The effect of NOM to TiO_2: interactions and photocatalytic behavior

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Natural organic matter (NOM) is ubiquitous in aquatic environment, which plays a predominant role in the sorption of pharmaceuticals onto the TiO_2 nanoparticles. It is a matter of concern whether NOM could act as a surface sensitizer of TiO_2 or not. In this context, the role of NOM is investigated for the photocatalytic degradation of carbamazepine (CBZ) using TiO_2. Four different ratios of NOM:TiO_2 were used varying from $400\,\mu g\,g^{-1}$ to $400\,mg\,g^{-1}$. The findings reveal that small amounts of NOM could enhance the TiO_2 efficiency up to 8%. Electron paramagnetic spectroscopy (EPR), along with size exclusion chromatography with dissolved organic carbon detection (SEC-OCD) and nuclear magnetic resonance spectroscopy (NMR) reveal the occurring mechanism. TiO_2 binds small molecular size fractions of NOM and breaks aromatic bonds of adsorbed NOM transforming it to stranded alkyl groups. This modified TiO_2 bears a significant amount of electrons (e^-) and lesser holes (h^+) than the purified TiO_2 and when irradiated, produces hydroxyl radicals which degrade CBZ.

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1. Introduction

Titanium oxide is used in a wide variety of technological applications where surface properties play a role. It is used in heterogeneous catalysis, as photocatalyst; in solar cells for the production of hydrogen and electric energy, as white pigment, as corrosion-protective or optical coating, as spacer material in magnetic spin-value systems, and it is important in earth sciences [1].

By far, the most actively pursued applied research on TiO_2 is its use for photo-assisted degradation of organic molecules. TiO_2 is a semiconductor where the electron–hole pair, created upon irradiation with sunlight, became separated and the resulting charge carriers migrate to the surface. These react with adsorbed water and oxygen to produce radical species, which attack any adsorbed organic molecule and can, ultimately, lead to their complete decomposition into CO_2 and H_2O [2].

Photocatalysis based on TiO_2 has been intensively investigated in order to improve photocatalytic efficiency for different applications such as decomposition of various organic pollutants in aqueous media [3]. Studies on the doping of non-metal and transition-metal ions into TiO_2 have become attractive in the area of photocatalysis [4].

Natural organic matter (NOM) is ubiquitous in aquatic environment and plays a predominant role in the sorption of toxic substances onto the TiO_2 nanoparticles (NPs) [5]. Once released in the environment, NPs will inevitably interact with abundant NOM [6]. Fulvic acid (FA) and humic acid (HA) are the main constituents of NOM from water resources responsible for water color and odor [7], and also responsible for membrane fouling in water treatment [8]. It is reported that TiO_2 has a strong affinity for HA [9–11], especially at a low pH value. Previous investigations showed that certain groups of organic compounds, such as carboxylic acids, strongly adsorb onto the TiO_2 surface at low pH values whilst others, such as alcohols and saturated long-chain aliphatic compounds, do not [12].

The research on the NOM/TiO_2 interactions was so far limited to the photodegradation of NOM by TiO_2 [7,9–11,13–16]. However, it is reported that the removal of Cr(IV), by using TiO_2 photocatalysis, was greatly enhanced when the system contained both HA and Cr(VI) [16] and also that HA coating enhanced the adsorption of Cd(II) to nano-TiO_2 [6].

It is a matter of concern whether NOM could act as a TiO_2 surface sensitizer or not. So far, only activated carbon has been used as a catalyst support for the photocatalytic degradation [17]. Carbon doping has been shown to be more active than doping with nitrogen [18]. For example, Khan et al. [19] first demonstrated the high photoactivity of carbon-doped TiO_2 in the photoelectrochemical context by measuring the rate of water splitting to H_2 and O_2. Previously, it was reported by Doll et al. that low concentrations of NOM could accelerate the degradation of carbamazepine

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due to the photochemical formation of reactive species by NOM, but at higher concentrations of NOM, the acceleration of the degradation decreased [20]. It is suggested that for the best evaluation of the photocatalytic degradation of NOM by TiO_2, NOM should be characterized in detail [13]. Therefore, the aim of this work was to evaluate the photodegradation efficiency of NOM-modified TiO_2 to CBZ, by using a well-characterized lignite humic acid, as a model NOM, to elucidate the effect of NOM to the photocatalytic behavior of TiO_2.

2. Experimental

2.1. Reagents

Millipore Milli-Q Water (resistivity = 18 MΩ cm) and P25 titanium oxide (nano-TiO_2) (Evonik Degussa GmbH, Düsseldorf, Germany) with purity >99.5% were used for all the experiments. The pH adjustments were carried out using NaOH and HNO_3 from Fluka. The fairly homogeneous humic acid, used as NOM model, is a lignite humic acid (LHA2) previously characterized by Drosos et al. [21] and also named $L_{Parental}HA$ in [22]. Carbamazepine (99%) was obtained from Sigma Aldrich.

2.2. Purification

In order to obtain a completely DOC-free TiO_2, a purification step was required by baking P25 TiO_2 at 500 °C for 60 min. An aqueous solution (Milli-Q water) of the baked TiO_2 (20 g L^{-1}) was irradiated for 60 min, under a Solar UV Simulator (Oriel Corp., Stratfort, CT, USA) with additional WG 295 filters (6 mm, Schott Glaswerke, Germany). The scheme and detailed description of the solar simulator used for the irradiation experiments was given by Doll et al. [20]. The radiation source was a 1000-W Xe short-arc lamp, which was turned on at least 30 min prior to irradiation in order to insure a constant photon flux.

The irradiated TiO_2 solution was centrifuged at 4000 rpm for 15 min. The filtered TiO_2 was placed into an oven at 60 °C for 24 h, in order to remove moisture completely. The purified TiO_2 was then grained to obtain fine powder. The supernatant was collected and measured by total organic carbon detection (TOC) and size exclusion chromatography with organic carbon detector (SEC-OCD) after filtration using 0.45 μm filter supor 450.

2.3. Samples preparation

One gram of purified TiO_2 was placed in 50 ml of an LHA2 solution at pH 5, stirred overnight and centrifuged at 4000 rpm for 15 min. The supernatant was collected, filtered using 0.45 μm filter supor 450 and measured by total organic carbon detection (TOC) and size exclusion chromatography with organic carbon detector (SEC-OCD). The different LHA2 solutions used were 8000, 800, 80, and 8 mg L^{-1} respectively, giving four TiO_2-LHA2 ratios. By using 50 ml of Milli-Q instead of the LHA2 solution, the TiO_2 obtained was used as a blank (Blank TiO_2). The materials were placed into an oven at 60 °C for 24 h, in order to remove moisture completely and were grained to obtain a fine powder. The four LHA2-modified TiO_2 samples are named here as it follows: (1) LT04 for the LHA2:TiO_2 ratio of 400 μg g^{-1}, (2) LT4 for the 4 mg g^{-1} ratio, (3) LT40 for the 40 mg g^{-1} ratio and (4) LT400 for the 400 mg g^{-1} ratio.

All CBZ samples were prepared by dissolving CBZ in Milli-Q water, stirred for 6 h and placed in an ultrasonic bath for 15 min to ensure complete dissolution.

The catalysis samples were prepared by adding 1 g L^{-1} LHA2-modified TiO_2 material in 10 mg L^{-1} pharmaceutical solution at pH 7. The sample volume was 50 ml. Samples were irradiated by the Solar UV Simulator introduced by Doll et al. [20].

All samples were stirred and irradiated simultaneously from above by a homogenous light field. During photoreaction, samples were collected at different time intervals for analysis. Before irradiation, adsorption was allowed to take place for 30 min in the dark.

2.4. EPR spectroscopy

Electron paramagnetic resonance (EPR) spectra were recorded at liquid-nitrogen temperature (77 K) with a Bruker ER200D spectrometer equipped with an Agilent 5310A frequency counter. Typically, adequate signal-to-noise ratio was obtained after 20–40 scans. Samples were cooled to 77 K and illuminated in the cavity while spectra were recorded. A 450 W lamp (Oriel model 66929) was used as illumination source. EPR samples were prepared by pasting the wet pellet of each material into 5 mm suprasil (Willmad Co.) quartz tube with no further treatment. g-values were calibrated versus DPPH, g = 2.0036, as described earlier [23].

2.5. SEC-OCD chromatography and TOC analysis

Size exclusion chromatography coupled with organic carbon and UV (254 nm) detector used a TSK HW 50S Column. The mobile phase was 1.5 g L^{-1} $Na_2HPO_4 \cdot 2H_2O$ and 2.5 g L^{-1} KH_2PO_4 with 1 mL min^{-1} flow rate, followed by acidification using 5 mL L^{-1} phosphoric acid 85% with a flow rate of 0.5 mL min^{-1} under nitrogen 5.0 (28 L h^{-1}) with 0.5–1 bar pressure. The contact time in the reactor was 80 s, 60 s UV radiation and rotation time of the reactor 400 rpm. For the determination of the apparent molecular size, calibration using PEGs was performed. In detail, Vo was determined by blue dextran (2×10^6 Da), Vp by methanol and the calibration PEG standards used varied in molecular weight (200 kDa, 100 kDa, 40 kDa, 20 kDa, 10 kDa, 6 kDa, 4 kDa, 1550 Da, 1000 Da, 400 Da, 200 Da). DOC concentrations were measured both by SEC-OCD and a TOC 5000 Carbon Analyzer (Shimadzu).

2.6. NMR spectroscopy

Solid state ^{13}C NMR spectra of powder samples were recorded on a Bruker NMR spectrometer at a resonance frequency of 400 MHz, using a Ramped-Cross Polarization MAS with a spinning speed of 6.8 kHz [24]. A contact time of (1 ms) and a pulse delay of (400 ms) were used. A ramped ^1H-pulse decreasing the power from 100 to 50% was used to circumvent spin modulation of Hartmann–Hahn conditions [24]. At least 50,000 single scans were collected for each sample.

2.7. HPLC analysis

The concentration of CBZ was measured by high-performance liquid chromatography (HPLC) using an HP 1100 HPLC system (column RP 18e, 5 μm; mobile-phase acetonitrile: water 60:40; 1 mL min^{-1}) with detection at 280 nm by a UV detector.

3. Results and discussion

3.1. TOC and samples

LHA2 was proved to contain 44% of carbon both by elemental analysis in [22] and TOC analysis. More information about LHA2 is summarized in Table 1. The adsorbed carbon on 1 g of purified TiO_2 was 160 μg L^{-1} for LT04 and 670 μg L^{-1} for LT4, close to the concentration found in drinking water. The adsorbed carbon for LT40 was 8 mg L^{-1}, and for LT400 was 44 mg L^{-1}, which are values,