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Screening of factors influencing the photocatalytic activity of TiO_2:Ln (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) in the degradation of dyes

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ABSTRACT

In this work, we analyzed the photocatalytic activity of TiO_2:Ln (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) systems in the degradation of two organic dyes by means of a probabilistic approach to screen the factors influencing their photocatalytic activity. The photocatalytic properties were described by six responses (crystallite size, band gap energy, visible light absorption, specific surface area, zeta potential and photocatalytic conversion) as a function of lanthanide type (seven elements), lanthanide concentration (two), pH level (two) and dye type (methyl orange and crystal violet). We analyzed 140 experiments using the analysis of variance (ANOVA) method. The results show that band gap energy and specific surface area exhibited behavior that depended on the atomic number of the element used. However, visible light absorption was not modified by the type of lanthanide element or its concentration in the range studied (0.1 and 0.3 wt.% lanthanides/TiO_2 ratio), and the zeta potential depended mainly on pH. Photocatalytic conversion depended on pH, dye type and doping element. The experimental factorial design of the photocatalytic system allowed us to find the best conditions for enhancing the degradation of these two dyes.

1. Introduction

The discharge of dye-contaminated wastewater by different types of industry seriously damages microorganisms, aquatic life and humans [1]. Due to their complexity, a variety of non-biodegradable and highly water-soluble dyes are difficult to remove from wastewater by conventional methods [2]. TiO_2-based photocatalysts are commonly used agents for the decomposition of organic pollutants present in wastewaters from various industries, factories, laboratories, etc., which represent a serious problem for the environment [3–5]. More recently, hybrid materials, such as doped or decorated TiO_2 particles, have become available to improve this photocatalysis process.

The photocatalytic oxidation process consists of the activation of particles of semiconducting materials, such as the abovementioned titanium dioxide, which is excited with light having energy greater than or equal to the difference between the valence band and the conduction band ($h\upsilon \geqslant E_g$) [6,7]. This generates an exciton or electron–hole pair within the semiconductor; these migrate to the material's surface and initiate a series of redox reactions. The final outcome of these events is the oxidation of pollutants that are present in the reaction medium. The mean lifetime of an electron–hole pair is short (30 ± 15 ns) [7]. The incorporation of lanthanide ions onto the TiO_2 surface increases the lifetime of charge carriers due to energy transfer phenomena between the host and dopant ions in TiO_2 [8,9].

Experimentation has been used to understand and/or improve these catalytic systems; however, there may be a large number of factors, but usually only a handful of them are important or significant. A screening experiment is therefore important to identify the influential factors. Once these factors are identified, the next stage of the investigation focuses on the elucidation and optimization of the relationship between the response and the factors. The experiments to screen the factors are usually performed at the early stages of a design project when many of the factors initially considered have very little or no effect on the performance. To conduct the experiment, the control factors and noise factors should be identified [10–12]. The effects of these factors are then investigated at different levels. As the number of levels increases for each

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control and noise factor, the number of combinations becomes large and unmanageable. Therefore, running experiments with all these combinations becomes uneconomical and time consuming.

In this work, we present a screening of factors that may influence the photocatalytic properties of TiO_2–Ln systems. We analyzed six responses: crystalline size, band gap energy, visible light absorption, surface area, zeta potential and photocatalytic conversion. These responses were studied as a function of four factors: (A) seven lanthanide elements, (B) two lanthanide concentrations, (C) two pH levels and (D) two dye types. We used dyes with opposite electrical natures, i.e. crystal violet is a cation at both reaction pH levels, while methyl orange is an anion under natural conditions. These dyes also possess different electrical characteristics than the TiO_2–Ln system, as well as chemical stability and minor discoloration when exposed to light for a long period of time. As a result we find that photocatalytic activity of all doped samples does not depend on the type of Ln, nor on its concentration, nevertheless if we compare the doped and the undoped samples, the doped samples have better photocatalytic activity (for any Ln). This is because the addition of lanthanides inhibits crystal growth, and this increases SSA. We are confident that our statistical analysis will help the understanding of the role of each factor studied in the photocatalytic activity.

2. Experimental

TiO_2–Ln powders were synthesized and characterized as previously reported [13]. Briefly, these systems were obtained by the sol–gel method using titanium n-butoxide as the precursor. The materials were doped with lanthanides (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) by the addition of lanthanide nitrate as a precursor salt. Lanthanide aqueous solutions were prepared by stoichiometric addition to obtain 0.1 and 0.3 wt.% Ln on the TiO_2. The obtained gel was dried in an oven at 120 °C for 12 h and finally annealed at 500 °C for 4 h using a heating rate of 2 °C/min.

Photocatalytic tests were carried out in a microscale photoreactor equipped with a 5.5 W low-pressure cold-cathode mercury lamp (UVP Pen-Ray 90-0012-01). In a typical experiment [13–15], 10 mg of the photocatalyst was added to 10 mL of a solution containing 35 ppm of methyl orange (mo) or crystal violet (cv); the pH was adjusted to 5.6 or 3.1 with HCl. The suspension was kept in the dark under magnetic stirring for 30 min. After 60 min under UV–vis light, the suspension was filtered and the dye concentration was determined by UV–vis absorption spectroscopy using a Hewlett Packard 8453 spectrophotometer.

X-ray diffraction patterns were collected using a Siemens D500 diffractometer with a Cu tube with Ka radiation at 1.5405 Å, scanning in the 20–70° 2θ range with increments of 0.021 and as wept time of 1 s. Nitrogen adsorption isotherms were measured at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020 spectrometer in order to determine the specific surface area (SSA) of the photocatalysts by BET. Before the measurements, the samples were outgassed at 350 °C for 2 h [16]. Electrophoretic measurements of zeta potential (Zp) at different pH values were performed using a Zeta-Meter 3.0+ unit equipped with a molybdenum anode and a platinum cathode [17,18]. All the experiments (or measurements) are summarized in Table 1.

3. Results and discussions

Analysis of variance (ANOVA) is an effective analysis tool that allows the simultaneous comparison of factors to determine if they are identical or significantly different. ANOVA tell us if the variance in our data is significant and measures that significance [19,20]. The experimental results are organized in three ANOVA designs (see Table 1). In the first ANOVA, we analyzed four responses: crystallite size, band gap energy, visible light absorption and surface area as a function of two factors: (A) seven lanthanide elements and (B) two concentrations, i.e. 0.1 or 0.3 wt.% Ln. The number of experiments (or measurements) in this first ANOVA was $4 \times 7 \times 2 = 56$. The average crystallite size d was estimated using the Scherrer equation and diffraction spectra (see Fig. 1): $d = K\lambda/b \cos\theta$, where b is the full width at half maximum (FWHM) of the anatase peak (28.17°). The band gap energy (E_g) was estimated from the spectra in percent reflectance mode by means of the Kubelka–Munk function: $F(R) = (1-R)^2/2R$, where R is the diffuse reflectance, through the corresponding Tauc plots: $(F(R) \times E)^{1/2}$ and E is the energy of absorbed light, by extrapolation of the straight line to the abscissa [21–23]. The visible light absorption (VLA) was calculated from the spectra of absorbance mode by numerical integration in the range of 400–700 nm [24,25]. All

Table 1
It shows the experimental design with related factors and responses. Four factors: (*A*) lanthanide type, (*B*) concentration, with – and + equal to 0.1 and 0.3 wt.%, (*C*) two pH conditions, with – and + equal to 3.1 and 5.6 and (*D*) two dyes, with – and + equal to crystal violet and methyl orange, respectively. Five responses: energy gap, UV–visible absorption, surface area, zeta potential and photocatalytic conversion.

								D			
								–		+	
						C					
						–	+	–	+	–	+
A	*B*	Size (nm)	E_g (eV)	VLA	SSA (cm^2/g)	Pz		Conversion%			
La	–	8.4	3.23	33.99	90	9.5	−18.7	34.1	34.9	29.5	14
Ce	–	8.4	3.18	32.06	98	9.5	−23.9	28.5	38.5	35.9	13,5
Pr	–	8.4	3.25	29.45	99	7.8	−−27.3	20.8	41.3	51.9	8,2
Nd	–	8.4	3.22	27.99	99	7.8	−24.2	22.3	38.5	57.1	11,1
Sm	–	8.4	3.18	25.59	106	7.8	−25.0	27.5	38.4	46.7	12
Eu	–	8.3	3.18	31.16	102	9.5	−20.4	26.2	43.5	45.9	15,4
Gd	–	9.9	3.17	32.62	111	7.7	−16.3	35.2	45.0	39.2	17,6
La	+	7.2	3.15	31.70	119	25.8	−25.8	30.3	40.9	40.2	13,5
Ce	+	9.0	3.13	53.96	109	14.5	−18.2	19.7	40.1	50.2	17,3
Pr	+	8.4	3.19	38.87	112	8.7	−17.0	32.3	41.7	38.2	11,9
Nd	+	8.4	3.22	33.96	112	9.4	−31.2	25.4	54.0	30.3	6,7
Sm	+	7.1	3.18	32.15	110	15.5	−22.5	24.0	35.6	52	15,2
Eu	+	8.3	3.20	30.55	101	16.4	−13.6	21.7	40.9	42.5	12,4
Gd	+	8.3	3.22	29.37	94	−10.4	−20.9	27.6	58.3	43.4	8,5
Undoped		9.9	3.18	33.99	86	6.3	−33.1	25.8	35.1	31.5	13.4
Designs		(1)				(2)		(3)			