

Developing Composites of Polymer Microgels and Titania Nanoparticles for Photocatalytic Degradation

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ABSTRACT

Microcomposites composed of titanium dioxide nanoparticles embedded within cross-linked, thermally responsive microgels of poly(*N*-isopropylacrylamide) were prepared. These microcomposites showed rapid sedimentation, which is useful for gravity separation of the titania nanoparticles in applications such as environmental remediation. To investigate the degradation kinetics using these microcomposites in aqueous suspensions, methyl orange was employed as a model contaminant. The decline in the methyl orange concentration was monitored using UV-Vis spectroscopy. Degradation of methyl orange was also measured using only nanoparticles TiO₂ (Degussa™ P25) for comparison with the microcomposites. Experiments were performed at different pH conditions that spanned acidic, neutral, and basic conditions to gain insight into the interplay of TiO₂ surface charge, ionization of the polyelectrolyte chains in the microcomposites, and ionization of the methyl orange.

INTRODUCTION

Titanium dioxide is a common and widely studied photocatalyst due to its appealing attributes such as non-toxicity, chemical inertness and high photocatalytic activity¹⁻³. The large band gap of TiO₂ (3.2eV) permits it to absorb photons in the UV region, which results in production of electron-hole pairs that participate in redox reactions known to degrade simple organic species⁴. In recent years, there has been increased interest in use of nanosized titania powders due to enhancements in photocatalytic activity⁵⁻⁷. Because separation of suspended titania nanoparticles from water has been a major obstacle, use of very fine particles of titania in applications such as waste-water treatment have been limited. In a recent report⁸, we demonstrated the synthesis of novel microcomposites in aqueous media comprising of polymer gels on micron length scales that were loaded with Degussa™ P25 TiO₂ nanoparticles. Microcomposites with high mass fractions of titania (50-75wt%) were prepared that showed rapid sedimentation (~minutes), which is a useful characteristic for gravity separations. In this study we build on our previous body of work by investigating the photodegradation of a model organic dye, methyl orange, using the novel polymer-titania microcomposites. Kinetics of the photodegradation are evaluated by monitoring the changes in the methyl orange concentration using UV-Vis spectroscopy. The influence of pH of the solution, which influences the interactions between the poly(acrylic acid) (PAAc) in the polymer microgels, the titania surface and the methyl orange adsorbate is studied. Degradation of methyl orange using freely suspended titania is also conducted for comparison with the microcomposites.

EXPERIMENTAL: PHOTOCATALYTIC STUDY

Degradation studies were done using aqueous solutions containing 5 ppm of methyl orange (MO) and suspended microcomposites or free Degussa™ P25 particles such that the overall concentration of TiO₂ was 50, 100, or 200 ppm. The pH was adjusted using 0.1M HCl or 0.1M NaOH and degradation kinetics are reported here at a pH of 2±0.1 and 6.5±0.2. Photocatalysis was performed under illumination using two commercially available 15W Philips F15T8 black-light fluorescent bulbs

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(model 392233) that have spectral energy distribution centered at 352 nm (UVB radiation). The intensity of the radiation reaching the solution surface ($3.5\text{mJ}/\text{cm}^2$) was detected using a Chromaline UV Minder radiometer (UVM226) connected to a remote probe (UVM226S). Control experiments were performed under UV irradiation without the addition of any catalyst or microcomposites. Negligible decolorization (<1%) of the MO was observed confirming that the degradation of MO predominately occurs by photocatalysis using titania rather than photolysis. Dark adsorption was conducted for at least three hours before irradiation for adsorption of MO onto the TiO_2 surface. Aliquots of 1.5ml of the suspension were collected at regular intervals during the degradation experiments, centrifuged (10000g, 30mins) to completely remove any particles, and the peak absorbance was analyzed using a V-530 UV-Vis spectrophotometer (Jasco, MD).

RESULTS AND DISCUSSION

The microcomposites used in this study consist of porous, cross-linked PNIPAM microspheres with interpenetrating chains of PAAc that allow easy and efficient loading of titania nanoparticles within the IP-microgels⁸. The degradation of MO by both the microcomposite particles and freely suspended titania (Figure 1) is well described by a mono-exponential curve, suggesting that a pseudo-first-order reaction model can be used for describing the kinetic behavior of the photocatalysis. The apparent rate constant was obtained directly using a regression analysis of the experimentally observed decline in the peak height of MO absorbance as a function of time.

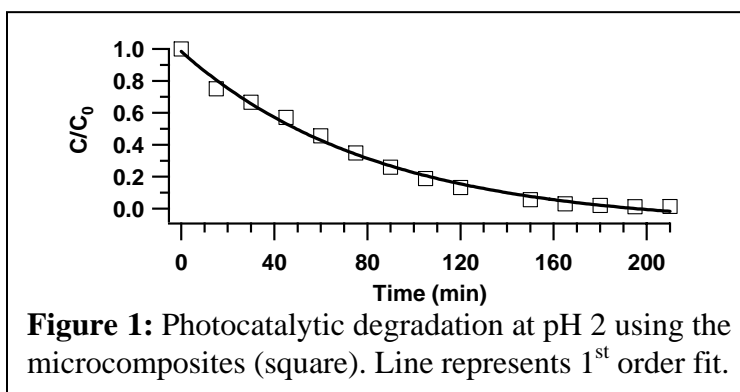


Figure 1: Photocatalytic degradation at pH 2 using the microcomposites (square). Line represents 1st order fit.

Table 1: Degradation rate constants

Concentration (PPM)	Freely Suspended TiO_2		Microcomposite	
	k (min^{-1}) pH 2	k (min^{-1}) pH 6.5	k (min^{-1}) pH 2	k (min^{-1}) pH 6.5
200	0.0130	0.0189	0.0136	0.0046
100	0.0093	0.0154	0.0084	0.0053
50	0.0036	0.0086	0.0033	0.0036

Table 1 shows that the reaction rate constant for the photodegradation of MO by the freely suspended TiO_2 at the acidic pH (~2) is 57% higher than the value obtained when the pH is near neutral conditions (~6.5). This effect has been reported in literature^{9, 10} and can be attributed to the increased active sites available for MO degradation. Regarding the pH variation our results correlate well with that of Kansal and co-workers¹¹, who also reported faster degradation kinetics under neutral (or basic) conditions using freely suspended TiO_2 . At a basic pH, both the surface of the titania (ISP ~ 6.5) and the MO are negatively charged, which impacts surface adsorption of MO. However, the presence of large quantities of hydroxyl ions on the particle surface as well as in the reaction medium favors the formation of $\text{OH}\cdot$ radicals that are responsible for the photocatalytic degradation of MO. Even though the concentration of OH^- ions in bulk solution is reduced at a neutral pH, the electrostatic repulsion between the titania surface, which is now relatively uncharged, and the MO is reduced favoring adsorption of the dye and its oxidation. In an acidic medium, although the adsorption of the MO is improved on the positively charged TiO_2 surface, the reduction in the concentration of the OH^- ions leads to a decrease in the rate constant.

Table 1 shows that a number of significant observations can be made when comparing the performance of the freely suspended titania with the microcomposites. At acidic conditions, the photodegradation by the microcomposites and the free titania show similar rate constants and variation with the concentration of titania. In contrast, near a neutral pH the photocatalytic degradation of MO using the microcomposites has much smaller rate constant and remains largely unaffected even when the concentration of titania is increased. A closer look at the structure of the microcomposite can give some insight into these differences. The PAAc chains that are present as interpenetrating chains⁸ in the microcomposite contain carboxylic acid groups that are mostly deprotonated above pH 4 and known to functionalize inorganic oxide surfaces¹²⁻¹⁴. Near a neutral pH, photocatalytic degradation of MO using the microcomposites is less because the negatively charged carboxylate groups interact with the oxide surface and can disrupt the adsorption of negatively charged hydroxyl species onto the titania surface due to electrostatic repulsion. Since the number of oxidative species is diminished, the lower photocatalytic oxidation reaction is experimentally manifested as a lower reaction rate constant. However, at pH 2 the PAAc is protonated and the titania surface within the microcomposite remains primarily unhindered. As a result, the photocatalytic performance of both the microcomposites and the freely suspended titania are comparable under acidic conditions.

Increasing the overall TiO₂ concentration in the solution from 50 to 200 ppm requires increasing the weight fraction of microcomposites in the solution. The resulting increase in polymer fraction has little influence at acidic conditions and the primary effect from increased titania surface sites dominates leading to faster photocatalysis. In contrast, at neutral pH conditions, the increase in the PAAc fraction balances the increase in titania and little change in the reaction rate constant can be observed as TiO₂ content changes from 50 ppm to 200 ppm.

CONCLUSIONS

The photocatalytic behavior of novel polymer-titania microcomposites that show rapid sedimentation in aqueous dispersions was studied. Using the photodegradation of a model organic dye, methyl orange, the photocatalytic behavior of the microcomposites was compared with freely suspended titania over a range of pH values. Under acidic conditions, the reaction rates were found to be identical while at a pH of 6.5, the freely suspended titania showed faster rate kinetics. However, at both pH values the microcomposites showed rapid sedimentation with settling velocities nearly 100 times faster than the freely suspended titania, which makes them promising candidates for applications such as wastewater remediation where the use of nanoparticles of TiO₂ is advantageous for photocatalysis but separation of the nanoparticles is difficult and time consuming.

ACKNOWLEDGEMENT

Financial support in the form of a graduate teaching assistantship from a NSF grant on Curriculum Reform (EEC-0530444) to CAC is gratefully acknowledged. The authors would also like to thank Bijith D. Mankidy for help with photocatalytic experimentation.

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