

Photodegradation of rhodamine B in aqueous solution via SiO₂@TiO₂ nano-spheres

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Abstract

Titania coated silica spheres (SiO₂@TiO₂) prepared by heterocoagulation of silica and titania nano-particles were investigated as catalyst in the photodegradation of rhodamine B (RB) in aqueous solution. The silica spheres were prepared by the well-known Stöber method and titania sol by a hydrolysis–condensation reaction in acidic media. The uncoated and coated particles were characterized by zeta potential measurements, acoustic attenuation spectroscopy and scanning electron microscopy. The degradation of the dye was induced by illuminating the coated spheres in aqueous solution with artificial solar light. The spectral distribution of the applied light corresponds to the sunlight spectrum on the earth's surface. Rhodamine B was used as model dye and decomposed completely to colourless end products after illumination. The decrease in concentration of rhodamine B was monitored by UV–vis spectroscopy and the total organic carbon (TOC) was determined in order to verify the degradation mechanism described elsewhere.

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1. Introduction

The application of semiconductors in heterogeneous photocatalysis to eliminate various pollutants in aqueous systems as well as in the air has gained significant attention in the last decade [1,2]. Especially titania (anatase), as it is non-toxic, highly chemically resistant and available at low cost, is investigated and already widely used as photocatalyst [3,4] in various applications, like degradation of air pollutants (NO_x, aromats, chlorofluorocarbons) [5–7] and water purification, e.g. degradation of various pollutants in waste waters [8–10] or detoxification of drinking [11–14] and surface waters, respectively [15].

The basic principle of titania photocatalysis in presence of moisture and oxygen under illumination with solar light is as follows: after excitation with light of an energy higher than the band gap (e.g. 3.2 eV for anatase), pairs of holes (h⁺) and electrons (e⁻) are formed, which can either recombine inside or on the surface of titania or react with adsorbed electron donors

(e.g. hydroxide ions) or acceptors (e.g. oxygen). The resulting hydroxyl radicals OH[•] and superoxide ions O₂^{-•} are known to be oxidants capable of oxidizing organic compounds [2,3,7].

Recently, titania films [16,17] were investigated as photocatalyst, as they are considered to be more applicable in practise than titania suspensions [18], as the films have not to be reclaimed from the reaction mixture as the powder suspensions have to. The main disadvantage for the application of titania films is that the photocatalytic activity is reduced compared to titania powder, due to less surface area. In this study, we present the application of titania coated silica spheres (SiO₂@TiO₂) as catalyst in the photodegradation of rhodamine B in aqueous solution, which can easily be reclaimed by sedimentation or filtration of the reaction mixture. The spheres were synthesized by heterocoagulation [19] of silica and titania nano-particles prepared by sol–gel techniques [20,21] and characterized by scanning electron microscopy (SEM), zeta potential measurements and acoustic attenuation spectroscopy. A main advantage of core–shell systems is that their properties can be varied with the size, composition and thickness of both core and shell [22,23]. Another advantage is the cost-reduction in the preparation of the catalyst. Since the described photocatalytic effects mainly concern

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the surface of the catalyst, the $\text{SiO}_2@\text{TiO}_2$ core–shell system is cheaper than pure titania as the inert silica core is well available as industrial by-product.

Rhodamine B is used as model organic dye, as it is the most important xanthene dye and dye pollutants from the textile industry are an important factor in environmental pollution and its degradation mechanism has been studied quite well [24–26]. The photodegradation of rhodamine B in aqueous solution via coated spheres was investigated by UV–vis spectroscopy and determination of the total organic carbon (TOC).

2. Experimental

2.1. Preparation of $\text{SiO}_2@\text{TiO}_2$

$\text{SiO}_2@\text{TiO}_2$ [19,27,28] was synthesized through heterocoagulation of silica spheres and titania nanosol. The silica particles were synthesized according to the method described by Stöber et al. [20]. To obtain particles in different sizes, the concentration of the used reagents was varied. Titania sol was prepared by a hydrolysis–condensation reaction of tetrapropylorthotitanate in ethanol as solvent. To peptize the intermediate gel, hydrochloric acid was added to the solution [21]. The coating was performed by gradual addition of titania sol to silica particles dispersed in ultra-pure water. The coating progress was monitored by zeta potential measurements. After complete coating of the silica particles, excess titania was removed through centrifugation (10,000 g, 10 min) and discarding the supernatant. The coated particles were then redispersed in ultra-pure deionized water. More details about the preparation are given elsewhere [19].

2.2. Characterization of $\text{SiO}_2@\text{TiO}_2$

The size of titania, silica and coated silica was measured using acoustic attenuation spectroscopy. The zeta potential of the particles was calculated from the colloidal vibration current (CVI) determined by electroacoustic measurements [29]. Both methods were performed by using a DT 1200 from Dispersion Technology. The phase composition of titania nano-particles was determined using Rietveld refining techniques with the fundamental parameter approach (Bruker AXS, Topas 2.1). The morphologies of silica and $\text{SiO}_2@\text{TiO}_2$ were investigated by scanning electron microscopy studies (SEM) (Philips XL 30 ESEM FEG).

2.3. Photodegradation of rhodamine B

The photodegradation of rhodamine B (RB) was investigated using a Suntest CPS+ from Atlas Material Testing Solutions as source for artificial sunlight. The applied radiation intensity for the experiments was 550 W/m^2 , which is equivalent to the solar intensity at high noon in the equatorial region. The test was performed with 100 mL of water containing 10^{-5} mol/L RB and $1.5 \cdot 10^{-3} \text{ wt\%}$ titania and dispersed $\text{SiO}_2@\text{TiO}_2$, respectively. The mixture was irradiated at the described intensity and the progress of the degradation of rhodamine B was monitored every hour by UV–vis spectroscopy (Varian Cary 50). In order

to quantify the concentration of rhodamine B, the UV–vis spectrometer was calibrated to a concentration range between 10^{-7} and 10^{-5} mol/L at a wavelength of 554 nm, which corresponds to the absorption maximum of RB. As a reference measurement 100 mL of water with 10^{-5} mol/L RB was also irradiated and monitored by UV–vis spectroscopy to investigate if degradation also occurs in the absence of the photocatalyst.

Additionally, TOC in the mixture was determined by using a highTOC II from Elementar Analysensysteme in order to investigate if the dye is only photobleached or completely degraded. For these investigations, a solution of 75 mL $4 \cdot 10^{-5} \text{ mol/L}$ RB plus 75 mL titania sol was used. This solution was also irradiated at the described conditions except for the fact that the UV filter was removed from the Suntest CPS+ in order to accelerate the degradation reaction as UV rays up to a wavelength of 250 nm are applied to the system. Samples at the beginning, in the middle and at the end of the experiment were taken for TOC analysis.

3. Results and discussion

3.1. Characteristics of $\text{SiO}_2@\text{TiO}_2$

The size of the titania nanosol was 10 nm according to acoustic attenuation measurements. Its isoelectric point (IEP) determined by zeta potential measurements is at pH 6.7 (Fig. 1). Besides that X-ray diffraction (XRD) studies were made to determine the phase composition via Rietveld quantification. These studies revealed anatase as major phase and rutile as minor phase. Exact quantification was not possible due to the lack of sharp reflection signals in the diffraction pattern, as consequence of the nano-crystalline character of titania.

Silica spheres with a diameter of 220, 470 and 590 nm according to acoustic attenuation spectroscopy were synthesized. Zeta potential measurements showed that in the investigated pH range (3.0–11.0) the zeta potential is negative. The IEP for the particles is at pH 1.0–2.0 depending on the particle size. Fig. 1 shows the zeta potential versus the pH value for 220 nm sized silica particles. In order to investigate the morphology of the synthesized

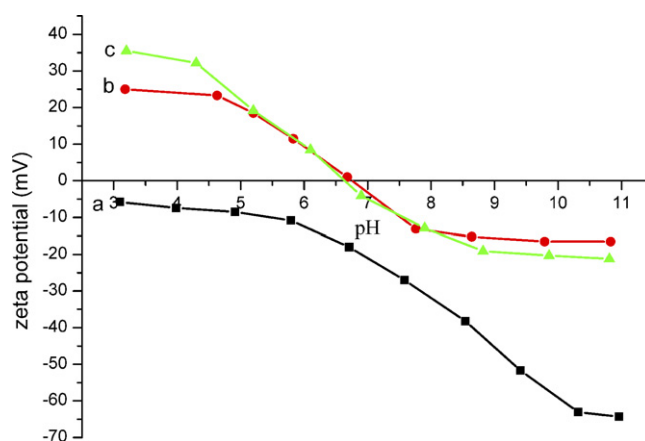


Fig. 1. Change in zeta potential with the pH of silica (220 nm) (a), titania nanosol (10 nm) (b) and $\text{SiO}_2@\text{TiO}_2$ (470 nm) (c).

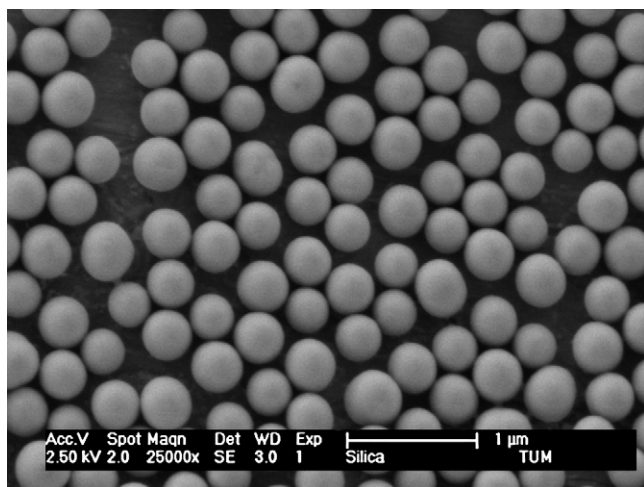


Fig. 2. SEM image of the synthesized silica particles.

particles, SEM studies were performed. Fig. 2 shows a SEM image of the silica particles. The image illustrates that the particles are spherical and have a smooth surface.

The coating was carried out by gradual addition of titania sol to the aqueous silica dispersion, which leads to heterocoagulation. In terms of this experiment, the smaller titania particles are bound on the surface of the silica spheres (Fig. 3). Important for this approach is the control of the pH value, as the particles have to be oppositionally charged for the coating to take place. A pH of 7.5 for silica and 2.0 for titania was used, as it appeared to be a good compromise between colloidal stability and surface charge.

The progress of coating was monitored by zeta potential measurements. In the course of the experiment, the pH drops from 7.5 to 2.5–3.0 after the last addition of titania sol and the zeta potential becomes more and more positive, which is a consequence of the decreasing pH and the coating with titania, until a plateau is reached. At this plateau, where the zeta potential does not change anymore (except for small changes related to fluctuations in pH), the coating process is complete and the silica spheres are fully covered by titania. To verify the success of the coating, the zeta potential of the coated silica spheres was measured in dependency of the pH. As can be seen in Fig. 1,

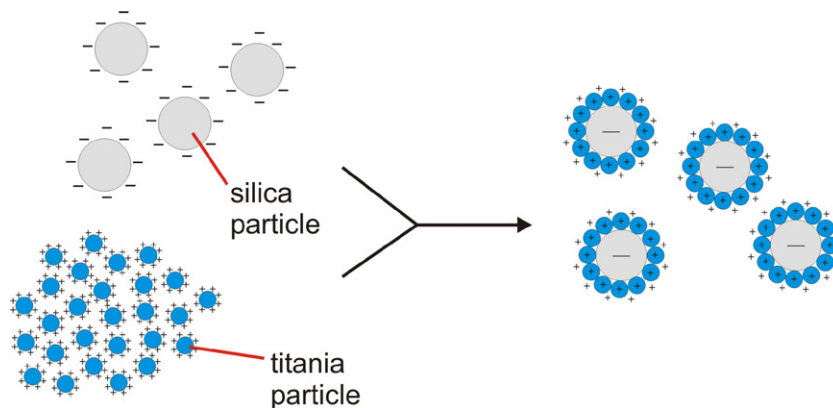


Fig. 3. Schematic drawing of the coating process by heterocoagulation.

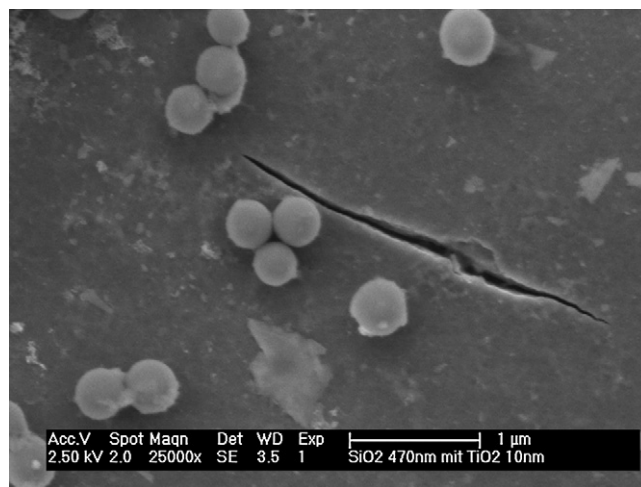


Fig. 4. SEM image of the titania coated silica spheres.

the coated particles exhibit almost the same pH dependency as pure titania, which leads to the conclusion that the silica spheres were successfully coated with titania. Furthermore, SEM studies of the coated spheres were performed, which illustrate that the particles are still monodisperse and spherical, but the surface is not smooth anymore (Fig. 4). This rough surface is related to the coating with titania.

3.2. Photodegradation of rhodamine B in the absence of TiO_2

Fig. 5 shows the decrease in RB concentration determined by UV–vis spectroscopy versus illumination time in presence of titania nano-particles, coated silica spheres and absence of both. The reference sample is not photodegraded to a great extent. The concentration only decreases by about 10% during the experiment. The reaction mechanism in absence of titania and presence of oxygen includes the following possible steps [16,17,24,26]:



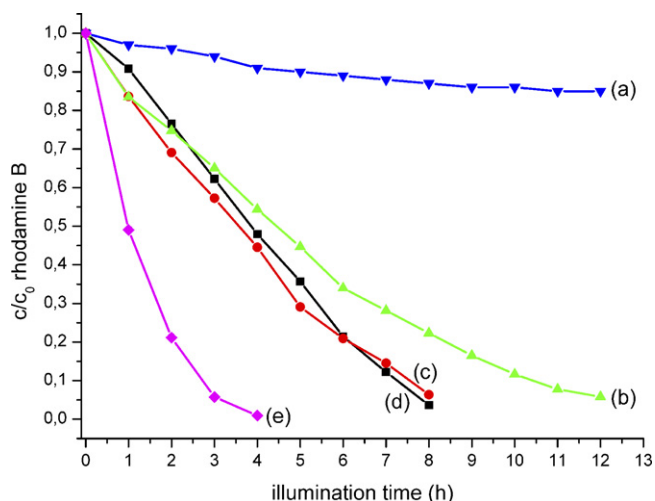


Fig. 5. Decrease in rhodamine B concentration over the time of pure rhodamine B aqueous solution (a) and in presence of SiO₂@TiO₂ (590 nm) (b), SiO₂@TiO₂ (470 nm) (c), SiO₂@TiO₂ (220 nm) (d) and titania nanosol (e).



The excitation of RB (Eq. (1)) and irradiation with visible light/UV rays is followed by the reduction of O₂ to O₂^{-•} by RB^{*} (Eq. (2)). O₂^{-•} reacts with a proton (from the autoprotolysis of the solvent water) to OOH[•] (Eq. (3)). In total, the cationic dye radical is degraded to carbon dioxide, water and mineral acids via rhodamine as intermediate (Eq. (4)). In case of our experiment, the rhodamine intermediate could not be detected in the UV–vis spectroscopy (Fig. 6), only a decrease in RB concentration was found. Qu et al. [26] reported that OOH[•] and OH[•] are necessary for the *N*-deethylation of RB, which in turn is necessary for the complete degradation of the dye. Qu et al. also reported that Eq. (2) is a very slow reaction compared to the reaction of the excited dye with titania (Eq. (5)). The very slow *N*-deethylation followed by a much faster degradation of RB through OOH[•] is a possible explanation for the decrease in absorbance of the dye. The fact that the degradation without a detectable rhodamine intermediate occurs was also reported by

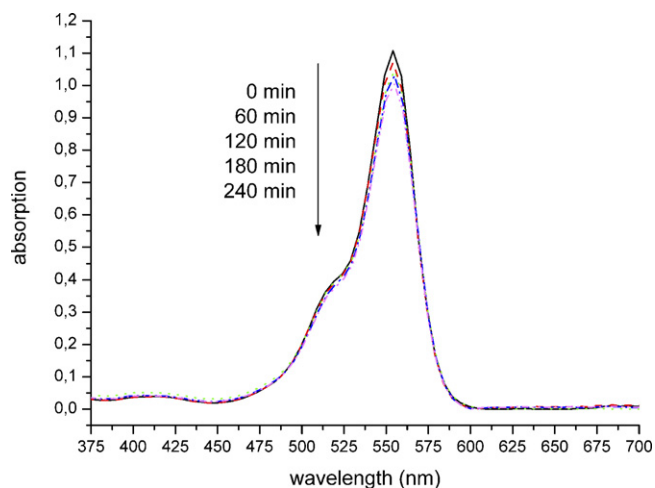


Fig. 6. Absorption spectra of rhodamine B aqueous solution during illumination.

Wu and Zhang [17]. Pure photobleaching, with aromatic hydrocarbons as final product is no possible explanation, as no rise in absorption at 225 nm – typical for aromatic rings – can be found.

3.3. Photodegradation of rhodamine B in the presence of TiO₂

In case of titania nanosol, the degradation is fastest and the concentration follows an exponential decay. After an irradiation time of about 4 h, the rhodamine is completely decomposed according to UV–vis spectroscopy (Figs. 5 and 7) and a colourless solution is obtained. The degradation of the dye assisted by SiO₂@TiO₂. Fig. 5 shows almost a linear decay for the decrease in concentration for all particle sizes. Comparing differently sized coated silica particles, the degradation slows down with rising particle diameter. This is related to the fact that smaller particles have a higher specific surface area than larger ones; hence, the mass proportion of titania as coating on the silica surface is increasing with decreasing particle diameter.

The illumination time for complete degradation doubles if pure titania sol is compared with 220 nm sized SiO₂@TiO₂, but the difference between 220 and 470 nm sized SiO₂@TiO₂ is quite small. After 8 h of illumination, the RB concentration in case of the 470 nm sized particles is only slightly higher than the one of the 220 nm sized particles. The 590 nm sized SiO₂@TiO₂ behave different, the degradation is much slower. Compared with the 470 nm sized particles, it takes about additional 3.5 h until complete degradation of the dye according to UV–vis spectroscopy. For the largest particles, the degradation reaction slows down significantly at longer irradiation times. This is not observed in case of the smaller particles. The slow-down of the reaction is possibly due to the faster sedimentation of the 590 nm sized particles. Without stirring, the particles do not stay in suspension as long as the smaller particles do and therefore the diffusion path for unreacted molecules towards the active titania surface increases, resulting in a slowdown of the overall degradation process.

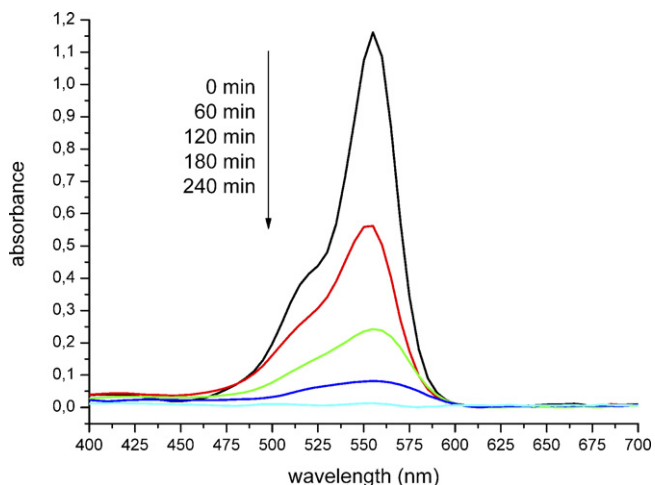


Fig. 7. Absorption spectra of rhodamine B aqueous solution in presence of titania nanosol during illumination.

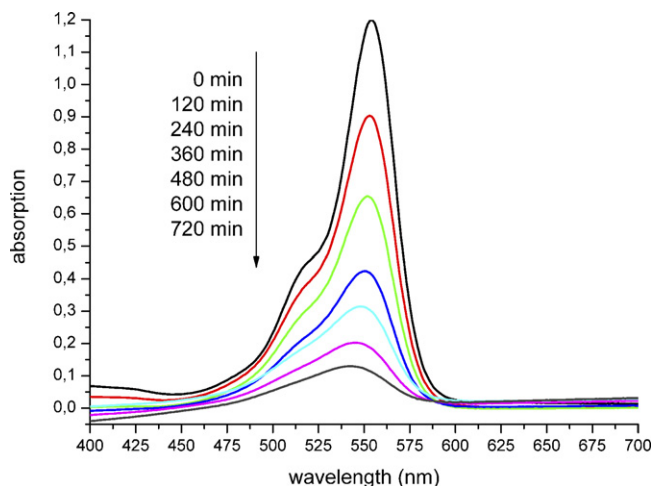


Fig. 8. Absorption spectra of rhodamine B aqueous solution in presence of $\text{SiO}_2@\text{TiO}_2$ (590 nm) during illumination.

In Fig. 8, UV–vis spectra after different illumination times of a rhodamine B solution with the 590 nm sized $\text{SiO}_2@\text{TiO}_2$ spheres are shown. As can be seen from the figure, the maximum absorption peak at 554 nm gradually decreases during the illumination. Like in the case of RB without any additives, no blue-shift of the absorption maximum to 498 nm could be observed at any time of illumination. According to Watanabe et al. [24] the blue-shift in the absorption maximum is related to the *N*-deethylation of rhodamine B to rhodamine (Fig. 9), the major intermediate in the degradation of rhodamine B. As mentioned above, the absence of the rhodamine peak does not necessarily mean that the *N*-deethylation does not take place in presence of TiO_2 or $\text{SiO}_2@\text{TiO}_2$. Since there are no additional peaks appearing in the UV–vis spectra in the course of the experiment either using titania nano-particles or $\text{SiO}_2@\text{TiO}_2$, the dye is completely degraded and not only photobleached. In presence of titania or $\text{SiO}_2@\text{TiO}_2$ under visible light/UV illumination additional reactions can occur [16,17,24,26]:

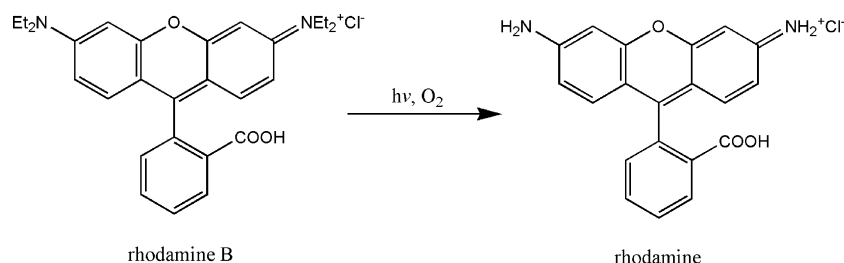
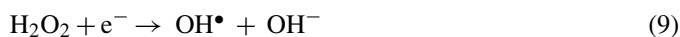
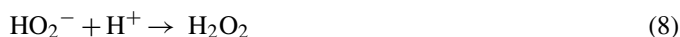
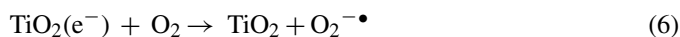
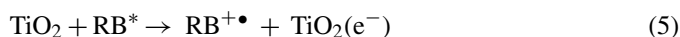
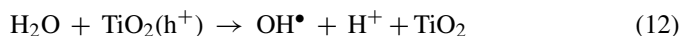
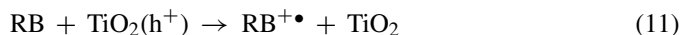
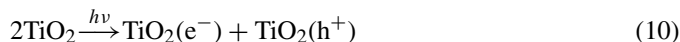


Fig. 9. *N*-deethylation of rhodamine B to rhodamine [23].

These equations refer to the case of visible light illumination, under UV irradiation; titania is excited directly, leading to the following reactions:



Titania can be excited directly or indirectly through RB. If excited indirectly, the reaction with oxygen leads to the formation of $\text{O}_2^{\bullet-}$ (Eq. (6)). From subsequent reactions after the formation of the superoxide ion (Eqs. (7)–(9)) hydroxyl radicals are formed. The direct excitation of titania through UV rays also leads to the cationic dye radical $\text{RB}^{\bullet+}$ and OH^\bullet (Eqs. (10)–(12)). For the reaction of water respectively RB with the electron holes of the excited titania, the adsorption of both on the titania surface is necessary. As already mentioned above, the formation of OH^\bullet is necessary for the *N*-deethylation of RB and therefore required for the complete degradation of RB.

According to UV–vis spectroscopy after illumination of the samples RB has disappeared and no other products detectable by UV–vis spectroscopy are left in the reaction mixture. To prove if the concentration of the organic carbon decreases in course of the experiment, TOC measurements were carried out. A complete disappearance of organic carbon would confirm the complete degradation of RB, whereas only a small decrease in TOC would lead to the assumption that only photobleaching occurs. Fig. 10 shows the normalized TOC in dependency of the illumination time for the RB degradation assisted by titania sol. After 3 h illumination time, no RB could be detected by UV–vis spectroscopy and the carbon concentration decreased by about 70% of the initial concentration. This demonstrates that no RB is left in the reaction mixture, but it also seems to be certain that after the decolorization of the dye, there is still some organic carbon left – likely aldehydes/carboxylic acids – but no aromatic rings, since these also could not be detected. So the reaction time for the complete degradation is longer than for complete disappearance of RB in UV–vis spectra.

Additionally, the rate constants for the degradation of RB according to UV–vis spectroscopy were determined, assuming pseudo-first-order reaction kinetics [17]:

$$\ln\left(\frac{c}{c_0}\right) = -kt \quad (13)$$

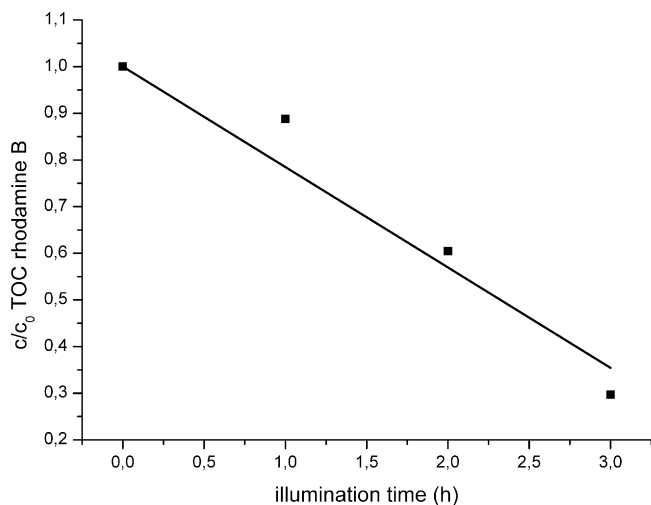


Fig. 10. Decrease in TOC of rhodamine B aqueous solution in presence of titania nanosol during illumination.

where c/c_0 is the normalized RB concentration and k is the rate constant. In comparison to the data of Wu and Zhang [17] who determined k as 0.01173 min^{-1} , our determined rate constants for pure titania and $\text{SiO}_2@ \text{TiO}_2$ were 0.01719 min^{-1} for the titania sol, respectively 0.00348 min^{-1} for $\text{SiO}_2@ \text{TiO}_2$ (590 nm), 0.00465 min^{-1} for $\text{SiO}_2@ \text{TiO}_2$ (470 nm) and 0.00473 min^{-1} for $\text{SiO}_2@ \text{TiO}_2$ (220 nm) (Fig. 11). This confirms the fact mentioned in the beginning that the sol is more reactive than the film, but cannot be reclaimed. The coated spheres show a significant lower reactivity compared to titania sol or film, but can be easily reclaimed.

All experiments demonstrated that the titania coated silica particles have a significant photocatalytic activity towards degrading the dye in aqueous solution. Only the large $\text{SiO}_2@ \text{TiO}_2$ particles do not perform very well in this experimental setup due to sedimentation effects. For further experiments and practical applications this can be prevented by stirring or pumping the suspension. The experiments also showed that RB was completely degraded and not only photobleached according to the known degradation mechanisms.

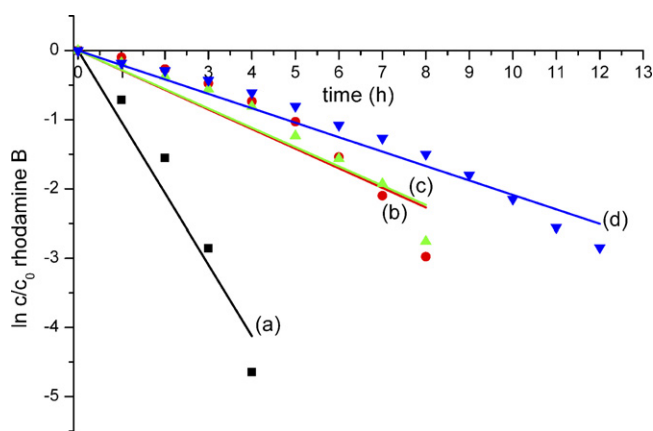


Fig. 11. $\ln(c/c_0)$ of rhodamine B concentration versus time for titania sol (a), $\text{SiO}_2@ \text{TiO}_2$ (220 nm) (b), $\text{SiO}_2@ \text{TiO}_2$ (470 nm) (c) and $\text{SiO}_2@ \text{TiO}_2$ (590 nm) (d). The slope refers to the rate constant k .

It must be stated that the experimental conditions do not represent the solar radiation in middle Europe, as the solar radiation in middle Europe is not as high as the one applied in the experiment, so degradation under European conditions should be slower. Even though the particles have their advantages as they are non-toxic and can be reclaimed and therefore can be used in cycle. The fast sedimentation of coarse particles could be utilized for example in water purification plants. In comparison with the titania nano-particles, which have a higher photocatalytic activity, the coated particles could be used as one step in water purification as they easily can be separated from the purified water through sedimentation, e.g. simply stopping to stir or pump the water. This separation is not possible when using the titania sol, as it will not sediment without flocculation aids due to its colloidal particle size. Before the application of the $\text{SiO}_2@ \text{TiO}_2$ particles for real waste waters, more investigations have to be made in order to test the photocatalytic activity regarding other organic as well as biological pollutants, get more experience in recovering the catalyst and collect data about the activity of recovered particles.

4. Summary

The experiments showed that the titania coated silica particles have a significant photocatalytic activity regarding the degradation of rhodamine B in aqueous solution under solar light irradiation and that the dye was completely degraded and not only photobleached. The coated particles are easily available through well-known one-step synthesis followed by a heterocoagulation. Further investigations will be made in order to determine the photocatalytic activity when using other hydrocarbons as pollutants in water.

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