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Parameter optimization of a semi-batch water decontamination slurry photocatalytic reactor using Taguchi-Grey technique

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The aim of the present research work was to optimize the input parameters and the efficiency of operation of a slurry semi-batch water purification photocatalytic reactor, aiming at maximum efficiency. The response function upon varying the input parameters was the conversion degree of the model water contaminant Acid Black 194 azo dye (AB194). The optimization procedure is based on the application of combined methodology – experimental plan, which is based on Taguchi L9 Orthogonal Array (OA 3^4) and Grey Relational Analysis (GRA). The highest conversion degree (degree of decolorization – response function) was achieved at the lowest AB194 azo dye initial concentration, under UV-C illumination intensity of 0.07 W/cm^2, and 400 rpm magnetic stirrer operation rate, while increasing the O_2 flow rate above 10 L/h did not give any substantial increase in the decolorization degree.

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

INTRODUCTION

Chromium Acidic Black Diazo Dye (Colour Index Acid Black 194) is used for colouring textiles and anodized aluminium articles [1]. Discharging it into the waterways is strictly forbidden by the present day safety regulations, because it represents a health hazard. It is manufactured by the Bulgarian factory BULCOLOR in the town of Kostenetz and it is known that this dye is especially stable to UV-light irradiation, which is of great advantage in view of its practical application [1]. This fact makes it also suitable to be a model waste water contaminant in view of its stability (see Fig. 1).

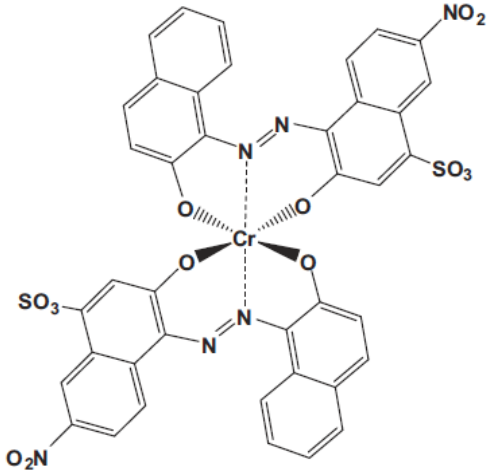

Figure 1. Chromium Acidic Black Diazo Dye AB194 – structural formula

Different configurations of slurry photocatalytic reactors have already been proposed and studied aiming at simpler mathematical models for designing the reactors and improving their efficiency [2]. The present study was carried out using a semi-batch photocatalytic slurry reactor, reported by us previously [3]. The batch consisted of a fixed volume of model contaminant waste water and fixed amount of suspended TiO_2 Degussa P25 photocatalytic material. The construction of the reactor enables feeding a continuous flow of oxygen – for this reason the reactor belongs to the group of semi-batch reactors, i.e. one of the reactants (the pollutant) is in a fixed amount and the other reactant (the oxygen) is in continuous flow – photocatalytic oxidation reaction. A horizontal quartz tube is mounted in the reactor enabling insertion of different types of cylindrical illumination lamps – UV-A, UV-C and visible light lamps. The lamp in the quartz tube is situated perpendicularly to the shaft of the Pyrex glass reactor (see Fig. 2).

One possible approach in the optimization of the operational input parameters is based on the Design of Experiments (DoE) ranging from complete factorial design to Taguchi's method [4-6] which is time saving and lowering the expenses for the experimental runs. The latter statistical method [4] observes the values of the response function upon varying many input factors. In our case of photocatalytic reactor for waste water decontamina-

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tion using azo dye model contaminant (AB194) the response function is the degree of decolorization of the dye solution in the course of illumination followed spectrophotometrically or we can take the time interval needed for achieving complete decolorization (i.e. 99.9% photo-oxidative conversion degree). Taguchi's method is based on using orthogonal arrays (OAs) of different kinds – in our previous study on photocatalytic air purification [7] we made use of L32 OA for the case of 5 input parameters on 5 levels (5^5). The present study applies a much simpler case of statistical analysis for the specific case of a water decontamination photocatalytic reactor. This is the L9 OA which involves 4 parameters on 3 levels (3^4) making only 9 experiments, while the complete factorial design 3^4 means carrying out 81 experiments.

The aim of the study was to improve the efficiency of a semi-batch slurry photocatalytic reactor for oxidative degradation of azo dye model waste water contaminant over commercial TiO_2 semiconductor material Degussa P25, upon varying the photo-oxidation process input parameters. The parameters were as follows: initial concentration of the dye: 1 mmol\L to 5 mmol\L (P1), different types of illumination - UV-C, UV-A and visible light at intensities 0.07 W/cm^2 to 8.9 W/cm^2 (P2) measured by Cole-Parmer radiometer VLX-3W, different speed of the magnetic stirrer in the slurry 400-600 rpm (P3) and different oxygen flow rates 8L/h up to 12 L/h (P4). Then Grey Relational Analysis (GRA) [8, 9] 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 conversion degree based on ANOVA Analysis of Variance statistical tool.

EXPERIMENTAL

In order to develop a statistical model to analyze the effect of input parameters P1-P4 a first order linear mathematical model and ANOVA technique were used to verify the model competency. The investigation was focused on the direct effect of the input process parameters on the single response function – degree of decolorization of the azo dye Acid Black 194 (conversion degree). The investigated input parameters were the initial azo dye concentration, the type of illumination source, the magnetic stirrer speed of operation and the oxygen feed flow rate into the reactor. The Taguchi L9 orthogonal array was used for the design of the experiments and to optimize the parameters. Regression coefficients were calculated using 4 factors on a three levels central composite design with 95% of confidence level. The central composite first order design is the most efficient tool in response with a minimal number of experimental runs without great loss of accuracy. The ANOVA comprises the sum of squares and degrees of freedom. The sum of squares is transformed into contributions from regression model as well as residual error. A first-order linear model was developed to predict the resultant response function F – decolorization degree: $F = f(C^0_{ad}, I_{uv}, R_{st}, O_{2fl})$ – the regression coefficients were calculated using a four factor – three level central composite design. If the calculated confidence value – deviation of predicted conversions from the experimentally measured conversions, i.e. the model deviation is less than 0.05 % – is greater than the standard tabulated value of 95 % for confidence level, then the model is considered to be adequate within the confidence limits. This validates the significance of the model – the testing was done using the ANOVA. The value of deviation was less than 0.05 %, which proves the significance of the model. The determination coefficient of the square quadratic error R^2 exhibits the goodness of fit of the model.

In the experimental runs a semi-batch semi-continuous flow slurry photocatalytic reactor for water purification (Fig. 2) was applied and the degree of decolorization of a solution of Acid Black 194 azo dye was evaluated using CAMSPEC spectrophotometer Model M501 (UK) monitoring the wave length of maximum extinction (absorbance) at 570 nm for this specific azo dye. Different types of lamps were used – UV-A (polychromatic BLB i.e. Black Light Blue lamp with maximum at 365 nm), UV-C (monochromatic 254 nm TUV lamp) – both giving intensity of illumination of 0.07 W per cm^2 and visible light of 8.9 W per cm^2.

RESULTS AND DISCUSSION

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 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 [3] between anatase and rutile – their band gaps are different (3.0 eV for rutile corresponding to adsorption edge λ_{max} = 413 nm and 3.2 eV for anatase corresponding to adsorption edge λ_{max} = 388 nm). The positions of the conduction and the valence bands of these two semiconductors allow charge carrier separation as the valence bands merge – therefore the holes are migrating freely. However, the conduction bands (A/R) are separated and the photoexcited electrons remain localized. The company Degussa has made use of this synergistic effect and it produces the best commercially available photocatalyst (having ratio A:R = 3:1). If this charge separation model is correct, then the best ratio A:R would be 1:1, however in this specific case the surface area would be too low because of the high content of rutile [3]. So obviously Degussa Co. has found out an optimal combination between synergism and specific surface area at 3:1.

The measure of the photocatalytic activity was taken to be the azo dye degree of decolorization (single response function) as a result of varying the four input parameters on three levels (Table 1). The O_2 feed flow rate created a large oxygen excess with respect to the stoichiometrically required amount for oxidation reaction.

Table 1. Four input parameters of the photoreactor on three levels

Symbol	Input Parameter	Level 1 -1	Level 2 0	Level 3 1
P1	AB194 initial concentration	1 mmol/L	3 mmol/L	5 mmol/L
P2	Type of illumination	UV-C 0.07 W/cm^2	UV-A 0.07 W/cm^2	Visible 8.9 W/cm^2
P3	Magnetic stirrer speed	400 rpm	500 rpm	600 rpm
P4	Oxygen flow rate	8 L per hour	10 L per hour	12 L per hour

The first variable input parameter was the azo dye Acid Black194 initial concentration from 1 mmol/L to 5 mmol/L (P1), while the type of illumination UV-C (TUV), UV-A (BLB) 0.07 W/cm^2 and visible light 8.9 W/cm^2 was the second input parameter (P2), the speed of the magnetic stirrer in the slurry from 400 to 600 rpm was the third input parameter (P3) and the oxygen flow rate from 8 to 12 L/h was the fourth input parameter (P4). In all the experimental runs the oxygen concentration was in large excess with respect to the stoichiometrically required oxygen amount to achieve 99.9% conversion (Table 2).

The main task of the study was the development of a mathematical function (statistical model), based on four input parameters on three levels to predict the values of the single response function, which have already been measured experimentally (Table 2) with the possibly smallest model deviation. The model should describe the relationship between the input process parameters and the response function. This would enable the determination of the optimal levels of process variable parameters that could produce a desirable output (the highest conversion degree).

Table 2. Experimental design – central composite design matrix

Trial No	P1	P2	P3	P4	Response conversion %
1	-1	-1	-1	-1	83.70
2	-1	0	0	0	72.40
3	-1	+1	+1	+1	50.10
4	0	-1	0	+1	80.00
5	0	0	+1	-1	61.50
6	0	+1	-1	0	39.50
7	+1	-1	+1	0	70.10
8	+1	0	-1	+1	52.90
9	+1	+1	0	-1	30.80

Therefore, in the current investigation a first-order linear model was developed to predict the resultant conversion degree. The response function can be expressed as follows:

$$F = f(C^0_{ad}, I_{uv}, R_{st}, O_{2fl}) \quad (1)$$

where C^0_{ad} is the inlet concentration of azo dye AB194, I_{uv} is the type of illumination and its intensity, R_{st} is the rate of stirring and O_{2fl} is the oxygen flow rate. The regression coefficients were calculated using a four factor - three 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 F is given by the following expression (2):

$$F = A + B\,C^{0}_{ad} + C\,I_{uv} + D\,R_{st} + E\,O_{2fl} = A + B\,P1 + C\,P2 + D\,P3 + E\,P4 \quad (2)$$

Validating the adequacy of the model. Analysis of variance (ANOVA) was used to assess the relationship between the response variable and one or more predictor variables. We obtained the following values for the coefficients:

$$F = 60.1 - 8.7\,P1 - 18.9\,P2 + 0.93\,P3 + 1.16\,P4 \quad (3)$$

This model predicts the following values of the conversion (response function), which are compared with the experimentally observed values in Table 3.

As we can see, the percentages of the errors are varying between 0.2% (exp. 4) up to 4.9% in only one case (exp. 2) – these errors are acceptable. The coefficients of parameters P3 and P4 are very small, compared to the coefficients for P1 and P3 as it can be seen in equation (3). This suggests that we are probably in a situation of superparametrization. Let us check this point - so we can make one more iteration – let us first eliminate P3 (influence of stirrer speed) and vary the other three parameters P1, P2, P4 – now we obtain the following equation:

$$F = 60.1 - 8.7\,P1 - 18.9\,P2 + 0.93\,P3 + 1.7\,P4 \quad (4)$$

Table 4 lists the experimental conversions and the simulated values, as well as the errors.

Table 3. Comparison of the observed values and the predicted values of AB194 degree of decolorization (response function) with all four parameters P1, P2, P3, P4 and the resulting percentage of error.

Trial No	P1 P2 P3 P4	Observed conversion	Predicted conversion	% Error
1	-1 -1 -1 -1	83.70	85.6	2.3
2	-1 0 0 0	72.40	68.8	4.9
3	-1 1 1 1	50.10	52.0	3.7
4	0 -1 0 1	80.00	80.2	0.2
5	0 0 1 -1	61.50	59.9	2.6
6	0 1 -1 0	39.50	40.3	1.9
7	1 -1 1 0	70.10	71.2	1.6
8	1 0 -1 1	52.90	51.6	2.4
9	1 1 0 -1	30.80	31.3	1.6

Table 4. Comparison of the observed values and the predicted values of AB194 degree of decolorization (response function) with three parameters P1, P2, P4 and the resulting percentage of error

Trial No	P1 P2 P4	Observed conversion	Predicted conversion	% Error
1	-1 -1 -1	83.70	86.6	3.3
2	-1 0 0	72.40	68.8	4.9
3	-1 1 1	50.10	51.1	2.0
4	0 -1 1	80.00	80.2	0.2
5	0 0 -1	61.50	58.9	4.2
6	0 1 0	39.50	41.2	4.2
7	1 -1 0	70.10	70.3	0.3
8	1 0 1	52.90	52.5	0.7
9	1 1 -1	30.80	31.3	1.6

Now let us make one last iteration eliminating both P3 and P4 and leaving only P1 and P2 as significant input parameters for the semi-batch photoreactor – these data are listed in Table 5. Eliminating two of the parameters of the square average deviation it becomes double (these values are not listed in Table 5). The final conclusion is that the input parameters P3 and P4 must also be taken into account, although their contributions are not so significant as the contributions of input parameters P1 and P2.

Table 5. Comparison of the observed values and the predicted values of AB194 degree of decolorization (response function) with two main parameters P1, P2 and the resulting percentage of error.

Trial No	P1	P2	Observed conversion	Predicted conversion	% Error
1	-1	-1	83.70	87.7	4.6
2	-1	0	72.40	68.8	4.9
3	-1	1	50.10	49.9	0.3
4	0	-1	80.00	79.0	1.2
5	0	0	61.50	60.1	2.3
6	0	1	39.50	41.2	4.2
7	1	-1	70.10	70.3	0.3
8	1	0	52.90	51.4	2.9
9	1	1	30.80	32.5	5.2

CONCLUSIONS

The highest degree of decolorization in a semi-batch slurry photoreactor for waste water decontamination was achieved at the lowest concentration of the azo dye model waste water pollutant of 1 mmol/L AB194, UV-C illumination, 400 rpm magnetic stirrer rate, while increasing the O_2 flow rate above 10 L/h did not give any substantial increase in the decolorization degree. All four input parameters must be taken into account in spite of the fact that the contributions of P1 and P2 (dye concentration and illumination) are much more significant but nevertheless, the other two input parameters (rate of stirring the suspension P3 and oxygen feed flow rate P4) cannot be entirely disregarded.

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