Design equation with mathematical kinetic modeling for photooxidative degradation of C.I. Acid Orange 7 in an annular continuous-flow photoreactor

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ABSTRACT

The decolorization of C.I. Acid Orange 7 (AO7), an anionic monoazo dye of acid class was investigated using UV/H$_2$O$_2$ process in an annular continuous-flow photoreactor (ACFP) as a function of oxidant, dye concentrations, reactor length and volumetric flow rate. The removal efficiency of AO7 was a function of operational parameters and increased with increasing initial concentration of H$_2$O$_2$ but it was low at high flow rate and initial concentration of AO7. Results indicated that the decolorization rate was pseudo-first order kinetic with respect to the dye concentration. A rate equation for decolorization of AO7 was obtained by kinetic modeling. Design equation for ACFP reactor was obtained with combination of kinetic model and rearranged tubular reactor design equation. Design equation was used for predicting concentration of AO7 and also electrical energy per order (E_{EO}) at different conditions. The calculated results obtained from design equation and kinetic model were in good agreement with experimental data.

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1. Introduction

Approximately 10,000 different dyestuffs are used in textile industry and among them, azo dyes such as C.I. Acid Orange 7 (AO7) is used over 50% of all dyes [1]. Textile industry wastewater is heavily charged with unconsumed dyes because 1–15% of the dyes are lost during dyeing process [2]. Some azo dyes and degradation products such as aromatic amines are highly carcinogenic [3]. If these effluents are release to the environment without treatment, they will threat ecosystem [4].

Conventional biological treatment methods are ineffective for decolorization and degradation because of the presence of large degree of aromatics in these dyes. Physical techniques, such as adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation and electrocoagulation are widely used for removal of these pollutants efficiently but they just transport contaminants from water to sludge and produce secondary wastes which need more treatment [5]. The alternatives to non-destructive physical water treatment processes are advanced oxidation processes (AOPs), because they mineralize organic water contaminants [6]. There are different AOPs reacting systems which are almost characterized by the efficient production of hydroxyl radicals. These radicals are powerful

and highly reactive oxidant with short-lived time and non-selectively attack to pollutants. Among the AOPs, UV/H$_2$O$_2$ process has been applied successfully to treat different pollutants in water [7–9]. In this process UV light is absorbed directly by H$_2$O$_2$, hydroxyl radicals are generated by photolysis of peroxide bond and the highest hydroxyl radical yields are obtained when short-wave ultraviolet radiations (200–280 nm) are used [10].

Various types of kinetic models have been postulated to describe the kinetics of the UV/H$_2$O$_2$ process (Table 1). The first type is the power law model which was tested for many organic compounds. For example Ku and Ho [11], Sundstrom et al. [12] and Elkanzi and Kheng [13] tested and obtained reaction order for various operational parameters. The second type is kinetic model on the basis of reaction mechanism and known chemical and photochemical reactions. Most of kinetic models of second type utilize the pseudo-steady state approximation for the free radical species in the system [8,14,15]; these kinetic models were developed for constant concentration of H$_2$O$_2$ in the decolorization course. Most of the past efforts on the treatment of dye wastewater by the UV/H$_2$O$_2$ process was mainly studied in a batch or recirculated photoreactor. Therefore, the study on the development of the kinetic modeling of the dye removal by UV/H$_2$O$_2$ process in a continuous photoreactor is scarce.

The objective of the present study is to develop a kinetic model and design equation for the decolorization of AO7 using UV/H$_2$O$_2$ process in an annular continuous-flow photoreactor (ACFP). Design

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Table 1
Review of some kinetic rate expressions for removal of various organic compounds with the UV/H_2O_2 process.

Type of kinetic models	Organic compound	Reactor type	Rate equation	References
First category of kinetic models	Chlorophenols	Batch	$-\frac{dC_s}{dt} = k_{H_2O_2} C_s^m C_{H_2O_2}^n + k_{uv} C_s^0 I^p + k_h C_s^q C_{H_2O_2}^r I^s$	[11]
	Benzene, toluene, phenol, dimethylphtalate	Batch	$-\frac{dC_s}{dt} = k_{uv} C_s^m + k_h C_{H_2O_2}^n C_s^0$	[12]
	Isoprene	Batch	$-\frac{dC_s}{dt} = k_{uv} C_s^m I^n + k_h C_s^0 C_{H_2O_2}^p I^q$	[13]
Second category of kinetic models	Acid Orange 7	Batch and continuous circulation	$-\frac{dC_s}{dt} = \frac{2\emptyset f_{H_2O_2} k_h I}{k_b C_{SO}} C_s$ $f_{H_2O_2} = \frac{\varepsilon_{H_2O_2} C_{H_2O_2}}{\varepsilon_s C_s + \varepsilon_{H_2O_2} C_{H_2O_2}}$	[8,15]
	Reactive Black 5	Re-circulation	$-\frac{dC_s}{dt} = \frac{k_b I C_{H_2O_2}}{(k_{b1} I + k_{b2}) C_{SO} + C_{H_2O_2}} C_s$	[14]

m, n, o, p, q, r, s reaction order.
k_b, k_{b1}, k_{b2} constants used for the kinetic modeling.
k_h reaction rate constant for UV/H_2O_2 system, min^{-1}.
k_{UV} reaction rate constant for UV alone, min^{-1}.
$\emptyset$ quantum yield.
ε molar absorption coefficient $M^{-1}\,\text{cm}^{-1}$.

equation and kinetic model can be used in order to predict the concentration of AO7 and electrical energy consumption at different conditions.

2. Experimental

2.1. Materials

AO7, a monoazo anionic dye, was obtained from Fluka (Switzerland) as a model compound from monoazo textile dyes. The hydrogen peroxide solution (30%) was purchased from Merck (Germany).

2.2. Photoreactor

All experiments were carried out in an annular continuous-flow photoreactor (Fig. 1). The photoreactor comprises Pyrex reactor (70 mm i.d., 72.5 mm o.d., 80 cm long), which has three sampling ports at 20 cm distance from each other. In center of the photoreactor, a mercury UV lamp (30 W, UV-C, $\lambda_{max} = 254$ nm manufactured by Philips, Holland) in vertical array was placed in the quartz tube (30 mm i.d., 32.5 mm o.d., 80 cm long).

2.3. Procedure

For photooxidative degradation of AO7, a solution containing known concentrations of dye and H_2O_2 was prepared and then 3 L of the prepared solution was transferred into a Pyrex beaker and agitated with a magnetic stirrer during experiment. AO7 concentrations were set at values, in most cases 40 mg L^{-1}, which were within the range of typical concentration of real textile wastewater. The solution was pumped with a peristaltic pump (Heidolph, PD 5001) through the ACFP reactor without any circulation. AO7 concentration at the inlet and outlets was analyzed with a UV–vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 485 nm. The light intensity in the center of the photoreactor was measured by a Lux-UV-IR meter (Leybold Co.). The volumetric flow rate was measured with a graduated cylinder and a stopwatch.

3. Results and discussion

3.1. Mathematical kinetic modeling and design equation

The decolorization efficiency versus photoreactor length at different initial concentrations of H_2O_2 was summarized in Fig. 2. The decolorization efficiency increased with increasing H_2O_2 concen-
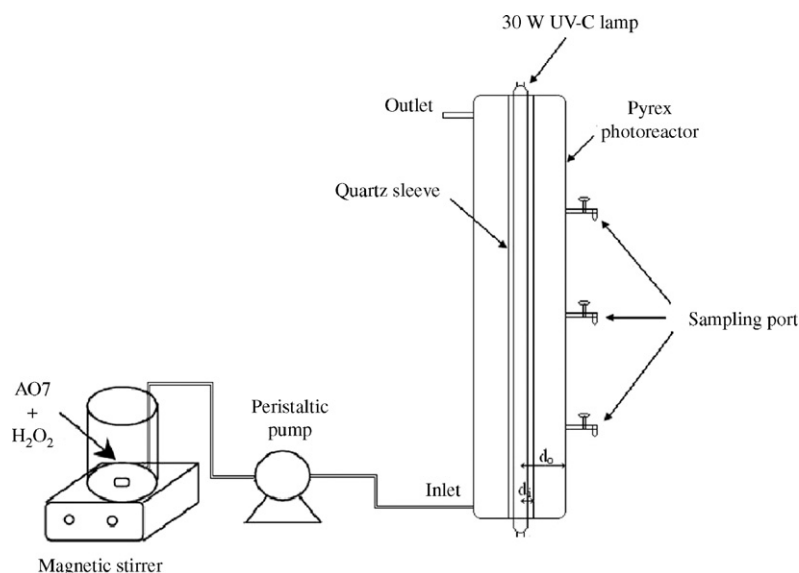

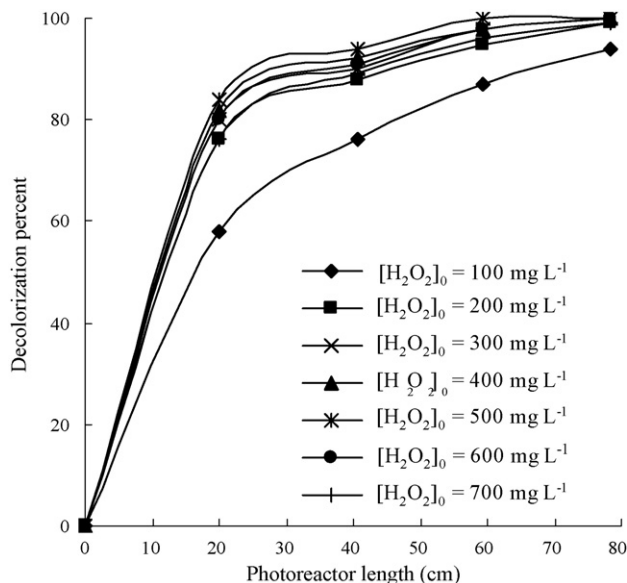**Fig. 1.** Scheme of annular continuous-flow photoreactor. For details refer to the text.

Fig. 2. Decolorization percent versus photoreactor length at the different initial concentrations of H_2O_2. $[AO7]_0 = 40$ mg L^{-1}, flow rate = 140 mL min^{-1}, pH $\cong$ 5, $I_0 = 60$ W m^{-2}.

tration from 100 to 500 mg L^{-1}. The enhancement of decolorization of AO7 in this course is due to an increase in the hydroxyl radical concentration. The improvement was not sustained above a critical value and the reaction rate constant decreased. This is reasonable, since increasing H_2O_2 concentration has two opposing effects:

1. As the concentration of H_2O_2 is increased, more hydroxyl radicals are available to attack the aromatic rings. Therefore, the rate of reaction increases.
2. When H_2O_2 is used in excess, hydroxyl radical efficiently reacts with H_2O_2 and produces $HO_2^\bullet$, also $^\bullet OH$ radicals generated at high concentration, dimerize to H_2O_2 [9].

Fig. 3 shows that the decolorization efficiency over photoreactor length as a function of the initial dye concentration using constant initial H_2O_2 concentration. From this plot, it can be seen that decolorization efficiency decreased with increasing initial dye
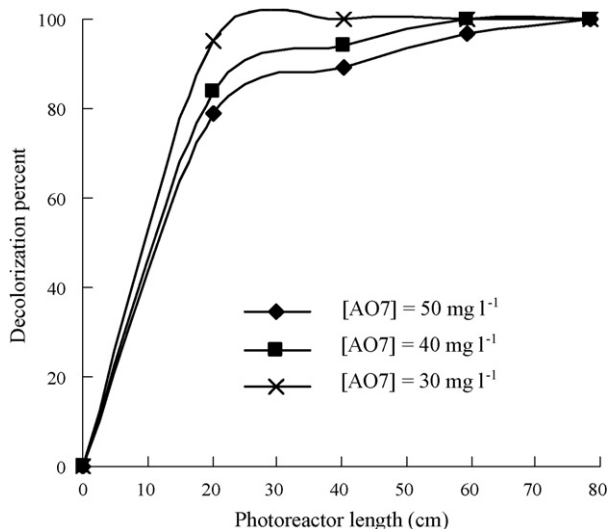
concentration. At high concentrations of AO7, the penetration of photons entering in to the solution decreases, so that an inner filter effect is induced and hence the solution becomes more and more impermeable to UV radiation, consequently, hydroxyl radical concentration decreases [8]. Also, at higher concentrations of AO7, higher intermediates are formed. These intermediates are also highly reactive towards hydroxyl radicals. Thus, AO7 and its intermediates compete effectively for hydroxyl radicals, reducing the removal efficiency.

The decolorization efficiency versus photoreactor length at different volumetric flow rates was summarized in Fig. 4. The results indicated that with decreasing volumetric flow rate from 140 to 120 ml min^{-1}, removal efficiency increased, so that the complete decolorization was obtained around 40 cm from photoreactor length. This is logical, because with decreasing volumetric flow rate the residence time of the reactant increases in the reactor [6].

The semi-logarithmic graphs of the AO7 concentration versus photoreactor length at different initial H_2O_2 concentration yield
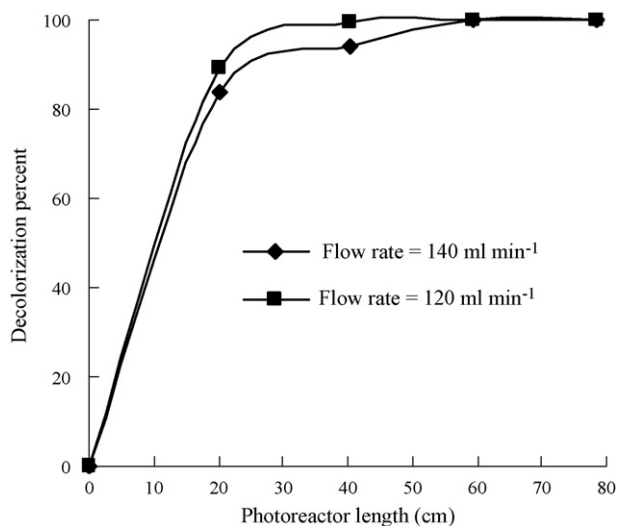

Fig. 3. Decolorization percent versus photoreactor length at the different initial concentrations of AO7. $[H_2O_2]_0 = 500$ mg L^{-1}, flow rate = 140 mL min^{-1}, pH $\cong$ 5, $I_0 = 60$ W m^{-2}.

Fig. 4. Decolorization percent versus photoreactor length at the different volumetric flow rates. $[AO7]_o = 40$ mg L^{-1}, $[H_2O_2]_0 = 500$ mg L^{-1}, pH $\cong$ 5, $I_0 = 60$ W m^{-2}.

Table 2
Apparent reaction rate constant for removal of AO7 at ACFP reactor in the presence of different initial concentrations of H_2O_2. For experimental details refer to Fig. 2.

H_2O_2 (mg L^{-1})	k_{ap} (min^{-1})	R^2
100	0.164	0.99
200	0.235	0.98
300	0.279	0.98
400	0.308	0.98
500	0.317	0.97
600	0.293	0.98
700	0.245	0.98

straight lines indicating pseudo-first-order reaction. The apparent reaction rate constant (k_{ap}) for decolorization of AO7 using different amounts of H_2O_2 was obtained from semi-logarithmic graphs were given in Table 2.

$$-\frac{d[AO7]}{dt} = k_{ap}[AO7] \tag{1}$$

In the above equation, [AO7] is the AO7 concentration and k_{ap} and t are the pseudo-first-order rate constant and irradiation time, respectively.
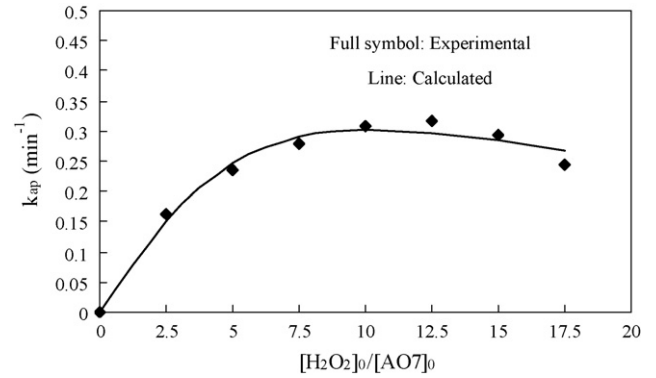

Fig. 5. Plot of k_{ap} versus the initial concentration ratio of AO7 to H_2O_2. [AO7]$_0$ = 40 mg L^{-1}, flow rate = 140 mL min^{-1}, I_0 = 60 W m^{-2}.

As it was previously reported [9], the relationship between the apparent reaction rate constant (k_{ap}) and the amount of H_2O_2 can be modeled using nonlinear regression. The model was defined by considering the inhibition reactions and negligible effect of direct
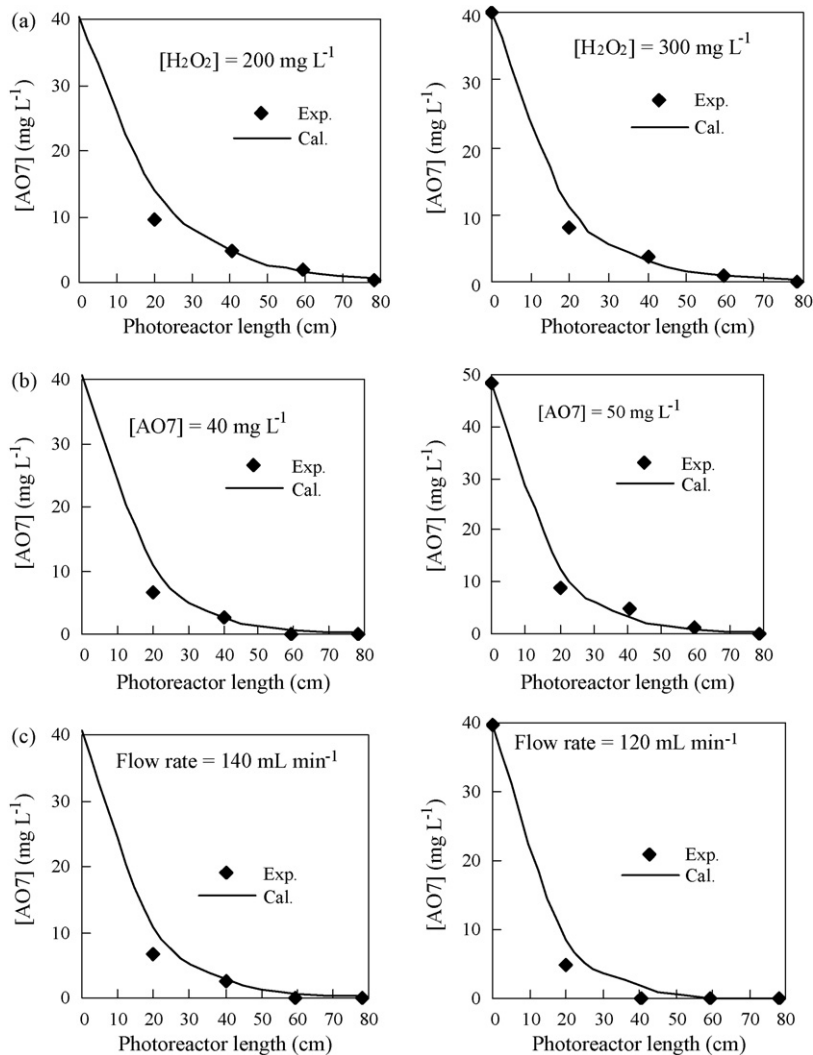

Fig. 6. Comparison between experimental and calculated data for the decolorization of AO7 in the UV/H_2O_2 process: (a) at different initial concentrations of H_2O_2. [AO7]$_0$ = 40 mg L^{-1}, flow rate = 140 mL min^{-1}. (b) at different initial concentrations of AO7. [H_2O_2]$_0$ = 500 mg L^{-1}, flow rate = 140 mL min^{-1}. (c) at different volumetric flow rates. [AO7]$_0$ = 40 mg L^{-1}, [H_2O_2]$_0$ = 500 mg L^{-1}. (I_0 = 60 W m^{-2} for all runs).

photolysis in photodegradation of AO7 as:

$$k_{ap} = \frac{a([H_2O_2]_0/[AO7]_0)}{1 + b([H_2O_2]_0/[AO7]_0) + c([H_2O_2]_0/[AO7]_0)^2} \quad (2)$$

where k_{ap} is the dependent variable, a, b and c are the model parameters and $[H_2O_2]$ is the H_2O_2 concentration. Fitting the experimental data to the proposed model (Eq. (2)) was presented in Fig. 5. The model parameters with 95% confidence level and Sum of Squares due to Error (SSE) as the error function were obtained with nonlinear regression using Polymath (version 6.5) software package. The values of a, b, c with 95% confidence level and SSE are 0.067 ± 0.0097, 0.025 ± 0.0036, 0.009 ± 0.002 and 0.0003, respectively. The proposed model predicts a maximum k_{ap} around 10 for $[H_2O_2]_0/[AO7]_0$, which was in good agreement with experimental data of 12.5. This model is useful in estimating the proper H_2O_2 concentration for photooxidative degradation of AO7, to prevent excess use of oxidant and a better control of operational costs.

Reynolds number calculations indicated that flow regime used in this work is laminar. Therefore we can consider reactor used in this work as ideal tubular reactor. For a tubular reactor, the design equation can be written as follows [16]:

$$\frac{-d[AO7]}{dV} = \frac{-r_{AO7}}{v_0} \quad (3)$$

with

$$V = \frac{\pi}{4}(d_o^2 - d_i^2)l \quad (4)$$

and

$$-r_{AO7} = \frac{-d[AO7]}{dt} \quad (5)$$

In the above equations V, v_0, d_o, d_i and l are the photoreactor volume, volumetric flow rate, inner diameter of pyrex annular photoreactor, outer diameter of quartz tube and photoreactor length, respectively.

With substitution of Eqs. (4) and (5) to Eq. (3), we obtain:

$$\frac{-d[AO7]}{dl} = \frac{\pi/4\,(d_o^2 - d_i^2)}{v_0}\left(\frac{-d[AO7]}{dt}\right) \quad (6)$$

Finally, with substitution of Eq. (2) into Eq. (6), we obtain:

$$\frac{-d[AO7]}{dl} =$$
$$\frac{\pi/4\,(d_o^2 - d_i^2)}{v_0}\left(\frac{a([H_2O_2]/[AO7]_0)}{1 + b([H_2O_2]/[AO7]_0) + c([H_2O_2]/[AO7]_0)^2}\right)$$
$$[AO7] \quad (7)$$

After substitution of the values of a, b, c, d_o and d_i to Eq. (7), the concentration of AO7 at different photoreactor lengths was obtained for varying initial concentrations of H_2O_2, AO7 and also for different flow rates. A comparison between experimental and calculated data for the decolorization of AO7 at different photoreactor lengths has been shown in Fig. 6. As can be seen from this figure, the model allows predicting AO7 concentration at different conditions.

3.2. Evaluation of electrical energy consumption for ACFP reactor

When we want to select a waste treatment technology, we have to consider important factors such as economics, economy of scale, regulations, effluent quality goals, operating and robustness, among mentioned factors economics is often paramount [17].

The UV/H_2O_2 process is electric-energy intensive and electric energy can represent a major fraction of the operating costs, simple
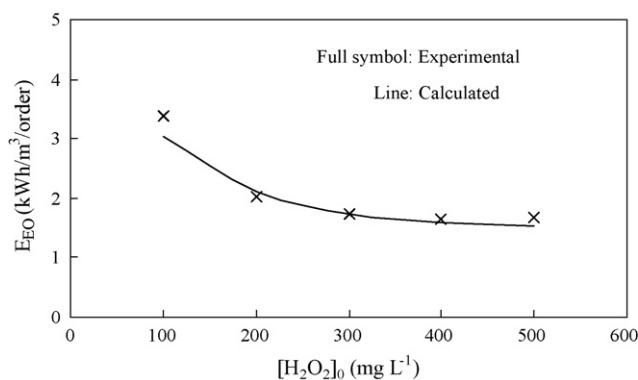

Fig. 7. Electrical energy per order versus the initial concentration of H_2O_2. $[AO7]_0 = 40\,mg\,L^{-1}$, flow rate = 140 mL min^{-1}, $I_0 = 60\,W\,m^{-2}$.

figures-of-merit based on electric energy consumption can be very informative. Therefore Bolton et al. defined the figures-of-merit electric energy per order (E_{EO}) to use in the first order kinetic regime of AOPs when the low pollutant concentrations (which apply here) are present in solution [18]. E_{EO} is defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in a unit volume of contaminated water. With assuming first-order kinetics, the E_{EO} can be calculated from the following equation for a batch-type reactor:

$$E_{EO} = \frac{P_{el} \times t \times 1000}{V \times 60 \times \log(C_0/C)} \quad (8)$$

where P_{el} is the input power (kW) from UV lamp to the AOPs system, t is the irradiation time (min), V is the volume of water (L) in reactor and C_0 and C are initial and final pollutant concentrations, respectively [18]. Above equation for a continuous-flow reactor changes to:

$$E_{EO} = \frac{P_{el}}{v_0 \times \log(C_0/C)} \quad (9)$$

where v_0 is the volumetric flow rate (m^3/h) in the flow-through system.

Fig. 7 shows the predicted E_{EO} values estimated from the design equation (Eqs. (7) and (9)) and experimental data as a function of H_2O_2 concentration. It can be seen that the model correctly predicts the trend of the E_{EO}. As can be seen from Fig. 7, E_{EO} decreased with increasing H_2O_2 concentration from 100 to 300 mg L^{-1} which is due to an increase in the hydroxyl radical concentration. The enhancement of decolorization rate was not very high in the range of 300–500 mg L^{-1} for H_2O_2 concentration. This is reasonable, because •OH radicals efficiently react with H_2O_2, hence the photooxidative degradation promoter itself contributes to the •OH-scavenging capacity and reduces the decolorization rate of AO7 [9].

4. Conclusions

It can be concluded that the UV/H_2O_2 process using annular continuous-flow photoreactor indicated satisfactory performance in the decolorization of AO7 as a model compound from textile industry. The results indicated that AO7 concentration at different lengths of photoreactor could be predicted with kinetic modeling at different conditions. For evaluation of electrical energy consumption, E_{EO} values based on experimental and calculated data were obtained at different conditions. The results of this study indicated that applying desired H_2O_2 concentration could reduce the E_{EO} value.

References

[1] Krik-Othmer, Encyclopedia of Chemical Technology, third ed., Wiley, New York, 1978.
[2] C.S. Poon, Q. Huang, P.C. Fung, Degradation kinetics of cuprophenyl yellow RL by UV/H_2O_2/ultrasonication (US) process in aqueous solution, Chemosphere 38 (1999) 1005–1014.
[3] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, Toxicol. Lett. 151 (2004) 203–210.
[4] H. Lachheb, E. Puzenat, A. Ksibi, M. Elaloui, E. Guillard, C. Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, Appl. Catal. B 39 (2002) 75–90.
[5] O.J. Hao, H. Kim, P.C. Chiang, Decolorization of wastewater, Crit. Rev. Env. Sci. Technol. 30 (2000) 449–505.
[6] N. Daneshvar, M. Rabbani, N. Modirshahla, M.A. Behnajady, Photooxidative degradation of Acid Red 27 in a tubular continuous-flow photoreactor: influence of operational parameters and mineralization products, J. Hazard. Mater. 118 (2005) 155–160.
[7] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.
[8] M.A. Behnajady, N. Modirshahla, M. Shokri, Photodestruction of Acid Orange 7 (AO7) in aqueous solutions by UV/H_2O_2: influence of operational parameters, Chemosphere 55 (2004) 129–134.
[9] N. Daneshvar, M. Rabbani, N. Modirshahla, M.A. Behnajady, Critical effect of hydrogen peroxide concentration in photochemical oxidative degradation of C.I. Acid Red 27 (AR27), Chemosphere 56 (2004) 895–900.
[10] A. Lopez, A. Bozzy, G. Mascolo, J. Kiwi, Kinetic investigation on UV and UV/H_2O_2 degradations of pharmaceutical intermediates in aqueous solution, J. Photochem. Photobiol. A 156 (2003) 121–126.
[11] Y. Ku, S.C. Ho, The effect of oxidants on UV destruction of chlorophenols, Environ. Prog. 9 (1990) 218–221.
[12] D.W. Sundstrom, B.A. Weir, H.E. Klei, Destruction of aromatic pollutants by UV light catalyzed oxidation with hydrogen peroxide, Environ. Prog. 8 (1989) 6–11.
[13] E.M. Elkanzi, G.B. Kheng, H_2O_2/UV degradation kinetics of isoprene in aqueous solution, J. Hazard. Mater. B 73 (2000) 55–62.
[14] A. Mohey El-Dein, J.A. Libra, U. Wiesmann, Mechanism and kinetic model for the decolorization of the azo dye Reactive Black 5 by hydrogen peroxide and UV radiation, Chemosphere 52 (2003) 1069–1077.
[15] A. Aleboyeh, Y. Moussa, H. Aleboyeh, Kinetics of oxidative decolourisation of Acid Orange 7 in water by ultraviolet radiation in the presence of hydrogen peroxide, Sep. Purif. Technol. 43 (2005) 143–148.
[16] O. Levenspiel, Chemical Reaction Engineering, Wiley, New York, 1972.
[17] M.A. Behnajady, N. Modirshahla, Evaluation of electrical energy per order (E_{EO}) with kinetic modeling on photooxidative degradation of C. I. Acid Orange 7 in a tubular continuous-flow photoreactor, Ind. Eng. Chem. Res. 45 (2006) 553–557.
[18] J.R. Bolton, K.G. Bircger, W. Tumas, C.A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems, Pure Appl. Chem. 73 (2001) 627–637.