Automate on-line monitoring of the TiO₂ based photocatalytic degradation of dimethyl phthalate and diethyl phthalate

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Chemicals

All standards used were of analytical grade quality. Dimethyl phthalate (DMP, purity 99.5%), diethyl phthalate (DEP, purity 99.5%) standards, dichlorometane (HPLC grade) and ethyl acetate (99.8 % purity) were obtained from Sigma Aldrich (St. Louis, MO, USA). Methanol and acetonitrile HPLC grade were purchased from TEDIA (Fairfield, OH, USA). Solid-phase extraction was performed with a 47 mm diameter × 0.5 mm thickness × 10 µm (nominal) particle size 3M Empore (St. Paul, MN, USA) membrane disk containing C18 (octadecyl-bonded silica). Stock solutions of each phthalate were prepared in water. A series of standard solutions were prepared by mixing an appropriate amount of the stock solutions with water in a 100 mL volumetric flask. All the standard solutions were stored at 4 °C and protected from light in amber glass bottles. Doubly distilled water was used for preparation of all solutions. Commercial catalyst: Degussa P25 and Hombikat were purchased from Aeroxide and Sigma Aldrich, respectively. The prepared material was synthesized by microwave assisted sol-gel method using isopropanol, titanium isopropoxide and water as precursors (8:1:3).³⁴

Run	Type of catalyst	Dosage of catalyst (g L ⁻¹)	рН	Degradation of DMP (%)	Degradation of DEP (%)
1	-1	-1	-1	15.42±0.24	20.16±0.84
2	-1	0	1	26.03±0.06	29.50±0.31
3	-1	1	0	25.45±0.06	25.84±0.18
4	0	-1	1	64.26±0.12	65.98±0.21
5	0	0	0	63.10±0.09	66.09±0.21
6	0	1	-1	61.11±0.10	63.69±0.12
7	1	-1	0	51.23±0.05	55.61±0.18
8	1	0	-1	55.07±0.14	57.38±0.55
9	1	1	1	60.23±0.19	62.32±0.34
10	0	0	0	59.03±0.08	62.42±0.11
11	0	0	0	63.32±0.04	65.67±0.08

 Table S1. Design of experiment (DOE) arrangement and experimental results (n=3).

Characterization of TiO₂ base photocatalysts

The catalysts were characterized by different techniques. The surface area and porosity were analyzed by adsorption-desorption of nitrogen gas at 77 K using a TriStar II analyzer and calculated by applying the BET and BJH methods. All samples were degassed at 423 K for 6 h before analysis. To determine the crystalline phases composition and the crystallite size, X-ray diffraction patterns (XRD) were obtained using CuK α radiation ($\lambda = 1.54056$ Å) in a Siemens D5000 equipment. The morphology was analyzed by scanning electron microscopy (SEM) using a Hitachi S-3400N microscope operated at 15 kV. UV-Vis spectroscopy with diffuse reflectance (Carry 300 Bio spectrophotometer) was used to obtain the absorption spectra of the solids (from 190 to 800 nm); and the band gap energy values were calculated using the Kubelka-Munk function.³⁴ The isoelectric point was determined using a zeta-meter apparatus (Zetasizer Malvern).



Figure S1. X-ray diffraction patterns of TiO₂ based materials.

The diffractograms of the material used in the degradation of PAEs are shown in **Figure S1**. The three materials presented diffraction signals attributed to planes (101), (004), (200), (105), (211), (204), (116), (220), (215) of the crystalline phase anatase of TiO₂ (JCPDS No. 21-1272). It can also be observed that two commercial materials showed additional signals in planes (110), (101) and (111) which are attributed to the rutile phase of TiO₂ (JCPDS No. 21 - 1276), suggesting that the rutile and anatase phases of TiO₂ coexist in the materials

that were commercially acquired, and the material synthesized by the sol-gel method presented only the anatase phase. However, it can also be observed that the intensity of the peak (101) corresponding to the anatase phase was the strongest in all samples, indicating that the growth of TiO_2 is oriented along this plane and the anatase phase is the predominant crystalline phase in the three materials.

The percentage of anatase and rutile phase present in the materials were determined by the **Equation S1**.

$$A(\%) = \frac{100}{\left[1 + 1.265 \left(\frac{I_R}{I_A}\right)\right]}$$
 (Equation S1)

where I_R and I_A are the intensities of the peaks of anatase and rutile, respectively.³⁵

The crystallite size of the anatase phase was calculated with the diffractograms and the Scherrer equation (**Equation S2**).

$$D = \frac{K\lambda}{\beta Cos\theta} \quad (\text{Equation S2})$$

where: K is a constant of the shape of the crystal (0.9), D is the average normal crystalline dimension to the diffracted planes, λ is the wavelength (1.5418 Å), β is the peak width at half- maximum intensity and θ is the Bragg angle.³⁶

N₂ adsorption



Figure S2. N₂ adsorption isotherms of TiO₂ based materials.

The N₂ adsorption-desorption isotherms at 77 K are presented in **Figure S2**. According to the IUPAC classification,⁴¹ the commercial materials (Degussa P25 and Hombikat) presented isotherms type III characteristics of macroporous materials. The isotherms exhibit a low adsorption region for relative pressures less than 0.5 and high adsorption at P/P_0 values higher than 0.8 which indicates the presence of macropores. It can also be observed a hysteresis loop type H3 characteristic of networks macroporous. On the other hand, the catalysts synthesized by the sol-gel method presented an isotherm type V,⁴¹ characteristic of micro and mesoporous materials, in which low adsorption can be observed

at P/P_0 values lower than 0.6 and higher than 0.8. A H2 hysteresis loop characteristic of ordered mesoporous materials was also observed.

Diffuse reflectance UV-Vis

Figure S3 showed $(F(R)hv)^{1/2}$ vs energy graph in which the straight line was extrapolated towards the axis of the abscissa to obtain the Eg values of the materials.



Figure S3. Diffuse reflectance UV-Vis of TiO₂ based materials.

Zeta potential

The zeta-potentials of the three catalysts as a function of the solution pH are given in **Figure S4**. Suspensions were made by adding 0.03 g of each catalyst in 10 mL of a 1 mM NaCl solution; these were adjusted to different pH values in a range between 4 to 8 with 0.1 mM NaOH and 0.1 mM HCl,³⁶ and then, all the suspensions were analyzed in the zetasizer.



Figure S4. Zeta potential of TiO₂ based materials with respect to pH.



Figure S5. SEM micrographs of the TiO_2 based materials (10 000 X): a) Sol-gel, b) Degussa P25, and c) Hombikat.



Figure S6. Pareto charts from three-level fractional factorial design for the response variables, degradation of A) DMP, and B) DEP.

Significance of process variables and empirical model development for PAEs photocatalytic degradation

Equation S3 and **S4** represent the second order polynomial regression models for prediction of the degradation of DMP and DEP in terms of coded variables, containing only the statistically significant terms.

 $DMP = 62.1739 + 16.6050 \, TC + 11.7452 \, TC^2 + 2.6466 \, CC + 4.2216 \, pH \qquad (Equation S3)$ $DEP = 64.8826 + 16.6350 \, TC + 11.4986 \, TC^2 + 1.6833 \, CC + 2.7617 \, pH \qquad (Equation S4)$



Figure S7. Profile of predicted values and desirability for the degradation of DMP and DEP.