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TREATMENT OF INDUSTRIAL WASTEWATER BY USING ADVANCED OXIDATION TECHNOLOGY

معالجة مياه الصرف الصناعى بإستخدام تكنولوجيا الأكسدة المتقدمة

***I.G. Rashed, *A.A. Al-Sarawy, *M.M. El-Halwany and **H.M. Nashaat**

*Mathematical and Physical Engineering Department, Faculty of Engineering, Mansoura University, Egypt.

** Huawei Technology Company, Egypt

الملخص العربى

تهدف هذه الدراسة الى تطبيق أحد طرق الأكسدة المتقدمة (تفاعلات فينتون للأكسدة) وتقييم نتائج الدراسة لتحديد إمكانية إستخدام هذه الطريقة لإزالة المتبقى من هذه الأصباغ – بعد إستخدامها فى عمليات الصباغة – فى أحواض الصباغة ومياه الصرف الصناعى. ويعتمد تفاعل فينتون على وجود فوق أكسيد الهيدروجين مع كبريتات الحديدوز فى وسط حامضى حيث ينتج شق الهيدروكسيد الحر الذى له القدره على تكسير المركبات العضوية وإزالة ألوانها من محاليلها المائية ومن مياه الصرف الصناعى. ولذلك فقد تم تحديد أنسب الظروف لإتمام عملية الأكسدة فى تفاعل فينتون حيث تم دراسة تأثير العوامل التالية على العملية وهى رقم الأس الهيدروجينى، جرعة فوق أكسيد الهيدروجين، جرعة كبريتات الحديدوز، التركيز الإبتدائى للصبغة والزمن. ولقد أثبتت الدراسة أن أفضل الظروف لإزالة هذه الأصباغ تكون عند رقم الأس الهيدروجينى 3 ، 300 ملجم /لتر من فوق أكسيد الهيدروجين ، 90 ملجم /لتر من كبريتات الحديدوز ، ويلزم زمن قدره 120 دقيقه لحدوث أفضل إزاله لألوان الأصباغ. وأثبتت القياسات أنه تم بنجاح إزالة هذه الألوان بنسبة إزالة أكبر من 95 %. وأيضاً تم دراسة الأكسجين الكيميائى المستهلك قبل وبعد عملية الأكسدة كمؤشر للمحتوى العضوى ، وقد أثبتت القياسات أنه تم اختزال كمية الأكسجين الكيميائى المستهلك بنسبة اختزال تتراوح بين 68%-77%.

ABSTRACT

The general strategy of this study was based on evaluation of the possibility of applying advanced photo-oxidation technique (Fenton oxidation process) for removal of the residuals from effluents of dyeing baths. Studying the different parameters that affect on the chemical oxidation process for dyes in their aqueous solutions by using Fenton's reaction. These parameters are pH, hydrogen peroxide dos, ferrous sulfate dose, Initial dye concentration, and time factor. The optimum conditions were found to be: pH = 3, H_2O_2 dose = 300 mg/l, $FeSO_4$ dose = 90 mg/l and reaction time 120 minutes. Finally Chemical oxygen demand (COD), before and after oxidation process was measured to ensure the entire destruction of organic dyes during their removal from wastewater. The experimental results show that Fenton's oxidation process successfully achieved very good removal efficiency (over 95%) in all dyes subjected to this study. This behavior was accompanied with a reduction in chemical oxygen demand (COD) in the range of 68-77%.

Key words: Fenton, Advanced Oxidation, Wastewater Treatment and Dye Removal.

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1.INTRODUCTION

Advanced oxidation processes (AOPs) generally means application of either advanced oxidation technologies using UV/O_3, O_3/H_2O_2, UV/H_2O_2 or the photo Fenton reaction ($UV/H_2O_2/Fe^{2+}$ or Fe^{3+}). Peyton gave a detailed overview and description of AOPs [1,2,3]. The Fenton's reagent was discovered by Fenton in 1894, [4]. Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals. The ferrous iron (Fe^{++}) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of these radicals is involves a complex reaction sequence in an aqueous solution [5]. H_2O_2 can act as an $OH^{\cdot}$ Scavenger as well as an initiator [6]. Generally Fenton's oxidation process are pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. So, the organic substances are removed at two stages of the oxidation and the coagulation [7]. A continuous photo-Fenton process for the degradation of gaseous dichloromethalane (DCM) can be used [8]. Solar photocatalytic degradation of the azo dye acid orange 24 by means of a photo-Fenton reaction promoted by solar energy was used [9]. The degradation of different commercial reactive dyes by using solar light assisted Fenton and photo-Fenton reaction was investigated [10]. Photocatalytic organic content reduction of two selected synthetic wastewater from the textile dyeing industry was studied by the use of heterogeneous and homogeneous photocatalytic methods under solar irradiation, at a pilot plant scale at the Plata forma Solar de Almeria [11]. The scavenging effect of phosphate and bicarbonate anions on the degradation of organic pollutants by means of the Fenton process may be somewhat reduced by the necessity of the application of this technique at moderately low pH [12]. Photo-Fenton processes could be applied in treating many industrial wastewater, i.e., treated wastewater containing wastewater from plastic industry, landfill leachate, dye house industry [13-16], quinoline (aromatic compound) [17,18,19] pesticides [20-24], organic compounds and phenolic wastes [25-27] trichloroethylene trihalomethanes [28], and wastewater from paper industry. The using of Fenton reaction in the decomposition of phenol and formaldehyde [29], from their aqueous solutions and from industrial wastewater containing them was studied which achieve a very good efficiency of removal over 90%. The removal of color and COD from a mixture of four reactive azo dyes using Fenton oxidation process was investigated which achieved a high efficiency more than 90% [30]. The color and COD removal from textile effluent by coagulation and advanced oxidation processes was studied. $FeSO_4$ and $FeCl_3$ were used as coagulants at varying doses [31]. Wastewater from the Afyon Alkaloids factory was subjected to low-pressure catalytic wet-air oxidation using Fenton's reagent, and the optimal reaction conditions were investigated [32]. The treatment of wastewater coming from painting processes by application of conventional and advanced oxidation technologies was discovered [33], The reduction of organic pollutants in landfill leachate and the effecting factors on the degradation of methyl tert-butyl ether, with fenton Reagent was reported [34].

In present study, we are interested in studying the possibility of application of Fenton oxidation process, as an advanced chemical technology technique, for removal of residual colors of dyes from wastewater of an artificial dying bath, as a preliminary treatment prior to biological oxidation.

2. MATERIALS AND METHODS

2.1Materials

The Fenton's reagent composed of H_2O_2 and ferrous iron were of AR grade (Sigma-Aldrich, Germany). All synthetic of each tasted dye solutions (which obtained from Dakahliatex company, mansoura, Egypt) were prepared by dissolving a known quantity in distilled water and used as a stock solution and diluted to the required initial concentration.

2.2 Equipments

Equipments used in this study are electrical balance Mettler model H-80, mechanical stirrer with various shaking speed, digital PH-meter (Cole-parmer chemadet 5986-50), COD instrument (VELP Scientifica, Eco, Itali) and Spectrophotometer (Galen kamp visi-spec SPR-590-010-W) with wavelength range 325-900nm and measuring absorbance at λ_{max} of each tested dye. Calibration curves were constructed to correlate concentrations to different absorbance values.

2.3 Methods

All reactions were performed in batch model, the experiments were conducted at room temperature (25±2°C). The processes were carried out in 1000 ml glass beakers with a 12cm diameter. In each beaker the aqueous solution was mixed with ferrous sulfate and hydrogen peroxide depending on the following steps

(1) A series of six glass beakers containing 500 ml of aqueous solutions of the used dye at initial concentration of 50 mg/l).
(2) All reaction mixture were subjected to rapid stirring (200r.p.m) by using mechanical stirrer for a period of 1 minute.
(3) The stirrer speed was reduced to 30 r.p.m and the mixture was kept stirred for additional period of 15 minutes.
(4) Stirring was stopped and the solution was left to stand for about 20 minutes to ensure complete settling of solid materials.
(5) The remaining dye concentration was determined spectrophotometerically.

3. RESULTS AND DISCUSSION

3.1 Effect of reaction time

To determine the effective reaction time for the best removal of these dyes by Fenton's reaction, the process was carried out at constant hydrogen peroxide dose (300 mg/l); initial dye concentration (50 mg/l), constant ferrous sulfate dose (90 mg/l), and pH=3. Samples were drawn at different intervals along the reaction time.

As shown in figures (1), it was found that the maximum removal of dyes from their aqueous solution reach over 95%. Moreover, the removal and degradation rate was increased sharply and reached a maximum as 120 minutes, then become constant until the end of the reaction time. This may be due to the consumption of hydrogen peroxide. This is in accordance with findings in literature.

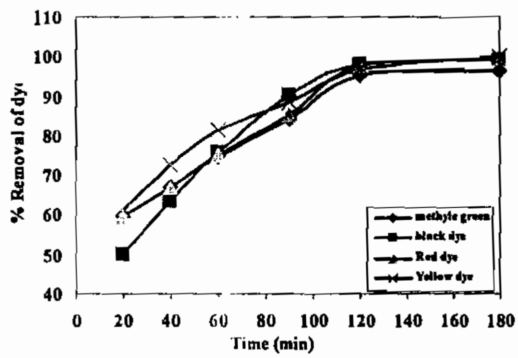

Fig. (1): Time course of the dye removal for different dyes.

3.2. Effect of pH

Fenton reaction is strongly affected by the pH value since it influences the generation of OH' radicals and thus the oxidation efficiency. Figure (2) shows that the remaining concentration was highly affected by the pH value. The results revealed that the optimum pH for the maximum removal of the color of the tested dye was 3. At pH values above 4 the degradation strongly decreases because ferrous catalyst deactivated by the formation of ferric hydroxide. Also at higher pH values iron precipitate as hydroxide and reducing the transmission of light and in turn, deactivate Fenton oxidation reagent (or reducing the efficiency of Fenton oxidation process. Therefore, all the studied systems were firstly adjusted at pH=3.

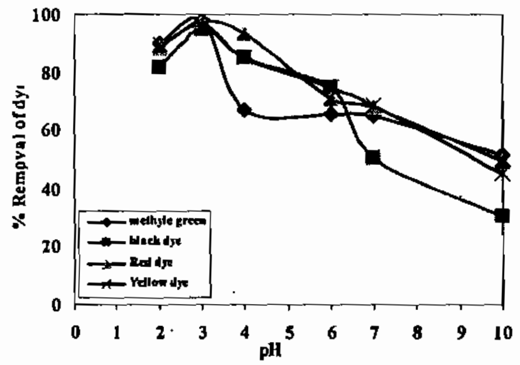

Fig. (2): Effect of pH on the dye removal for different dyes.

3.3. Effect of hydrogen peroxide dose

During Fenton processes the limiting reagent is hydrogen peroxide at the optimum pH. A significant enhancement of removal was noticed when the hydrogen peroxide dose increases, however up to 300 mg/l. At higher doses there was a slight increase in the degradation of dyes. Results obtained in figure (3) indicated that the destruction of the tested dye in their aqueous solutions increases by increasing hydrogen peroxide. The effect of hydrogen peroxide is not significantly effective at doses higher than 300 mg/l. Also it can be seen from figure that, the percent of removal was over 95% at 300 mg/l hydrogen peroxide. At higher doses than 300 mg/l, there was a slight increase of dye removal and destruction. Generally, the removal rate of organic compounds increases as the dose of hydrogen peroxide increases until critical value, after this critical value, the rate of removal may be decrease or not significantly increase.

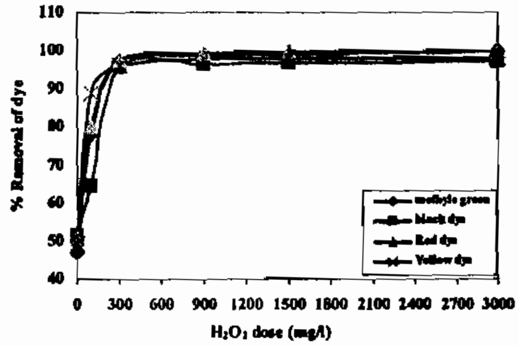

Fig. (3): Effect of H_2O_2 dose on the dye removal for different dyes.

The optimum hydrogen peroxide dose was found to be 300 mg/l, This is in agreement with the fact that an excess amount of hydrogen peroxide in the solution will slightly retard the destruction and removal of dyes, This behavior may be due to auto-decomposition of H_2O_2 to oxygen and water and the recombination of $OH^{\cdot}$ radicals. Since $OH^{\cdot}$ radicals react with H_2O_2, itself contributes to the $OH^{\cdot}$ scavenging capacity, so that H_2O_2 should be added at an optimal concentration to achieve the best degradation. We can conclude that, on using iron as a catalyst it is essential to use the smallest amount of iron in order to avoid the problems associated with their elimination.

3.4. Effect of ferrous sulfate dose

Iron in its ferrous and ferric forms acts as photocatalyst and requires a working pH below 4 to start the catalytic decomposition and the removal of the tested dyes. To obtain the optimal Fe (II) or Fe (III) amounts, the processes were carried out with various amounts of iron salt under these conditions, pH=3, initial dye concentration (50 mg/l) and at hydrogen peroxide dose of 300 mg/l. The results shown in figure (4) indicated that the destruction of the tested dyes in their aqueous solutions increase by increasing ferrous sulfate dose, the effect of ferrous sulfate not significantly effective at doses higher than 90 mg/l. It can be seen from the figure that the percent removal of dye was over 95% at 90 mg/l ferrous sulfate. In case of higher doses of ferrous sulfate Fe^{2+} will be oxidized to Fe^{3+}, which at higher pH values precipitate and reduce the transmission of light which is necessary to activate the reaction, so that ferrous sulfate must added an optimal dose to achieve the best removal.

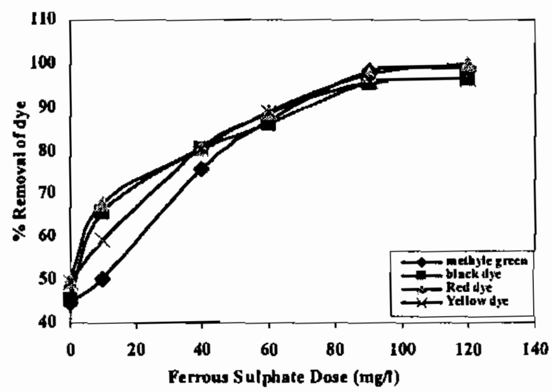

Fig. (4): Effect of ferrous sulphate dose on the dye removal for different dyes.

3.5. Effect of initial dye concentration

The effect of initial dye concentration was studied at constant hydrogen peroxide dose (300 mg/l), constant ferrous sulfate dose (90 mg/l), and constant pH (pH = 3), the sample was drawn at different intervals along the reaction time. As shown in figure (5) we can conclude that, the removal of the tested dyes was over 95% at low initial concentration (25 and 50 mg/l), but in case of high initial dye concentration (equal to or higher than 75 mg/l), the percent removal decreases to about 70% or less. The optimum contaminant concentration in water before the photocatalytic treatment must permit the maximum reaction rate. So, the initial concentration of contaminants in the wastewater can be optimized, when possible.

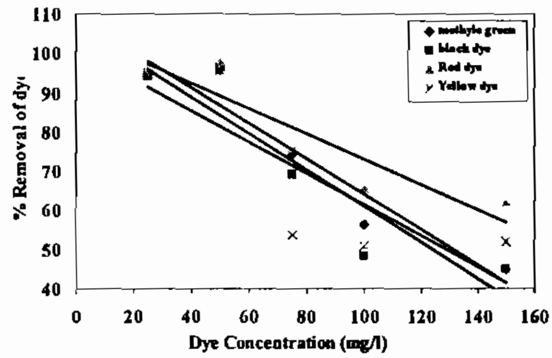

Fig. (5): Effect of intial dye concentration on percent removal for different dyes.

3.6. Evaluation of dye removal and destruction via COD determination

Wastewater obtained from dyeing industry contain a various pollutants including high content of organic matter and color problem depending on forms of dyes, surface active materials, and textile additive materials used in the process. Azo dyes are resistant to biodegradation under aerobic conditions, whereas anaerobic color removal due to reductive -N=N- cleavage was applied by many researchers successfully. Fenton oxidation process has the advantage of both oxidation and coagulation processes. During the process, the organic substances are reacted with hydrogen peroxide (H_2O_2) in the presence of inexpensive ferrous sulfate ($FeSO_4$) to reduce COD content and color. In current study the application of Fenton oxidation process not only led to color removal of the hitherto prepared direct dyes from wastewater but also led to a large decrease in COD and in turn, might enhance the biodegradability of these oxidized wastewater. This adapt the resultant water to be subjected to biological treatment. To evaluate the effect of Fenton oxidation process on COD removal, COD was measured before and after the oxidation process. Results indicated that reduction in COD was in the range 68-77%. This achieve a very good removal which in accordance of the dye degradation of these dyes by Fenton oxidation process and, this step must followed by raising pH again to neutral condition to help in the coagulation process, this will adapt wastewater to biological oxidation especially with the presence of remaining hydrogen peroxide which increase amount of dissolved oxygen.

4. CONCLUSION

The following conclusions might be drawn as a result of application of an advanced chemical oxidation technology (Fenton oxidation process) for removal of the residuals from effluents of dyeing baths:-

- The optimum conditions for the best color removal were determined by studying different parameters which affect the process of chemical oxidation.
- It was found as pH = 3, H_2O_2 dose = 300 mg/l, Fe_2SO_4 = 90 mg/l and reaction time = 120 minutes.
- Fenton's oxidation process successfully achieved a very good removal efficiency (over 95%) in all dyes subjected to this study. This behavior was accompanied with a reduction in chemical oxygen demand (COD) in the range of 68-77%.
- Finally, from this study, it is highly recommended to apply the used technique (Fenton's oxidation process) as a preliminary treatment of wastewater resulting from dyeing baths.

5. REFRENCES

1. Jian C., Ph. D. Thesis, Univ. docent bijhet sub Dep. Milieu Technologie, Holland (1997).
2. Glaze, W.H., Kang, J.W. and Chapin, D.H., Ozone Sci. Eng., 9, 335-352, (1987).
3. Gomez L.C., Water Res., 27, 985, (1993).
4. Fenton, H.J.H., J. Chem. Soc., 65, 899-910, (1894).
5. Pingatello J.J., Environ. Sci. Technol., 26, 944-951, (1992).
6. Venkatadri R. and Peters R.W., Haz. Waste Haz. Mat., 10, 107-149, (1993).
7. Kange, Y.W. and Hwang , K.Y., Wat. Res. 34, 10, 2786-2790, (2000).
8. Feitz Z.J., Guan J., Chattopadahay G. and David T.W., Chemosph., 48(2), 401-406, (2002).
9. Juan M.C., Teresa Ma.L., Manuel S., Erick R.B. Dyes and Pigm., 69, 144-150, (2006).
10. Francesc T., Julia G.M., Jose A.G., Xavier D., Jose P., Solar Energy 77, 573–581, (2004).
11. Kositzi M., Antoniadis A., Poulios I., Kiridis I., Malato S., Solar Energy, 77, 591–600, (2004).
12. Nogueria R. F. P., Silva M. R. A. and Trovo A. G., Solar Energy, (2005).
13. Bauer and Fallmann H., Res. Chemi Intermed., 23, 4, 341-354, (1997).
14. Feng J., Xijium H., Polock Y., Huai Y. Z. and Gao Q. L., Ind. Eng. Chem. Res., 42, 2058-2066, (2003).
15. Sheng H. Lin and Cho C. Lo, Wat. Res. 31, 8, 2050-2056, (1997).
16. Keiichi T., K. P. and Teruaki H. N., Wat. Res. 34, 1, 327-333, (2000).
17. Sundstorm, D., Wier B. and Klie H., Environ. Progress, 8, 6-11, (1989).
18. Malato S., Blanco J., Fernandez-Ibanez P. and Campos A., Appl. Cata. B: Environ., 28, 163-174, (2000).
19. Faust B. C. and Hoigne J., Atmos. Environ., 24A, 79-89, (1990).
20. Chiron S., Fernandez A. A., Rodriguez A. and Calvo E. G., Wat. Res., 34(2), (2000).
21. Mujeebur M.S.M., Pistone L., Trifiro F. and Miertus S., ICS-UNIDO Publisher, 38, (2000).
22. Fallmann H., Krutzler T. R., Malato and Blanco J., Physic. Chemie, 213, 67-74, (1999).
23. Safarzadeh-Amiri A., Bolton J.R. and Cater S.R., Solar Energy, 56, 5, 439-

443, (1996).

24. Eisenhauer H., Wat. Pollut. Control Fed., 36, 5, 1116-1128, (1994).
25. Zahng, X.Q., peijing, (1980). As cites in Parra S. et al., Water Sci. and Technol., 44, No. 5, 219-227, IWA Publisher, (2001).
26. Ilisz I. and Dombi A., Applied catalysis A: General 180, 35-45, (1999).
27. Rashed, I.G., Hanna, M.A., El-Gamal, H.F., Al-Sarawy, A.A. and Wali, F.K.M., J. for Environ. Sci., 2, 15-30, (2004).
28. Amy L.T., Christopher R., Warberg, D. Atkinson A. and Richard, Wat. Res. 35, No. 4, 977-984, (2001).
29. Rashed, I.G., Hanna, M.A., El-Gamal, H.F., Al-Sarawy, A.A. and Wali, F.K.M., Engineering Research Journal, University of Helwan, 92, 97-107, (2004).
30. Sureyya M., Deniz K. and Olcay T. , J. of Environ. Sci. and Health, A38, 10, 2241-2250, (2003).
31. Solmaz, S.K., Birgül, A. and Üstün, G.E., Coloration Technology, 122, 2, (2006).
32. Bıçaksız, Z., Aytimur, G. and Atalay, S. Water Environ. Res., 80, 6, 540-546(7), (2008).
33. Consejo, C., Ormad, M.P., Sarasa, J. and Ovelleiro, J.L., Ozone: Science and Engineering, 27, 4, 279-286(8), (2005).
34. Ma, X., Zhou, M., J. of Chem. Technology & Biotechnology, 84, 10, 1544-1549(6), (2009).