



Oxidative power of aqueous non-irradiated TiO₂-H₂O₂ suspensions: Methylene blue degradation and the role of reactive oxygen species

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ABSTRACT

In the present study, the degradation of methylene blue in non-irradiated TiO₂-H₂O₂ suspensions was investigated. Five commercially available catalysts were characterized (BET surface area, zeta potential, hydrodynamic diameter) and their oxidative power was assessed by means of the degradation of methylene blue. A subsequent EPR study was made to verify and identify potential oxidative radicals. The results showed that all suspensions could degrade methylene blue significantly stronger compared to hydrogen peroxide alone. A broad variation between the different catalysts in their capability to adsorb dye molecules was found which was essential for decomposition of methylene blue in darkness. The highest degradation rate of all samples was found for Degussa P25 at neutral pH. EPR studies of this sample verified the presence of oxygen centred radicals namely hydroxyl ($\cdot\text{OH}$) and superoxide radicals ($\text{O}_2^{\cdot-}/\cdot\text{OOH}$). Non-irradiated TiO₂-H₂O₂ systems show great potential not only in dye removal applications but also in the field of disinfection where low concentrations of hydrogen peroxide are required and irradiation may not be feasible.

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1. Introduction

Titanium dioxide (TiO₂) is widely used as a catalyst in heterogeneous photocatalysis in applications such as waste water treatment [1], air purification [1] and disinfection [2] due to its photostability, chemical resistance and cost effectiveness [3]. The oxidative power of TiO₂ particles in aqueous suspension originates from the photogeneration of an electron-hole pair when irradiated ($h\nu > E_g$) and successive redox reactions with O₂/H₂O [4]. The capacity of TiO₂-UV-systems to degrade organic compounds is strongly related to the generation of reactive products or intermediates of these redox reactions, namely hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\text{O}_2^{\cdot-}$), hydroperoxyl radicals ($\cdot\text{OOH}$) and hydrogen peroxide (H₂O₂) [4]. The addition of H₂O₂ has been shown to accelerate TiO₂-assisted photodegradation by its intrinsic oxidative power, repression of electron-hole recombination and photocatalytic reduction to form $\cdot\text{OH}$ [5].

Current research focuses strongly on catalyst modifications to make oxidation processes accessible for visible light irradiation and thereby overcome the limitations of UV-irradiation [6–8]. How-

ever, TiO₂ particles have also shown to possess oxidative power in the absence of any light when interacting with H₂O₂ [9,10]. Hence, the intrinsic oxidative power of H₂O₂ could be enhanced by the addition of TiO₂ particles. The mechanism behind this Fenton-like reaction is still elusive and contrary studies on the topic have been published [11,12]. While the underlying reaction pathway is controversial, there is evidence that the oxidative behaviour is due to the generation of reactive oxygen species (ROS) at the catalyst surface [13,14]. This effect has mostly been studied in the context of nanoparticle toxicity [15–17] and only a few studies have investigated the potential of TiO₂-H₂O₂ systems to degrade organic compounds [9,10,18].

The possibility to degrade organic dyes such as methylene blue (MB) in the absence of light would greatly extend the range of applications for TiO₂ based degradation processes. The oxidative power of a vast selection of photocatalysts has been assessed and relevant operating parameters for the photodegradation of dyes have been addressed [19–22]. To our best knowledge, no such study exists for non-irradiated TiO₂-H₂O₂ systems. The aim of this study was to confirm and assess the oxidative power of five different catalysts in non-irradiated TiO₂-H₂O₂ systems. Special focus was placed on the role of pH dependent adsorption of MB onto the catalyst surface and its influence on the degradation efficacy. Furthermore, an EPR spin trapping study was conducted to verify the presence of ROS

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and contribute to the knowledge about the degradation mechanism of these systems.

2. Materials and methods

2.1. Materials

Five different TiO₂ powders were used in the present study (Table S1 1): Degussa P25 (**P25**; Evonik Degussa GmbH, Hanau Wolfgang, Germany), Kronos 1171 (**Kro**; Kronos International, Leverkusen, Germany), Hombitan Anatase (**Hom**; Sachtleben Chemie, Duisburg, Germany), Sigma Aldrich rutile (**Ald**; Sigma Aldrich, St. Louis Missouri, United States) and Sensient Eurovit (**Eur**; Sensient colours UK, Lynn Kings, United Kingdom). All powders are commercially available and were used as received without further purification.

Laboratory agent MB and H₂O₂ were used and dilutions were prepared using deionised water (Millipore, Billerica, MA, US). HCl and NaOH were used to adjust the pH. NaCl was used as an inert electrolyte for zeta-potential and hydrodynamic size measurements. For EPR studies, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was used as a spin trap without further purification. All chemicals apart from DMPO (Dojindo Molecular Technologies, Inc, Munich, Germany) were purchased from Sigma Aldrich.

2.2. Zeta potential, hydrodynamic diameter and BET surface area

For zeta potential and hydrodynamic diameter measurements, 50 mg of TiO₂ was added to 1 L 0.001 M NaCl and bath sonicated for 10 min to break up agglomerates. After a resting time of 20 min to allow aggregates to sediment, 300 ml of the supernatant was taken and divided in three stock solutions. Each stock solution was adjusted to pH 3, 6.7 and 9 using HCl and NaOH and stirred for 4 h for pH stabilisation. 1 mL of the sample was then introduced to a disposable folded cuvette (DTS1070, Malvern Instruments, Worcestershire, United Kingdom) and characterized with a Malvern Nano ZS Zetasizer (Malvern Instruments, Worcestershire, United Kingdom). Electrophoretic light scattering (ELS) was utilized to measure the zeta potential using the Smoluchowski equation. Dynamic light scattering (DLS) was used to determine the hydrodynamic diameter calculated derived from the Stokes-Einstein equation. Three measurements were performed for each sample and the same sample was used to measure zeta potential and hydrodynamic diameter.

The specific surface area (SSA) was determined by the adsorption of N₂ at -196 °C using a Micromeritics ASAP 2020 (Norcross, GA, USA). Prior to measurement, all samples were degassed for 12 h at 90 °C. The SSA was calculated using the multipoint Brunauer-Emmett-Teller (BET) method for adsorption values in the relative pressure range between 0.05 and 0.40.

2.3. Methylene blue adsorption and degradation

The oxidative power of all five TiO₂ powders were tested as followed: 50 mg TiO₂ (C_f = 1 g/L) was added to 47 mL 0.03 mM MB (stirred at 650 rpm) and the pH was adjusted with HCl or NaOH to pH 3, 6.7 or 9. The beaker was covered by an aluminium hood which was only removed quickly for the introduction of titrants or sample extraction to keep the exposure to ambient light at minimum. The suspension was stirred for 60 min to reach the adsorption equilibrium of MB on the TiO₂ particles. For UV-vis measurements of MB absorption, 2 mL samples were taken at 0 (no TiO₂-particles), 5, 10, 15, 30 and 60 min and centrifuged at 10 000 rpm for 1 min. 1.5 mL of the supernatant was then put in a disposable cuvette and analysed using a UVvis spectrophotometer (Lambda 25, PerkinElmer,

instruments, MA, USA). The absorbance was recorded for a wavelength range of 750 nm–500 nm and the sample was returned to the stock solution. A pre-study confirmed a maximum absorbance peak at 664 nm with no peak shift in the spectra during the degradation process. A Beer-Lambert diagram was established to correlate the maximum absorbance at 664 nm with different MB concentrations (0.005 mM–0.03 mM). Linear correlation (R² = 0.994) was found between absorbance and dye concentration within this range of concentrations.

After one hour of MB absorption, 3 mL of 50 vol.% H₂O₂ was introduced to the suspension to obtain a final concentration of C_f = 3 vol.% H₂O₂. Changes in pH caused by the introduction of H₂O₂ were adjusted with HCl or NaOH. For determination of MB degradation, samples were taken and measured according to the procedure described above at 0, 5, 10, 15, 30 and 60 min. All powders were tested in triplicates for each pH.

2.4. Electron paramagnetic resonance spectroscopy (EPR)

All EPR experiments were carried out under minimum ambient light. 20 mg TiO₂ was mixed with 10 ml 6% H₂O₂ for 30 s. 200 µL of this suspension was taken and introduced to 400 mM DMPO of the same volume. After handshaking for 5 s a sample of approximately 0.05 mL was introduced to a 1.7 mm OD capillary (WILMAD, Vineland, NJ, USA), sealed and inserted into a 707-SQ-250 quartz tube with 4 mm outer diameter (WILMAD, Vineland, NJ, USA). The sample was then placed in a universal rectangular TE₁₀₂ cavity and EPR measurements were started immediately using a BRUKER EleXsyS 560 X-band spectrometer (Rheinstetten, Germany). All measurements were performed at a microwave frequency of 9771 MHz and microwave power of 12.6 mW. Measurements were done at a centre field of 348.2 mT, a sweep field of 8 mT and a field scan rate of 0.048 mT/s. The field modulation frequency was set to 100 kHz with a modulation width of 0.08 mT. A time constant of 167 ms was used. A first harmonic order spectrum was recorded for each sample approx. 90 s after the introduction of the spin trap.

2.5. Statistics

Datasets were analysed using a normality and equal variance test prior to further statistical testing. One-way analysis of variance (ANOVA) and a subsequent pairwise comparison of data groups (TiO₂ + H₂O₂) versus a control group (H₂O₂ only) using Holm-Sidak method was done to determine statistical significance in dye degradation, zeta potential and hydrodynamic size. Probability of p < 0.05 was considered significant with n = 3 samples for each group. All statistical analyses were performed using SigmaPlot 13.0 (Systat Software Inc., Chicago, IL).

3. Results & discussion

3.1. Zeta potential, hydrodynamic diameter and BET surface area

The adsorption of dye molecules onto the catalyst surface may play an essential role in the irradiation independent degradation of MB. Therefore, all tested TiO₂ powders were characterized regarding surface charge (zeta potential) and potentially available adsorption sites (BET surface area and hydrodynamic diameter). Table 1 presents the zeta potential, hydrodynamic diameter and BET surface area of the five TiO₂ powders tested. An increase in pH resulted in more negative zeta potentials for all tested TiO₂ powders and the absolute values measured are consistent with previous results [23–25]. Interestingly, zeta potentials close to the isoelectric point (iep) were observed for Kro and Eur at pH 3. This was different from the other TiO₂ samples for which positive zeta potentials were

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