

Kinetics of Fenton Like Cotton Reactive Dyeing Wastewater Discoloration Process

ANISOARA BERTEA¹, LILIANA ROZEMARIE MANEA^{1,2} ANDREI PETRU BERTEA^{1*}, ION SANDU^{2,3*}

¹ Gheorghe Asachi Technical University Iasi, Faculty of Textile and Leather Engineering and Industrial Management, 29 Dimitrie Mangeron Blvd., 700050 Iasi, Romania

² Romanian Inventors Forum, 3, Sf.P.Movila St., Bloc L11, III/3, 700089 Iasi, Romania

³ Alexandru Ioan Cuza University of Iasi, ARHEOINVEST Interdisciplinary Platform, 11 Carol I Blvd., Corp G demisol, 700506 Iasi, Romania

Textile dyeing processes are responsible for the colour of the textile wastewater, major environmental problems for the textile sector. In order to meet legislative requirements, coloured wastewaters have to be treated. Oxidative treatments proved to be among the most efficient and one of the most effective oxidation agents is the hydrogen peroxide. In this paper the kinetics of the colour removal of wastewater produced in the reactive dyeing of cellulose fibers when using a Fenton like system (hydrogen peroxide – CuO/Al₂O₃ catalyst) was investigated. Different dyes and dyeing concentrations are tested, and chemical oxygen demand decrease is monitored as well. The results are compared with those obtained when using a classical Fenton process for removing the colour of the wastewater. Plotting ln(C_i/C) versus time for each of the studied reactive dyes linear dependencies have been obtained, leading to the conclusion that the process follows a pseudo-first order kinetic model at each pH. The rate constant at different pH values and the half-life were calculated as well. Regression analyses conducted to a model of the process that match well with experimental data.

Keywords: coloured wastewater, reactive dyes, Fenton like discoloration kinetics

Dyeing operations generate a large portion of the textile industry's total wastewater [1-5]. The primary source of wastewater in dyeing operations is spent dye bath and wash water. The residual colour in the textile effluent depends upon the nature of the dye that have been used and the dyeing procedure. Among the various dye classes, reactive dyes are characterised by low fixation rates, and therefore contribute more significantly to the colour of the textile wastewater [6-12]. Studied proved that, in general, dyes are not toxic to the environment, but even so colour in the water streams reduce light penetration, affecting the growth of plants and impacting of other forms of life.

In order to meet legislative requirements, coloured wastewaters are usually treated in a chemical-physical or in an active sludge biochemical plant. Many methods, though effective, yield high waste treatment cost in terms of sludge handling and disposal. From this point of view, oxidative treatments seem to be promising because they involve negligible sludge quantities. One of the most efficient oxidation agents is the hydrogen peroxide. The speed of the decolourisation process and its efficiency are

of major importance [13-16].

In this paper the kinetics of the colour removal of wastewater produced in the reactive dyeing of cellulose fibers when using a Fenton like system (hydrogen peroxide – CuO/Al₂O₃ catalyst) was investigated. We have analyzed three reactive dyes, at common dye house effluent concentration. Beside the decolourisation process, chemical oxygen demand decrease was monitored. The results were compared with those obtained when using a classical Fenton reactive for removing the colour of the wastewater.

Experimental part

Materials

The reactive dyes that have been used were Reactive Yellow 145, Reactive Red 40 and Reactive Violet 4 (chemical structures are shown in Table 1). Dyeing was performed on 100% cotton knitted fabric using producer's prescription, by a batch process. The catalyst was prepared using (Cu(NO₃)₂ · 3H₂O) and Al₂O₃, by wet mixing at a molecular ratio of 3:1 in a semi wet system, followed by drying at 110°C and calcination at 600°C.

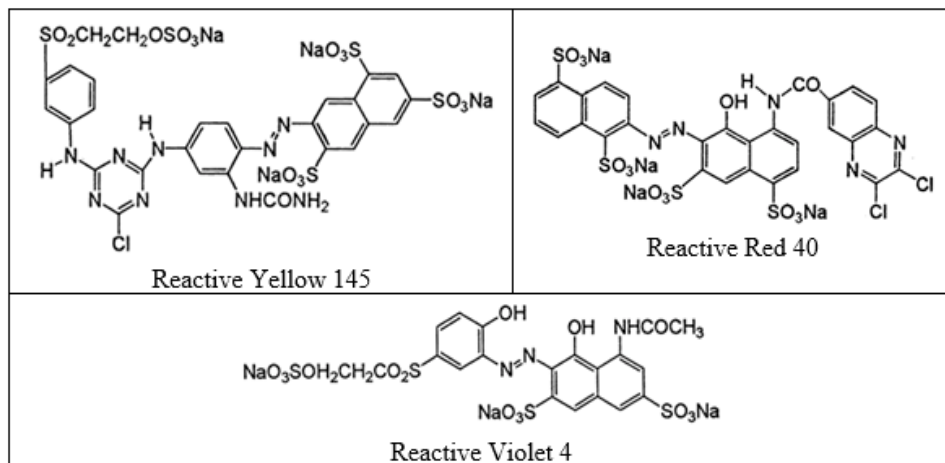


Table 1
CHEMICAL STRUCTURES OF THE
ANALYSED REACTIVE DYES

* email: andrei_bertea@yahoo.co.uk, (+40) 729113212; sandu_i03@yahoo.com, (+40) 744431709

Discoloration procedure

We have used synthetically produced wastewater, which contains besides the dye all the other auxiliaries used in a genuine dyeing process, which are sodium sulfate, used as electrolyte for dye exhaustion, and sodium carbonate, that generates the alkaline medium for dye fixation. The catalytical oxidation of the wastewater was made in a laboratory device that consisted in a 500mL Erlenmeyer flask with magnetically stirring. The catalyst in powder form was suspended in the solution during the treatment. After 30 min the catalyst was separated by centrifugation and the colour was measured spectrophotometrically. For every discoloration treatment, the parameters were as follows: 120mg/L dye concentration; 100mL wastewater; 100mg catalyst (concentration 1 g/L solution); 2mL H₂O₂ (30% w/w); neutral pH (pH was adjusted using hydrochloric acid 1M); 26°C room temperature.

Degree of discoloration determination

The percentage degree of discoloration was calculated as ratio between the decrease in the absorbance and the absorbance of the untreated sample.

$$\text{Discoloration degree} = \frac{Abs_o - Abs_f}{Abs_o} \times 100, [\%], \quad (1)$$

where:

Abs_o - absorbance of the untreated sample;

Abs_f - absorbance of the treated sample.

The absorbance was measured at maximum absorption wavelength (416nm for Reactive Yellow 145, 520 for Reactive Red 40 and 545nm for Reactive Violet 4) using a Spectro UV/ Vis Dual Beam Labomed UVS-2800 spectrophotometer.

Chemical Oxygen Demand (COD) measurement

The COD value was determined according to the Romanian standard method: a sample of the wastewater

(treated and untreated) is refluxed in strongly acidic solution with a known excess of potassium dichromate in the presence of silver sulfate. The organic matter that exists in the sample is oxidized by the potassium dichromate. The dichromate that exceeds the stoichiometric value was titrated with ferrous ammonium sulfate, using ferroin as an indicator. At equivalence point the colour of the solution changes from green blue to reddish blue. The amount of K₂Cr₂O₇ consumed is converted in the oxidizable matter that is calculated in terms of oxygen equivalent.

Results and discussions

The UV - VIS absorption spectra for each dye solution proved that the oxidation takes place at the chromophore bonds level, resulting in a significant discoloration of the residual solution (the peaks in the visible range are levelled) [17-21]. The variation of the dye content in the synthetical baths during the oxidation treatment is shown in figure 1.

It can be seen that the dye concentration decrease significantly, reaching under 0.04 g/L for the yellow and the violet dye, and less then 0.06 mg/L for the red dye.

When graphing $\ln(C_o/C_t)$ versus time, where C_o represents the initial dye concentration, and C_t the dye concentration at time t, the graph that we have obtain is linear, then leads to the conclusion that we deal with a first order reaction, described by an equation of the sort:

$$\ln \frac{C_o}{C_t} = k \cdot t$$

where:

C_o - initial dye concentration;

C_t - dye concentration at time t;

k - rate constant (proportionality constant).

The graphs $\ln(C_o/C_t)$ versus time for the three studied reactive dyes [22-25] is shown in figure 2.

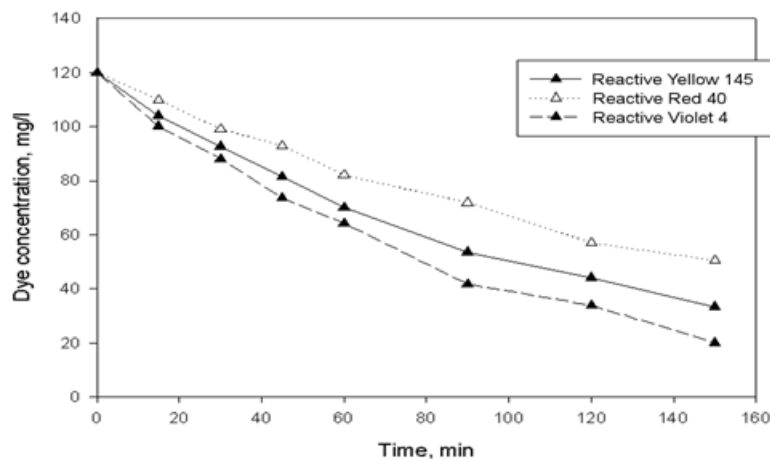


Fig. 1. Dye concentration vs. oxidative discoloration time

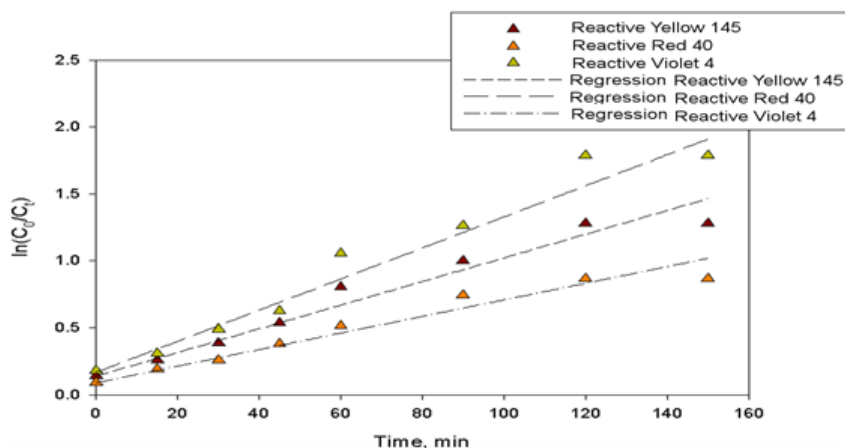


Fig. 2. $\ln(C_o/C_t)$ versus time and fitting of the kinetic curves

Table 2
KINETICAL DATA AND CORRELATION COEFFICIENT

Dye	Dye concentration decrease, (%)	k (min ⁻¹)	Correlation coefficient	Half time (min)
Reactive Yellow 145	72.14	8.49·10 ⁻³	0.9992	81.64
Reactive Red 40	57.86	5.89·10 ⁻³	0.9981	117.68
Reactive Violet 4	83.25	11.49·10 ⁻³	0.9965	60.32

Dye	Chemical Oxygen Demand (mg O ₂ /l)		Conversion, (%)
	Initial	Final	
Reactive Yellow 145	672.84	405.9	39.67
Reactive Red 40	922.98	710.56	23.01
Reactive Violet 4	845.85	472.4	44.15

Table 3
INITIAL AND FINAL VALUES OF THE COD

Dye	Colour Removal degree	
	H ₂ O ₂ catalysed with CuO/Al ₂ O ₃	Fenton's Reagent
Reactive Yellow 145	72.14	68.4
Reactive Red 40	57.86	64.6
Reactive Violet 4	83.25	81.2

Table 4
DISCOLORATION EFFICIENCY COMPARISON

For all the three discoloration processes half time ($t_{1/2}$)

was calculated using the relation: $t_{1/2} = \frac{\ln 2}{k}$

The kinetical data and the correlation coefficient for the decolourisation processes are shown in table 2.

Table 3 shows the initial and final values of the COD. It can be seen that the COD decrease (23- 45%) is not as important as the colour decrease (60-80%), which leads to the conclusion that the action of the oxygen peroxide was focused on the chromophore of the dye. A slight reflectance decrease in the UV range ($\lambda = 250\text{nm}$) could suggest that the aromatical part of the dye molecule has been primarily attacked by the oxidant.

As it can be seen from table 4, Fenton's Reagent is more efficient in the case of the dye that is more resistant to oxidation, but in the case of easy oxidized dyes the system H₂O₂/ CuO/Al₂O₃ proves to be more effective.

Conclusions

Colour removal of wastewater from cellulose dyeing with reactive dyes can be performed using a Fenton like system consisting in hydrogen peroxide associated with a CuO/Al₂O₃ catalyst. The discoloration reaction follows a first order law, and its efficiency is at least similar if not better than the Fenton's discoloration process. The decrease in chemical oxygen demand is important, but smaller than the colour decrease, which suggests that the destruction is focused on the chromophore of the dye.

References

1. RAJENDIRAN, S., SHRIRAM, B., KANMANI, S., IARJSET, 3, no. 3, 2016, p. 107.
2. SOARES, PA., SILVA, T.F.C.V., MANENTI, D., SOUZA, S., BOAVENTURA, R., VILAR, V., Environ. Sci. Pollut. Res., 21, no. 2, 2014, p. 932.
3. JEDRZEJCZAK, M., WOJCIECHOWSKI, K., Chemik, 70, no. 3, 2016, p. 150.
4. WANG, J., TAN, H.C., ZHANG, YL., PAN, YZ., Mod. Appl. Sci., 10, no. 5, 2016, p. 87.
5. BABU, S.V., RAGHUPATHY, S., RAJASIMMAN, M., J. Adv. Chem. Sci., 2, no. 2, 2016, p. 233.

6. SALA, M., LOPEZ-GRIMAU, V., GUTIERREZ-BOUZAN, C., Materials, 9, no. 3, 2016, p. 211.
7. LI, H., LIUB, S., ZHAOB, J., FENG, N., Colloids and Surfaces A: Physicochem. Eng. Aspects, 494, 2016, p. 222.
8. GHALWA, N., SAQER, A., FARHAT, N., J. Chem. Eng. Process Technol., 7, no. 1, 2016, p. 1.
9. MILED, W., SOULA, S., LADHARI, N., IJSET, 3, no. 2, 2015, p. 102.
10. KAMAT D. V, KAMAT S.D., Int. J. Environ. Sci., 5, no.6, 2015, p. 1078.
11. FETTOUCHE, S., TAHIRI, M., MADHOUNI, R., CHERKAOU, O., J. Mater. Environ. Sci., 6, no.1, 2015, p. 129.
12. KARADAG, R., TORGAN, E., International Journal of Conservation Science, 7, Special Issue: 1, 2016, p. 357.
13. WALL, F., Int J Waste Resources, 5, no. 1, 2015, p. 1.
14. MOJTABA, A., PEGAH, A., SHAHRAM, S., NEGAR, A., Adv. Arch. City Env., 1, no. 2, p. 12.
15. RIBEIRO, M.C.M., STARLING, M.C.V.M., LEO, M.M.D., Environ. Sci. Pollut. Res., 23, no. 9, 2016, p. 10146.
16. PATIL, A., RAUT, P.D., IOSR-JESTFT, 8, no. 10, 2014, p. 29.
17. POPA, A., BUCEVSCI, A., PUSTIANU, M., MANEA, L.R., SANDU, I., Mat. Plast., 53, no.2, 2016, p. 316.
18. MANEA, L.R., BERTEA, A., NECHITA, E., POPESCU, C.V., SANDU, I., Rev. Chim.(Bucharest), 67, no. 8, 2016, p. 1607.
19. MANEA, L.R., BERTEA, A., NECHITA, E., POPESCU, C.V., SANDU, I., Rev. Chim. (Bucharest), 67, no. 7, 2016, p. 1284.
20. MANEA, L.R. SCARLET, R., LEON, A.L., SANDU, I., Rev. Chim. (Bucharest), 66, no.5, 2015, p. 640.
21. MANEA, L.R. CHIRITA, M., HRISTIAN, L., SANDU, I., Mat. Plast., 53, no. 3, 2016, p. 361.
22. MANEA, L.R., DANU, M.C., SANDU, I., Rev. Chim. (Bucharest), 66, no. 6, 2015, p. 868.
23. STANESCU, I., MANEA, L.R., BERTEA, A., BERTEA A.P., SANDU I.C.A., Rev. Chim. (Bucharest), 67, no. 10, 2016, p. 2086.
24. STANESCU, I., MANEA, L.R., BERTEA, A., BERTEA A.P., SANDU I., Rev. Chim. (Bucharest), 67, no. 11, 2016, p. 2276.
25. NEJNERU, C., NICUTA, A., CONSTANTIN, B., MANEA, L.R., TEODORESCU, M., AGOP, M., Journal of Applied Mathematics, vol. 2013, 137056, 2013, doi: 10.1155/2013/137056

Manuscript received: 27.04.2016