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Optimization of removal of colour and organic pollutants from textile wastewater treated with UV/H_2O_2 adopting the Plackett–Burman factorial design

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ABSTRACT

In the research work presented here, a Plackett–Burman two-level partial factorial design was adopted as a multivariate strategy to determine the optimum UV/H_2O_2 process conditions for maximizing the treatment efficiency of dye-rich textile effluents. The influence of wastewater parameters, i.e. type and concentration of dye (C_{Dye}), 100–300 mg/L; concentration of NaCl (C_{NaCl}), 2.5–3.5 g/L; and concentration of urea (C_{Urea}), 5–15 g/L; and the amount of NaOH (C_{NaOH}), 1–2.4 mL/L; as well as the operational parameters, i.e. intensity of UV irradiation (I_{UV}), 1.2–1.4 kW; the amount of H_2O_2 ($C_{H_2O_2}$, 0.7–8.3 mL/L; and treatment time (t), 6–30 min; on the colour and the removal of organic pollutants was investigated. After determining seven variables, laboratory-scale experiments were conducted using two synthetically-prepared wastewaters solutions that were polluted with two structurally different reactive dyes and selected chemicals. The assessment of the UV/H_2O_2 pilot plant's performance was by monitoring the absorbance and total organic carbon in the treated samples. The obtained results showed that the treatment time and dye concentration had a major impact on the reduction of both reactive dyes. At the same time, the amount of urea and the intensity of UV radiation had a notable influence on the organic pollutant reduction.

Keywords: Textile wastewaters; UV/H_2O_2 treatment; Decoloration; Placket–Burman factorial design; Process optimization

1. Introduction

Coloured textile effluents represent severe environmental problems as they contain mixture of unconsumed dyestuffs of diverse chemical structures and associated chemicals with elevated organic and inorganic parameters [1]. A literature review regarding dye-bath wastewater treatments reveals the consideration of different approaches and techniques to handle such effluents including advanced oxidation processes (AOPs), biodegradation, adsorption onto carbon or various low-cost materials, membrane (ultra)filtration, etc. [1–6]. In the AOPs, highly reactive species, mainly hydroxyl radicals, act as primary oxidants that have one unpaired electron and are very strong and non-selective oxidizing agents, able to oxidize organic

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compounds in various wastewaters [2]. Among AOPs, the UV/H_2O_2 treatment was believed to be one of the most promising technologies, as no sludge is formed during the treatment, although it is relatively expensive in comparison to the conventional purification processes [7]. Thus, to offer a technology that is industrially applicable and cost-effective, the UV/H_2O_2 process needs to be optimized. Any decolourisation process as well as organic pollutant removal involves many problems as the processes are dependent on several operational conditions and have to be optimized using different statistical multivariate approaches such as Plackett–Burman experimental design, Taguchi method, artificial neural network (ANN), response surface methodology (RSM), etc. [7–11].

Plackett–Burman factorial design provides a fast and effective way to identify the important factors among a large number of variables, therefore, saving time and maintaining convincing information on each parameter [9]. The main steps of experimental design, usually two-level, are the selection of initial variables and responses as well as the selection of experimental domain (extreme values at which the factors are studied) [11].

The main goal of this research is to find out which variables (dye, NaCl, urea, UV irradiation, H_2O_2 or treatment time) have a significant influence on the UV/H_2O_2 decoloration and organic pollutant removal efficiency using the Plackett–Burman two-level partial factorial design.

2. Materials and methods

2.1. Synthetic wastewaters

A series of experiments were carried-out using 6 L of synthetically prepared wastewaters that were polluted with structurally-different reactive vinylsulphone dyes, i.e. C.I. Reactive Red 112 (RR112) or C.I. Reactive Blue 19 (RB19), and chemicals (NaCl, NaOH and urea) in different concentrations, thus simulating cotton dye-house effluents. Wastewaters were composed and treated according to the presented factorial design (Table 1), in order to establish which components have the superior (positive or negative) influence on colour and organic pollutants reduction during UV/H_2O_2 treatment on pilot plant.

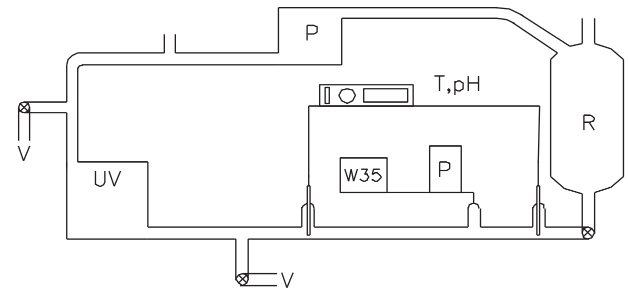

Fig. 1. Schematic view of the pilot plant for UV/H_2O_2 purification: *R* is the reservoir for wastewater, UV is the reactor with UV lamp *P* is the pump, W35 is the dosing system for H_2O_2, *V* is sampling.

All chemicals used for trials were of analytical grade: sodium hydroxide (NaOH) was purchased from Fluka, and sodium chloride (NaCl), urea and H_2O_2 (35% w/w, with $\rho = 1.13$ g/mL) from Merck.

2.2. Photo-reactor setup

Photo-oxidation experiments were performed on a pilot photo-reactor setup designed by Solvay Interlox (Fig. 1) with a maximum working volume of 6 L, flow rate of 180 L/h (3 L/min) and UV irradiation from 400 up to 2000 W. To maintain the temperature of the prepared wastewaters during the experiment constant, the reservoir was cooled using cooling water.

The assessment of a UV/H_2O_2 pilot plant's performance was verified by monitoring the absorbance and total organic carbon (TOC) in treated samples (response values). All experiments were performed in triplicate, and the average measurement value of the three independent experiments was shown as a result.

2.3. Plackett–Burman factorial design

In the present research, two-level Plackett–Burman partial factorial design was used. Each of the selected seven variables (preliminary determined as the most significant parameters for decoloration), i.e. concentra-

Table 1
Levels of selected seven variables tested in a Plackett–Burman experimental design

Experimental value	Variables						
	C_{Dye} (mg/L)	C_{NaCl} (g/L)	C_{NaOH} (mL/L)	C_{Urea} (g/L)	$C_{H_2O_2}$ (mL/L)	I_{UV} (W)	*t* (min)
Maximal (+1)	300	3.5	2.4	15	8.3	1,600	30
Optimum (0)	200	3	1.7	10	4.5	1,400	18
Minimal (−1)	100	2.5	1	5	0.7	1,200	6

tion of dye (C_{Dye}), NaCl (C_{NaCl}), NaOH (C_{NaOH}), urea (C_{Urea}) and H_2O_2 ($C_{H_2O_2}$), UV irradiation (I_{UV}), and treatment time (t), is four times at nominal (optimal) level and four times at an extreme level (once at the maximal and once at the minimal level), which is exposed in Table 1 (input variables) and Table 2 (coded levels).

The significance of the influence on each of selected seven variables was calculated using Eqs. (1) and (2) [10,11]. The influence of a variable is significant (positive or negative) if the difference D_i were greater than the experimental error (EE), and insignificant when D_i is smaller than EE. EE occurs on account of the measurement imperfection. When the increase in variable value causes a decrease in absorbance and TOC, the variable is considered to have a positive influence on the result. On the other hand, when the increase in variable value causes an increase in absorbance and TOC, the variable is considered to have a negative influence on the result.

$$D_{i\,\max} = \sum_{j=1}^{p} \frac{y_{i_j}{}^{(pri\,oi)}}{p} - \sum_{j=1}^{p} \frac{y_{i_j}{}^{(pri+i)}}{p} \quad (1)$$

$$D_{i\,\min} = \sum_{j=1}^{p} \frac{y_{i_j}{}^{(pri\,oi)}}{p} - \sum_{j=1}^{p} \frac{y_{i_j}{}^{(pri-i)}}{p} \quad (2)$$

where D_i is the influence of variable; p is the number of experiments, where the variable i has a constant value, y_i is the experimental result (response), oi is the experiment, where the variable i has an optimum value, $+i$ is the experiment, where the variable i has an extreme (high) value, and $-i$ is the experiment, where the variable i has an extreme (low) value.

2.4. Analytical procedures

To determine the influence of an individual variable, the absorbance (A) and the TOC content were measured in treated samples. The TOC was determined using a DC-190 Analyzer (Dohrmann), and the absorbance was recorded at a wavelength of maximum absorption for each dye, at 510 nm for RR112 and at 592 nm for RB19, according to standard EN ISO 105-Z10 by means of a Carry 50 UV–VIS spectrophotometer (Varian) using a cuvette with a 10 mm optical length.

3. Results and discussion

The statistical methods for optimization of operational parameters have proved to be a powerful and useful tool for various wastewaters treatments. Therefore, to improve the efficiency of UV/H_2O_2 pilot plant's performance for effluents originated by textile dye-houses, Plackett–Burman two-level partial design was employed in the present study. Previously selected and tested factors included different concentrations of dyestuff, NaCl, NaOH and urea as well as different concentration of hydrogen peroxide, UV irra-

Table 2
Plackett–Burman two-level partial design of variables in coded levels*

Experiment	Variables						
	C_{Dye} (mg/L)	C_{NaCl} (g/L)	C_{NaOH} (mL/L)	C_{Urea} (g/L)	$C_{H_2O_2}$ (mL/L)	I_{UV} (W)	t (min)
1	0	0	0	0	0	0	0
2	0	0	1	0	1	1	1
3	0	1	0	1	0	1	1
4	0	1	1	1	1	0	0
5	1	0	0	1	1	0	1
6	1	0	1	1	0	1	0
7	1	1	0	0	1	1	0
8	1	1	1	0	0	0	1
9	0	0	−1	0	−1	−1	−1
10	0	−1	0	−1	0	−1	−1
11	0	−1	−1	−1	−1	0	0
12	−1	0	0	−1	−1	0	−1
13	−1	0	−1	−1	0	−1	0
14	−1	−1	0	0	−1	−1	0
15	−1	−1	−1	0	0	0	−1

*0 is the optimal level; 1 is the extreme level (−1 is minimal and +1 is maximal level).

Table 3
The response values obtained by the UV/H_2O_2 treatment

Experiment	RR112		RB19	
	A	TOC (mg/L)	A	TOC (mg/L)
1	0.056	202	0.047	275
2	0.018	312	0.041	340
3	0.005	302	0.022	391
4	0.205	203	0.39	243
5	0.003	262	0.01	232
6	0.087	279	0.285	245
7	0.044	378	0.074	311
8	0.009	199	0.018	215
9	0.227	108	0.246	108
10	0.777	112	1.011	109
11	0.027	194	0.04	207
12	1.238	193	0.769	162
13	0.016	107	0.021	111
14	0.178	103	0.502	109
15	0.435	197	0.382	206

Table 4
The effects of the variables on the colour and organic pollutants (TOC) removal

Effluent	Response	Variable influences						
		UV	H_2O_2	Dye	NaCl	NaOH	Urea	Time
RR112	A	neg/pos	neg/neg	neg/pos	neg/pos	neg/pos	neg/pos	pos/ins
	TOC	pos/neg	pos/ins	pos/ins	pos/ins	pos/neg	neg/neg	neg/ins
RB19	A	neg/pos	neg/pos	neg/pos	pos/pos	neg/neg	ins/pos	pos/pos
	TOC	pos/neg	ins/ins	pos/ins	neg/neg	poz/poz	neg/neg	ins/pos

Note: Pos, positive effect; neg, negative effect and ins, insignificant effect; at maximal level/at minimal level.

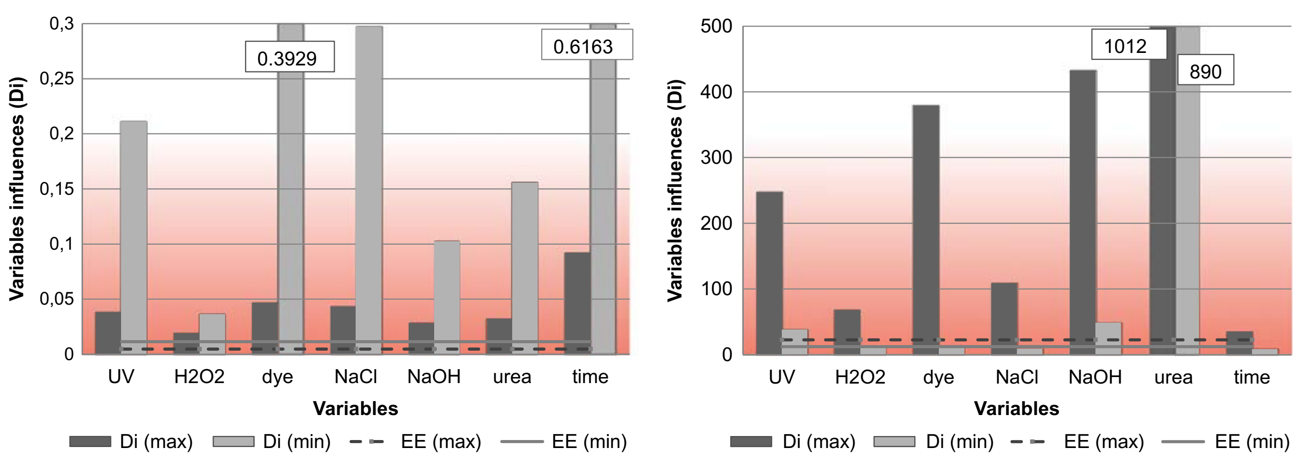

Fig. 2. The influence of the variables on the absorbance (left) and the TOC (right) at maximal and minimal levels of wastewater polluted with the RR112 dye.

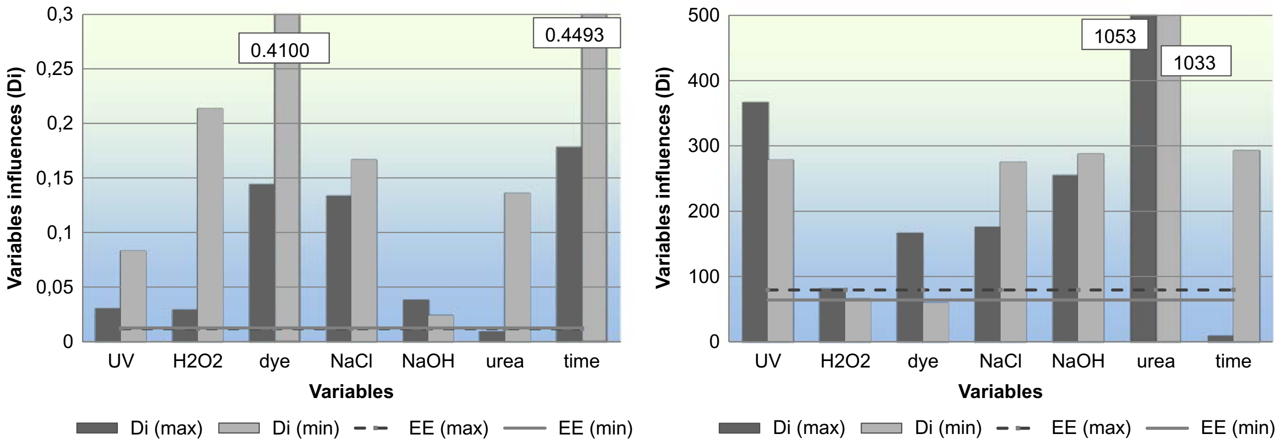

Fig. 3. The influence of the variables on the absorbance (left) and the TOC (right) at maximal and minimal levels of wastewater polluted with the RB19 dye.

diation and treatment time (Table 2). A summary of the response values (measured absorbance and TOC) after each treatment experiment is given in Table 3, and the effect of the variables on the decoloration and the TOC removal in Table 4.

The influence of the variables on colour and organic pollutant removal at maximal and minimal levels is presented in Figs. 2 and 3, separately for wastewaters included RR112 and RB19.

The symbols used in Figs. 2 and 3 are as follows:

D_i (max) is the influence of variables at maximum levels,
D_i (min) is the influence of variables at minimum levels,
EE (max) is the experimental error when the variables are at maximum levels, and
EE (min) is the experimental error when the variables are at minimum levels.

It is evident from Table 3 that the two response values, absorbance and TOC, are almost identical for both wastewaters, polluted with structurally-different reactive vinylsulphone dyes. Moreover, the given results show that the maximum removal efficiency of both dyes, Reactive Red 112 and Reactive Blue 19, was obtained at maximal level by the Experiment 5 using the following conditions: C_{dye} 200 mg/L, C_{NaCl} 3.5 g/L, C_{urea} 10 g/L, C_{NaOH} 2.4 mL/L, I_{UV} 1.6 kW, $C_{H_2O_2}$ 4.5 mL/L and time 30 min, and at minimal level by the Experiment 13 using C_{dye} 100 mg/L, C_{NaCl} 2.5 g/L, C_{urea} 5 g/L, C_{NaOH} 1.7 mL/L, I_{UV} 1.2 kW, $C_{H_2O_2}$ 4.5 mL/L and time 18 min. Meantime, the maximum TOC removal efficiency for both wastewaters was gained at maximal level by the Experiment 8 under the next variables: C_{dye} 300 mg/L, C_{NaCl} 3 g/L, C_{urea} 10 g/L, C_{NaOH} 1.7 mL/L, I_{UV} 1.6 kW, $C_{H_2O_2}$ 8.3 mL/L and time 30 min, and at minimal level by the Experiment 9 using C_{dye} 100 mg/L, C_{NaCl} 3 g/L, C_{urea} 5 g/L, C_{NaOH} 1 mL/L, I_{UV} 1.4 kW, $C_{H_2O_2}$ 4.5 mL/L and time 6 min.

As could be perceived from Table 4, and Figs. 2 and 3, there are some differences between influences of variables on the treatment results regarding the wastewater composition. All the variables except time have a significant influence on wastewater absorbance polluted with RR112, and all variables except time have a significant influence on wastewater absorbance polluted with RB19 at both maximum and minimum levels, since their D_i values are bigger than the EE. Moreover, the treatment time and the dye concentration are the deciding parameters playing a role in the reduction of both reactive dyes, at maximal and minimal levels; the longer the treatment time and the lowest the amount of dye, the lowest the absorbance.

On the other hand, the most important parameters for organic pollutant (TOC) reduction were the amount of urea and the intensity of UV irradiation. Influences of urea in both wastewaters and at both levels are negative, since urea contains organically bonded carbon, which results in higher TOC values. Higher intensity of UV irradiation influencing on major degradation of presented compounds into smaller products and consecutively, reducing TOC in treated sample.

The three variables, NaCl, NaOH and H_2O_2 have a very major influence on the colour and the removal of organic substituents regardless of the dye used.

4. Conclusions

Two synthetically-prepared wastewaters were treated utilizing a pilot UV photo-reactor setup. In order to determine the significant variable influencing UV/H_2O_2 treatment process and consecutively, to optimize the process parameters, the Plackett–Burman factorial design was used. Seven variables were selected, i.e. four parameters that are characteristics for textile dyebath wastewaters (concentration of dye, urea, NaCl and NaOH) and three operational parameters of treatment plant (intensity of UV irradiation, amount of H_2O_2 and treatment time), which were arranged on two levels, i.e. optimal level and extreme level (maximal and minimal level).

This present study indicated that mainly the intensity of UV irradiation has a major influence on decolouration and TOC reduction at both levels and for both wastewaters, although the treatment time and the dye concentration are the most important parameters that positively affected the colour removal. On the other hand, the intensity of UV radiation and the concentration of urea are two the most significant variables that influencing on TOC reduction.

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