DOI: 10.2429/proc.2013.7(1)002 2013;7(1)

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STUDIES OF OPTIMIZATION OF COLORED WASTEWATER TREATMENT BY FENTON'S REAGENT (PART I)

BADANIA W CELU OPTYMALIZACJI OCZYSZCZANIA ŚCIEKÓW BARWNYCH ODCZYNNIKIEM FENTONA (CZĘŚĆ I)

Abstract: The constant industry development results in the increase of number and diversity of substances deposited with wastewater. Moreover, requirements for wastewater utilization are constantly restricted, thus there is the need of treatment methods improvement. In recent studies significant attention is devoted to advanced oxidation processes (AOPs), in which highly reactive radicals able to treat concentrated, hardly degradable and toxic industrial wastewaters are generated. Colored wastewaters produced during industrial processes usually characterize with significant content of refractive organic compounds which additionally posses mutagenic and cancerogenic properties. Classical treatment methods of such wastewaters (e.g. sorption, coagulation) hardly ever guarantee efficient dyes degradation. Thus, the treatment of colored wastewater with the use of one of AOP ie Fenton reagent was performed. First, preliminary studies focused on the influence of H_2O_2 dose, initial pH value, reaction time and Fe^{2+}/H_2O_2 weight ratio on treatment effect were performed. Obtained results will be further used for development of crucial studies plan in which Surface Response Method will be used. The study will allow to formulate mathematical models describing changes of wastewater decolorization effects as a function of investigated parameters. Thus, the optimization of the process will be possible.

Keywords: advanced oxidation processes, Fenton's reagent, dye wastewater, response surface methodology

Introduction

One of the results of the civilization development is the global application of organic dyes applied in many branches of the industry. Nowadays almost all produced goods - including food, cosmetic products, pharmaceuticals, plastics, textiles or even natural material are dyed. Colored wastewaters produced during technological processes characterize with significant content of hardly decomposing organic compounds, which posses toxic or cancerogenic properties. Thus, the degradation of dyes must be performed in order not only to protect water ecosystems but also humans' health and safety [1-3].

According to wide diversity of dyes used in industry there are many treatment technologies applied for removal of those contaminants. It includes coagulation, sorption, chemical oxidation with ozone or hydrogen peroxide or separation. In many cases combination of those processes together with biological treatment is applied [1, 4-7]. Advanced oxidation processes (AOPs) *ie* UV/H_2O_2 [1], UV/TiO_2 [8] or Fenton reagent are also a solution used for colored wastewater treatment. The high effectiveness of those processes is obtained by the action of highly reactive hydroxyl free radicals $OH^{\bullet}$. Those radicals characterize with significant redox potential (2.8 V) as well as fast and non-selective oxidation of many organic compounds. However, many scientists state that in case of Fenton reaction ferryl ion (FeO^{2+}) acts as an oxidizing agent [4].

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The application of Fenton method for contaminants degradation has many advantages *ie* no toxic effect, low price of reagent components and no formation of chloroorganic compounds. The evaluation of treatment of wastewater containing Acid Yellow 36 dye by means of Fenton method is discussed in the presented paper. The results obtained during the study will be a base for further treatment via *Surface Response Method*. The second part of the study will focus on the development of mathematical models describing changes of wastewater decolorization effects as a function of investigated parameters. Thus, the optimization of the process will be possible.

Methodology of the study

The treatment of colored wastewater containing acidic dye Acid Yellow 36 extra (250%) by BORUTA-KOLOR Sp. z o.o. was performed. The dye is mainly used in textile industry and according to its properties it must be removed from wastewaters before their deposition to the receiving body [9]. The aim of the experiment was to determine the influence of H_2O_2 dose, initial pH, reaction time and weight ratio of Fe^{2+}/H_2O_2 on wastewater decolorization effects. The synthetic wastewater was prepared via dissolution of 100 mg of dye in 1 dm^3 of deionized water. The obtained solution characterized with yellow color and clarity. Next, the solution was acidified until the desired pH was established. Next, hydrogen peroxide and solid $FeSO_4 \cdot 7H_2O$ were added. Fenton reaction occurs in acidic environment and after it is finished, the neutralization was needed. The wastewater neutralization caused their further decolorization and precipitation of well-settling iron(III) hydroxide $Fe(OH)_3$. The degradation of dye was carried out in beakers of 1 dm^3 volume which were constantly mixed using magnetic stirrer with the speed of 300 rpm. The determination of dye concentration in treated wastewater was made after their neutralization and centrifugation (used to remove formed precipitate) by means of absorbance measurements using SPEKOL UV VIS spectrometer at wavelength $\lambda = 485$ nm. The visual evaluation of decolorization rate was also made.

Results and discussion

In the preliminary studies hydrogen peroxide doses in the range 40÷200 mg/dm^3 increased by 20 mg/dm^3 step-wisely were applied. The first part of experiments was carried out at constant pH = 3.5 and Fe^{2+}/H_2O_2 weight ratio equal to 0.33. Basing on previous studies performed at Division of Water and Wastewater Technology 15 and 30 min reaction times were accepted. Obtained results revealed that the increase of hydrogen peroxide dose caused the decrease of absorbance value at treated wastewater (Fig. 1). The visual decolorization was already obtained for the oxidant dose equal to 140 mg/dm^3 for which absorbance value was at the level of 0.078. The best degradation effect was noted for the oxidant dose equal to 180 mg H_2O_2/dm^3. In the next stage of the study the decolorization effectiveness at constant pH = 3.5, H_2O_2 dose - 180 mg H_2O_2/dm^3 and various Fe^{2+}/H_2O_2 weight ratios in the range 0.05-0.5 was investigated. The reaction times were also equal to 15 and 30 min. The best treatment effect was obtained for Fe^{2+}/H_2O_2 ratios 0.05 and 0.1 (measured absorbance values after 15 min were equal to 0.1216 and 0.0714 and after 30 min 0.0674 and 0.0648, respectively).

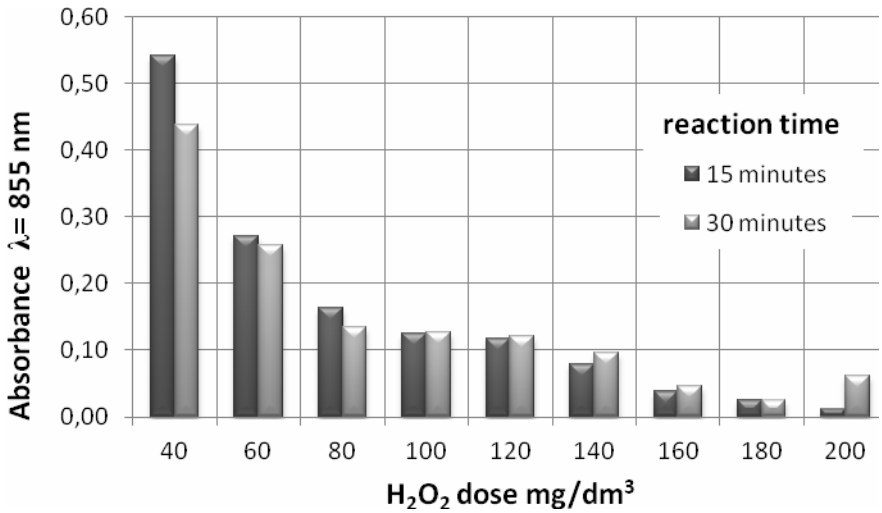

Fig. 1. The influence of H_2O_2 dose on the decolorization effect for the following process parameters: mass ratio of $Fe^{2+}/H_2O_2 = 0.33$; pH = 3.5

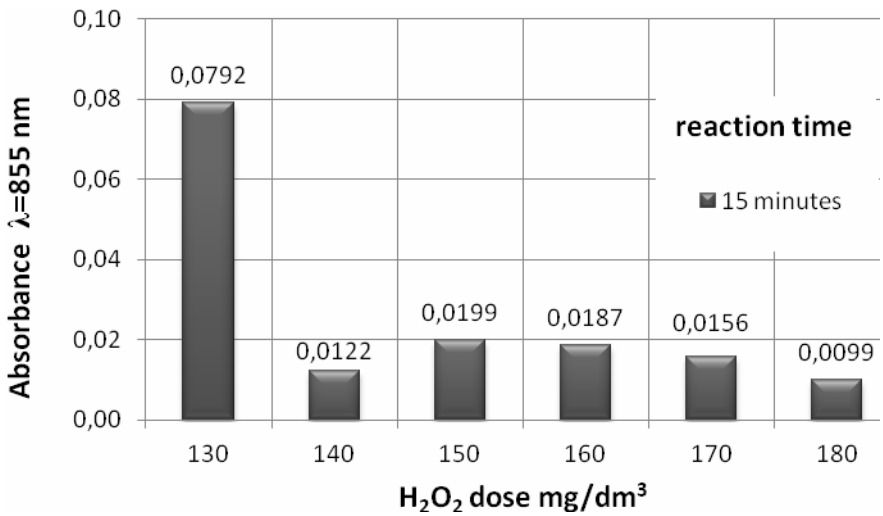

Fig. 2. The influence of H_2O_2 dose on the decolorization effect for the following process parameters mass ratio of $Fe^{2+}/H_2O_2 = 0.1$; pH = 3.5

The next study step was to investigate the influence of the initial pH value on Acid Yellow 36 dye degradation. The applied pH values were equal to 2, 2.5 and 3.5. Other process conditions *ie* H_2O_2 dose and Fe^{2+}/H_2O_2 weight ratios were equal to 180 mg/dm^3, and 0.05 and 0.1, respectively. The analysis of obtained results caused the modification of process conditions. Thus, the effect of decolorization at pH = 3.5, Fe^{2+}/H_2O_2 weight ratio

0.1 and the oxidant dose range 130-180 mg/dm^3 was investigated (Fig. 2). The visual decolorization was obtained for H_2O_2 doses above mg/dm^3.

On the basis of obtained results optimal conditions of classical Fenton reaction were established *ie* oxidant dose = 140 mg/dm^3, Fe^{2+}/H_2O_2 weight ratio 0.1, pH = 3.5, and reaction time 15 min. Nevertheless, the final stage of the study was focused on the influence of reaction time on process effectiveness. The study of reaction kinetic revealed that visual decolorization could be obtained already after 7 minutes for which absorbance value was equal to 0.0904 (Table 1).

Table 1

The influence of reaction time on the decolorization effect

Dose of H_2O_2 = 140 Mass ratio of Fe^{2+}/H_2O_2 = 0.1 pH = 3.5		
Reaction time [min]	**Post-neutralization color**	**Absorbance**
1	Intensive yellow	0.7173
2	Light yellow	0.4052
3	Light bright yellow	0.1933
4	Light bright yellow	0.1323
5	Light bright yellow	0.1168
7	Visual decolorization	0.0904
10	Visual decolorization	0.0899
12	Visual decolorization	0.0833
15	Visual decolorization	0.0822
20	Visual decolorization	0.0835
25	Visual decolorization	0.0875
30	Visual decolorization	0.0885

Conclusion

The study revealed that degradation Acid Yellow 36 degradation can be made using Fenton reagent. At proper process conditions visual decolorization can be obtained after 7 minutes of reaction run. The effectiveness of the wastewater treatment is also depended on the oxidant dose and Fe^{2+}/H_2O_2 weight ratio optimal values of which are established at 140 mg/dm^3 and 0.1. The process environment should be acidified up to pH = 3.5 and during a further research check the effect of decolorization of sewages for higher pH values.

The proposed treatment method is easy to perform, however one must remember about post-process neutralization of wastewater. Additionally, the alkalization of wastewater also improves the decolorization effect. The presented studies allow to generate the plan for further investigations focused on optimization of treatment of wastewater containing Acid Yellow 36 using Fenton reagent.

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BADANIA W CELU OPTYMALIZACJI OCZYSZCZANIA ŚCIEKÓW BARWNYCH ODCZYNNIKIEM FENTONA (CZĘŚĆ I)

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Abstrakt: W wyniku ciągłego rozwoju przemysłu wzrasta ilość i różnorodność zanieczyszczeń odprowadzanych ze ściekami. Ponadto wymagania dotyczące unieszkodliwiania ścieków ulegają ciągłym zaostrzeniom, dlatego istnieje duża potrzeba doskonalenia metod oczyszczania. W ostatnich latach dużą uwagę poświęca się badaniom i wdrażaniu tzw. metod pogłębionego utleniania, które polegają na generowaniu wysoko reaktywnych rodników mających zdolność oczyszczania stężonych, trudno degradowanych i toksycznych ścieków przemysłowych. Ścieki barwne powstające w wyniku procesów produkcyjnych zazwyczaj charakteryzują się dużą zawartością trudno rozkładalnych związków organicznych, mających często charakter muta- i kancerogenny. Klasyczne metody oczyszczania takich ścieków (np. koagulacja, sorpcja) rzadko umożliwiają skuteczną degradację barwników, dlatego przeprowadzono oczyszczanie ścieków barwnych, wykorzystując jedną z metod pogłębionego utleniania - odczynnik Fentona. W pierwszej kolejności przeprowadzono badania wstępne, mające na celu określenie wpływu wielkości dawki H_2O_2, początkowej wartości pH, czasu reakcji oraz wartości stosunku masowego Fe^{2+}/H_2O_2 na efekty odbarwiania ścieków. Uzyskane w ten sposób wyniki były następnie podstawą do opracowania planu badań właściwych, prowadzonych przy użyciu tzw. metody powierzchni odpowiedzi. Na podstawie wyników tych badań opracowane zostaną modele matematyczne zmian efektów odbarwiania ścieków w funkcji badanych czynników, umożliwiające przeprowadzenie optymalizacji tego procesu.

Słowa kluczowe: metody pogłębionego utleniania (AOPs), odczynnik Fentona, ścieki barwne, metoda powierzchni odpowiedzi