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Parameter optimization of photocatalytic reactors using Taguchi-Grey technique

A. E. Eliyas[1]*, G. Munteanu[2], P. Karakashkova[1], M. Fabian[3]

[1] *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bl. 11, 1113 Sofia, Bulgaria*
[2] *Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei St., 060021 Bucharest, Romania*
[3] *Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 040 01 Košice, Slovak Republic*

Dedicated to the 80th anniversary of Professor Lachezar Petrov, DSc,
Corresponding Member of the Bulgarian Academy of Sciences

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The aim of the present study is to optimize the input parameters and the operation of a flat-plate gas-phase continuous flow photocatalytic reactor for air purification in order to achieve maximum efficiency, i.e. maximum conversion degree of ethylene as model air pollutant. The optimization procedure is based on the application of a combined methodology – an experimental plan, which is designed using Taguchi L32 Orthogonal Array and Grey Relational Analysis. The highest conversion degree is achieved at the highest ethylene feed concentration of 10000 ppm, the highest ethylene contact time of 6 min, and the maximal UV-C illumination intensity of 15 mW/cm^2, achieved at zero distance of illumination and five TiO_2 thin film coatings on the flat plate. Relative humidity has a small effect on the photocatalytic oxidation reaction.

Keywords: photocatalytic reactor, air purification, Taguchi-Grey methodology

INTRODUCTION

Different types and design configurations of photocatalytic reactors are used for air decontamination from volatile organic compounds (VOCs) originating from the industry, presenting a serious environmental problem [1]. One specific type of these photocatalytic reactors is the flat-plate continuous flow reactor [2]. All these types of reactors require operational input parameters optimization in order to achieve maximum efficiency. One possible approach is the procedure, which is based on Design of Experiments (DoE) proposed by different authors, applying different approaches: from complete factorial design to Taguchi's method, which is time-saving and lowering expenses for experimental runs [3–5]. It is a statistical technique used to study many factors simultaneously and most economically. By studying the effects of individual input parameters on the response function the optimal factor combination can be determined. When applied to a design Taguchi's technique helps to seek out the best design among the many alternatives, it is a powerful tool in optimization of experimental setup configuration, including catalytic reactors configuration and operational conditions.

Taguchi is implying orthogonal arrays (OAs), and in our case, five input parameters were selected considering five levels for each input parameter. Most often, it is L25 or L32 orthogonal arrays that are applied for evaluation of the measured output response; here, the conversion degree of photocatalytic oxidation of ethylene over TiO_2 on single layer or multilayer thin film coatings under UV-light irradiation.

The aim of the study is to improve the efficiency of the photocatalytic oxidation of ethylene in a recently designed and constructed gas-phase flat-plate continuous flow photocatalytic reactor (Fig. 1a, 1b) over commercial TiO_2 semiconductor material Degussa P25, upon varying the photooxidation process parameters. The parameters were feed concentration of ethylene: 1000 to 10 000 ppm (P1), ethylene contact time 120–360 s (P2), under different UV-C illumination intensities of 1.3–15 mW/cm^2 (P3) at illumination distances from 40 cm to 0 cm, relative humidity RH of the feed of 10–30% (P4) and number of TiO_2 coats from 1 to 5 (P5). Then Grey Relational Analysis (GRA) [6, 7] was applied to find out which ones of the input parameters are significant and what is the percentage of their contribution to the conversion degree and what is the optimal set of the operational conditions to achieve a maximum of the ethylene conversion based on Analysis of Variance statistical tool (ANOVA).

EXPERIMENTAL METHODS

In order to develop a statistical model to analyse the effect of input parameters P1-P5 a first-order mathematical model and ANOVA technique were used to verify model competency. The investigation was focused on the direct effect of the input process parameters on the single response function: degree

* To whom all correspondence should be sent:
E-mail: alel@ic.bas.bg

of complete oxidation of ethylene (conversion degree).

The significant input parameters are: intensity of illumination, ethylene contact time, and humidity. The Taguchi L32 orthogonal array was used for the design of the experiments and to optimize the parameters. Regression coefficients were calculated using five factors on five levels central composite design with 95% confidence level. The central composite first-order design is the most efficient tool in response with a minimal number of experimental runs without significant loss of accuracy. The ANOVA comprises the sum of values and degrees of freedom. The sum is transformed into contributions from the regression model, as well as residual error. A first-order model was developed to predict the resultant response function F (conversion degree): $F = f(Ce, \tau e, I, RH, Nc)$; the regression coefficients were calculated using a five-factor on a five-level central composite design. If the calculated value of F is greater than the standard tabulated value for 95% confidence level, then the model is considered to be adequate inside the confidence limit. This validates the significance of the model – the testing was done using the ANOVA. The value of probability 95% means that model deviation is less than 0.05, which proves the significance of the model. The determination coefficient R2 exhibits the goodness of fit of the model.

In the gas-phase experimental runs a continuous flow flat-plate steady-state reactor for air purification (Fig. 1a, Fig. 1b) was applied and the degree of conversion of ethylene was evaluated using LANCOM III gas analyzer (UK) at different flow rates of ethylene or nitrogen flow rates through the water vapor saturator (different contact times).

The relative humidity of the feed mixture as an important reaction parameter was varied without any variation of the O_2/C_2H_4 feed ratio. Different light intensities were achieved by varying the distance between the lamp and the flat plate quartz glass illumination window. The illumination intensity was 1.3 to 15 mW/cm^2 for the UV-C light. Ethylene was selected as contaminant; its feed concentration was varied by changing the Matheson settings.

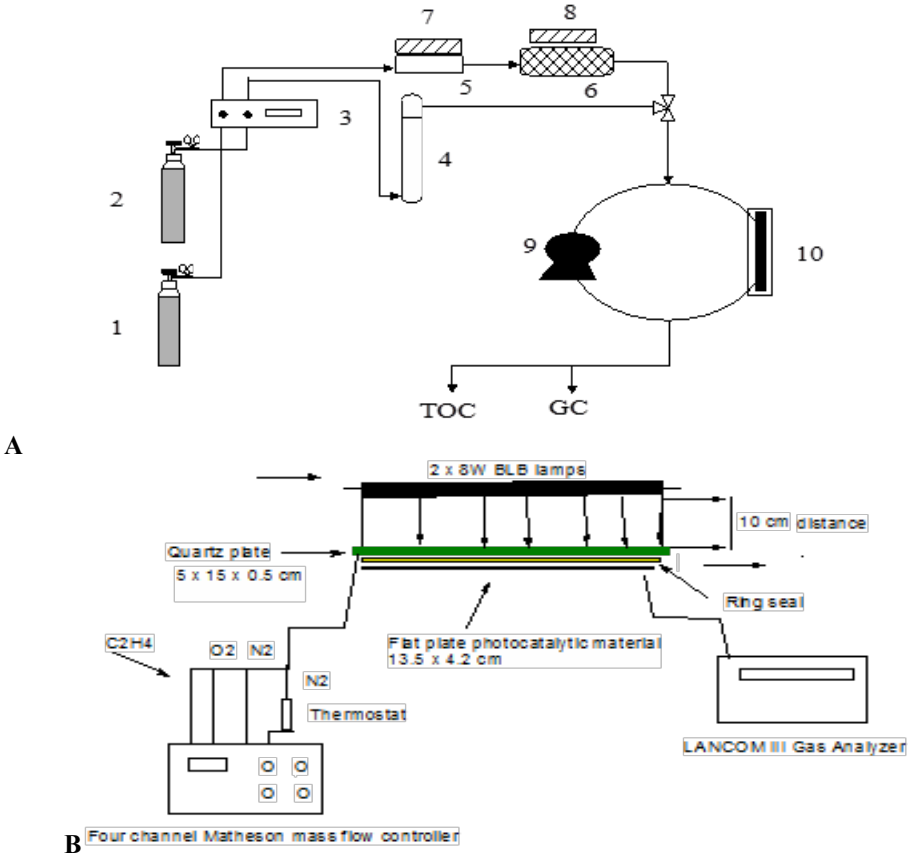

Fig. 1. A. Gas-phase flow-circulation photocatalytic reactor equipped with GC and TOC: 1&2 – O_2 and C_2H_4 gas cylinders, 3 – Matheson mass flow controller; 4 – water vapor saturator; 5 – zeolite dehumidifier; 6 – flat plate reactor; 7 – heating tape; 8 – light source; 9 – gas circulation pump; 10 – cylindrical thin film reactor with built in lamp. **B**. Flat-plate reactor with quartz glass illumination window: Matheson mass flow controller for the feed gaseous mixture and LANCOM III gas analyzer for the converted mixture.

Prior to layered deposition of the photocatalytic material as powder form on a TLC sheet (Al foil, Merck, pre-coated with a 0.2 μm SiO_2 film) it was dispersed in H_2O by sonication to obtain a stable slurry (UP200S Hielscher ultrasonic processor 24 kHz, Germany). The regime of operation of this photocatalytic reactor has already been described in a previous work [2]. The authors have specified the optimal experimental conditions to achieve maximal conversion degree, namely, optimal coating thickness to guarantee kinetic region of operation avoiding any diffusion limitations, as well as the time interval on stream to achieve steady state operation for a such size of photocatalytic reactor.

RESULTS AND DISCUSSION

We paid special attention to the preparation of TiO_2 layers. The commercially available photocatalyst Degussa P25 TiO_2 (75% anatase and 25% rutile) was used as standard material. The single-point BET method (30% N_2 + 70% He mixture at inlet flow rate of 15 ml/min – adsorption of N_2 as a monolayer at the boiling temperature of liquid nitrogen 77 K) showed that the Degussa P25 TiO_2 specific surface area was 50 m^2/g.

The suspension of nanosized particles was sonicated for 30 min in impulse regime: 24 kHz, 100% amplitude, cycle 0.5, which turned out to be more efficient than the continuous cycle 1.0. Thereafter it was deposited on thin layer chromatography sheets (SiO_2 coated) by the capillary technique with directing air stream until obtaining the optimal coating thickness of 1 mg/cm^2 [2]. This is a standard reference coating for making comparison between different photocatalytic materials. TiO_2 over-layer is located on the sub-layer of large angular micrometer-sized SiO_2 crystals (SEM) on the TLC sheet. Anatase (A) is generally accepted to be the better photocatalyst under UV-illumination than rutile (R) whose crystals are more compact and therefore the specific surface area is smaller. However, there exists a synergistic effect between anatase and rutile since their band gaps are different (3.0 eV for rutile corresponding to an absorption edge $\lambda_{max} = 413$ nm). The positions of the conduction and the valence bands of these two semiconductors allow charge carrier separation as the valence bands merge and therefore the holes are migrating freely. However, the conduction bands of A and R are separated and the photoexcited electrons remain localized. The Degussa company has made use of this synergistic effect and produces the best commercially available photocatalyst having an A/R ratio of 3:1. If this charge separation model is correct then the best A/R ratio would be 1:1; however, in this specific case the surface area would be too low because of the high content of rutile. So, Degussa have found an optimal combination between synergism and specific surface area at 3:1.

The measure of the photocatalytic activity was taken to be the ethylene degree of conversion (single response function) as a result of varying the five input parameters (Table 1). The O_2 feed flow rate created a large excess of oxygen with respect to the stoichiometrically required amount for the oxidation reaction. This allowed us to disregard the difference between the inlet and outlet oxygen concentrations under illumination. Thus, the sixth variable P6 was not included in the consideration, which simplifies the reaction picture. So, the bimolecular reaction of Langmuir-Hinshelwood type of mechanism is reduced to a pseudo first-order kinetic equation following only the pollutant concentration decrease with the time. In the case of the air purification photocatalytic reactor (continuous air flow mode or flow-circulation regime of operation) the conversion degree of the pollutant (ethylene flow) is measured as a function of the pollutant contact time.

Feeding C_2H_4 and O_2 by two independently regulated channels allows varying the feed ethylene concentration (P1) but at the same time also the ethylene contact time (P2). In all the experimental runs the oxygen concentration is in large excess with respect to the stoichiometrically required oxygen amount to achieve 100% conversion of ethylene. So, this parameter can be disregarded in our analysis as we can accept that the outlet concentration of oxygen remains practically unchanged, i.e. it is practically the same as the inlet concentration in the photocatalytic reactor and, therefore, it can be included in the value of the effective kinetic constant in the kinetic equation.

The illumination intensity parameter can be varied by changing the UV-C lamp distance to the TiO_2 thin film coating. The use of two independently regulated channels for feeding N_2 enables the variation of the humidity of the gaseous mixture (parameter P4). This is a very important operational parameter [8] during photocatalytic oxidation processes as the water vapour is the source of the hydroxyl radicals formed under UV-light irradiation [9], being the main active particles oxidizing practically all classes of organic compounds. The number of TiO_2 thin film coatings deposited on the TLC sheet was also varied (P5). All these considerations make a set of 5 parameters on 5 levels (Table 1), which is described by an orthogonal array L32 (5^5) of the central composite design matrix (Table 2).

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Table 1. Five input parameters on five levels under UV-C light illumination

Symbol	Input parameter	Level 1 -2	Level 2 -1	Level 3 0	Level 4 1	Level 5 2
P1	C_2H_4 inlet concentration	1 000 ppm	3 000 ppm	5 000 ppm	7 000 ppm	10 000 ppm
P2	C_2H_4 contact time	2 min	3 min	4 min	5 min	6 min
P3	Illumination distance	0 cm	10 cm	20 cm	30 cm	40 cm
	Intensity	15 mW/cm^2	11.5 mW/cm^2	8.1 mW/cm^2	4.7 mW/cm^2	1.3 mW/cm^2
P4	Relative humidity	10%	15%	20%	25%	30%
P5	Number of TiO_2 coats	1	2	3	4	5

Table 2. Experimental design based on the central composite plan matrix.

Trial No	P1	P2	P3	P4	P5	Response conversion
1	−1	−1	−1	−1	1	26.1
2	1	−1	−1	−1	−1	37.8
3	−1	1	−1	−1	−1	30.4
4	1	1	−1	−1	1	53.0
5	−1	−1	1	−1	−1	10.3
6	1	−1	1	−1	1	22.4
7	−1	1	1	−1	1	31.8
8	1	1	1	−1	−1	26.4
9	−1	−1	−1	1	−1	20.5
10	1	−1	−1	1	1	18.3
11	−1	1	−1	1	1	20.6
12	1	1	−1	1	−1	50.0
13	−1	−1	1	1	1	26.8
14	1	−1	1	1	−1	25.4
15	−1	1	1	1	−1	46.9
16	1	1	1	1	1	39.3
17	−2	0	0	0	0	22.8
18	2	0	0	0	0	37.5
19	0	−2	0	0	0	28.9
20	0	2	0	0	0	49.5
21	0	0	−2	0	0	42.6
22	0	0	2	0	0	38.9
23	0	0	0	−2	0	31.42
24	0	0	0	2	0	27.7
25	0	0	0	0	−2	33.9
26	0	0	0	0	2	53.3
27	0	0	0	0	0	44.0
28	0	0	0	0	0	45.1
29	0	0	0	0	0	43.8
30	0	0	0	0	0	44.1
31	0	0	0	0	0	46.4
32	0	0	0	0	0	44.7

The main task of the study was the development of a mathematical function (statistical model), based on five input parameters on five levels, to predict the values of the single response function, which have already been measured experimentally (Table 2) with possibly small model deviation. This function linearly depends on all the five input parameters; its expression being determined by multilinear regression. In the regression procedure, the real values of the input parameters are replaced with the corresponding Taguchi parameters (Table 2). The model should describe the relation between the input process parameters and the response. This would enable to determine the optimal process variable levels that could produce a desirable output (the highest conversion degree). Therefore, in the current investigation a first-order mathematic model consistent with first-order kinetics [10] was developed to predict the resultant conversion degree.

The response function F can be expressed as follows:

$$F = f(C_e^0, \tau_e, I_{uv}, RH, N_c) \equiv C_1P_1 + C_2P_2 + C_3P_3 + C_4P_4 + C_5P_5 + b,$$

where C_e^0 is the inlet concentration of ethylene, τ_e, is the ethylene contact time, I_{uv} is the intensity of UV- C light irradiation, RH is the relative humidity, N_c is the number of TiO_2 coatings on the TLC flat plate and P_1, P_2, … P_5 are the corresponding Taguchi working parameters (Table 2). The regression coefficients C_1, C_2, … C_5, and b were calculated by multilinear regression using a five-factor five-level central composite design in MINITAB 15 BASICS statistical software with 95% confidence level.

The mathematical model developed using the evaluated regression coefficients for calculating the resultant conversion degree is given by the following expression:

$$F = 33.18 + 3.69P_1 + 6.33P_2 – 1.45P_3 + 0.09P_4 + + 1.22P_5.$$

According to the above expression the optimal maximum conversion is obtained when $P_1 = 2$, $P_2 = 2$, $P_3 = −2$, $P_4 = 2$ and $P_5 = 2$, i.e. when $C_e^0 = 10000$ ppm C_2H_4, the contact time $\tau_e = 6$ min, $I_{uv} = 15$ mW/cm^2, RH = 30% and $N_c = 5$. In Table 2 no trial is characterized by these Taguchi parameters: 2, 2, -2, 2, 2 and, consequently, it is not possible to check whether this mathematical prediction is in agreement or not with experimental data. In spite of this fact, we have to mention that the results obtained in trials 4, 12, 18, 20, 21, and 26 are in accord with the expression above.

Another item that could be concluded taking into account the values of the coefficients from this expression, is whether a hierarchy between the input parameters can be established: the higher the value of a coefficient, the greater is the importance of the corresponding parameter. Consequently, the order of

the importance of the parameters is the following: contact time, ethylene concentration, illumination intensity, and number of coats. According to the obtained expression the conversion is only slightly sensitive to the change of the relative humidity.

Table 3. Comparison of the observed values and the predicted values of ethylene conversion degree (response function) and the resulting percentage of error.

Trial No	Observed conversion	Predicted conversion	Error, %
1	26.1	25.74	1.38
2	37.8	30.68	18.84
3	30.4	35.96	15.46
4	53.0	45.78	13.62
5	10.3	20.40	49.51
6	22.4	30.22	25.88
7	31.8	35.50	10.42
8	26.4	40.44	34.72
9	20.5	23.48	12.69
10	18.3	33.30	45.05
11	20.6	38.58	46.60
12	50.0	43.52	12.96
13	26.8	23.02	14.10
14	25.4	27.96	9.16
15	46.9	33.24	29.13
16	39.3	43.06	8.73
17	22.8	25.80	11.63
18	37.5	40.56	7.54
19	28.9	20.52	29.00
20	49.5	45.84	7.39
21	42.6	36.08	15.31
22	38.9	30.28	22.16
23	31.42	33.00	4.85
24	27.7	33.36	16.97
25	33.9	30.74	9.32
26	53.3	35.62	33.17
27	44.0	33.18	24.59
28	45.1	33.18	26.43
29	43.8	33.18	24.25
30	44.1	33.18	24.76
31	46.4	33.18	28.49
32	44.7	33.18	25.77

Validating the adequacy of the model, ANOVA was used to assess the relationship between the response variable and one or more predictor variables. Thus, the significance of each process variable is evaluated for determining the quality characteristic. Table 3 compares the observed and predicted values and the resulting percentage of error.

CONCLUSION

The highest conversion degree was achieved at the highest concentration of 10000 ppm C_2H_4, the maximal illumination intensity at 0 distance of illumination, the highest contact time of 6 min, and five TiO_2 thin film coatings, whatever the relative humidity.

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