effect of NaCl and Perigen LDR addition

The same conditions of Fenton reaction as for aqueous solution of BDPT (75 mg/dm^3 $FeSO_4$ and reagent ratio $FeSO_4$:H_2O_2 1:10) have been used for discoloration of dyestuff solution BDPT containing 1, 5, 10, 20, 40, 80 g NaCl /dm^3. As it can be observed in Figure 4 only for 1 g/dm^3 NaCl no meaningful decrease of discoloration efficiency appeared compared with tests without NaCl. However, the color reduction for a sample including 10 g NaCl /dm^3 amounted already 63%, and for the one including 80 g NaCl /dm^3 - 40% after 45 min.

The NaCl impact on discoloration efficiency can be explained as follows. In the presence of excess Cl^- ions due to reaction of $HO^\bullet$ radicals with Cl^- ions the ion-radicals $Cl_2^{-\bullet}$ are produced which possess much lower oxidative potential than $HO^\bullet$ radicals [15]:

$$HO^\bullet + Cl^- \longleftrightarrow HOCl^{\bullet-}$$

$$HOCl^{\bullet-} + H^+ \longrightarrow H_2O + Cl^\bullet$$

$$Cl^\bullet + Cl^- \longrightarrow Cl_2^{-\bullet}$$

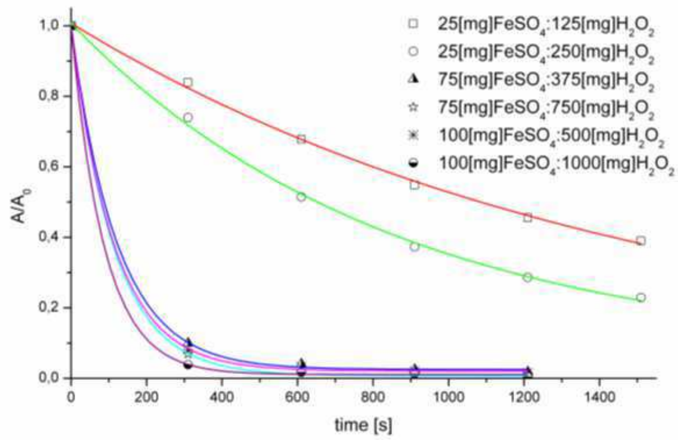

Fig. 3. Dependence of discoloration extent of dyestuff BDPT aqueous solutions on $FeSO_4$ dose

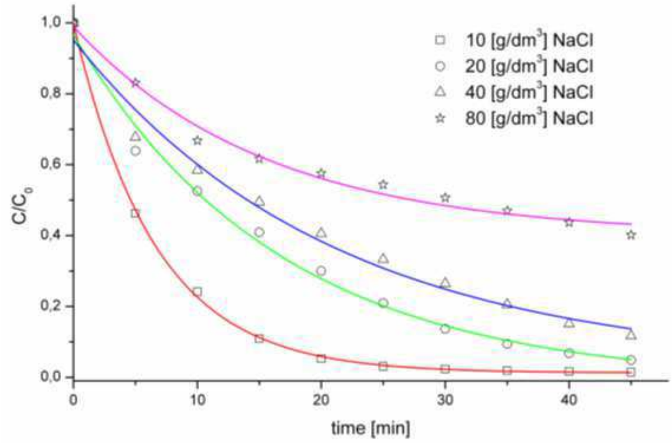

Fig. 4. Dependence of discoloration extent of dyestuff BDPT aqueous solutions on NaCl concentration

After increasing the $FeSO_4$ dose up to 200 mg/dm^3 and keeping the ratio $FeSO_4$:H_2O_2 = 1:10 the test has been repeated for samples of BDPT solution containing 0.5, 1.0, 2.0 g/dm^3 of auxiliary agent - Perigen LDR. In the case of samples containing 0.5 and 1.0 g/dm^3 Perigen LDR the Fenton reaction enabled 99% color reduction, however for the samples containing 2.0 g/dm^3 LDR the degree of color reduction decreased to 75% after 45 min, what was shown in Figure 5. The presence of surfactants in the concentration above the *Critical Micelle Concentration* (CMC) causes emulsification of dyestuff molecule shielding it against the attack of radicals, which in consequence decreased the efficiency of discoloration.

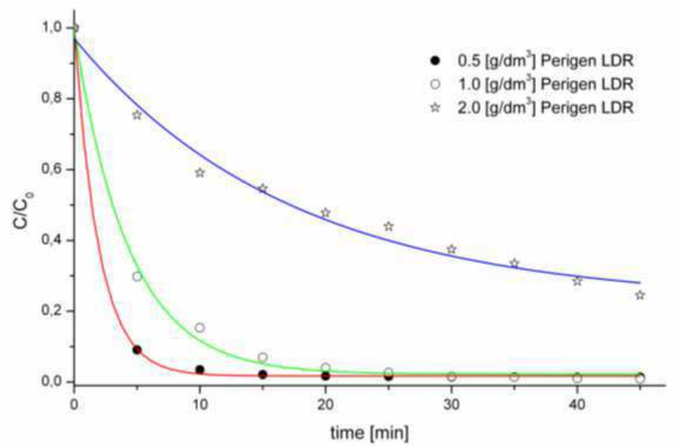

Fig. 5. Time dependence of discoloration of BDPT in the presence of surfactant Perigen LDR

Discoloration of simulated wastewater and real industrial textile effluents

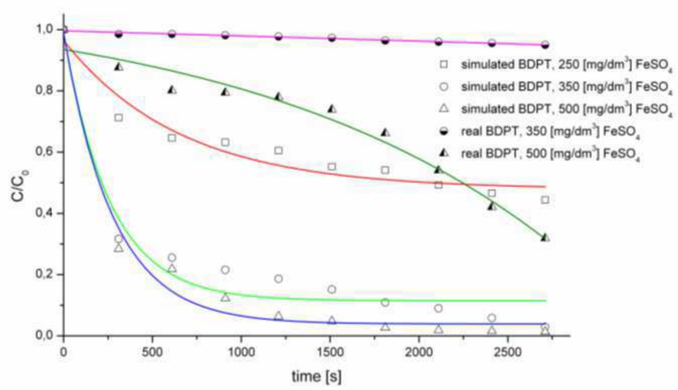

Fig. 6. Comparison of discoloration of simulated textile wastewater with real industrial one of the same reagents concentration

In the next experiment an aqueous solution with concentration of 200 mg/dm^3 BDPT containing 80 g/dm^3 NaCl and 0.5 g/dm^3 Perigen LDR, simulating the composition of real textile wastewater has been subjected to discoloration with Fenton's reagent. The doses of reagent amounting 250, 350, 500 mg/dm^3 $FeSO_4$ with the ratio $FeSO_4$:H_2O_2 = 1:10 were used. As it is seen in Figure 6 satisfactory degree of color reduction above 90 and 97% both for $FeSO_4$ dose 350 mg/dm^3 and 500 mg/dm^3 was achieved.

Finally the corresponding test for a real industrial wastewater after dyeing process with 350, 500 mg/dm^3 $FeSO_4$ and reagent ratio $FeSO_4$:H_2O_2 = 1:10, pH value equal to 3 has been performed. Unexpectedly the results of discoloration were incomparable with that obtained for the simulated wastewater. In the case of usage of 350 mg/dm^3 $FeSO_4$ almost none color reduction was observed, however for 500 mg/dm^3 $FeSO_4$ 70% of color was reduced during

45 min. It is difficult to explain these results of discoloration of real industrial wastewater, what needs further investigation. One can conclude that simulated textile wastewater is not the same as real wastewater generated during reactive dying in industrial scale.

Conclusions

Fenton reagent appeared to be very effective method in degradation of aqueous solution of many dyestuffs. Inhibition effect of NaCl presence in textile wastewater on discoloration has been found: the higher content of NaCl the poorer is discoloration degree. The emulsification effect of surfactants present in textile wastewater in the concentration above critical micelle concentration causes a decrease of discoloration rate.

Simulated textile wastewater are not the same with respect to discoloration by Fenton reagent as real wastewater generated during reactive dying in industrial scale.

It was proved, that nearly 5 times more reagent dose had to be used to discolor a mixture simulating the composition of real textile wastewater, than it is in the case of dyestuff solution without any additional substances. Moreover, to discolor real wastewater generated in industrial reactive dyeing process 500 mg/dm^3 $FeSO_4$: 5000 mg/dm^3 H_2O_2 reagent dosage, ie 7 times higher dose than in case dyestuff solution, have to be applied.

It becomes legitimate to make further study concerning discoloration of model wastewater including dyestuffs, NaCl, auxiliary agents and real wastewater, with Fenton's reagent as well as with other deep oxidation techniques.

References

[1] Czajkowski W. Nowoczesne barwniki dla włókiennictwa. Łódź: Wyd Polit Łódzkiej; 2006.

[2] Constapel M, Schellentrager M, Marzinkowski JM, Gab S. Degradation of reactive dyes in wastewater from the textile industry by ozone: Analysis of the products by accurate masses. Water Res. 2009;43:733-743. DOI: 10.1016/j.watres.2008.11.006.

[3] Ahmed Nahed SE, El-Shishtawy Reda M. The use of new technologies in coloration of textile fibers. J Mater Sci. 2010;45:1143-1153. DOI: 10.1007/s10853-009-4111-6.

[4] Xu H, Zhang D, Xu W. Monitoring of decolorization kinetics of Reactive Brilliant Blue X-BR by nline pectrophotometric method in Fenton oxidation process. J Hazard Mater. 2008;158:445-453. DOI: 10.1016/j.jhazmat.2008.01.109.

[5] Papić S, Vujević D., Koprivanac N, Sinko D. Decolourization and mineralization of commercial reactive des by using homogeneous and heterogeneous Fenton and UV/Fenton processes. J Hazard Mater. 2009;164:1137-1145. DOI: 10.1016/j.jhazmat.2008.09.008.

[6] Kusić H, Loncarić BA, Koprivanac N, Papić S. Fenton type processes for minimization of organic content in coloured wastewaters. Part II: Combination with zeolites. Dyes Pigments. 2007;74:388-395. DOI: 10.1016/j.dyepig.2006.01.050.

[7] Tantak NP, Chaudhari S. Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment. J Hazard Mater. 2006;B136:698-705. DOI: 10.1016/j.jhazmat.2005.12.049.

[8] Arslan-Alaton I, Gursoy Betul H, Schmidt JE. Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes. Dyes Pigments. 2008;78:117-130. DOI: 10.1016/j.dyepig.2007.11.001.

[9] Wang S. A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. Dyes Pigments. 2008;76:714-720. DOI: 10.1016/j.dyepig.2007.01.012.

[10] Gulkaya I, Surucu GA, Dilek FB. Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater. J Hazard Mater. 2006;B136:763-769. DOI: 10.1016/j.jhazmat.2006.01.006.

[11] Bianco B, De Michelis I, Vegliň F. Fenton treatment of complex industrial wastewater - Optimization of process conditions by surface response method. J Hazard Mater. 2011;186:1733-1738. DOI: 10.1016/j.jhazmat.2010.12.054.

[12] Alnuaimi Maitha M, Rauf MA, Ashraf S. A comparative study of Neutral Red decoloration by photo-Fenton and photocatalytic processes. Dyes Pigments. 2008;76:332-337. DOI: 10.1016/j.dyepig.2006.08.051.
[13] Riga A, Soutsas K, Ntampegliotis K, Karayannis V, Papapolymerou G. Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of H_2O_2/UV, Fenton, UV/Fenton, TiO_2/UV and TiO_2/UV/H_2O_2 processes. Desalination. 2007;211:72-86. DOI: 10.1016/j.desal.2006.04.082.
[14] Arslan-Alaton I, Tureli G, Olmez-Hanci T. Treatment of azo dye production wastewaters using Photo Fenton-like advanced oxidation processes - Optimization by response surface methodology. J Photoch Photobio A. 2009;202:142-153. DOI: 10.1016/j.jphotochem.2008.11.019.
[15] Ledakowicz S, Maciejewska R, Gębicka L, Perkowski J. Kinetics of the decolorisation by Fenton's reagent. Ozone Sci Eng. 2000;22:195-205. DOI: 10.1080/01919510008547220.

ZASTOSOWANIE ODCZYNNIKA FENTONA DO OCZYSZCZANIA ŚCIEKÓW WŁÓKIENNICZYCH W WARUNKACH PRZEMYSŁOWYCH

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Abstrakt: Barwniki reaktywne wyróżnia szereg cech, które sprawiają, iż są one powszechnie stosowane w praktyce przemysłu włókienniczego. Constapel i in. oszacowali roczną produkcję tego typu barwników na ponad 140 000 Mg. Przy czym barwniki reaktywne są w większości (50%) stosowane do barwienia włókien celulozowych, jednakże mogą one być również stosowane do wełny i poliamidu. Niestety, barwniki reaktywne wyróżnia niski stopień wyczerpania z kąpieli, wynoszący od 50 do 90%. Oznacza to, iż w przemysłowych procesach barwienia używany jest nadmiar barwnika, który nie wiąże się z włóknem i w postaci hydrolizatu trafia do ścieków, stanowiąc obciążenie dla środowiska. Procesy barwienia reaktywnego wymagają użycia elektrolitu w postaci: roztworu NaCl lub Na_2SO_4 o stężeniu do 100 g/l, wytworzenia silnie alkalicznego pH oraz użycia środków powierzchniowoczynnych - SPC. To sprawia, iż ścieki generowane w procesach barwienia reaktywnego charakteryzuje: wysokie zasolenie i zabarwienie, wysoka wartość pH, obecność SPC. Ponadto te ścieki ze względu na niski stosunek BZT_5/ChZT są mało podatne na procesy biologicznego oczyszczania. Alternatywą dla oczyszczania tego typu ścieków mogą być metody AOP, wśród których na uwagę ze względu na niskie koszty i łatwość stosowania zasługuje odczynnik Fentona. Na podstawie przeglądu najnowszych doniesień literaturowych można stwierdzić, iż zostało przeprowadzone wiele udanych prób głównie dekoloryzacji roztworów. Niewiele natomiast uwagi poświęcono odbarwianiu ścieków rzeczywistych czy symulowanych mieszanin zbliżonych składem do ścieków rzeczywistych, czyli zawierających barwniki oraz NaCl, Na_2SO_4, SPC, (Sun i in. 2009; Arslan-Alaton i in. 2008). Eksperymenty przeprowadzone w skali laboratoryjnej były ukierunkowane na analizę wpływu NaCl i włókienniczych środków pomocniczych (środki dyspergujące i sekwestrujące) na hamowanie procesu odbarwiania odczynnikiem Fentona. Przedmiotem badań były zarówno syntetyczne ścieki symulujące skład rzeczywistych ścieków włókienniczych, jak również rzeczywiste ścieki powstałe w procesie barwienia reaktywnego. Wykazano zjawisko hamowania odbarwiania odczynnikiem Fentona w obecności NaCl, jak i środków dyspergujących i sekwestrujących.

Słowa kluczowe: odczynnik Fentona, ścieki włókiennicze, odbarwianie, inhibicja