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Research paper

Influence of methanol when used as a water-miscible carrier of pharmaceuticals in TiO_2 photocatalytic degradation experiments

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ABSTRACT

Research on the use of titanium dioxide (TiO_2) for water treatment has expanded to include the degradation of pharmaceuticals and personal care products (PPCPs). PPCPs are typically introduced in aqueous solutions during TiO_2 photocatalysis experiments using a water-miscible carrier solvent (e.g. methanol) to improve their solubility; however, carrier solvents may be detrimental to photocatalysis due to their scavenging effect. Although it is advisable to maintain the solvent at low concentrations, the influence of elevated concentrations of methanol or other solvents on photocatalysis has not been carefully explored. In this study, we examined the impacts of different methanol concentrations (0–0.2% v/v) on photocatalysis using P25 (commercial TiO_2) and TiO_2 nanomaterial synthesized via thermal and chemical oxidation (TCO). Scavenging of hydroxyl radicals by methanol was evident for both P25 and TCO but the effect was more prominent on TCO. Also, the photodegradation of some compounds using P25 were enhanced at low levels of methanol. Overall, this study highlights that trace amounts of methanol used as a carrier solvent can affect photocatalysis, especially in TiO_2 nanomaterials with low reactivity. This should be considered carefully in future experiments so that the results are not biased by the introduction of carrier solvents.

1. Introduction

Studies on the use of titanium dioxide (TiO_2) for environmental applications has grown rapidly since the discovery of its photocatalytic potential over four decades ago [1]. Among the semiconductors that can initiate photocatalytic processes, TiO_2 is the most widely used material due to its relatively higher activity, non-toxic effects, inert qualities, resistance to corrosion, and low associated costs [2]. The use of TiO_2 for a variety of industrial applications began in the 1990s, mainly as a paint additive and glass coating because of its self-cleaning and anti-fogging functions [3]. With advances in nanoscience and nanotechnology, alternative synthesis methods and improvement in TiO_2 structural properties continue to progress. Alongside this development is the pressing need for advanced, low-cost, and efficient water treatment technologies to address the declining clean water sources worldwide [4]. In addition, long-term droughts and increased water demands have motivated the development of new water reuse, recycling, and reclamation strategies (i.e., indirect potable or non-potable reuse systems) that stress the need for robust treatment technologies to handle a diversity of contaminants emanating from unconventional water sources [5]. The ubiquity of the so-called emerging contaminants of concern in source waters, primarily pharmaceuticals and personal care products (PPCPs), has been a subject of water research for a number of years due to their potential risks to aquatic and human health [6]. These combined challenges have encouraged several research and development studies that highlighted the potential use of TiO_2 photocatalysis for water treatment applications.

Numerous studies have suggested the use of TiO_2 photocatalysis in the effective degradation of PPCPs in water [7–9]. Much of the current work has also employed methanol as a carrier solvent when conducting TiO_2 photocatalytic degradation experiments on PPCPs (Table 1). This practice facilitates the introduction of the compounds into aqueous matrices, as some are poorly soluble in water. However, the presence of methanol can be detrimental to PPCP removal due to its ability to scavenge the electron holes [10] and/or the hydroxyl radicals [11] produced during photocatalysis. When an organic compound is present,

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Table 1
Selected studies that employed carrier solvents during experimental investigations of photocatalytic decomposition of pharmaceuticals.

Carrier Solvent	No. of compounds	Carrier solvent concentration (v/v)	Reference
Methanol	15	0.004%[a]	[9]
Methanol	1	0.17%	[17]
Acetonitirile	4	0.953%[a]	[33]
Methanol	15	0.004%[a]	[8]
Methanol	2	0.5%[b]	[34]
Methanol	1	0.01%	[35]
Methanol	3	N/A	[36]
Methanol	33	0.4%[a]	[37]
Methanol	15	0.004%[a]	[38]
Methanol	2	0.1%	[39]
Ethanol	2	0.075%[a]	[40]
Methanol	14	0.002%	[16]
Methanol	5	0.002%	[23]

[a] Calculated based on the data provided in the study.
[b] Calculated based on the highest concentration of the target chemical in the mixture (~5 mg/L). N/A = not available nor cannot be calculated from the information provided.

its degradation via TiO_2 photocatalysis occurs in two main pathways: (1) reactions via singlet electron transfer (SET) (i.e. hole-mediated and electron-donating processes); or, (2) reactions with hydroxyl radicals and other generated reactive oxygen species [12]. Methanol degradation is typically initiated by SET chemistry (i.e. hole-mediated) [12,13] and, in fact, it has been used as an efficient hole scavenger in photocatalytic experiments [12]. However, there is still a mixed interpretation of the degradation pathway of alcohols as studies have utilized methanol as a hydroxyl radical scavenger rather than a hole scavenger [11,14]. This practice was derived from experiments that did not observe the presence of ketone- and aldehyde-type intermediates which are indicator compounds for SET reactions [12]. Regardless of the mechanism, only a few studies have discussed the effects of the carrier solvent on their photocatalysis experiments [15–19]. Although methanol and other carrier solvents are typically maintained at low concentrations from 0.002% to 0.5% v/v (Table 1), it is still important to assess the scavenging effects of these low concentrations of solvents when determining the overall efficiency of TiO_2 photocatalysis in degrading pharmaceuticals or other similar chemicals.

In this study, we explored the influence of low levels of methanol additions (0%, 0.002%, 0.02% and 0.2% v/v) on photocatalytic degradation of 15 target compounds typically discharged in wastewater streams [20,21]. The photocatalysis of these representative contaminants using commercially available TiO_2 nanopowder (P25) was compared to a TiO_2 material synthesized using the thermal-chemical oxidation of titanium powder (TCO). The study examines the overall confounding effects of the use of methanol when conducting TiO_2 photocatalysis tests on PPCPs.

2. Materials and methods

2.1. Reagents and chemicals

Titanium powder (~325 mesh, 99.95%), hydrochloric acid (HCl), sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2) were purchased from Sigma-Aldrich while the commercial P25 powder (Aeroxide) was purchased from Evonik Industries. HPLC grade methanol (BDH) was purchased from VWR (Mississauga, ON) while ultrapure water was obtained from a MilliQ water purification system (MilliQ, EMD Millipore, Mississauga, ON). The 15 compounds included in this study have varying solubility and physical-chemical properties (Table 2) and were purchased from Sigma-Aldrich. Their chemical structures are presented in Fig. S4 (Supplementary information). Designated isotopically labeled standards were used for LC–MS/MS analysis and quantitation (except for monensin) and lorazepam was used as an internal standard (Table S2). These standards were purchased from CDN Isotopes Inc. (Pointe-Claire, QC, Canada), except for atorvastatin-d_5, which was purchased from Toronto Research Chemicals (Toronto, ON, Canada). The complete list of the deuterated standards employed in this study is provided in Table S2 (Supplementary material). All compounds (regular and deuterated standards) were dissolved in methanol as 1 g/L stock solutions and stored in amber glass vials in a −20 °C freezer.

2.2. Thermal-chemical oxidation method (TCO) for nanomaterial synthesis

Titanium powder (1 g) was soaked in 50 mL of 30% H_2O_2 in a 500-mL clear glass jar which was capped and heat treated for 4 h at 80 °C producing a titanium–titanium dioxide complex in solution. The remaining liquid (yellowish in appearance) was transferred into a second glass jar and dried at 80 °C for 12 h. The powdered material that remained after evaporation was pulverised and heat treated again at 600 °C for 4 h. After the heat treatment, the material was stored in a glass vial and kept in the dark at room temperature.

2.2.1. Nanomaterial characterization

The surface morphology of TiO_2 nanomaterials was characterized by a high resolution transmission electron microscope (HRTEM, JEOL 2010F) at the Canadian Centre for Electron Microscopy (CCEM). TEM samples were prepared by drop casting powder dispersions onto carbon grids. The X-ray photoelectron spectroscopy (XPS) was carried out to verify the presence of TiO_2. Measurement was conducted using VG Scientific ESCALab 250 system with an aluminum radiation source ($h\nu$ = 1486.6 eV) under ultra-high vacuum. A survey scan was collected at 50 eV pass energy, whereas individual scans (Ti2p and O1s) were collected at 20 eV pass energy. The atomic concentration was calculated using the CasaXPS software (Casa Software Ltd.).

The specific surface area was determined using Brunauer-Emmett-Teller (BET) surface analyzer (Quantachrome Autosorb iQ) using $N_{2(g)}$ adsorption data. The band gap of TiO_2 samples was determined by the diffuse reflectance spectra (DRS) using a Shimadzu UV-2501PC UV–vis-NIR spectrophotometer equipped with an integrating sphere accessory, using $N_{2(g)}$ as the reference. The details regarding the band gap analysis are described by Hu et al. [22]. A Raman spectrometer (Renishaw Ramanscope) equipped with a He-Ne laser (5 mW incident power, 633 nm wavelength) was used to obtain spectra associated with different TiO_2 crystalline phases. Specific information on the TiO_2 Raman mode description is found elsewhere [16].

2.3. Experimental setup

Two types of TiO_2 nanomaterials were tested in this study: (1) P25, a commercially available TiO_2 powder and (2) TCO, a powder derived from the thermal-chemical oxidation of titanium powder. Different concentrations of methanol were selected based on the range of values observed in published studies that used methanol as a carrier solvent (Table 1). For each set of experiments, an empty 1 L amber glass solvent bottle was spiked with 200 µL of the 10 mg/L pharmaceutical stock solution in methanol (diluted from 1 g/L solution) and dried at room temperature using $N_{2(g)}$. For P25 experiments, the pharmaceutical compounds were re-solubilized in 1 L ultrapure water and stirred at 1100 rpm for 5 min. Aliquots (300 mL) of this solution containing 2 µg/L of pharmaceuticals were transferred into three beakers for replication were then magnetically stirred (600 rpm) on a four-position stir plate equipped with an in-house designed UV-LED light source casing. Pre-measured P25 powder (30 mg) was added into each beaker and methanol was spiked immediately at different volumes (6, 60, and 600 µL) to obtain 0.002%, 0.02%, and 0.2% of methanol concentration (v/v). The experimental specifications of the photocatalytic batch reactors, including the light intensity, wavelength, and relative distance of the