ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Chemometric study of thermal treatment effect on the P25 photoactivity for degradation of tartrazine yellow dye

Isis P.A.F. Souza, Osvaldo Pezoti, Karen C. Bedin, André L. Cazetta, Sandra A.R. Melo, Lucas S. Souza, Marcela C. Silva, Vitor C. Almeida*

Laboratory of Environmental and Agrochemistry, Department of Chemistry, State University of Maringá, Av. Colombo 5790, CEP 87020-900 Maringá, Paraná, Brazil

ARTICLE INFO

Keywords:
Photocatalysis
P25
TiO_2
Thermal treatment
RSM
Tartrazine yellow

ABSTRACT

In the present work, a chemometric study was carried out using a central composite rotatable design (CCRD) to evaluate the effect of thermal treatment on the P25 photoactivity for degradation of tartrazine dye. The factors investigated for thermal treatment were: temperature, heating rate and heating time, and the experimental design response was the photodegradation constant (k_{app}). The response surface methodology (RSM) was employed to obtain the material with higher k_{app} value for tartrazine photodegradation, under UV radiation, and investigate the interactions between factors of thermal treatment. The P25 used as precursor, as well as the obtained material from the optimized conditions (TTP_{op}), and the material with worst photocatalytic activity (TTP-17) were characterized from the N_2 physiosorption, FT-IR, SEM, XRD, DSC/TGA and PAS. The TTP_{op} was obtained under conditions of temperature of 298 °C, heating rate of 10 °C min^{-1} and heating time of 177 min. TTP_{op} showed k_{app} value of 25.7, while P25 and TTP-17 presented k_{app} values of 20.2 and 10.0, respectively.

1. Introduction

Photocatalytic degradation is classified as an advanced oxidation process (AOP), being described as an efficient, easy-to-handle and moderate cost method for the degradation of various types of organic compounds [1–3]. This process is initially based on the generation of oxidizing radical species, such as hydroxyl radicals ($HO^{\bullet}$), on the catalyst surface [2,4]. When a catalyst is irradiated with UV radiation, it acts as a reductant and absorbs photons from the light, causing the transference of electrons located in the valence layer to the conduction layer, giving rise electron-hole pairs [2,5]. Consequently, the electron-hole pairs give rise to $HO^{\bullet}$ radicals on the photocatalyst surface that react with pollutants by oxidation reactions, generating carbon dioxide and water (mineralization) [1,2,6].

Titanium dioxide (TiO_2) is easily found in nature in mineral form from the three different crystalline phases; brookite (orthorhombic), anatase (tetragonal) and rutile (tetragonal) [7]. In recent years, the use of TiO_2 as photocatalyst has attracted attention of the scientific community due to its high availability, low cost, photochemical stability, high photocatalytic activity and low toxicity [5,8]. These TiO_2 characteristics allow that it is applied in various treatment methods, aiming the photodegradation of many pollutants [9,10], including alkenes, olefin, aliphatic compounds, phenols, organic compounds, pesticides, herbicides, among others [8,11]. The commercial TiO_2 (P25,Evonik-formerly Degussa) consists at a mixture of TiO_2 anatase and rutile phases, containing 0–13% of amorphous material, with particle size between 20 and 50 nm [12–14].

Anatase is the crystalline phase of TiO_2 that shows the best response in photodegradation processes [15,16] Therefore, most of the works that report the synthesis or treatment of this photocatalyst have been carried out with the aim of obtaining materials with higher percentages of anatase phase. This has been demonstrated in the literature from the studies that use photocatalyst surface modifying agents and thermal treatments [17,18].

TiO_2 photocatalytic efficiency depends on several parameters such as the quality and content of the anatase phase, including crystallinity and the presence of impurities on its surface [19,20] A strategy to improve the efficiency of catalysts is the realization some kinds of treatments or modifications on the materials. In this way, an option is the employ of thermal treatment, which has a determinant influence on the photocatalytic, morphological and structural properties of the materials [18]. The treatment parameters, such as temperature, time and heating rate usually are evaluated to obtain materials with better photocatalytic activities.

Studies involving thermal treatments on the TiO_2 have been reported in the literature [12,19,21,22]. In general, these works have as focus the investigation of the temperature effect on the photocatalytic activity, and on structural and textural features of TiO_2 based materials.

* Corresponding author.
E-mail address: vcalmeida@uem.br (V.C. Almeida).

https://doi.org/10.1016/j.ceramint.2018.04.016
Received 7 February 2018; Received in revised form 3 April 2018; Accepted 3 April 2018

In addition, thermal treatment conditions were evaluated from the univariate studies, in which one factor was varied, keeping others stable, e.g, varying the temperature and keeping the heating rate and time stable. This way, studies have neglected possible synergistic effects between parameters involved in the thermal treatments. Therefore, becomes important investigating these parameters, considering its synergism effects, and that best performances of obtained materials may be reached from the optimized experimental conditions.

The response surface methodology (RSM) consists of a mathematical set and statistical multivariate methods, which allow to evaluate experimental conditions related to response from the mathematical model [23,24]. Additionally, it has as great advantages optimizing the procedures, aiming to find appropriated experimental conditions to obtain the best responses, allied to the accomplishment of a minimum number of experiments. In this sense, the RSM have been applied in the optimization of material syntheses [25–27] as well as in the analytical methods [28,29].

Moreover, the information provide from this study, will can useful for studies that use P25 for photodegradation of organic compounds, besides gives support to future works that carry out thermal activation on photocatalysts.

Dyes are organic compounds widely used in various industrial sectors such as textile, paper, leather, food and plastics [17,30]. The discharge of dye-containing wastewaters in natural water bodies is considered a big threat to the environment, since it promotes a strong coloration to the water body, which besides the aesthetic factor, also inhibits the photosynthesis processes and severely affects the water quality parameters [5,30].

The tartrazine, also known as Yellow 5, is a synthetic dye that belong to the azo-dye group (N = N), and that has been widely used in industries because it confers a vibrant color to food products [6]. However, although it is used in food industries, an extended and/or repeated exposure to this kind of synthetic dye can cause several diseases in humans, including allergies, headaches, diarrhea and even cancer if consumed in excess [31]. In this way, different methods of effluent treatment for removal of dyes from the aqueous solutions have been reported in the literature, such as biological treatments, flocculation, sedimentation, adsorption and photocatalytic procedures [5,32,33].

In the present work, we propose to investigate and optimize the experimental conditions of thermal treatment on the P25, using RSM, to obtain a material with best photocatalytic performance for degradation of tartrazine dye. Several analytical techniques were used to evaluate the changes that occurred with materials which were submitted to the thermal treatment. To our best knowledge, it is the first time that RSM has been applied with the aim to optimize the thermal treatment on the P25, as well as to investigate the influence and interactions of factors as temperature, heating rate and heating time on the photocatalytic activity. Additionally, the information provide from this study, will can useful for studies that use P25 for photodegradation of organic compounds, besides gives support to future works that carry out thermal activation on photocatalysts.

2. Experimental

2.1. Materials

All used chemicals were of analytical grade. Titanium dioxide (TiO_2 – P25 with about 80% anatase and 20% rutile; size of 20–50 nm) was purchased from Evonik. The food dye tartrazine was acquired from Duas Rodas Company and diluted in distilled water to prepare the working solutions.

2.2. Thermal treatment of P25

The thermal treatments were performed using 1.0 g of P25, which was placed in a porcelain crucible and heated in a muffle furnace (EDG 7000-3PS). The experimental conditions such as, temperature, heating rate and heating time, were defined by experimental matrix established from the central composite rotatable design (CCRD). The levels of each factor were selected according to a previous review of the literature. The temperature ranged from 200 to 700 °C, heating rate from 1 to 11 °C min^{-1} and heating time from 60 to 240 min. After each thermal treatment, the materials were stored in sealed bottles for further analysis.

2.3. Experimental design and response surface methodology (RSM)

The central composite rotatable design (CCRD) and RSM were applied to investigate the interaction between studied variables and optimize the conditions of thermal treatment for enhance the photocatalytic activity of P25. In this work, the independent variables were x_1, x_2 and x_3, corresponding to temperature (°C), heating rate (°C min^{-1}) and heating time (min), respectively, while the response (Y) was the apparent first order rate constant (k_{app}, see Eq. (2)). According to the experimental design used, each independent variable was investigated in five levels coded as −1.68, −1, 0, +1 and +1.68 [34]. The real and coded values of the factors studied are shown in Table 1.

The CCRD consisted of 18 experiments, including 8 factorial points relative to the complete 2^3 factorial design, 6 axial points and 4 central points. The experimental data were evaluated by adjusting a second-order polynomial regression model, defined by Eq. (1).

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \tag{1}$$

where Y is the response variable, β_0 is the constant term and β_i, β_{ii} and β_{ij} are linear, quadratic and interaction effect terms, respectively. The statistical significance of the model and regression terms was evaluated by variance analysis (ANOVA) at 95% confidence level. The experimental design and data processing were performed using Design Expert 7.0.0 software.

2.4. Photocatalytic procedure

The photocatalytic activities of thermally treated P25 were evaluated by the photodegradation of tartrazine dye. The experiments were performed in jacketed beaker, containing 400 mL of dye solution (50 mg L^{-1}) and 0.200 g of catalyst (dosage = 0.5 g L^{-1}). Initially, the solutions were kept under magnetic stirring for 30 min in the dark to establish the adsorption equilibrium. Then, the suspensions were irradiated with UV light by germicide lamp (Osram, German, 18 W). During the irradiation, aliquots of 4.0 mL were sampled every 30 min and measurements were carried out by a UV–vis spectrophotometer (Agilent, Cary 50). The tartrazine photolysis experiment was carried out in the maximum irradiation time of 240 min. The response of the experimental design was given by the apparent first order rate constant (k_{app}) obtained from the adjustments of the nonlinear pseudo-first order kinetic model to the experimental data of photodegradation kinetic [35]. The k_{app} was calculated according to the photodegradation reaction of tartrazine dye represented by Eq. (2).

$$\frac{C}{C0} = exp^{-kapp.t} \tag{2}$$

Table 1
Real variables and their coded values.

Factors	Coded values				
	−1.68	−1	0	+1	+1.68
	Real values				
Temperature (°C) (X_1)	200	300	450	600	700
Heating rate (°C min^{-1}) (X_2)	1	3	6	9	11
Heating time (min) (X_3)	60	96	150	204	240