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Application of Box–Wilson experimental design method for the photodegradation of textile dyestuff with UV/H_2O_2 process

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Abstract

Photodegradation of textile dyestuffs Chrysophenine Yellow (DY12), Congo Red (DR28) and Remazol Black B (RB5) by the UV/H_2O_2 process was investigated in a laboratory scale photoreactor equipped with a 16-W low-pressure mercury vapour lamp. The Box–Wilson experimental design was employed to evaluate the effects of major process variables, dyestuff and hydrogen peroxide concentrations and irradiation time on decolorization efficiency. Response function coefficients were determined by regression analysis of experimental data and predictions were found to be in good agreement with the experimental results. For 100 mg l^{-1} DY12, RB5 and DR28 for instance, the optimum hydrogen peroxide concentration and irradiation time were found to be 45 mM for 58 min, 45 mM for 58 min and 60 mM for 120 min with 100, 100 and 85.7% efficiencies, respectively. Further increases in oxidant concentration led to slight decreases in decolorization efficiencies according to the response function, most probably due to the scavenging effect of excess hydrogen peroxide on hydroxyl radicals. And this was confirmed by the repeated experiments performed at the points of concern. Increasing the dyestuff concentration also decreased the decolorization efficiency even at higher concentrations of oxidant and longer irradiation times. The photodegradation of dyestuffs were found to follow a first-order reaction law.

Keywords: Box–Wilson design; Decolorization; Photodegradation; Textile; Dyestuff; UV/H_2O_2 process

1. Introduction

Synthetic dyestuffs are present in certain industrial wastewaters, in concentrations sufficient to impart noticeable colour to the effluent. Dyestuffs have a complex chemical structure which is hard to degrade biologically and numerous biodegradability studies on dyes have shown that azo dyes are not likely to be biodegradable under aerobic conditions [1,2]. They are either sorbed or trapped in bioflocs [3,4]. Thus, ecosystems of streams can be seriously affected. Consequently, dyes have to be removed in dye wastewater before discharge. In the past, effluents containing azo dyes have been treated by adsorption onto activated carbon or by chemical coagulation [5,6]. However, these traditional methods mainly transfer the contaminants

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from wastewater to solid wastes. Therefore, advanced oxidation is a potential alternative to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents [2]. Chemical oxidation using ultraviolet radiation (UV) in the presence of hydrogen peroxide (H_2O_2) is a very promising technique. UV wavelengths of 200–280 nm lead to disassociation of H_2O_2, with mercury lamps emitting at 254 nm being the most commonly used. UV/H_2O_2 systems generate hydroxyl radicals (OH•) which are highly powerful oxidizing species. Hydroxyl radicals can oxidize organic compounds (RH) producing organic radicals (R•), which are highly reactive and can be further oxidized. The main reactions that occur during UV/H_2O_2 oxidation are as follows [7]:

$$H_2O_2 + UV \rightarrow 2OH\bullet \quad (1)$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \quad (2)$$

$$RH + OH\bullet \rightarrow H_2O + R\bullet \rightarrow \text{further oxidation.} \quad (3)$$

Several dyes utilized by textile industries (including azo-reactive ones) have been successfully degraded by the above technique [8–12]. However, a literature survey has shown that most of the studies were carried out within a certain range of H_2O_2 concentration and most frequently at a constant dye concentration without optimizing the oxidant concentration for any concentration of a dye.

In this study, we have investigated the ability of the oxidative UV/H_2O_2 process to decolorize aqueous solutions of three azo dyes (Direct Red 28, Direct Yellow 12, Reactive Black 5). The Box–Wilson experimental design was used in order to investigate the effects of important process variables on colour removal performance. The Box–Wilson experimental design is a response surface methodology used for evaluation of a dependent variable as functions of independent variables [13,14]. Dyestuff and H_2O_2 concentrations and reaction time were considered as independent variables and colour removal efficiency was considered as dependent variable in the Box–Wilson statistical design method. In addition to dyestuff removal efficiency, total organic carbon (TOC) has also been determined in order to evaluate the mineralization rate, as an important indicator of the treatment effectiveness.

2. Experimental

2.1. Reagents

The azo dyes, Direct Red 28 (DR28), Direct Yellow 12 (DY12), Reactive Black 5 (RB5) are widely used textile dyestuffs in the Turkish textile industry and were obtained from Far-East as commercially available dyes and used without further purification. Further characteristics of the azo dyes used in the study are listed in Table 1. The H_2O_2 solution (35%,w/w) of analytical grade was obtained from Merck, Germany. Aqueous solutions of azo dyes were prepared with distilled water.

2.2. Photoreactor

All experiments were performed in a well-stirred, batch, cylindrical photoreactor with a total volume of 2.2 l. The reactor is made of glass and does not contain any metal parts. The outside of

Table 1
Main characteristics of the azo dyes used

	RB5	DY12	DR28
Colour index number	17095-24-8	24895	22120
Synonyms	Remazol Black B	Chrysophenine Yellow	Kongo Red
Molecular formula	$C_{26}H_{25}N_5O_{19}S_6$	$C_{30}H_{26}N_4O_8S_2Na_2$	$C_{32}H_{24}N_6O_6S_2$
Molecular weight (g mol)	991.82	680.7	696.67
λmax (nm)	597	405	497
Purity (%)	~55	~65	~85

the reactor was covered with an aluminium sheet. At the top, the reactor has inlets for feeding reactants, and ports for measuring temperature and withdrawing samples. The reactor was open to air with a teflon-coated magnetic stirring bar placed in the bottom to provide proper mixing. The UV irradiation source was a 16-W low-pressure mercury vapour lamp (maximum emission at 254 nm) encased in a quartz tube. Because the light source produces heat, in order to conduct experiments at room or controlled temperatures, the lamp was surrounded with a water-cooling jacket to maintain a constant temperature. The lamp was axially centered and was immersed in the dye solution. Fig. 1 shows the schematic diagram of the laboratory-scale photochemical installation used in the study.

2.3. Experimental procedure and analytical methods

For a standard reaction run, 2 l of aqueous solution was used. All experiments were conducted at neutral pH without buffering. Following the adjustment of dyestuff concentration in the solution, it was poured into the reactor. Then, H_2O_2 at different amounts was injected in the reactor before the beginning of each run. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of H_2O_2. The temperature of the solution was kept constant at 25±2 °C throughout all experiments. Each run in this study was performed two times and each sample was analyzed twice to confirm the results. In case of an error higher than 5%, a third run was conducted to fit at least two values. The results used in this study are the average values derived from the repeated experiments, the results of which were within 5% of each other.

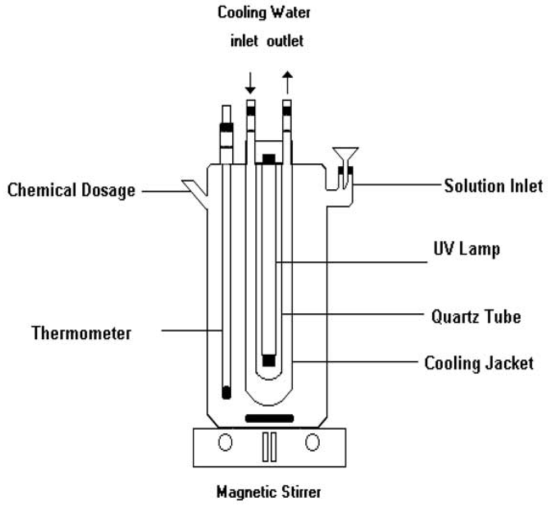

Fig. 1. Schematic diagram of the laboratory-scale photochemical installation.

Samples were taken at predetermined reaction times to measure absorbance, TOC and pH. The samples were analyzed immediately to avoid further reaction. A spectrophotometer of Novaspec II, Pharmacia Biotech. was used to measure the absorbance. TOC measurements were carried out using a DOHRMAN DC 190 model TOC analyzer. pH was measured by using a NEL pH 890 pH meter.

2.4. Box–Wilson experimental design

The Box–Wilson statistical experimental design was employed to determine the effects of operating variables on dyestuff removal efficiency and to find the combination of variables resulting in maximum dyestuff removal efficiency. The Box–Wilson design is a response surface methodology which is an empirical modeling technique devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. Basically this optimization process involves three major steps, performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the adequacy of the model. The significant variables like dyestuff concentration, H_2O_2 concentration and reaction time were chosen as the independent variables and designated as X_1, X_2 and X_3 respectively. The dyestuff concentration (X_1) was varied between 50 and 250 mg/l, the H_2O_2 concentration (X_2) between 5 and 75 mM and the reaction time (X_3) between 10 and 120 min. Experimental conditions determined by the Box–Wilson statistical design are presented in Table 2. The experiments consist of six axial (A), eight factorial (F) and centre points. The centre point was repeated three times for each set of experiments. Computation was carried out using multiple regression analysis using the least squares method.

The following response function was used in correlating the colour removal efficiency (Y) with other independent parameters (X_1, X_2, X_3). A SCIENTIST computer program was used for determination of the coefficients of Eq. (1) by regression analysis of the experimental data.

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

where, Y = predicted yield; b_o = constant; b_1, b_2, b_3 = linear coefficients; b_{12}, b_{13}, b_{23} = cross product coefficients; b_{11}, b_{22}, b_{33} = quadratic coefficients.

3. Results and discussion

The TOC and colour removal efficiencies obtained from the experiments which consisted of six axial (A), eight factorial (F) and centre points are summarised in Table 3 and observed colour removal efficiencies were compared with the predicted ones obtained from the response function. The observed colour removal efficiencies varied between 10 and 85%, 40 and 100% and 44 and 100% for the dyes DR28, DY12 and RB5 respectively. In terms of TOC, the removal efficiencies varied between 0 and 13, 0 and 50 and 0 and 34% for DR28, DY12 and RB5 respectively.

Experimental results were used in a SCIENTIST regression analysis program to determine the coefficients of the response function [Eq. (1)]. The calculated coefficients are listed in Table 4 and were used in calculating predicted values of colour removal efficiencies. The correlation coefficients (R^2) between the observed and predicted values were 0.996, 0.982 and 0.976 for DR28, DY12 and RB5 respectively indicating a good agreement between the observed and predicted values of colour removal efficiencies.

The effects of the operating variables on the system's colour removal performance were determined by obtaining projections of the response functions on certain planes of known parameter values. In order to determine the effect of H_2O_2 concentration on dyestuff removal efficiency at a dyestuff concentration of D_o: 100 mg/l, Fig. 2 was developed as a function of irradiation time for different values of H_2O_2 concentration for DR28, DY12 and RB5 respectively.

The efficiency increased with increasing H_2O_2 concentration. The colour removal efficiency for DR28 increased from 64.2 to 85.7% at the end of 120 min of irradiation when the initial H_2O_2 concentration was increased from 5 to 60 mM (Fig. 2a). Further increasing H_2O_2 concentration to 75 mM did not change the efficiency. DR28 was found to be the one which was the most difficult to degrade among the three dyestuffs studied. The degradation rate of DY12 and RB5 were almost similar and higher than that of DR28. The colour

Table 2
Experimental conditions according to a Box–Wilson statistical design

Axial points				Factorial points			
No.	Dye_o (mg/l)	$H_2O_{2\ o}$ (mM)	t (min)	No.	Dye_o (mg/l)	$H_2O_{2\ o}$ (mM)	t (min)
A1	250	40	65	F1	207.8	60.2	96.8
A2	50	40	65	F2	207.8	60.2	33.2
A3	150	75	65	F3	207.8	19.8	96.8
A4	150	5	65	F4	207.8	19.8	33.2
A5	150	40	120	F5	92.2	60.2	96.8
A6	150	40	10	F6	92.2	60.2	33.2
Centre point				F7	92.2	19.8	96.8
C	150	40	65	F8	92.2	19.8	33.2

removal efficiency increased from 87.5 to 100% for DY12 after only 58 min of irradiation when the initial H_2O_2 concentration was increased from 5 to 45 mM (Fig. 2b) and again decreased to 95% when the H_2O_2 concentration was further increased to 75 mM. For RB5, the efficiency increased from 77.6 to 100% after 58 min of irradiation when the initial H_2O_2 concentration was increased from 5 to 45 mM (Fig. 2c) and again decreased to 90.7% when the oxidant concentration was further increased to 75 mM. The decreases in removal efficiency at high oxidant concentrations is thought to be due to the side reactions taking place between the $OH\bullet$ radicals and the excess H_2O_2. In order to verify this scavenging effect, additional experiments were performed at a hydrogen peroxide concentration of 75 mM and irradiation time of 120 min for DR28 and 58 min for DY12 and RB5. Experimentally determined decolorization efficiencies at these points were 88, 93 and 86% for DR28, DY12 and RB5 respectively indicating not more than a 5% deviation from the values determined from the response function.

For an initial dyestuff concentration of 100 mg/l, optimum $[H_2O_2]/[\text{Dyestuff}]$ molar ratios

Table 3
Observed and predicted colour removal efficiency with TOC removal efficiencies

Exp. No.	Obs. col. rem. efficiency			Pred. col. rem. efficiency			TOC rem. efficiency (%)		
	DR28	DY12	RB5	DR28	DY12	RB5	DR28	DY12	RB5
*A*1	26	79	70	28	78	69	3	9	3
*A*2	85	99	1	82	1	1	13	50	34
*A*3	46	98	96	44	97	92	4	18	11
*A*4	26	80	62	27	83	68	0	8	7
*A*5	61	1	1	59	96	98	0	38	27
*A*6	10	40	46	11	45	50	0	0	4
*F*1	43	98	95	43	1	98	2	19	20
*F*2	19	65	63	19	63	64	0	11	11
*F*3	32	91	78	32	92	78	8	20	7
*F*4	14	51	44	11	49	40	1	5	0
*F*5	77	1	1	80	1	1	13	31	34
*F*6	43	86	86	45	84	85	0	13	10
*F*7	68	99	1	69	99	97	10	35	14
*F*8	36	84	82	37	79	77	0	21	11
C (Ave)	41	98	95	41	98	95	1	21	21

Table 4
Coefficients of the response function

Coefficients	Values		
	DR28	DY12	RB5
b_o	4.81×10^{-1}	4.86×10^{-1}	5.07×10^{-1}
b_1	-5.87×10^{-3}	-1.51×10^{-3}	-1.95×10^{-3}
b_2	5.08×10^{-3}	5.34×10^{-3}	8.8×10^{-3}
b_3	8.65×10^{-3}	1.24×10^{-2}	1.03×10^{-2}
b_{12}	-7.84×10^{-8}	1.93×10^{-5}	3.43×10^{-5}
b_{13}	-1.52×10^{-5}	2.99×10^{-5}	2.31×10^{-5}
b_{23}	1.33×10^{-5}	-1.56×10^{-5}	-1.17×10^{-5}
b_{11}	1.38×10^{-5}	-8.07×10^{-6}	-8.83×10^{-6}
b_{22}	-4.49×10^{-5}	-6.59×10^{-5}	-1.21×10^{-4}
b_{33}	-1.93×10^{-5}	-8.95×10^{-5}	-6.89×10^{-5}

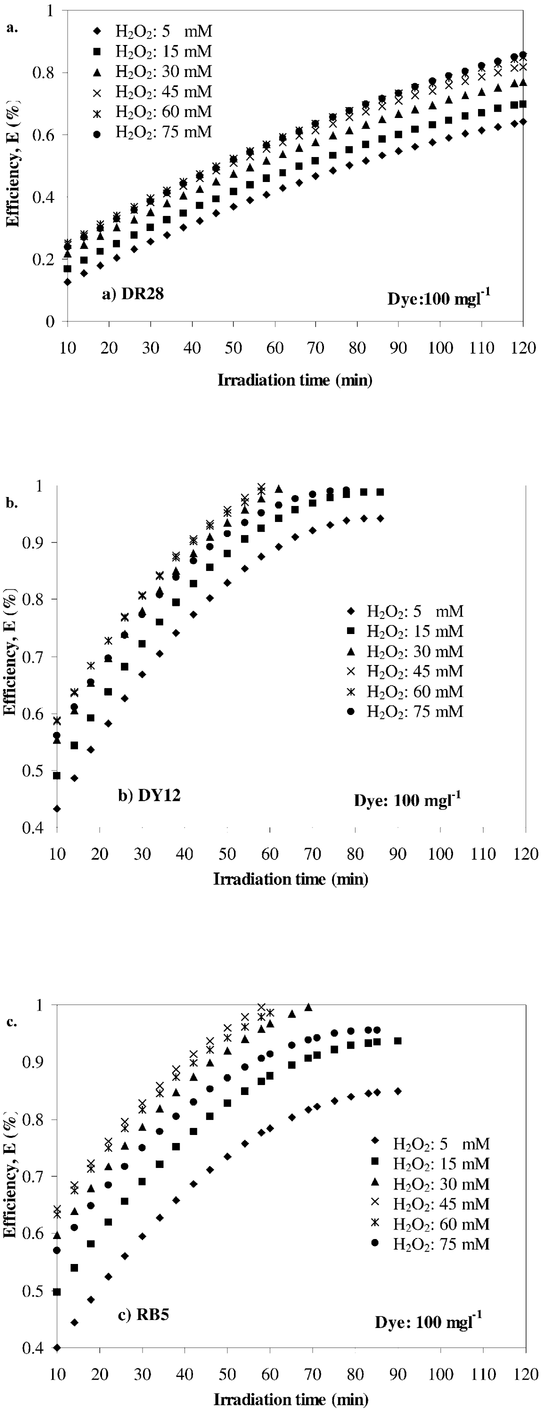

Fig. 2. Variation of decolorization efficiency with time as a function of initial H_2O_2 concentration; (a) for DR28; (b) for DY12; (c) for RB5.

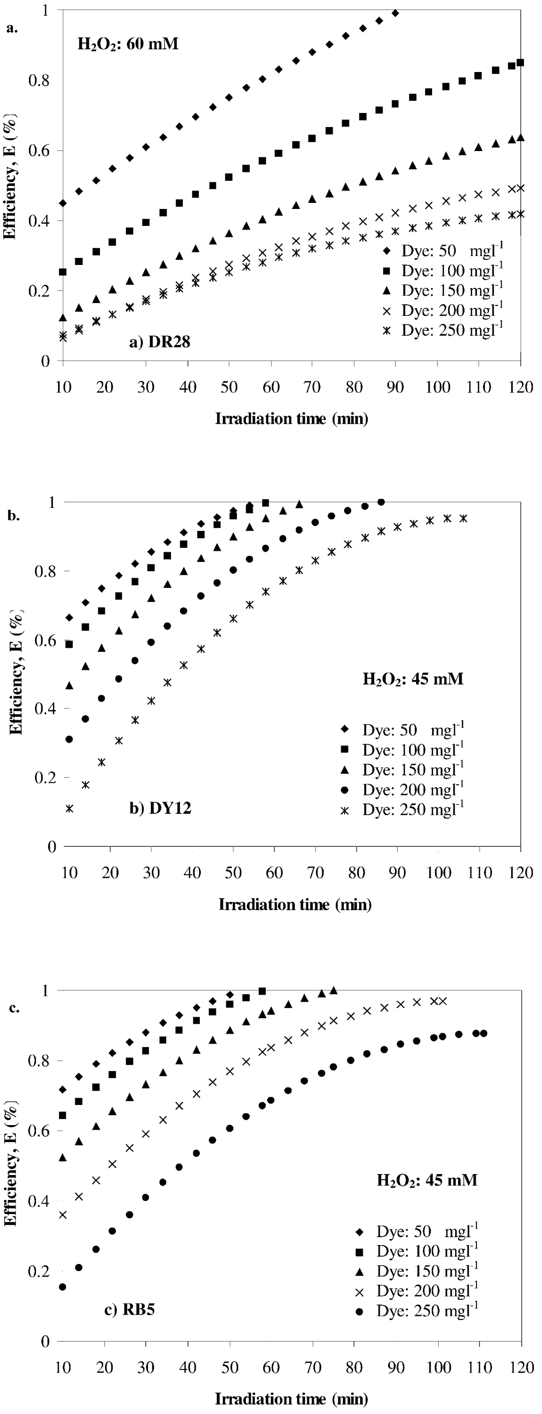

Fig. 3. Variation of decolorization efficiency with time as a function of initial dyestuff concentration; (a) for DR28; (b) for DY12; (c) for RB5.

Table 5
Variation of the first-order reaction rate constant with H_2O_2 concentration (C_{dye}: 100 mg/l)

$C_{H_2O_2}$ (mM)	DR28		DY12		RB5	
	k (min^{-1})	r^2	k (min^{-1})	r^2	k (min^{-1})	r^2
5	8.3×10^{-3}	0.999	3.41×10^{-2}	0.996	2.16×10^{-2}	0.983
15	9.5×10^{-3}	0.998	3.96×10^{-2}	0.987	3.02×10^{-2}	0.991
30	1.13×10^{-2}	0.996	4.7×10^{-2}	0.981	4.55×10^{-2}	0.974
45	1.31×10^{-2}	0.994	5.27×10^{-2}	0.979	5.52×10^{-2}	0.969
60	1.44×10^{-2}	0.99	5.11×10^{-2}	0.979	5.21×10^{-2}	0.97
75	1.5×10^{-2}	0.988	4.67×10^{-2}	0.982	3.52×10^{-2}	0.988

Table 6
Variation of the first-order reaction rate constant with dyestuff concentration

C_{dye} (mg l^{-1})	DR28		DY12		RB5	
	k (min^{-1})	r^2	k (min^{-1})	r^2	k (min^{-1})	r^2
50	26.6×10^{-3}	0.97	60.4×10^{-3}	0.973	65.7×10^{-3}	0.962
100	14.4×10^{-3}	0.99	52.7×10^{-3}	0.979	55.2×10^{-3}	0.969
150	8.2×10^{-3}	0.999	44.1×10^{-3}	0.982	39.5×10^{-3}	0.98
200	5.7×10^{-3}	0.995	37.8×10^{-3}	0.972	34.8×10^{-3}	0.985
250	4.4×10^{-3}	0.983	31.8×10^{-3}	0.983	21.1×10^{-3}	0.98

were, thus, found to be 500, 473 and 818 for DR28, DY12 and RB5, respectively, taking into account the purity of the dyestuffs. However, this does not necessarily mean that these ratios are also valid for different concentrations of the dyestuffs because it has already been reported [15] that although the $[H_2O_2]/[\text{pollutant}]$ molar ratio was kept constant, the removal efficiency decreased with increasing concentrations of pollutant due to, (a) the scavanging effect of high concentrations of H_2O_2 on OH• radicals, (b) the scavanging effect of intermediate products produced during the decomposition of pollutant; and (c) the decrease in the fraction of light absorbed by hydrogen peroxide due to the intermediate products. It is actually possible to understand whether this is valid when the pollutant of concern is a dyestuff using the response function.

The degradation kinetics of the dyestuffs was found to follow a first order reaction law and the reaction rate constants were calculated and are given in Table 5. There is, however, one point to note, after reaching the maximum efficiency that can be achieved at a certain H_2O_2 concentration and irradiation time, a trend of a decrease in predicted efficiencies with time was observed for DY12 and RB5 and this decrease in removal efficiency increased with increasing H_2O_2 concentration. Since recolourization cannot take place as far as there is enough H_2O_2 in the medium and reaction goes on, this could be related with the response function. And since the observed removal efficiencies of DY12 and RB5 were high, deviations after reaching maximum values is normal as far as these deviations are not significant ($<5\%$) and the predicted efficiency values after the maximum one should not taken into consideration.

Fig. 3 depicts the variation of colour removal efficiency with irradiation time at constant H_2O_2 concentrations of 60, 45 and 45 mM (optimum concentrations according to Fig. 2) for DR28, DY12 and RB5 respectively, but at different concentrations of dyestuffs. The colour removal efficiency decreased with increasing dyestuff concentration. Maximum removal efficiency decreased from 100% for an initial dyestuff concentration of 50 mg/l to 41.8, 95.4 and 87.7% when the dyestuff concentration was increased to 250 mg/l for DR28, DY12 and RB5, respectively.

Although the decrease in removal efficiencies seems not to be significant for DY12 and RB5, the difference in required reaction time to achieve the efficiencies of concern was considerable. For DY12, for instance, while complete removal of 50 mg/l was obtained in 54 minutes, 95.4% efficiency for 250 mg/l was reached after 106 minutes of irradiation. Another observation for this set of experiments was the occurrence of a stationary phase in dyestuff removal efficiency after a certain period of reaction time especially at high dyestuff concentrations such as 200–250 mg/l. At low dyestuff concentrations, such as 50–100 mg/l, the efficiency increased almost linearly with time. This may be attributed to two factors, one of which is the higher light absorption of the intermediate products of the dyestuff and the second is the preference of OH• radicals for the intermediate products.

The first order reaction rate constants calculated for different dyestuff concentrations for this set of experiments are given in Table 6.

Variation of dyestuff removal efficiency with hydrogen peroxide concentration at different levels of dyestuff concentration but at a constant reaction time of 120 min for DR28 and 90 min for DY12 and RB5 [these reaction periods were found to be limit values after which no increase in dyestuff removal efficiency was observed (Fig. 3)] is depicted in Fig. 4. Two important conclusions can be derived from Fig. 4. First, for 50 mg/l DR28, for instance, while it was possible to achieve complete removal in 90 min at a hydrogen peroxide concentration of 60 mM (Fig. 3), complete removal at an oxidant concentration of 17 mM was also possible, however, after 120 min of irradiation (Fig. 4) indicating approximately a four fold decrease in oxidant concentration but a 4/3 fold increase in the required reaction time for complete removal. Similar results are also valid for other dyestuffs, especially for low concentrations. This means that complete removal was possible at a hydrogen peroxide concentration of 60 mM after 90 min but there was still residual hydrogen peroxide in the solution. This gives the engineer the opportunity to make a cost evaluation of the system. One can design a small volume reactor (short reaction period) and decrease the investment costs,

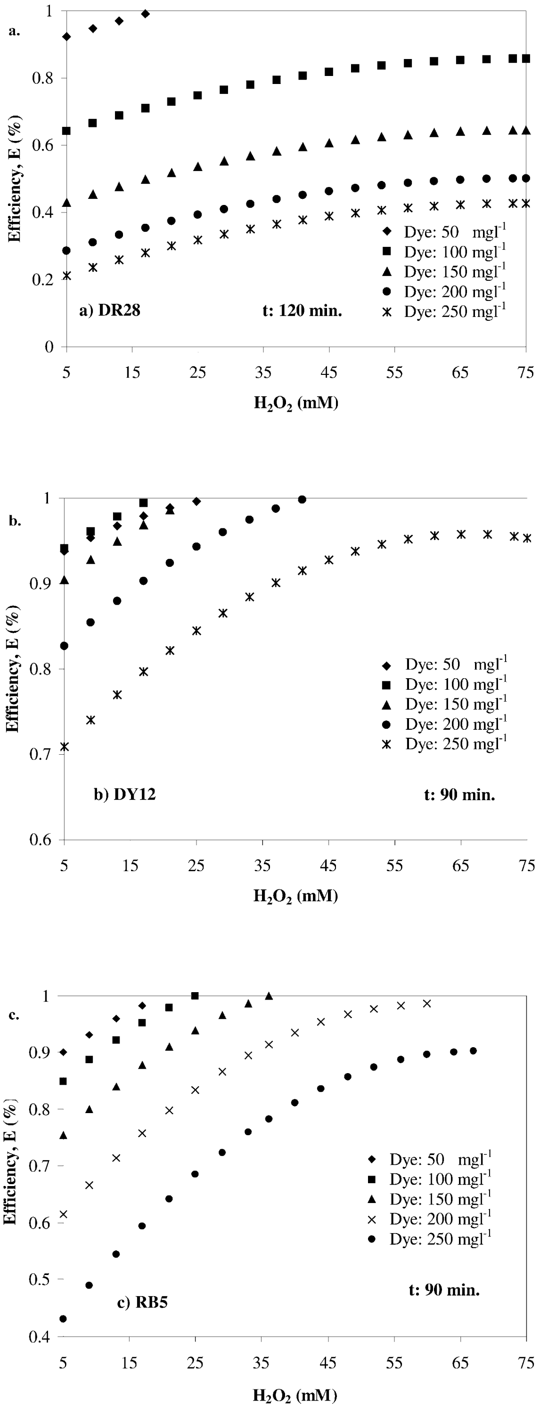

Fig. 4. Variation of decolorization efficiency with initial hydrogen peroxide concentration for different initial dyestuff concentrations; (a) for DR28; (b) for DY12; (c) for RB5.

however, this uses more chemicals and increases the operational costs. Alternatively, one may construct a slightly bigger reactor and use less chemicals. Depending on the data that can be obtained from the response function, an optimization can be made for the system to be cost–effective. Secondly, as far as a reaction period of 120 min is accepted to be reasonable, the required concentration of hydrogen peroxide needed to achieve the desired removal efficiency for any concentration of dyestuff can be determined. From Fig. 4, it can be seen that it may sometimes be more cost–effective to take a hydrogen peroxide concentration lower than that at which maximum efficiency was achieved due to small differences in removal efficiencies at different oxidant concentrations.

4. Conclusions

Photodegradation of textile dyestuffs Chrysophenine Yellow (DY12), Kongo Red (DR28) and Remazol Black B (RB5) by the UV/H_2O_2 process was investigated using Box–Wilson experimental design.

Statistical analysis using response surface methodology appears to be a valuable tool for studying the optimization of the process variables of the UV/H_2O_2 advanced oxidation process for the decolorization of textile dyestuffs. The second order response function seems to fit reasonably well.

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