

Photocatalytic activity evaluation of TiO₂ nanoparticles based on COD analyses for water treatment applications: a standardization attempt

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Abstract Evaluation of the photocatalytic activities of TiO₂ nanomaterials based on the chemical oxygen demand (COD) analyses under identical experimental conditions was not previously reported. In this work, COD has been selected as an adequate industrial water quality measure toward the establishment of a representative standard test method. The initial COD values of six organic pollutants representing dye, surfactants, phenols and alcohol were set at 30 ± 2 mg/L. Ten of different commercial and synthesized TiO₂ samples representing anatase, rutile and mixed phases were used and characterized. The data of photocatalytic processes were compared to that obtained using the commonly widespread Degussa-P25 TiO₂ (TD). The COD of all pollutants was completely removed by TD at UV exposure dose ≤ 9.36 mWh/cm². Consequently, the maximum irradiation dose was set at this value in all experiments. The percentages of COD removal as well as the values of the accumulated UV doses required for complete removal of pollutants were measured using the different TiO₂ samples. TiO₂ samples show different performance abilities toward the various pollutants compared to TD. Based on the obtained data, TiO₂ photocatalysts were divided into two categories according to the hydroxyl radical formation rates. Comparison with previous studies reveals that the photocatalytic efficiency evaluation depends on the method of measurement. COD is

recommended to be used as an adequate technique of analysis that meets the purpose of water treatment applications.

Keywords Photocatalytic activity · Nanosized TiO₂ · Organic pollutants · Water treatment · Chemical oxygen demand (COD) · Standard test method

Introduction

Municipal and industrial wastewaters are often polluted by various synthetic organic compounds such as surfactants, dyes, pharmaceuticals and other industrial chemicals and by-products (Li et al. 2012a; Sirtori et al. 2009; Li et al. 2012b; Gupta et al. 2013; Saleh et al. 2014; Mahmoodian et al. 2015; Ali and Gupta 2006; Ali 2010; Ali 2012; Ali et al. 2012; Ali 2014). Many of these compounds are characterized as recalcitrant pollutants that resist the conventional biological treatment systems. These recalcitrant pollutants most likely cause serious health risks to the living creatures and the environment. Removal of contaminants and reuse of the treated water utilizing nanotechnology would provide significant reduction in time and labor (Saleh and Gupta 2012a).

Photocatalytic oxidation processes have been widely considered as powerful methods to remove non-biodegradable organic pollutants in water. The photocatalytic processes have the potential to mineralize complicated organics and reduce toxicity without the generation of sludge and by-products (Li et al. 2012b; Saleh and Gupta 2012b). Titanium dioxide (TiO₂) is the most common and practical material as the environmental photocatalyst (Murgolo et al. 2015; Barakat 2011; Saif et al. 2013; EL-Mekkawi and Galal 2013; Saleh and Gupta 2012b; Gupta

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et al. 2012). Different features of TiO_2 photocatalysts have an influence on the photocatalytic performance, such as particle size, crystalline structure, phase composition, BET surface area and surface hydroxyl groups (Tryba et al. 2007). Scientific literature reports many studies addressing the photocatalytic activity quantification of TiO_2 as an essential investigation. However, the photocatalytic activities reported in the literature were evaluated using a large number of organic pollutants. Besides, many different methods and techniques have been used in the activity evaluation processes under widely varying experimental conditions. Generally, the percentage of degradation, degradation rate constant and the half-life of a model compound are the most common performance indicators. However, because of different experimental factors, it is difficult to use these data for comparison. For instance, the photocatalytic activities of TiO_2 in the literature were often expressed in terms of the first-order rate constants for the removal of organic pollutants. Meanwhile, using the rate constant values to evaluate the activity of a photocatalyst toward the removal of various pollutants is not expected to be totally precise. Most of the photocatalytic reactions follow the first-order kinetics only at the initial period of irradiation. Upon further light irradiation, the reactions often tend to show some deviations from the first-order reaction kinetics. This is probably due to the formation of new reaction products. That is why most of studies express the photocatalytic activities in terms of the initial rate constant. In addition, various analytical techniques have been used to follow up the change occurring during the photocatalytic reactions according to the type of pollutants. For example, the UV/visible spectrophotometry was often used to follow up the color change in degraded pollutants. Further, chromatography analyses were used to investigate the disappearance of reactants and/or the formation of new products (Sabin et al. 1992; Theurich et al. 1996; Ryu and Choi 2008; Murgolo et al. 2015). These wide variations in the used techniques lead to inaccurate assessments of different TiO_2 photocatalysts. Consequently, the need for an activity data set that is obtained under identical experimental conditions becomes a necessity for reliable comparisons (Ryu and Choi 2008). An adequate representative method of analysis for TiO_2 photocatalytic activity toward the actual removal of pollutants should be carefully selected.

There are several standardization attempts that aimed to quantify the performance ability of semiconductor photocatalysts. For example, the fluorescent probe method is one of these important standardization efforts (Ishibashi et al. 2000; Černigoj et al. 2009; Xiang et al. 2011; Saif et al. 2012). In this new method, the hydroxyl radicals ($\cdot\text{OH}$) produced on the surface of TiO_2 nanoparticles quantitatively convert the non-fluorescent coumarin species to

7-hydroxycoumarin fluorescent species under UV irradiation. The apparent rate constant for the photo-oxidation of coumarin, in turn, can be used as a photocatalytic activity measure of TiO_2 nanoparticles. Moreover, a comprehensive method to standardize and compare process efficiencies in heterogeneous photocatalysis was proposed by describing the relative photonic efficiency ζ_r (Serpone et al. 1996). Recently, the international standards organization (ISO) has begun to release a series of standards that cover air purification, water purification, self-cleaning and photosterilization for supported photocatalyst. The published ISO standards for water purification were used to test the activity of supported photocatalyst based on the rate of degradation of methylene blue dye MB or DMSO. The evaluation using one substrate does not always represent the real activity of the photocatalyst. Some experimental techniques may measure the conversion rate of a certain pollutant rather than the evaluation of the water quality upon the photocatalytic treatment. For example, it was found that the mineralization process of methylene blue dye (MB) occurs on a longer timescale than the oxidative photobleaching of the dye. Therefore, the measurement of the rate of photobleaching of MB is not equivalent to the rate of mineralization of the dye, which is usually a slower process (Mills et al. 2012).

In many countries including Egypt, chemical oxygen demand (COD) has been accepted as a national standard for organic pollution evaluation (Law 93 1962; Law 4 1994; Zhou et al. 2012). COD represents the amount of oxygen consumed to completely chemically oxidize the organic water constituents to inorganic end products. COD has been considered as a key parameter for monitoring water quality upon assessment of the effect of polluting agents (Silvestre et al. 2011). COD is an arbitrary empirical measurement typically carried out by subjecting the sample to oxidation to strong oxidants such as potassium dichromate in acid solution under working conditions well established by official methods.

High levels of COD in water often correlate with threats to human health including toxic algae blooms bacteria from organic wastes and seafood contamination (Karthikeyan et al. 2013). Wastewater containing high COD levels is mainly one of the major industrial problems that many industrial sectors face (Eremektar et al. 2007; Kaczala et al. 2010). Sources of COD in wastewater are varied. However, soluble organic compounds are most likely to contribute to escalated COD concentrations.

Many studies have interpreted the efficiencies of different photocatalysts toward various organic pollutants by monitoring the COD removal upon light irradiation. However, the initial COD values were always not the same. This inequality probably leads to imprecise methods of evaluation.

Herein, the evaluation of the photocatalytic activities of various synthesized and commercial TiO₂ nanomaterials based on the chemical oxygen demand (COD) analyses has been studied. The initial COD concentrations of pollutants were set at a given constant value. The photocatalytic degradability of various substrates with respect to their COD values was measured as a function of irradiation time (in terms of the irradiation dose). The light dose required for complete mineralization (i.e., zero COD value) or partial degrade of organic substrates is used to assess the photocatalytic activities of TiO₂ photocatalysts. Under identical experimental conditions, the photocatalytic activities of ten nanosized TiO₂ toward the removal of six soluble organic pollutants have been evaluated. Data interpretations as well as comparisons with previous studies were also given.

Materials and methods

Materials

Six water-soluble organic substrates were selected in this activity test: Methylene blue MB (C₁₆H₁₈ClN₃S, Fluka), p-nitrophenol PNP (C₆H₅NO₃, Sigma-Aldrich), p-chlorophenol PCP (ClC₆H₄OH, Sigma-Aldrich), *N*-cetyl-*N,N,N*-tri-methyl-ammonium bromide CTAB (C₁₉H₄₂BrN, Merk), sodium dodecyl sulfate SDS (C₁₂H₂₅O₄SNa, Sigma) and propanol PrOL (CH₃CH₂CH₂OH, Sigma-Aldrich). The initial COD values were the same for all organic substrate and were set to 30 ± 2 mg/L.

Ten TiO₂ samples were selected for this study, and they include Degussa P25 (abbreviated as TD throughout the text, Degussa-Hüls company), anatase (AC1, China), anatase (AC2, Aldrich) and rutile (RC1, Aldrich) all of which were commercially available and used without further treatment. In addition, the prepared samples T1, T2, T3 T4, T5 and T6 were synthesized according to the methods given in the mentioned references, respectively (Hafez et al. 2009; Papageorgiou et al. 1998; Huang et al. 2008). Factors such as pH, calcination temperatures, reaction media and various additives have been controlled to obtain different crystalline phases.

Characterization of TiO₂ samples

To determine the crystal phase composition of the synthesized and commercial TiO₂ catalysts, X-ray diffraction (XRD) measurements were taken using a Bruker D8 advance instrument with CuKα1 target with secondary monochromator 40 kV, 40 mA. Based on the XRD data, the percentages of anatase and rutile in the TiO₂ nanoparticles samples can be estimated from the respective XRD peak intensities using the following equation (Patterson, 1939):

$$X\% = 100/(1 + 1.265I_R/I_A) \quad (1)$$

where I_A represents the intensity of the anatase peak and I_R is that of the rutile peak and X is the weight percentage of anatase in the sample.

Also the crystallite size can be determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula (Patterson 1939):

$$L = K\lambda/\beta \cos \theta \quad (2)$$

where L is the crystallite size, λ is the wavelength of the X-ray radiation (Cu Kα = 1.54056 Å), K is usually taken as 0.9, and β is the linewidth at half-maximum height.

Mean particle size of TiO₂ samples were examined by N5 submicron particle size analyzer, Beckman Coulter, Miami, FL, USA).

Nitrogen adsorption–desorption isotherms were measured at −196 °C using SA 3100 surface area analyzer (Beckman Coulter, Miami, FL, USA). Specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method.

The surface hydroxyl group concentration on TiO₂ nanoparticles was estimated by FTIR analyses, TiO₂ powder was mixed with KBr (TiO₂:KBr) 1:32 by weight), and then 100 mg of the powder mixture was pelletized to a thin disk with a high-pressure pelletizer (Carver). These pellets were analyzed with FTIR spectrophotometer (Jasco, 4600) at the wavenumber of 1625 cm^{−1} (OH band).

The rate of the generated hydroxyl radicals by TiO₂ powders was estimated using fluorescent probe method (Saif et al. 2013). Illumination of the TiO₂ nanoparticles were carried out using the air cooled UV photoreactor (Photon Co., Egypt). The UV photoreactor lamps emitted the photons in the range from 320 to 410 nm. The intensity of UV radiation was 0.9 mW/cm². The photoluminescence spectra were measured using LS55 spectrofluorometer (PerkinElmer, USA). The apparent rate constant (k_f) was calculated using the slope of the fluorescence intensity–illumination time curves.

The pH of the point of zero charge pH_{pzc} was measured by pH drift method (Bessekhouad et al. 2004; Saleh and Gupta 2011). The method followed to determine the PZC of the TiO₂ comprised of the following steps. Five-hundred milliliters of 0.01 M NaCl solution was degassed using He in order to eliminate and prevent further dissolution of carbon dioxide. From this preliminary solution, eight solutions with pH values of 1.0–11.0 were prepared (by adding either HCl or NaOH). Ten milligrams of each TiO₂ sample was added into 10 ml of each solution. Flasks were capped and placed on a shaker for 24 h. The final pH was then measured and plotted as a function of initial pH. The intersection of each curve with the straight line at the slope of 45° is identified as the pH_{zpc} of the given TiO₂ sample. The pH values were measured using Jenway pH meter model 3510.



Photocatalytic activity experiments

The experiments of the photocatalytic activity evaluation were carried out using the batch method. Batch experiments were conducted using 0.05 g TiO₂ suspended in 100 ml of solutions containing the pollutant to be degraded at constant temperature (25 °C). The pH of pollutant solutions was adjusted by adding HCl using Jenway scientific experiment pH meter. Prior to UV irradiation, the suspension was stirred in the dark for 1 h to allow the equilibrium adsorption of substrates on TiO₂. The UV irradiation was made by UVA light bulbs (15 W). The light intensity was measured by YK-35UV radiometer, Taiwan, and it was 2.34 mW/cm².

At varied time intervals, aliquots were removed from the sample and centrifuged at 6000 rpm. Chemical oxygen demand (COD) measurements were measured by using COD meter and multiparameter photometer HI 83099.

The percentages of the COD removal of various pollutants upon adsorption and photodegradation in the absence and in the presence of TiO₂ nanoparticles were calculated by applying Eqs. (3), (4) and (5), respectively:

$$\% \text{ COD}_{\text{ads}} = 100 \times (C_{0\text{B}} - C_{0\text{A}}) / C_{0\text{B}} \quad (3)$$

$$\% \text{ COD}_{\text{st}} = 100 \times (C_{0\text{B}} - C_{\text{UV}}) / C_{0\text{B}} \quad (4)$$

$$\% \text{ COD}_{\text{cat}} = 100 \times (C_{0\text{A}} - C_{\text{UV}}) / C_{0\text{A}} \quad (5)$$

where $C_{0\text{B}}$ and $C_{0\text{A}}$ are the initial COD values before and after the addition of TiO₂. C_{UV} is the COD value at each time interval after UV light irradiation.

The amount of the accumulated UV light radiation over the irradiated pollutant solution was calculated at different intervals of illumination time by Eq. (6):

$$E_{\text{UV,ac}} = tE_{\text{UV}} \quad (6)$$

where $E_{\text{UV,ac}}$ is the accumulated UV radiation (mWh/cm²) incident on the reactor for each sample taken during the experiment at different intervals of illumination time. E_{UV} is the measured initial UV light intensity, and t is the experimental time at which each sample was taken.

Results and discussion

Preparation and characterization of TiO₂ nanoparticles

Preparation of TiO₂ nanoparticles

In this work, TiO₂ samples possessing different photocatalytically active phases (i.e., anatase, rutile and mixed phases) were selected. Some of TiO₂ samples under investigation are commercial (TD, AC1, AC2, RC1), while others (T1, T2, T3 T4, T5 and T6) are prepared. Sol–gel,

hydrothermal and combustion methods have been utilized in the preparation of TiO₂ nanoparticles (Hafez et al. 2009; Papageorgiou et al. 1998; Huang et al. 2008). Several preliminarily studies preceding the preparation of titanium oxide particles have been conducted in order to obtain pure nanosized TiO₂ representing different crystalline phases. Factors such as pH, calcination temperatures, reaction media, reaction temperature, calcination time and various additives have been controlled to obtain TiO₂ of different crystalline phases.

Characterization of TiO₂ nanoparticles

Characterization of both synthesized and commercial TiO₂ nanoparticles was conducted in this study. The crystalline phases, particle sizes, the points of zero charge, surface areas, density of surface hydroxyl groups and the rates of hydroxyl radical formation were identified and are given in Table 1.

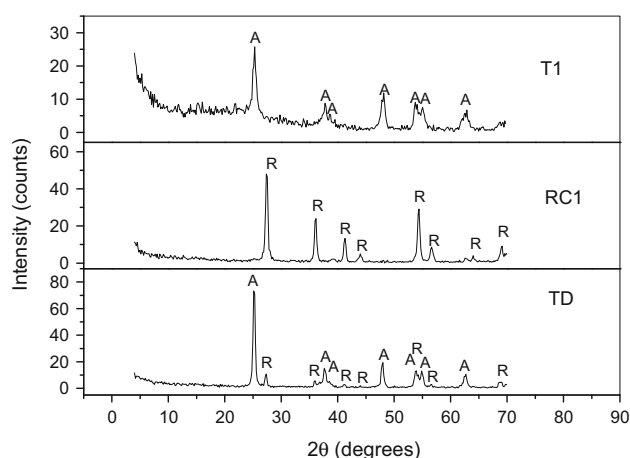
XRD analyses indicate the crystal type for TiO₂ samples. The XRD peaks at $2\theta = 25.17^\circ$, 37.77° , 48.03° , 55.08° and 62.56° in the spectrum of pure TiO₂ are identified as the crystal of anatase form (89-4921-JCPDS-ICDD, Copyright, 2001). On the other hand, peaks at $2\theta = 27.40^\circ$, 36.17° , 41.33° , 54.41° , 56.69° , 64.15° and 69.09° are taken as the crystal of rutile form (89-4920-JCPDS-ICDD, Copyright, 2001). For example, Fig. 1 shows XRD diffractograms of T1, RC1 and TD representing the anatase, rutile and mixture of anatase and rutile phases, respectively. The percentage ratios of anatase and rutile in each sample were estimated from the respective XRD peak intensities according to Eq. (1). Besides, the crystallites size was determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula as indicated in Eq. (2). Table 1 summarizes the crystal phases and the crystal sizes of the commercial and prepared TiO₂ samples. As shown in Table 1, different crystalline phases of TiO₂ representing anatase, rutile and mixture of anatase and rutile have been used in our studies. Overall, data in Table 1 revealed the nanosized dimensions of TiO₂ samples. Generally, the crystal sizes of the rutile phases are larger than that of the anatase since most of rutile samples are obtained at high calcination temperatures. It is worth mentioning that Degussa P25 (TD) has been widely considered as a de facto standard photocatalyst due to its superiority for most organic pollutants (Mills and Morris 1993; Theurich et al. 1996; Ryu and Choi 2008; Xiang et al. 2011; Sabin et al. 1992). Therefore, TD was used in this work as a reference photocatalyst as discussed later.

Figure 2 shows the determination of the pH of the point of zero charge (pH_{pzc}) measured by pH drift method. The pH of the reaction medium is one of the major factors that influence the adsorption of the ionic or polar form(s) of



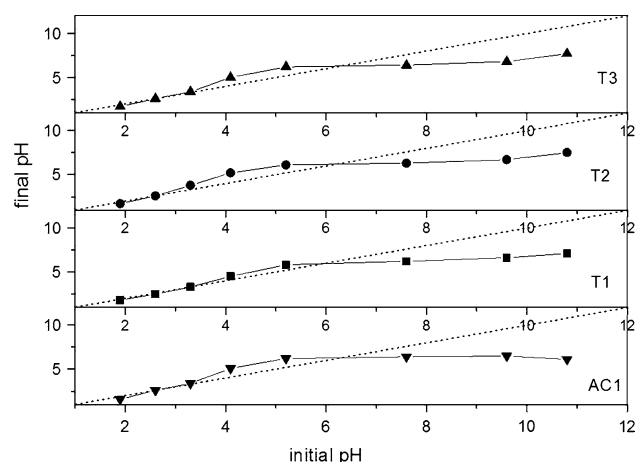
Table 1 Characterization of TiO₂ samples

Property	TD	AC1	AC2	RC1	T1	T2	T3	T4	T5	T6
Crystalline phase	Anatase: 80, rutile: 20	Anatase	Anatase	Rutile	Anatase	Anatase	Anatase: 43.2, rutile: 56.8	Anatase	Rutile	Anatase
Average crystal size (nm)	Anatase: 37, rutile: 90	120	56	75	13	8	Anatase: 49, rutile: 51	6	60	14
Hydrodynamic size (nm)	102.3	408.2	201.7	307.4	234.9	185.5	228.9	335.5	227.6	127.4
Surface area (m ² /g)	50	10.88	34.65	7.78	8.42	7.11	5.2	87.6	2.08	30.37
Surface OH conc.	163	109	217	100	106	103	62	117	45	149
OH [•] formation (k _f)	25.8	19.71	20.84	3.19	4.55	3.02	2.39	3.08	1.95	19.53
pH _{pzc}	6.25	6.30	6.01	5.91	5.93	6.19	6.30	6.50	6.11	6.23

**Fig. 1** X-ray diffractograms of some commercial (RC1 and TD) and synthesized (T1) TiO₂ samples. The crystalline phases were labeled as follows: A anatase, R rutile

pollutants on TiO₂ surfaces (Ryu and Choi 2008; EL Mekkawi and Abdel-Mottaleb 2005; Saleh 2015; Saleh and Gupta 2011). Point of net zero charge (pH_{pzc}) specifies the electrical neutrality of the TiO₂ at a particular value of pH under aqueous solution conditions. When TiO₂ is placed in solutions with pH higher than its PZC, the net surface charge becomes negative. However, at pH values below the ZPC, the surface has a net positive charge. These changes in the surface charge of TiO₂ may affect the adsorption pattern of ionic (or polar) pollutants via electrostatic interaction and therefore can affect the photocatalytic activity. Consequently, the measured values of pH_{pzc} have been considered as shown later to control the influence of the surface charge on the photocatalytic activity of TiO₂.

The concentration of the surface OH group (quantified in terms of the IR absorption) as well as the BET surface area of the TiO₂ samples was measured and is listed in Table 1. As shown in Table 1, the investigated TiO₂ samples have different OH group concentrations. The

**Fig. 2** The pH of the point of zero charge pH_{pzc} of some TiO₂ samples measured by pH drift method

surface hydroxyl groups may play a role in the enhancement of the photocatalytic activity. The role of the hydroxyl group is to facilitate the adsorption of pollutants on TiO₂ particles through the interaction with the surface hydroxyl groups (OH) which in turn may enhance their activity (Luo et al. 2010; Asuha et al. 2010; Takashi 2003). Examination of Table 1 shows that the surface OH group concentrations are directly proportional to their BET surface area among TiO₂ samples. This indicates that the surface-area-normalized OH group density on TiO₂ is to some extent constant for all TiO₂ samples tested in this study.

Additionally, the rates of hydroxyl radical formation upon the UV irradiation of TiO₂ particles were determined by using the fluorescent probe method. During the illumination of TiO₂ samples, the hydroxyl radicals (•OH) are produced. These produced radicals quantitatively convert coumarin (non-fluorescent species) to 7-hydroxycoumarin (fluorescent species) (Xiao et al. 2008; Tryba et al. 2007; Xiang et al. 2011; Saif et al. 2012; Ishibashi et al. 2000).



For example, Fig. 3 shows the change in the fluorescence spectrum of coumarin during illumination of TiO₂ (AC1) powder immersed in coumarin. As shown in Fig. 3, the generation of 7-hydroxycoumarin increases due to prolonged irradiation time. The estimated rate constant values of the hydroxyl radicals' formation (k_f) by different TiO₂ samples are summarized in Table 1. The given rate constant values indicate the discrepancies between TiO₂ samples toward the hydroxyl radicals' formations.

Setting up the identical experimental conditions

Minimization of the surface influence

The photocatalytic activities of various TiO₂ samples were examined under similar experimental conditions. Parameters affecting the photocatalytic performance such as pH of the reaction medium, surface OH group density, initial COD concentration, photostability of pollutants and irradiation dose were studied and controlled as shown below.

According to the measured points of zero charge values in Table 1, the surfaces of all TiO₂ samples carry positive charges at pH < 5.9. The influence of the surface charge on the photocatalytic activities of TiO₂ samples should be minimized (i.e., the initial pH should be set at a value where there is no tangible correlation between the photocatalytic activities and the surface charge of TiO₂ samples). Therefore, the initial pH in all activity experiments was set at pH 3 where the preliminary tests reveal that the pH change during the degradation reactions was only ± 0.2 for all activity tests.

On the other hand, the surface OH group concentration (quantified in terms of the IR absorption) was directly proportional to their BET surface area among TiO₂ samples (see Table 1). This indicates that the surface-area-

normalized OH group density on TiO₂ is constant for all TiO₂ samples tested in this study and that the effect of the surface OH group density is also minimized in the present photocatalytic activity evaluation.

Determination of pollutants

A huge number of organic substrates that belong to various classes (i.e., amines, phenols, carboxylic acids, alcohols, aliphatics, aromatics, surfactants, etc.) have been tested. Different non-volatile water-soluble organic substrates as representative models of pollutants from various categories were selected. We also mainly focused on choosing substrates that show acceptable degree of photostability toward prolonged UV light irradiation in the absence of TiO₂. Some organic substrates such as phenol, aniline and rhodamine B are excluded from this study due to their low photostabilities. Six substrate compounds were selected in this work. The substrates under investigation represent four organic classes: dye (MB), surfactants (SDS and CTAB), phenols (PCP and PNP) and alcohol (PrOL).

Setting the initial COD values

Setting of the initial COD of all pollutants at fixed value is necessary for precise photocatalytic activity evaluation of TiO₂ samples toward each pollutant. Previous studies have interpreted the efficiencies of different photocatalysts toward various organic pollutants by monitoring the COD removal upon light irradiation. However, the initial COD values were always not the same. This inequality probably leads to imprecise evaluation. Therefore, in this work, the initial COD values of all pollutants have been set at 30 ± 2 mg/L.

Photostability tests and irradiation dose

Prior to TiO₂ addition, the photostability of the selected organic pollutants was tested. In the photostability tests, the value of UV irradiation dose was $E_{UV,ac} = 9.36$ mWh/cm². This value corresponds to 4 h of the UV light illumination using the UVA light bulbs as discussed in “Materials and methods” section. This dose value was determined based on the collected data in the next section. As illustrated later, all pollutants under investigation are efficiently removed by TD upon exposing to this value of UV light dose. The selected pollutants showed high degrees of stability upon exposing to this value of UV dose in the absence of TiO₂. The percentage of COD decrease in the pollutants in the absence of TiO₂ upon the UV light illumination is calculated according to Eq. (4) and listed in Table 2. The photostability tests indicate that the prolonged UV light irradiation in the absence of TiO₂ as a

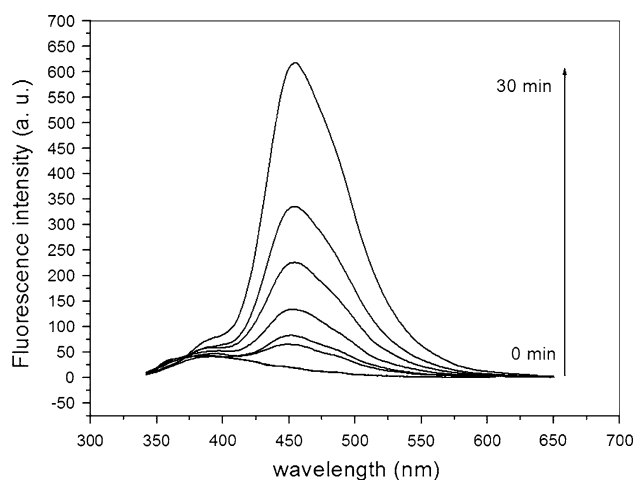


Fig. 3 Fluorescence spectral changes observed during illumination of TiO₂ (AC1) powder immersed in coumarin solution (1.0×10^{-3} M) ($\lambda_{ex} = 332$ nm)



photocatalyst is not sufficient to completely degrade the given organic substrates.

Photocatalytic activity evaluations of TiO₂ samples

Photoreactivities evaluation tests of TiO₂ samples were determined with various test pollutants under the identical experimental condition and are summarized in Table 3. The listed numbers represent the UV exposure dose ($E_{UV,ac}$; mWh/cm²) required for complete mineralization (i.e., 100 % COD removal). The listed percentage values represent the percentage of COD removal at UV exposure dose = 9.36 mWh/cm². As illustrated in Table 3, all pollutants are efficiently removed by TD upon exposing to UV light dose ≤ 9.36 mWh/cm². Therefore, the maximum irradiation dose was set at this value. For a given pollutant, we assume the TiO₂ samples that result in more than 60 % of COD removal are relatively the most active photocatalysts. The most active TiO₂ samples for a given substrate (i.e., in the same row) are indicated in bold numbers.

On the other side, the photostability of each pollutant toward UV illumination in the absence of TiO₂ should be considered. Considering the photostability data in Table 2, not all the high COD removal percentages in Table 3 indicate the high catalytic activities. For example, CTAB and PrOL are slightly photodegradable substrates showing 62 and 42.6 % decrease in COD values, respectively (see Table 2). Therefore, in case of both CTAB and PrOL, only TiO₂ samples which result in approximately complete COD removal were considered as the relatively most active photocatalysts.

Overall, based on the obtained data in Table 1 and 3, we have divided the TiO₂ photocatalysts into two categories. The first category is the TiO₂ samples that show high rates of hydroxyl radicals' formation (HRT) which includes TD, AC1, AC2 and T6. The second category is the TiO₂ samples that show low rates of hydroxyl radicals' formation (LRT) which includes RC1, T1, T2, T3, T4 and T5.

Table 2 Percentages of COD decrease in the substrates in the absence of TiO₂ upon UV light illumination

Substrate	% COD _{st}
MB	33.33
SDS	24.24
CTAB	62
PCP	0
PNP	20.9
PrOL	41.6

Initial COD concentration = 30 mg/L, initial volume = 100 ml, pH = 3, accumulated light dose = 9.36 mWh/cm²

The HRT photocatalysts are often the most effective photocatalysts for different organic substrates as shown in Table 3. TD, AC1, AC2 and T6 are the most active photocatalysts toward most pollutants under investigations. However, some limitations are obtained in case of PNP and surfactants (CTAB and SDS) upon using HRT catalysts. PNP is only completely removed when using TD as a photocatalyst, while CTAB and SDS are only removed by using TD and AC1. It has been noticed that the color of TiO₂ samples turns from white to yellow during the irradiation of PNP. This can be attributed to the formation of PNP–TiO₂ surface complex in the presence of UV light illumination. The surface complex may be formed via strong phenolate bonds which show high photostability. Further, CTAB and SDS—as surface active materials—show high adsorption on TiO₂ samples that have relatively smaller crystal sizes of AC2 and T6 (see Table 4).

These findings are different to that obtained by Ryu and Cho (2008). Ryu and Cho proposed similar experimental conditions in the photocatalytic activity assessment of TiO₂. They identified the photocatalytic activities of different TiO₂ samples toward various substrates in terms of their conversion rates in water. They found that there is no relation between the particle sizes and the photocatalytic activities evaluated in terms of the degradation rate constants. Their studies showed that the most active TiO₂ photocatalyst depends on what compound is used as a test substrate. They concluded that the relative activity of photocatalysts sensitively depends on the kind of test substrate. Accordingly, these observations suggest that the photocatalytic activity evaluation is affected by the method of measurement.

Adsorption of the organic pollutants on TiO₂ surfaces is another important factor that should be considered. Table 4 summarizes the percentages of COD decrease in the substrates upon the adsorption on TiO₂ surfaces. A survey of Tables 3 and 4 indicates that for a given pollutant, the most active photocatalysts often show slightly low adsorption tendencies (often <20 % COD removal). This can be attributed to the super tendencies of substrates toward TiO₂ surfaces adsorption that may block the photoactive sites in TiO₂ surfaces (EL-Mekkawi and Galal 2013).

Generally, there are mainly two routes in photocatalytic oxidation of organic pollutants, i.e., direct oxidation of substrates at the generated holes and indirect oxidation via the formed active free radical species (Henderson 2011). Accordingly, one can conclude that upon using HRT photocatalysts, the predominant mechanism is the indirect oxidative destruction via hydroxyl radicals. Efficient COD removal of all types of pollutants could be then achieved by using HRT photocatalysts whenever there is no surface interaction hindrance.



Table 3 Photocatalytic activities of TiO₂ samples based on the COD measurements

Substrate	TD	AC1	AC2	RC1	T1	T2	T3	T4	T5	T6
MB	8.78	8.19	9.36	23 %	0 %	0 %	8.89	59 %	5 %	8.58
SDS	6.44	9.36	68 %	33 %	64 %	0 %	72 %	60 %	7 %	33 %
CTAB	8.42	93 %	0 %	0 %	67 %	37 %	69 %	0 %	0 %	13 %
PCP	9.36	61 %	7.02	0 %	47 %	62 %	45 %	50 %	0 %	74 %
PNP	8.89	28 %	21.5 %	8.19	6 %	32 %	0 %	34 %	0 %	50 %
PrOL	95 %	ND ^a	8.19	47 %	62 %	37 %	55 %	ND ^a	0 %	8.19

Initial COD concentration = 30 mg/L, initial volume = 100 ml, pH = 3, TiO₂ = 0.5 g/L. The listed numbers represent the UV exposure dose ($E_{UV,ac}$; mWh/cm²) required for complete mineralization (i.e., 100 % COD removal). The listed percentage values represent the percentage of COD removal at UV exposure dose = 9.36 mWh/cm². The most active TiO₂ samples for a given substrate (i.e., in the same row) are indicated in **bold numbers**

^a Not detected because PrOL was completely adsorbed on TiO₂ surfaces

Table 4 Percentages of COD decrease in the substrates upon the adsorption on TiO₂ surfaces

Substrate	TD	AC1	AC2	RC1	T1	T2	T3	T4	T5	T6
MB	0	55.5	0	0	22.2	25.9	18	18.7	0	0
SDS	10	0	50	36.4	66.7	75.7	15.2	30	60	54.5
CTAB	31	55.2	40	0	0	34.5	10.3	37.9	55.1	25.8
PCP	0	0	0	0	11.1	0	0	50.6	0	0
PNP	20.5	0	0	0	0	8	0	0	0	10
PrOL	0	100	18.2	0	63.8	47.2	44.4	100	72	0

Initial COD concentration = 30 ± 2 mg/L, initial volume = 100 ml, pH = 3, TiO₂ = 0.5 g/L, relative standard deviation (SD) = 6.7 %

On the other hand, the behavior of the LRT group toward pollutants removal is different. Most of the TiO₂ samples show only partial or even zero COD removal of pollutants. However, some of TiO₂ samples that belong to LRT group seem to be selective to certain pollutants. Although LRT photocatalysts show only low rates of the active free radicals formation, RC1, T2 and T3 appear to be the most active for PNP, PCP and MB, respectively. We assume that upon using LRT photocatalysts, the predominant mechanism is mainly the direct oxidative destruction via the photogenerated holes. Rutile is generally believed to be much less active than anatase (Torimoto et al. 2002). Most rutile samples are obtained at high temperatures and tend to have low specific surface areas. Nevertheless, the activity of RC1 for PNP degradation is higher than some anatase samples. The formed yellow PNP–TiO₂ surface complex upon UV light illumination may be useful when the oxidation of pollutants occurs at the generated holes. The surface complex can probably facilitate the charge transfer from the pollutants into the surface of TiO₂ particle during the oxidation process. Similarly, the activity of T3 (mixture of rutile and anatase) for MB removal is higher than the other LRT photocatalysts. Previous studies indicate that among several prepared TiO₂ samples, the highest

photocatalytic activity was observed for TiO₂ powder composed of anatase and rutile phases owing to the similar phase composition with commercial Degussa P-25 (Arbuj et al. 2010).

Many studies and standardization efforts on the activity assessment of TiO₂ were made previously. In these studies, different organic pollutants including the current investigated pollutants were tested. Table 5 summarizes some of these efforts. Recently, the international standards organization (ISO) has begun to release a series of standards that cover air purification, water purification, self-cleaning and photosterilization for supported photocatalyst. The published ISO standards for water purification were used to test the activity of supported photocatalyst based on the rate of degradation of methylene blue dye MB or DMSO (see Table 5). The evaluation using one substrate does not always represent the real activity of the photocatalyst as shown in the manuscript. For example, although AC2 and T6 show high activities toward MB, they cannot be used in the removal of either PNP or the given surfactants. As shown in Table 5, the fluorescent probe method has been also recommended in previous studies as an adequate method for activity evaluation of photocatalyst (Tryba et al. 2007; Xiang et al.



Table 5 Summary of current and previously reported standardization efforts

Pollutants	Photocatalyst	Activity indices	Techniques and methods	References
MB	TiO ₂ (ST-01 and A11) heat-treated at 400–1000 °C	Rate of OH radical formation (fluorescent probe method)	Spectrofluorometry	Tryba et al. (2007)
		Rate constant of MB decomposition (absorbance change in MB)	UV–Vis spectrophotometry	
MB	Surfaces covered with photocatalytic coatings	Degradation rate and the associated photonic efficiency, ξ_{MB} (%)	UV–Vis spectrophotometry	ISO 10678: (2010)
DMSO	Surfaces covered with photocatalytic coatings	Concentration change in DMSO and its half-life in the photoreactor	HPLC	ISO 10676: (2010)
PCP	TD	Rate of CO ₂ photogeneration	Gas chromatography	Mills and Morris (1993)
PCP	Hombikat UV 100 and TD	Rate of PCP conversion	HPLC	Theurich et al. (1996)
		Rate of PCP mineralization	TOC	
Several pollutants including: PCP, MB and SDS	TD beside other seven types of TiO ₂ represent anatase, rutile and mixed phases	Rate constants of the conversion reaction	Different techniques according to the type pollutant such as: HPLC IC UV–Vis spectrophotometry TOC	Ryu and Choi (2008)
Cumarin	Different TiO ₂ films including TD	Degradation rate of CM Rate of OH radical formation	HPLC analyses Spectrofluorometry	Xiang et al. 2011; Saif et al. (2012); Ishibashi et al. (2000)
23 organic compounds (benzene, haloaromatics, chloroalkenes, haloalkanes, bis-(2-chloroethyl)ether, 1-hydroxyethane-1, 1-diphosphonate and ethylenediamine- <i>N,N,N',N'</i> -acetic acid)	TD	Rate constant of product formation or disappearance of reactants	Different techniques according to the type pollutant such as: –Titration –Ion selective electrode –Spectrophotometry	Sabin et al. (1992)
Phenols	TD	Relative photonic efficiencies based on initial rates of degradation	HPLC	Serpone et al. (1996)
MB, CTAB, SDS, PCP, PNP and PrOL	TD beside other 9 types of TiO ₂ represent anatase, rutile and mixed phases	UV irradiation dose based on the efficient COD removal	COD	Current study

2011; Saif et al. 2012; Ishibashi et al. 2000). These studies assumed that the photocatalytic activity depends on the amount of the OH radicals formed by the photocatalyst during the degradation reactions. However, according to

the current study, this method has some limitations arising from surface interactions or substrate-specific nature as discussed previously. Table 5 includes also some standardization attempts in which researchers used different



analytical techniques to follow up the degradation reaction rates of pollutants. These discrepancies in the used methods lead to inaccurate assessments as mentioned previously.

Finally, in the light of the previous interpretations, the method's merit can be summarized as follows:

1. The main advantage of this method is that it ensures the real treatment of the polluted wastewater.
2. This method is of low cost and easy to use.
3. The method is independent on the degradation pathway since the main activity indicator is the efficient removal of COD. The problem of the interference of reaction intermediates during the evaluation process does not exist.
4. The evaluation process does not depend on a specific nature of certain reactant or product so it can be used to evaluate the photocatalytic activity toward a mixture of organic pollutants.

Conclusion

This work puts a step on the establishment of a standard test method for the evaluation of photocatalytic activity of TiO_2 photocatalysts toward removal of organic pollutants. COD has been selected as an adequate industrial water quality measure toward the establishment of a representative test method for TiO_2 activity evaluation. We have focused on selecting different non-volatile, water-soluble organic substrates as representative models of pollutants from various categories. The initial COD values of all pollutants have been set at 30 ± 2 mg/L.

Ten of different commercial and synthesized TiO_2 samples were used in this study. All photocatalytic degradation experiments were conducted under identical conditions. The values of the accumulated UV doses required for complete or partial removal of pollutants based on the COD analyses were calculated and represented.

Photostability of pollutants and the adsorption behavior of pollutants on TiO_2 surfaces was measured and considered during the data interpretation. Based on the obtained data, TiO_2 photocatalysts were divided into two categories according to the hydroxyl radical formation rates. HRT and LRT represent TiO_2 samples that possess high and low rates of the hydroxyl radical formation, respectively. We assumed that upon using HRT photocatalysts, the predominant mechanism is the indirect oxidative destruction via hydroxyl radicals. Efficient COD removal of all types of pollutants was achieved by using HRT photocatalysts whenever there is no surface interaction hindrance.

However, some of TiO_2 samples that belong to LRT group were selective to certain pollutants. We assume that upon using LRT photocatalysts, the predominant mechanism is mainly the direct oxidative destruction via the photogenerated holes.

Finally, the evaluation test of TiO_2 photocatalysts using different types of substrates was mentioned in the earlier studies. However, COD is recommended as an adequate technique of analyses that meet the purpose of the water treatment applications.

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