Optimization for Degradation of Commercial Reactive Yellow Dye 145 Through Fenton's Reagent

Ayesha Mahmood[1], Shaukat Ali[1,*], Hamna Saleem[1] and Tanveer Hussain[2]

[1]Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad, Pakistan
[2]Department of Textile Chemistry, National Textile University, Faisalabad, Pakistan

*Corresponding author: Tel: +92 41 9200161 Ext. 3309; +92 333 6506013; E-mail: shaukatcolourist@yahoo.com

Among advanced oxidation processes, oxidation using Fenton's reagent is an attractive treatment for the effective decolourization and degradation of dye because of its low cost and the lack of toxicity of the reagents (*i.e.*, Fe^{2+} and H_2O_2 and solar radiation). The degradation of reactive yellow 145 dye by Fenton and photo-Fenton processes was investigated. The degradation rate was strongly dependent on pH, initial concentrations of Fe^{2+}, H_2O_2, temperature and light intensity. The effects of these parameters have been studied and optimum operational conditions of these two processes were found. The optimum conditions were found at pH 3 for these processes. The decolourization experiments indicate that dye can be effectively decolourized using Fenton and photo-Fenton processes with a little difference between the two processes, 91.4 and 97.8 % within 0.5 h, respectively for optimal conditions. The difference in docolourization is not similar to COD removal: with Fenton process there is significant increment (52.27 % COD removal) relatively to photo-Fenton process (only 38.63 % COD removal).

Key Words: Advanced oxidation processes, Fenton reagent, Photo-Fenton processes, Decolourization, Reactive dye, Oxidizing agent.

INTRODUCTION

Synthetic dyes are widely used in many industries such as leather, paper, textile, *etc*. to impart colours to the desired products. Many of these dyes are complex organic molecules consisting of substituted sites or linkages. On exposure to environmental conditions, the effluent discharge of these industries containing these dyes molecules pose a potential threat to living organisms and to water bodies at large which are the ultimate sources of life for all living species[1]. The reactive dyes are most important class of synthetic organic dyes used in the textile industries and are therefore common industrial pollutants. These dyes are found to be non-biodegradable[2]. Various physical/chemical processes (coagulation, flocculation, adsorption on activated carbon, reverse osmosis) and biological processes have been used for wastewater treatment. Biological processes are not effective enough to decolourize dyes of high photo stability while physical/chemical processes are not strong enough to decompose the dye. Hence sludge generation and adsorbent regeneration are the principal weaknesses of these processes[3]. Recently, advanced oxidation processes (AOPs) have been proposed as offering promise for wastewater treatment because advanced oxidation processes are able to oxidize a wide range of compounds that are otherwise difficult to degrade. Among advanced oxidation processes, oxidation using Fenton reagent is an attractive treatment for the effective decolourization and degradation of dyes because of its low cost, lack of toxicity of reagents, the absence of mass transfer limitation due to its homogenous nature and simplicity of technology[4].

Fenton's reagent, a mixture of Ferrous (Fe^{2+}) ion and hydrogen peroxide which produce hydroxyl radicals, has been used for oxidation of organic matter in water and to reduce the chemical oxygen demand (COD) and total organic carbon (TOC) content[5]. Fenton process can be adopted rapidly in a textile wastewater treatment system, without the need for reconstructing the existing coagulation unit. The only change in operating the process will be the addition of H_2O_2 and Fe^{2+} as well as pH adjustment. The use of Fe^{2+}/H_2O_2 as an oxidant is attractive since iron is highly abundant and non-toxic and a 34 % hydrogen peroxide aqueous solution is easy to handle and environmentally not harmful[6].

The main objective of this study is to analyze the feasibility of decolourization of commercially important reactive yellow 145 dye by Fenton processes as this dye's effluent has not been previously studied. That influenced by different operational parameters (pH, H_2O_2 dosage, Fe^{2+} dosage, temperature, time, reactive yellow 145 concentration, radiations), which affected the efficiency of Fenton and photo-Fenton process.

EXPERIMENTAL

Reactive yellow145 dye, hydrogen peroxide 35 %, ferrous sulphate ($FeSO_4 \cdot 7H_2O$), sulphuric acid, sodium hydroxide and sodium chloride were all laboratory grades. Distilled water was used throughout this study.

Experimental procedure: Appropriate volumes of dye solution, ferrous sulphate solution and hydrogen peroxide solution were mixed. The pH of each reaction solution was adjusted to desired value by using 1M sodium hydroxide and 1M sulphuric acid and was measured by pH meter. Magnetic stirrer provided continuous and uniform shaking. Temperature control was realized through hot plate. Aliquots were withdrawn from reactor periodically using pipette and were analyzed immediately.

Analytical methods: The UV-VIS spectra of dye were recorded from 400-800 nm using T60U UV/VIS spectrophotometer PG instruments Ltd. The maximum absorbance wavelength of dye was found at 422 nm. The peak at 422 nm was attributed to colour of dye solution. It was used to monitor decolourization of dye. Artificial light used in photo-Fenton was obtained from Tungsten filament lamp. Light intensity was measured using LX-9621 Lux meter.

## RESULTS AND DISCUSSION

Optimization of system parameters

Optimization of dye concentration and determination of λ_{max}: Measuring absorbance of five different concentrations including 0.001, 0.002, 0.003, 0.004 and 0.005 % optimized dye concentration. Spectrum of each solution was taken in visible range with UV/visible spectrophotometer. All the five solutions of dye gave maximum absorbance at 422 nm. Absorbance increased with increase in concentration of dye solution. So, λ_{max} of dye was 422 nm and optimized concentration was 0.005 % for conducting experiments.

Effect of pH on decolourization of dye: The pH value affects the oxidation of organic substances. Fenton's reactions are strongly pH dependent. pH influences the generation of hydroxyl radicals and thus oxidation efficiency[5]. The effect of initial pH on the decolourization by fenton oxidation process was studied in pH range of 2.5-6.0. Effect of pH from 2.5 to 6.0 on treatment efficiency was very dramatic as shown by Fig. 1. Decolourization of dye was 68 % after 1 h at pH 2.5. Further increase in pH from 2.5 to 3.0 caused surprising increase in % age colour removed from 68 to 96 % after 1 h. At pH 2.5 decolourization efficiency decreased. This could be explained by formation of oxonium ions $H_3O_2^+$ which enhanced the stability of H_2O_2 and restricted the generation of $^\bullet OH$ at low pH conditions[7]. An oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and to reduce reactivity with ferrous ions. Therefore, the amount of hydroxyl radicals would decrease as a result of the removal efficiency decreases[5]. Further increase in pH from 3.0 to 6.0 decreased decolourization rates. The difference in decolourization efficiencies is due to variation in hydrogen peroxide decomposition to $^\bullet OH$ radicals. Increase in pH from 3.0 to 6.0 caused decrease in % age colour removal from 96 to 8.39 %. In the pH range 3-6 the factors, which heavily influenced decomposition, are:

(1). At this pH range H_2O_2 spontaneously decomposed into water and oxygen rather than producing hydroxyl radicals.

$$2H_2O_2 \longrightarrow 2H_2O + O^\bullet_2$$
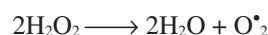
(2) At pH above 3, the concentration of hydroperoxy anions (HO_2^- conjugate base of H_2O_2) increases. These anions reduced the concentration of H_2O_2 and $^\bullet OH$ radicals[2].

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + {}^\bullet OH$$

$${}^\bullet OH + HO_2^- \longrightarrow H_2O + O_2^{\bullet -}$$
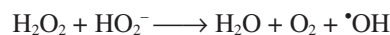
Increase in pH from 3 to 6, caused decreased in colour removal from 96 to 8.39 %. It is because iron starts to precipitate as hydroxide. Additionally, the oxidation potential of hydroxyl radicals was known to decrease[5] with increasing pH.
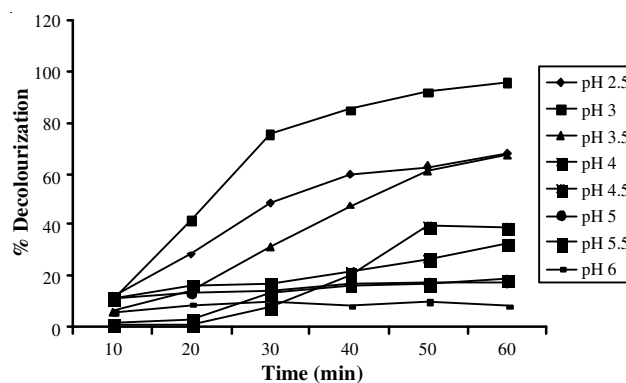

Fig. 1. Effect of pH on the decolourization of dye by Fenton oxidation. Experimental conditions: [dye] = 0.005 %, [H_2O_2] = 0.01 M, [$FeSO_4$] = 3.5×10^{-5} M and temperatute = 40 ºC

Effect of on decolourization of dye: H_2O_2 plays an important role as a source of $^\bullet OH$ generation in Fenton reaction. The effect of initial concentration of H_2O_2 (0.001, 0.005, 0.01, 0.02 and 0.04 M) on chemical efficiency of system was investigated using fixed concentration of $FeSO_4$ and dye at 3.5×10^{-5} M and 0.005 %, respectively. The results in Fig. 2 showed that by increasing concentration from 0.001 to 0.005 M % age decolourization increased from 42.8 to 95.8 % after 1 h. This can be explained by effect of additionally produced hydroxyl radicals[5].
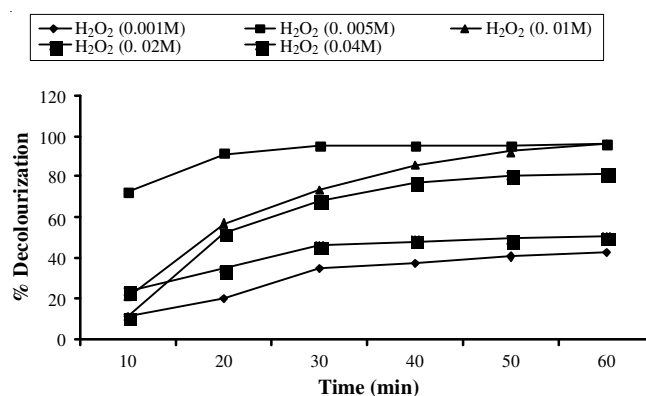

Fig. 2. Effect of H_2O_2 on decolourization of dye by Fenton oxidation. Experimental conditions: [dye] = 0.005 %, pH = 3.0, [$FeSO_4$] = 3.5×10^{-5} M and temperatute = 40 ºC

Further increase in H_2O_2 concentration from 0.005 to 0.01 M caused no significant change in decolourization. 94.9 % colour removal was observed with 0.005M H_2O_2 after 0.5 h while using 0.01M H_2O_2 73 % colour removal was observed after half hour. Whereas at the end of experiment % age colour removal of 96 % was observed by using 0.01M H_2O_2. This little increase is due to the fact that at higher H_2O_2 concentration scavenging of $HO^{\bullet}$ radicals will occur[8].

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet}$$

$$HO_2^{\bullet} + HO^{\bullet} \longrightarrow H_2O + O_2$$
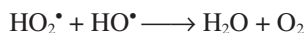
Further increase in H_2O_2 concentration from 0.01 to 0.02 M caused decrease in % age colour removal from 96 to 81 % after 1 h. Same result was observed while using 0.04M H_2O_2, which gave 50.4 % colour removal at end of 1 h.

This indicates that excess of H_2O_2 is decomposed without promoting further degradation or hindering the reaction. This decomposition may be attributed to the generation of water and oxygen ($2H_2O_2 \longrightarrow O_2 + 2H_2O$) since no detrimental effect is observed[9]. In addition recombination of $^{\bullet}OH$ also contributed for declining of decolourization[7].

$$HO^{\bullet} + {^{\bullet}OH} \longrightarrow H_2O_2$$

So optimal hydrogen peroxide concentration in Fenton oxidation of dye is 0.005 M, which caused 94.9 % age colour removal after 0.5 h.

Effect of FeSO4 dosage on decolourization: Iron in its ferrous and ferric forms act as catalyst and requires a working pH below 3.5. Amount of ferrous ion is one of the main parameters to influence the Fenton process. In this study, various concentrations of Fe^{2+} were applied to obtain its optimal original concentration. From Fig. 3, it is obvious that decolourization was limited at 0.5×10^{-5} M and only 55.22 % of dye was degraded within 1 h of reaction. In presence of 1.5×10^{-5} M, 2.5×10^{-5} M and 3.5×10^{-5} M of Fe^{2+}, a great improvement of decolourization efficiencies within 1 h of reaction achieved were 89.6, 92.73 and 95.6 %, respectively. The fact that higher decolourization efficiency achieved at high Fe^{2+} dosage was mainly attributed to higher production $^{\bullet}OH$ with more Fe^{2+} in Fenton's reaction[7].
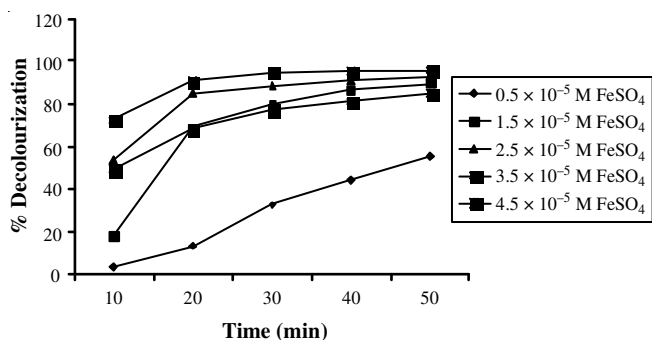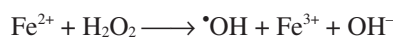

Fig. 3.   Effect of FeSO4 dosage on decolourization by Fenton oxidation. Experimental conditions: [dye] = 0.005 %, pH = 3.0, [H_2O_2] = 0.005 M and temperatute = 40 ℃

Decolourization of dye in Fenton process is due to hydroxyl radical generated by this reaction:

$$Fe^{2+} + H_2O_2 \longrightarrow {^{\bullet}OH} + Fe^{3+} + OH^-$$

Generated Ferric ion in solution reacts with residual H_2O_2 to produce hydroperoxy radicals and ferrous ion.

$$Fe^{3+} + H_2O_2 \longrightarrow [Fe^{3+} \text{----} OOH]^{2+} + H^+$$

Hydroperoxy radical did not play an important role in decolourization; hence Fe^{2+} is continuously generated from reaction mixture.

$$[Fe^{3+} \text{---} OOH]^{2+} + H^+ \longrightarrow HO_2^{\bullet} + Fe^{2+} + H^+$$
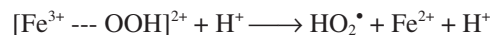
The decolourization continues until hydrogen peroxide is completely consumed in this reaction[2].

The decolourization percentage of dye began to decrease when concentration of Fe^{2+} was higher. Fe^{2+} have a catalytic decomposition effect on H_2O_2. When Fe^{2+} concentration is increased, the catalytic effect also increases accordingly and when its concentration was higher, a great amount of Fe^{3+} was produced. Fe^{3+} undergoes a reaction with hydroxyl ions to form $Fe(OH)^{2+}$ which has a strong absorption band causing higher absorbance and result in decrease percentage decolourization[5].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {^{\bullet}OH} + {^-OH}$$

$$Fe^{3+} + {^-OH} \longrightarrow Fe(OH)^{2+}$$
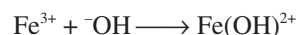
So increase in concentration of FeSO4 from 3.5×10^{-5} M caused decrease from 95.6 to 85.22 % at end of one hour. So optimum concentration of FeSO4 required for decolourization of dye is 3.5×10^{-5} M.

Effect of temperature on decolourization: The effect of temperature on decolourization of dye was studied at different temperatures 30, 40, 50 and 60 ℃. It is obvious from Fig. 4 that raising the temperature has a positive impact on decolourization of dye. The decolourization efficiency within 20 min of reaction increased from 24.64 to 80.22 % as increasing the temperature from 30 to 50 ℃. Additionally, the period of time required for decolourization of dye was much shorter at higher temperature. This can be explained that Fenton's reaction could be accelerated by raising the temperature, which improved the generation rate of $^{\bullet}OH$ and therefore to enhance the decolourization of dye[7].
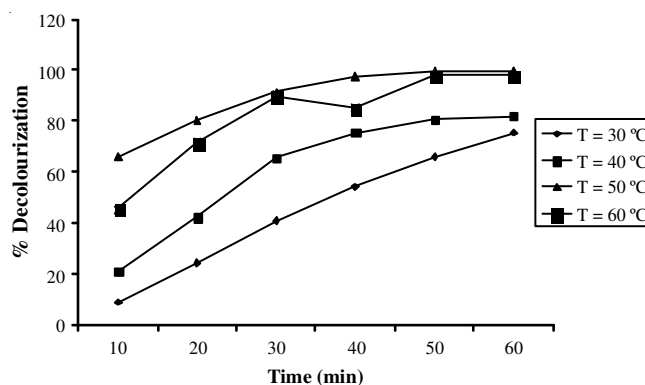

Fig. 4.   Effect of temperature on decolourization by Fenton oxidation. Experimental conditions: [dye] = 0.005 %, pH = 3.0, [H_2O_2] = 0.005 M and [FeSO4] = 3.5×10^{-5} M

Degradation rate decreased when temperature was 60 ℃ due to decomposition of H_2O_2 at higher temperature. Degradation efficiency decreased from 80.22 to 71.70 % within 20 min by increasing the temperature from 50 to 60 ℃ so optimum temperature required for decolourization of dye is 50 ℃.

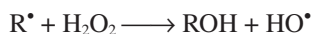**Effect of artificial light intensity on decolourization:**
Effect of artificial light intensity on decolourization of dye
yellow dye by photo-Fenton process was investigated by varying
the light intensity from 500 Lx to 2,000 Lx as shown by Fig. 5.
Decolorization efficiency of yellow dye increased by increasing
the intensity of light. Maximum decolourization was achieved
by using 2,000 Lx light which removed 98.78 % colour. In
general, the Fenton's reagent generates ferrous ions to react
with hydrogen peroxide, producing hydroxyl radicals, which
are strong oxidizing agents, to react with dye solution and
degrade it.

$$H_2O_2 + Fe^{2+} \longrightarrow {}^\bullet OH + OH^- + Fe^{3+}$$
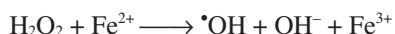
Additional amounts of ${}^\bullet OH$ radicals are also produced
from direct photolysis of H_2O_2

$$H_2O_2 \longrightarrow 2{}^\bullet OH$$

The hydroxyl radical's generated above propagate the
reaction by reacting with reactive yellow dye 145 to produce
further radicals, which can react in many different steps.

$${}^\bullet OH + RH \longrightarrow H_2O + R^\bullet$$

$$R^\bullet + H_2O_2 \longrightarrow ROH + HO^\bullet$$

Many other reactions are possible, which include the radical-
radical reaction or the reaction of ${}^\bullet OH$ radical with H_2O_2:

$${}^\bullet OH + {}^\bullet OH \longrightarrow H_2O_2$$

$${}^\bullet OH + H_2O_2 \longrightarrow H_2O + HO_2^\bullet$$

The peroxide radicals $(HO_2^\bullet)$ can produce H_2O_2 and
O_2 through disproportionation reaction or can react[1] with Fe^{2+}.

$$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2$$

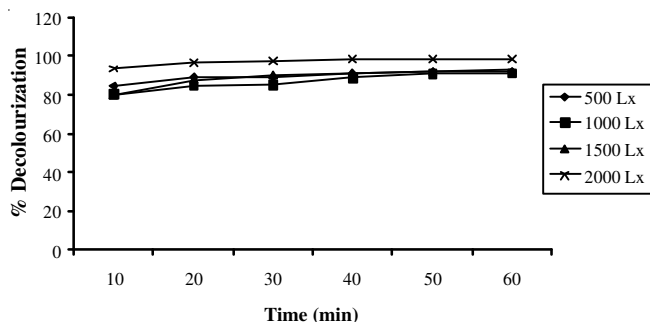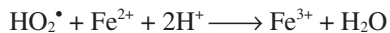$$HO_2^\bullet + Fe^{2+} + 2H^+ \longrightarrow Fe^{3+} + H_2O$$

Fig. 5.   Effect of artificial light intensity on decolourization by photo-Fenton
oxidation. Experimental conditions: [dye] = 0.005 %, pH = 3.0,
$[H_2O_2]$ = 0.005 M [FeSO$_4$] = 3.5 × 10^{-5} M and temperature = 50 ºC

The rate of photolysis of H_2O_2 depends upon directly on
incident light intensity. At low intensity, the photolysis of H_2O_2
was limited but at high intensity more hydroxyl radicals were
produced upon photo dissociation of H_2O_2, hence removal rate
increased. 93.90 % colour removal was achieved by using
2,000 Lx light within 10 minutes only. So optimum light
intensity was 2,000 Lx.

Effect of salts: Present study also examined the effects
of NaCl and Na_2CO_3 which are generally found in textile water
stream, on decolourization of dye. In absence of salts, the dye
decolourization was 99.42 %. The addition of NaCl and

Na_2CO_3 to dyesolution caused only 4 and 3 % decrease in
decolourization percentage as shown by Fig. 6. The small decrease
in removal efficiency is due to scavenging effect of Chloride
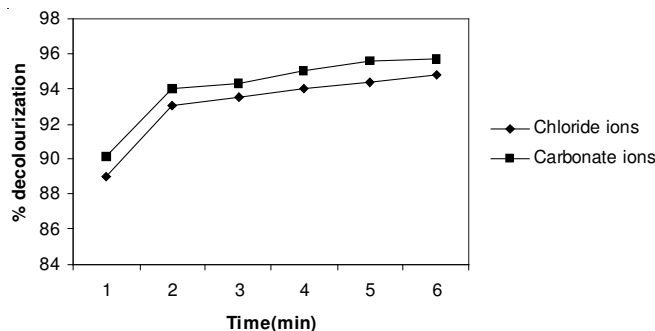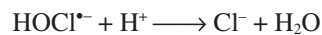and Carbonate ions as shown in following equations.

$$Cl^- + {}^\bullet OH \longrightarrow HOCl^{\bullet -}$$

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

$$CO_3^{2-} + {}^\bullet OH \longrightarrow {}^- OH + CO_3^-$$

Fig. 6.   Effect of salts on decolourization of dye by photo-Fenton oxidation.
Experimental conditions: [dye] = 0.005 %, pH = 3.0, $[H_2O_2]$ = 0.005
M [FeSO$_4$] = 3.5 × 10^{-5} M and temperature = 50 ºC and [salt]= 3 g/L

Chemical oxidation demand (COD): Chemical oxidation
demand values have been related to the total concentration of
organics in the solution and decrease of COD reflects the degree
of mineralization. It is important to measure the COD of dye
solution after oxidation in order to verify whether the dye is
actually mineralized. The experiments of Fenton and photo-
Fenton processes showed 52.27 and 38.63 % reduction of
COD. It appears that photo-Fenton process is more beneficial
for degradation as obvious from COD removal[5].

Conclusion

Decolourization of reactive yellow dye 145 in aqueous
solution by Fenton oxidation process has been studied on diffe-
rent experimental conditions, including pH, initial concentrations
of Fe^{2+}, H_2O_2, temperature and light intensity and presence of
salts. The results showed that Fenton and photo-Fenton processes
are powerful methods for decolourization of dye, but photo-
Fenton process is more efficient. The optimum conditions in
both processes were observed at pH = 3, with Fe^{2+} concentration
of 3.5 × 10^{-5} M and H_2O_2 concentration 0.005 M with dye
concentration of 0.005 %. Maximum decolourization was
achieved by photo-Fenton process.

REFERENCES

1. M.A. Alnuaimi, M.A. Rauf and S.S. Ashraf, *Dyes Pigments*, **76**, 332 (2008).
2. M. Muruganandham and M. Swaminatham, *Dyes Pigments*, **72**, 137 (2007).
3. T. Kurbus, A.M.L. Marechal and D.B. Vonina, *Dyes Pigments*, **58**, 245 (2003).
4. S. Wang, *Dyes Pigments*, **76**, 714 (2008).
5. N. Modirshahla, M.A. Behnajady and F. Ghanbary, *Dyes Pigments*, **73**, 305 (2007).
6. S.F. Kang, C.H. Liao and S.T. Po, *Chemosphere*, **41**, 1287 (2000).
7.   J.-H. Sun, S.-P. Sun, G.-L. Wang and L.-P. Qiao, *Dyes Pigments*, **74**, 647 (2007).
8. M. Lucas and J. Peres, *Dyes Pigments*, **71**, 236 (2006).
9. P.A. Carneiro, R.F.R. Nogueira and M.V.B. Zonini, *Dyes Pigments*, **74**, 127 (2007).