Photocatalytic Degradation of Antibiotics and Dyes in Wastewater by Hydrogenated Black Titanium Dioxide Nanoparticles Using Design of Experiment L9 Taguchi Orthogonal Array

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Abstract Aqueous pollution from industrial dyes and antibiotics has brought up much threat to our daily healthy life. In the present work, hydrogenated black TiO₂ nanoparticles (H-TiO₂) are synthesized, their properties are studied, and their potentials in removing dyes (methylene blue, M.B.) and antibiotics such as tetracycline hydrochloride (TC) and ciprofloxacin (CIP) are explored with the support of statistical optimization. The operational controlled parameters such as catalyst amount (g L⁻¹), pH and irradiation time (min) were optimized using Design of Experiment (DOE) L9 Taguchi Orthogonal Array. From Analysis of Variance (ANOVA) results, it can be seen that irradiation time is the most influencing parameter for % MB color removal, % Degradation of TC and CIP, over catalyst amount and pH. The optimal parameters found here are 0.50 g L⁻¹ of hydrogenated H-TiO₂-750 as catalyst, pH 4 for MB, pH 11 for TC and pH 2 for CIP, respectively. In addition, an irradiation time of 30 min shows a maximum MB color removal of 95.05%, TC 94.8% and CIP 92.25%. Irradiation time is found to be the most influencing parameter (71.08% for MB, 55.33% for TC and 52.77% for CIP) followed by catalyst amount (28.82% for MB, 44.19% for TC and 41.5% for CIP) and in the end pH (0.09% for MB, 0.47% for TC and 5.72% for CIP). With the use of hydrogenated H-TiO₂-750, the dye and antibiotics degradation reaches almost 40% more than using TiO₂ pristine anatase.

Keywords dyes & antibiotics, titanium (IV) oxide, statistical optimization, taguchi orthogonal array, black TiO₂

Introduction

Wastewater from the use of dyes and pharmaceutical products such as antibiotics contaminate a substantial and important part of our sources of consumable water. The increasing use of antibiotics such as tetracycline hydrochloride (TC) and ciprofloxacin (CIP) (Table S1) to treat bacterial infections in people is leading us to increasingly pollute different environmental compartments such as drinking water. Thus, it is necessary to address the environmental problems that have arisen due to the indispensable use of antibiotics used for human health.^[1] On the other hand, the use of dyes by industries, such as dyestuffs, textile, paper and plastics, consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater.^[2] The water resulting from the dyeing industry in particular constitutes one of the most difficult wastewater to be treated, due to among other things to suspended solids, its high content of toxic substances, in addition to color, which is the first pollutant recognized by the human eye. Dyes can significantly affect photosynthetic activity in aquatic life because of the reduction of light penetration and can be toxic to aquatic life due to the presence of aromatics, metals, chlorides, etc., in them.^[3] Synthetic dyes such as Methylene Blue (MB) (Table S1) is part of a group of organic pollutants that are used extensively in textile (*i.e.*, denim clothes). It is reported that there are over 100,000 commercially available dyes with a production of over 7×10^5 metric tons per year.^[4] Thus, researchers around the world are working for the remediation of contaminated water. As a result, there are different methods for cleaning wastewater by dyes and antibiotics, such as the case of biological treatments,^[5] adsorption,^[6-8] coagulation-flocculation,^[9,10] ozonation process,^[11] catalytic oxidation^[12]

and electrochemical methods.^[13]

In recent years, TiO₂ photocatalysis has gained particular interest because of heterogeneous nature that offers the possibility of catalyst reuse. TiO₂ is environmentally friendly, biocompatible, abundantly available, highly stable and low cost.^[14-20] TiO₂ has three polymorphs, rutile, anatase and brookite. Anatase is the most photoactive, which is improved by its high crystallinity and large surface area.^[21-24] Various methods have been developed for synthesizing nano-sized TiO₂ nanoparticles, such as vapor synthesis,^[25] thermal decomposition process,^[26-28] chemical vapor deposition,^[29] flame synthesis,^[30] heat-treated flame-synthesized,^[31] solvothermal method,^[32] among others. We have recently developed hydrogenation as a new method for making TiO₂ nanoparticles, which showed remarkably improved photocatalytic activity in hydrogen production from water and pollutant removal.^[16] Since that work, many methods and impressive work have been done to make black and colored TiO₂ nanoparticles. For example, Mao *et al.* prepared blue TiO₂ nanoparticles of high photocatalytic activity with hydrothermal and chemical reduction using N₂H₄.^[33] Huang *et al.*^[34] and Zhu *et al.*^[35] reported the synthesis of black TiO₂ by Al reduction at high temperature. Wang *et al.* prepared black TiO₂ nanoparticles in a thermal plasma furnace by hydrogen plasma at 500 °C.^[36] Kang *et al.* synthesized reduced black TiO₂ nanotubes by chemical reduction with NaBH₄.^[37] Xu *et al.* prepared hydrogenated black TiO₂ nanotubes by electrochemical reduction.^[38] Exciting photocatalytic activity has been reported on the black TiO₂, especially when compared to the normal white TiO₂.

In this work, we investigate the photocatalytic activity of hydrogenated black TiO₂ nanoparticles on the removal of MB and antibiotics TC and CIP % with the support of statistical

optimization, namely, with Design of Experiment (DOE) L9 Taguchi Orthogonal Array.

Materials and methods

Reagents and chemicals

All the chemicals used here were of the highest purity grade: methylene blue chloride powder (Basic blue 9) from Fisher Chemical was used at 10 mg L⁻¹, tetracycline hydrochloride powder > 98.0% from Tokyo Chemical Industry, Co. was used at 40 mg L⁻¹, ciprofloxacin powder 98% from Alfa Aesar at 40 mg L⁻¹, titanium (IV) dioxide anatase ≥ 99.0% was purchased Sigma-Aldrich. In order to maintain an acidic medium (*i.e.*, a pH of 2.0, 4.0 and 5.0) a solution of 0.010, 0.00010 and 0.000010 M of HCl (Fisher Chemical certified ACS plus) were used, respectively. In the case of the basic samples (*i.e.*, pH of 9 and 11), solutions of 0.0010 and 0.000010 M NaOH (LabChem, ACS 97.0%) were employed. Sodium Sulfate ≥ 99.0% was obtained from Sigma-Aldrich. In all experiments, deionized water from LabChem 100% pH 7.0 was used.

Hydrogenated TiO₂ black nanoparticles synthesis

Commercial anatase TiO₂ particles was obtained from Sigma-Aldrich and used without further purification. In a typical synthesis, 2.0 g of TiO₂ raw anatase was grinded *via* mortar and pestle for around 15 min and then placed in a high-temperature tube furnace and treated at certain temperatures (600, 650, 700 and 750 °C) and pressure (30 psi) under hydrogen atmosphere for 3 h. The cooled sample was removed from the tube furnace to obtain the hydrogen treated TiO₂ black nanoparticles, which was namely as H₂-TiO₂-X, where X was the temperature.

Materials characterization

The synthesized TiO₂ samples were characterized by several techniques. The ultraviolet-visible (UV-vis) spectra were measured using an Agilent Cary 60 spectrometer with a fiber optical reflectance unit. UV-vis diffusion reflectance spectra of the photocatalysts were collected using Cary 60 UV-vis Agilent Technologies spectrophotometer. MgO was used as reference sample, and its reflectance was assumed 100% throughout the spectrum. The X-ray diffraction (XRD) patterns were taken on a Rigaku Miniflex instrument with diffraction angle 2θ in between 20° and 70° using Cu Kα as the X-ray source (λ = 1.54056 Å). The transmission electron microscopy (TEM) analysis was taken on an FEI Tecnai F20 TEM machine with the electron accelerating voltage of 200 kV. A small amount of sample dispersed in water was dropped onto a thin holey carbon film and dried overnight before TEM measurement. The Brunauer-Emmett-Teller (BET) specific surface areas of raw TiO₂ anatase and hydrogenated TiO₂ black nanoparticles synthesized at different temperatures (600, 650, 700 and 750 °C, respectively) were performed by nitrogen sorption on a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. The pore size distribution (pore diameter and pore volume of the samples) was determined by the Barrett-Joyner-Halenda (BJH). For the ESR spectra active spectrum, MicroESR was run. In the case of photocurrent and impedance tests a potentiostat, BioLogic Science Instruments SP-150 was used. In addition, pH was monitored by pH meter Fisher Scientific Accumet® AE150 and a light source (Newport power supply, P = 150 W) was employed.

Photoelectrochemical measurements

Photocurrent intensity (PC) and electrochemical impedance spectroscopy (EIS) of the photocatalysts were carried out in a conventional three-electrode electrochemical cell with hydrogenated H₂-TiO₂ synthesized at different temperatures (600, 650, 700 and 750 °C, respectively) and pristine TiO₂ anatase samples as working electrodes, a platinum wire as counter

electrode and Ag/AgCl as reference electrode. The electrolyte employed here was a solution of Na₂SO₄, 0.5 M and a source of visible light (P = 150 W) was used. The working electrodes were prepared as follow: 32 mg of hydrogenated TiO₂ synthesized at different temperatures (600, 650, 700 and 750 °C, respectively) and pristine TiO₂ anatase, 4 mg of carbon black and 4 mg of polyvinylidene fluoride (PVDF). All above materials quantities were grinded together *via* mortar and pestle until homogeneous (about 15 min). After that, 4 drops of N-methyl-2-pyrrolidone (NMP) were added to the mixture, and continued grinding for about 5 min more. Previously several strips of titanium screen mesh - 2mil (1 cm width × 3 cm long) were washed and weighed in order to apply the resulting mixture on them. The mixture obtained above was deposited in the strips (about 1 cm² each); after that, they were allowed to dry on a stove overnight. Once the electrodes were ready, they were weighed and measured in an electrochemical workstation.

Photocatalytic evaluation

During the photocatalytic degradation of MB, TC and CIP, a beaker was used as a cell; 30 mL of 10 mg L⁻¹ MB, 40 mg L⁻¹ of TC and 40 mg L⁻¹ of CIP were deposited within it and irradiated by a source of visible light (P = 150 W), respectively. Then, a sample of 3 mL was taken from the cell at certain convenient time and analyzed. The absorbance of the sample was determined spectrophotometrically on an UV-vis spectrometer. The percentage of MB, TC and CIP dye degradation was calculated using the next expression:

$$\% \text{Deg} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A₀ and A_t are the absorbance at an initial time and a certain time t, respectively.

Design of experiments and statistical evaluation

Statistical Design of Experiments (DOE) is a structured and systematized method of experimentation, in which all factors are varied simultaneously over a set of experimental runs in order to determine the relationship between input factors affecting the output response during all the process. DOE technique can be useful for obtaining the relationship among variables and therefore save time by optimizing resources.^[39] DOE was carried out using Minitab® 19 as a statistical software.

To carry out this study, three factors have been considered such as (A) catalyst amount (CA) (g L⁻¹), (B) pH, and (C) irradiation time (IT) (min) (Table 1).

Table 1 Factors and levels to be considered in DOE L9 Taguchi Orthogonal array

Factors	Level 1	Level 2	Level 3
A	A1	A2	A3
Catalyst Amount (g L ⁻¹)	0.10	0.25	0.50
B	B1	B2	B3
MB pH	4	5	7
CIP pH	2	5	7
TC pH	7	9	11
C	C1	C2	C3
Irradiation Time (min)	10	20	30

The DOE by complete factorial design of three factors and three levels (3³) results in 27 experiments, because this is the minimum number of executions required to analyze the factorial effect of the entire process. Although in practice, it turns out to

Table 2 DOE L9 Taguchi Orthogonal array proposed for MB, TC and CIP degradation

Exp. #	Catalyst amount/(g L ⁻¹)	pH	Irradiation time/min
1	A1	B1	C1
2	A1	B2	C2
3	A1	B3	C3
4	A2	B1	C2
5	A2	B2	C3
6	A2	B3	C1
7	A3	B1	C3
8	A3	B2	C1
9	A3	B3	C2

be expensive and tedious because they must be done at least twice to ensure repeatability. Orthogonal array methods provide an alternative by reducing the entire factorial to a fractional one, therefore, reduce the minimum number of runs. With this array, the experiment can be carried out completely randomly (Table 2).

The response surface methodology (RSM) is a widely used mathematical and statistical method for modeling and analyzing a process, in which the response of interest is affected by various variables and the objective of this method is to optimize the response. The parameters that affect the process are called independent variables, while the responses are called dependent variables.^[40,41]

The parameters analyzed were optimized using RSM, considering as a response variable % color removal of MB, % degradation of TC and % degradation of CIP. In order to know the relationship between the controllable input parameters and the output response, the follow first order response surface model was used.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 \quad (2)$$

where Y = predicted response (response function), β_0 = Intercept coefficient (offset), β_1 , β_2 , and β_3 = linear terms (first order) and X_1 , X_2 and X_3 = Uncoded independent variables.

Results and Discussion

Photocatalyst characterization

The XRD patterns in Figure 1A with the well-defined diffraction peaks suggested that pristine and hydrogenated TiO₂ black nanoparticles synthesized at different temperatures (600, 650, 700 and 750 °C) had highly crystalline anatase phase. All peaks values matched well with anatase phase JCPDS card No. 21-1272 with the first peak at $2\theta = 24.8^\circ$ corresponding to the (101) plane, and other main peaks at $2\theta = 37.3^\circ$, 47.6° , 53.5° , 55.1° and 62.2° corresponding to the crystal planes (004), (200), (105), (211) and (204), respectively.^[14-19] The TEM images in Figure 1B showed that the pristine TiO₂ nanoparticles had an average primary particle size of 15 nm in diameter (Figure 1B-(1)) and were highly crystallized with well-defined lattice fringes and shape particle edges (Figure 1B-(2)), and the hydrogenated TiO₂ nanoparticles showed a similar average particle size around 15 nm in diameter (Figure 1B-(3)), and had a well crystallized core surrounded by a layer of disordered structure due to the formation of structural defects (Figure 1B-(4)).^[15,42,43]

It is well known that the photocatalytic activity will depends on how many photoexcited charges are created that is available for the photocatalysis process. Their numbers can be probed with the photocurrent measurement. Photocurrent density of pristine and hydrogenated TiO₂ nanoparticles is shown in

Figure 1 (A) XRD patterns of pristine and hydrogenated TiO₂ nanoparticles. (B) TEM images of TiO₂ nanoparticles. (1, 2) pristine TiO₂, (3, 4) hydrogenated TiO₂ treated at 600 °C.

Figure 2a. The measurements were taken using a voltage source at 0.4 V and measuring the response of each sample to the illumination generated from a Xe lamp (150 W) applied for 20 s and then turned off. The photocurrent was normalized with respect to the mass of the catalyst applied in the working electrodes. The intensity of the photocurrent density difference between light on and off or the net photocurrent density roughly reflects the amount of photoexcited charges that can be transported to the outside circuit. Normally, the more photoexcited charges are generated, the larger the intensity of the photocurrent density can be observed, assuming similar percentages of photoexcited charges are consumed or trapped within the photocatalysts. Apparently, more photoexcited charges that can be extracted are produced on the TiO₂ nanoparticles hydrogenated at higher temperatures, as higher photocurrent density is observed. Figure 2B displayed the comparison of the net photocurrent density. It increased from 2.52 to 3.52, 6.04, 6.94 and 8.47 mA/cm²g from pristine anatase to hydrogenated

Figure 2 (A) Time-dependent photocurrent density (J), (B) Comparison of photocurrent density (J), (C) EIS Nyquist plots, (D) UV-vis reflectance spectra, (E) BET surface area and BJH pore size distribution curve, (F) Comparison of surface areas and pore size of pristine anatase TiO₂ and hydrogenated TiO₂ nanoparticles at various temperatures.

TiO₂ at 600, 650, 700 and 750 °C, respectively. Compared with that of the pristine TiO₂ nanoparticles, the intensity of the hydrogenated TiO₂ nanoparticles at 750 °C increased 336%. Obviously, hydrogenation considerably increased the photocurrent density of TiO₂ nanoparticles.

Meanwhile, the photocatalytic activity also depends on how easy the charge transfer is on the surface of the photocatalyst. Such surface charge transfer resistance can be probed with EIS. Figure 2C displayed the EIS Nyquist plots. In the EIS plot, the diameter of the semicircle represents the charge transfer

resistance. A smaller semicircle means a smaller charge separation resistance. Judged from the diameter of the semicircle, the surface charge transfer resistance seemed to decrease with the increase of the hydrogenation temperature. In other words, the surface charge transfer resistance decreases in the order of anatase TiO₂ > 600 °C > 650 °C > 700 °C > 750 °C. Therefore, hydrogenation reduces the surface charge transfer for photocatalysis.

The amount of photoexcited charges is directly related to the amount of light absorbed by the photocatalyst. Figure 2D

Figure 3 (A) MB, (B) TC and (C) CIP degradation with various catalysts (0.25 g L^{-1}) after 30 min irradiation (10 mg L^{-1} MB (pH 7.0), 40 mg L^{-1} of TC (pH 9.0) and CIP (pH 7.0)). D) MB, TC and CIP degradation with various catalyst concentrations (irradiation time: 30 min, 10 mg L^{-1} MB (pH 7.0), 40 mg L^{-1} of TC (pH 9.0) and CIP (pH 7.0)).

showed the diffuse reflectance spectra pristine and hydrogenated TiO_2 nanoparticles. The bulk bandgaps of the pristine and hydrogenated TiO_2 nanoparticles were similar, around 3.0 eV, estimated from the intersection (about 410 nm) of the extensions of the sharp drop near 400 nm and of the flat reflection above 400 nm. This suggested that they had similar bulk optical absorption, consistent with the same highly crystalline anatase phase observed from their XRD patterns. Meanwhile, hydrogenated TiO_2 nanoparticles had less reflection in the visible-light region, above 400 nm, compared to the pristine anatase TiO_2 nanoparticles. The amount of non-reflected light increased in the order of anatase (4.1%) < 600 °C (17.3%) < 650 °C (19.6%) < 700 °C (24.0%) < 750 °C (32.6%). This indicated that the amount of light absorbed likely increased with the hydrogenated temperature, assuming the amount of scattered light was similar. This increased light absorption in the visible-light region was attributed to the disordered layer or structures created in the hydrogenated TiO_2 nanoparticles, as we reported previously and seen from the HRTEM images shown in Figure 1B–4.

The BET specific surface areas and pore size distribution were displayed in Figures 2E and S1–S4. The isotherms with a distinct hysteresis loops in relative pressure (P/P_0) range of 0.0–1.0 belong to type IV, indicating that a mesoporous structure. The changes of the BET surface area and pore size distribution with the hydrogenation temperature were displayed in Figure 2E. The BET surface area of the samples decreased with the increase of hydrogenation temperature. Specifically,

the surface area decreased from 3.96 to 3.86, 3.68, 3.04 and $2.97 \text{ m}^2/\text{g}$ from the pristine anatase TiO_2 nanoparticles to TiO_2 nanoparticles hydrogenated at 600, 650, 700 and 750 °C, respectively. This was probably due to the progressive aggregation of small crystallites into larger particles. Meanwhile, the main pore size increased after the hydrogenation treatment. Specifically, the centered pore size increased from 33.9 nm to 61.1, 65.5, 45.5 and 47.0 nm from the pristine anatase TiO_2 nanoparticles to TiO_2 nanoparticles hydrogenated at 600, 650, 700 and 750 °C, respectively.

DOE preliminary experiments

Preliminary assessments were carried out by one factor at a time approach in order to know the ranges of the main three parameters; such as catalyst amount (g L^{-1}) of dye and antibiotics, pH and irradiation time (min) for using later in the DOE Taguchi orthogonal array.

In the case of photocatalyst type, hydrogenated TiO_2 synthesized at different temperatures (600, 650, 700 and 750 °C) were used. During photocatalytic degradation, each experiment was repeated by triplicate under the same conditions in order to ensure the repeatability. Figures 3A–3C showed the degradation of MB, TC and CIP with various catalysts (0.25 g L^{-1}) after 30 min irradiation, respectively. Clearly, the amounts of MB, TC and CIP degraded within 30 min roughly followed the same order: TiO_2 nanoparticles hydrogenated at higher temperature displayed larger degradation and TiO_2 hydrogenated at 750 °C showed the largest degradation, all much better than the pris-

tine TiO₂ nanoparticles.

Photocatalytic degradation is also affected by the concentration of photocatalytic used during the experiment. Figure 3D showed the results of using H-TiO₂-750 as the catalyst with various concentration from 0.10 to 0.75 g L⁻¹. The increase in catalyst quantity enhances the number of active sites, increasing hydroxyl radicals production and as a result of this, it improves the degradation of dye and antibiotics. This behavior is consequential from 0.10 to 0.25 g/L. Further increase from 0.25 to 0.50 g/L only slightly increased the amount of degradation. When the concentration was larger than 0.50 g/L, the degradation decreased instead. This can be attributed to the fact that the solution becomes cloudy and hence does not allow the light to pass through, limiting the production of radicals that are responsible for the photocatalytic reaction with contaminants and decreasing the photocatalytic action.

The effect of pH is one of the most important factors to consider for the photocatalytic degradation. To investigate such effect, preliminary experiments were carried out at different pH values (from 2.0 to 11.0) using hydrogenated TiO₂ synthesized at 750 °C as catalyst, with a catalyst amount of 0.25 g L⁻¹ and an irradiation time of 30 min. Experiments were performed with irradiation axially to the sample using a stirrer magnetic in order to maintain samples homogeneously, all experiments were carried out at room temperature (≈ 23 °C). The results can be seen in Figure 4. The best efficiency found for a) MB degradation is in the pH acid to neutral (range between 4.0 and 7.0, Figure 4A). For TC degradation the better efficiency was observed in alkaline conditions (pH from 9.0 to 11.0) as seen in Figure 4B. Finally, the best results for CIP degradation were found from acid conditions to neutral (pH from 2.0 to 7.0), as displayed in Figure 4C.

In order to investigate the reaction kinetics of dye and antibiotics photodegradation, the pseudo-first order model was applied to simulate experiment date using equation (4):

$$k = \frac{C_0}{C_t} \quad (4)$$

where C_0 and C_t are the concentrations of the contaminants at time 0 and t , respectively, and k is the pseudo-first order rate constant. Figure 5A shows that the apparent rate constant for MB using a concentration of 0.10 g L⁻¹ of catalyst is 0.07179 min⁻¹, for 0.25 g L⁻¹ of catalyst k value is 0.07312 min⁻¹ and at last for 0.50 g L⁻¹ of catalyst used, k value is 0.08095 min⁻¹. The k value is higher for catalyst amount of 0.50 g L⁻¹, about 1.127 times more than 0.10 g L⁻¹ and 1.107 times more than 0.25 g L⁻¹, respectively. From Figure 5B, it can be seen that the apparent rate constant for TC using a concentration of 0.10 g L⁻¹ of catalyst is 0.07018 min⁻¹, for 0.25 g L⁻¹ of catalyst k value is 0.07020 min⁻¹ and at last for 0.50 g L⁻¹ of catalyst used, k value is 0.07720 min⁻¹. Using 0.50 g L⁻¹ as catalyst amount, the apparent rate constant reaches 1.1 times than 0.10 g L⁻¹ and 1.099 times more than 0.25 g L⁻¹ severally. Figure S5 showed that the apparent rate constant for CIP using a concentration of 0.10 g L⁻¹ of catalyst is 0.06963 min⁻¹, for 0.25 g L⁻¹ of catalyst k value is 0.07154 min⁻¹ and at last for 0.50 g L⁻¹ of catalyst used, k value is 0.07506 min⁻¹. It is clearly that the again k apparent rate constant value is higher for catalyst amount of 0.50 g L⁻¹ above the other values, about 1.078 times more than 0.10 g L⁻¹ and 1.049 more than 0.25 g L⁻¹.

Statistical analysis

With the above preliminary results, it was decided to make a complete study with the help of statistical optimization, varying three factors such as catalyst amount (0.10, 0.25 and 0.50 g L⁻¹), pH (depending on the case of the pollutant) and irradiation time (10, 20 and 30 min) using hydrogenated H₂-TiO₂-750 °C as

Figure 4 Degradation of (A) MB, (B) TC and (C) CIP after 30 min irradiation using H₂-TiO₂-750 (0.25 g/L) at various pH values (10 mg L⁻¹ MB (pH 7.0), 40 mg L⁻¹ of TC (pH 9.0) and CIP (pH 7.0)).

catalyst. A L9 Taguchi Orthogonal array was implemented (Table 2).

Taguchi orthogonal arrays are balanced to ensure that all levels of all factors are considered equally. For this reason, the factors can be evaluated independently of each other despite the fractionally of the design. From Minitab® 19 a L9 Taguchi array was obtained as can be seen in Table 2; the number of experiments was reduced from 27 to only 9. In order to ensure repeatability, the experiments were performed in triplicate. The results obtained by implementing DOE values from Table 2 are displayed in Figure 6. Figure 6A shows the degradation of MB: the best parameters for almost 100% of degradation are

Figure 5 The pseudo-first order rate constants for (A) MB and (B) CIP photodegradation with various concentrations of catalyst H₂-TiO₂-750.

catalyst concentration 0.50 g L⁻¹, pH 4.0 and 30 min of irradiation. Figure 6B shows the best parameters of TC degradation of about 95% are: catalyst concentration of 0.50 g L⁻¹, pH 7.0 and 30 min of irradiation. Figure 6C displayed that the best condition on degradation of CIP with almost 95% are catalyst concentration of 50 g L⁻¹, pH 2.0 and 30 min of irradiation.

Analysis of Variance (ANOVA) was used to investigate the influence of analyzed parameters such as catalyst amount, pH and irradiation time on the response variable MB, TC and CIP Degradation. The strategy of pooled sum of errors was conducted and the results of ANOVA for % MB color removal and antibiotics degradation response are shown in Table S2. From the ANOVA of experimental results, the MB degradation was influenced by irradiation time (71.08%) followed by catalyst concentration (28.83%) and finally pH (0.09%). The TC degradation was influenced by irradiation time (56.45%) followed by catalyst concentration (43.03%) and pH (0.24%). The CIP degradation was influenced by irradiation time (52.77%) followed by catalyst concentration (41.5%) and pH (5.72%).

The RSM method was used to optimize the response variable (% Deg) influenced by different controlled parameters such as catalyst concentration (C.A.), pH and irradiation time (I.T.). The relationship between input and output parameters was obtained by:

$$\% \text{ MB Deg} = -7.721 + 72.441 \text{ C.A.} - 0.538 \text{ pH} + 2.2987 \text{ I.T.} \quad (5)$$

$$\% \text{ TC Deg} = -13.86 + 87.85 \text{ C.A.} + 0.9210 \text{ pH} + 1.9863 \text{ I.T.} \quad (6)$$

$$\% \text{ CIP Deg} = 6.290 + 75.890 \text{ C.A.} - 2.263 \text{ pH} + 1.7291 \text{ I.T.} \quad (7)$$

Figure 6 (A) MB, (B) TC and (C) CIP degradation with H-TiO₂-750 using an array of L9 Taguchi Orthogonal.

The predicted values of % deg were obtained by substituting the values of the parameters considered into Eqs. (5), (6) and (7). R^2 adjusted was found for this model (L9 Taguchi Orthogonal array). Obtained (real) and predicted values (calculated) are appreciated in Table S3.

Figure 7 shows the response surface for optimization parameters. The optimized values obtained here are: (A) For MB, catalyst concentration 0.50 g L⁻¹, pH 4.0 and 30 min irradiation time, and with the maximum percentage of MB degradation of 95.30%. (B) For TC, catalyst concentration 0.50 g L⁻¹, pH 11.0 and irradiation time 30 min and with the maximum percentage

Figure 7 Response surface optimization parameters for (A) MB, (B) TC and (C) CIP.

of TC degradation of 99.78%. (C) For CIP, catalyst concentration 0.50 g L^{-1} , pH 2.0 and irradiation time 30 min and the maximum percentage degradation of 91.57% by keeping these parameters value.

Conclusions

The photocatalytic application of hydrogenated TiO_2 nanoparticles successfully carried out in the photocatalytic degradation of MB, TC and CIP. Several characterization techniques were used in order to know the catalyst's properties and photocatalytic performance. Each catalyst was subjected to the same tests and under the same circumstances by triplicate, in order to ensure repeatability. Hydrogenated TiO_2 nanoparticles showed much better performance than pristine TiO_2 nanoparticles, benefiting from the better photoexcited charge generation and separation that are needed for the photocatalysis. The $\text{H}_2\text{-TiO}_2\text{-750}$ showed the highest rate of photocatalytic power. Therefore, it was used for a more in-depth study with the support of statistical optimization. Degradation of MB, TC and CIP was implemented with the support of statistical optimization. A DOE Taguchi Orthogonal Array was performed in order to know the best factors influencing in the entire process. From ANOVA results, it can be seen that irradiation time is the most influencing parameter for the MB, TC and CIP degradation, over catalyst concentration and pH.

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Supporting Information

Supporting information for this article is available on the WWW under www.genchemistry.org/EN/10.21127/yaoyigc202

10006.

Conflict of Interest

The authors declare no conflict of interest.

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