Photocatalytic degradation of methylene blue by anatase TiO2 coating

Nikolai Desch[1], Angela Rheindorf[1], Cornelia Fassbender[1], Marc Sloot[1], and Markus Lake[1]

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Abstract

Photocatalytic coatings have the potential to contribute to the purification of water via an advanced oxidation process (AOP) [1]. A commonly used method for analyzing the mechanism of the photocatalytic performance of a given reactor type is to document the degradation behavior in a solution containing methylene blue. However, since methylene blue is rather unstable, the degradation results should be viewed critically. In this work, the degradation behavior of a test solution with methylene blue on quartz glass surfaces coated with photocatalytic titanium dioxide (TiO_2) of the anatase modification was investigated through a variety of different light sources. The coating was deposited by the reactive pulsed DC magnetron sputtering (MSIP-PVD) method described in [2], while the quartz glasses were coated with a 100 nm thick TiO_2 coating. The same glasses were used for all experiments with TiO_2. In the determination of the degradation rate, additional experiments were performed using pure quartz glass without any coating, which made it possible to examine the influence of different light sources on the degradation rate of methylene blue in general. Three different light sources, namely UV-A, UV-C, and simple fluorescent lamps were used in this study. The concentration of methylene blue was recorded by photo spectrometer in 10-minute increments throughout the experiment and the experiments were performed for 24 hours in all cases.

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Keywords: TiO_2, photocatalytic activity, anatase, photocatalytic dye removal, physical vapor deposition, methylene blue, quartz glass, methylene blue

Abstract

Photocatalytic coatings have the potential to contribute to the purification of water via an advanced oxidation process (AOP) [1]. A commonly used method for analyzing the mechanism of the photocatalytic performance of a given reactor type is to document the degradation behavior in a solution containing methylene blue. However, since methylene blue is rather unstable, the degradation results should be viewed critically. In this work, the degradation behavior of a test solution with methylene blue on quartz glass surfaces coated with photocatalytic titanium dioxide (TiO_2) of the anatase modification was investigated through a variety of

different light sources. The coating was deposited by the reactive pulsed DC magnetron sputtering (MSIP-PVD) method described in [2], while the quartz glasses were coated with a 100 nm thick TiO_2 coating. The same glasses were used for all experiments with TiO_2. In the determination of the degradation rate, additional experiments were performed using pure quartz glass without any coating, which made it possible to examine the influence of different light sources on the degradation rate of methylene blue in general. Three different light sources, namely UV-A, UV-C, and simple fluorescent lamps were used in this study. The concentration of methylene blue was recorded by photo spectrometer in 10-minute increments throughout the experiment and the experiments were performed for 24 hours in all cases.

1. Introduction

More than ever, our modern world is currently facing the threat of environmental pollution in many different forms. Particularly concerning the availability of clean drinking water and the treatment of wastewater, the need for novel environmentally friendly purification methods is rapidly gaining significance. Poor water quality and the lack of wastewater treatment are the root causes of a variety of diseases that severely impact human health around the world [3–6]. Research shows that even airborne aerosols from wastewater can carry microbial contamination and affect nearby regions, threatening the health of people living in coastal areas [3]. In addition, pollutants from wastewater runoff can seep into groundwater that is used as a drinking water source. Both chemical and microbiological contaminants from wastewater are still detectable in groundwater and thus have an impact on the quality of the clean water supply chain. Although groundwater contamination by wastewater is an indirect process, it is a serious and common problem in many regions [5].

The consequences of water pollution for human health and the environment have been studied extensively. In this context, it should be noted that contamination can occur at the water supply, during treatment, or at the point of delivery [4]. The results of such investigations show that although certain aspects of pollution – such as the region or the origin of the pollution – are often local factors, the common widespread problem is always a threat to human health and a clean environment. Pollutants can be microorganisms, heavy metals, pharmaceutical residues, pesticides, or other harmful chemical substances that may be present in wastewater. From the moment these components pollute water sources, it becomes complicated and costly to remove them [7].

Additionally, human consumption of pharmaceuticals, as well as the use of pharmaceuticals in the animal food chain, is a further source of increasing wastewater contamination since not all of the active ingredients of pharmaceuticals are absorbed by the body and some are released and subsequently enter the wastewater system. This is due to the design of some pharmaceuticals that are meant to be stable and not easily degradable to interact with the targeted molecules in the body. Conventional wastewater treatment systems are not efficient enough to remove all of these pharmaceuticals from wastewater and, as a result, the residues end up in surface waters and subsequently in drinking water supplies. The discharge of avoidable substances into waste water should be prevented as far as possible [8], whereby the maximum exposure limits in drinking water per liter are sometimes in the micro- or even nanogram range. Since conventional treatment methods are limited in their ability to remove a wide range of different nanoscale contaminants, often leaving many residues in the waste water [7, 8], extensive research and development efforts are currently being undertaken to develop novel water treatment concepts [7]. The advanced oxidation process (AOP) is an important component of water treatment methods that can be used to remove various contaminants from water. The degradation of contaminants occurs through the generation of strong oxidants such as HO, H_2O_2, O_3, and O_2 which react with the contaminants present in the water. The generated radicals provide many different pathways for the mineralization of various contaminants and, even in instances where the contaminants are not completely mineralized, their chemical bonds are broken and they are no longer harmful [9].

2. Photocatalytic Degradation via the Advanced Oxidation Process

TiO_2 in the anatase modification as a photocatalytic coating has the advantage of being chemically inert. While TiO_2 was previously classified as a potential carcinogen, due to a lack of evidence confirming this supposition in numerous in-depth studies, the opposite view is increasingly held. As a result, its EU classification of TiO_2as a potential carcinogen has also recently been withdrawn [10–12]. The discovery of the photocatalytic properties of TiO_2 has led to great interest in its potential for environmental applications [13]. Environmentally friendly production of the desired coating is possible with the use of modern coating technologies such as magnetron sputtering (MSIP-PVD), a commercial thin film deposition technique related to physical vapor deposition (PVD). Since a substrate temperature below 250 °C is preferred for the deposition of the anatase phase, and MSIP-PVD allows these temperatures to be maintained, this eliminates the need for post-deposition annealing [2, 14, 15]. When UV light is irradiated onto a TiO_2 photocatalytic surface and the photon energy is at least equal to or greater than its bandgap energy, an electron-hole pair – consisting of a free electron and a free electron hole – will simultaneously be formed. Both can move freely to the photocatalytic surface of TiO_2 and get trapped there. From this state, the trapped electron e^-_{tr} and the trapped electron hole h^+_{tr} will react with the molecules that are present. The trapped electrons and holes lead to a variety of reactions. One of many subsequent reactions is driven by photogenerated electrons causing reduction, ((1) in Figure 1), while another reaction is driven by photogenerated holes causing oxidation, ((2) in Figure 1) [16]. Concerning this aspect, we refer to the very thorough description and research on this topic that can be found in [16]. Furthermore, a great deal of research is also being conducted to explain other reaction kinetics that occur due to photocatalysis. The reactions shown in Figure 1 are just a few examples that generate free radicals which lead to the advanced oxidation process and have the potential to completely mineralize pollutants present in water. The radicals needed to drive the advanced oxidation process can subsequently be used to purify water. Photocatalytic coating systems are thus a promising approach to water purification and have a proven track record of excellent performance for continuous operation in photocatalytic water treatment reactors [9, 17–19].

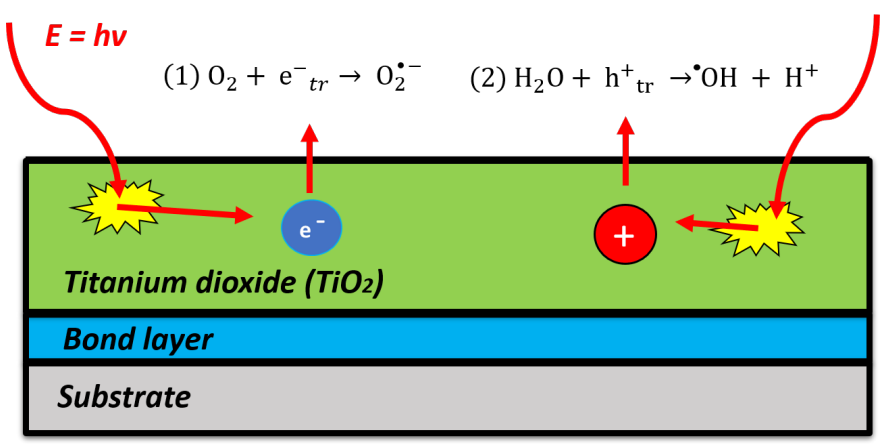


Figure 1: Example of processes occurring due to UV irradiation on a TiO_2 surface [16] , schematic illustration of the cross-section of the surface coating produced in this study

To demonstrate the general degradation mechanism, methylene blue degradation is often used in an aqueous solution as a testing fluid [13, 18–21]. However, examining the photocatalytic effect based on the degradation behavior of methylene blue may lead to misinterpretation of the data due to the poor stability of methylene blue, since the degradation of methylene blue may even occur in the absence of light exposure. As a result, the inclusion of reference experiments is important, which is why the DIN 52980 [20] recommends determining the degradation rate with and without light exposure for the same duration and subtracting

the dark degradation without light exposure from the light-exposed degradation. In this study, only the effect of the different light sources and the influence of the coating on the degradation of methylene blue was analyzed.

3. Experimental procedure

A scheme of the photocatalytic reactor configuration used for the degradation of methylene blue from an aqueous solution is shown in Figure 2. Two photocatalytic reactors were used in series and the methylene blue solution was stored in a closed tank. The solution was pumped from a 5 l reservoir through both photocatalytic reactors by a peristaltic pump and the pumping flow was kept constant at 0.5 l/minute during all experiments. The concentration of methylene blue was monitored through a bypass with a spectrometer (Perkin Elmer Lambda 2 UV/VIS Spectrometer). The absorbance of methylene blue was measured at the wavelength of 665 nm and the absorbance was recorded every 10 minutes for the duration of the experiment (24 hours).

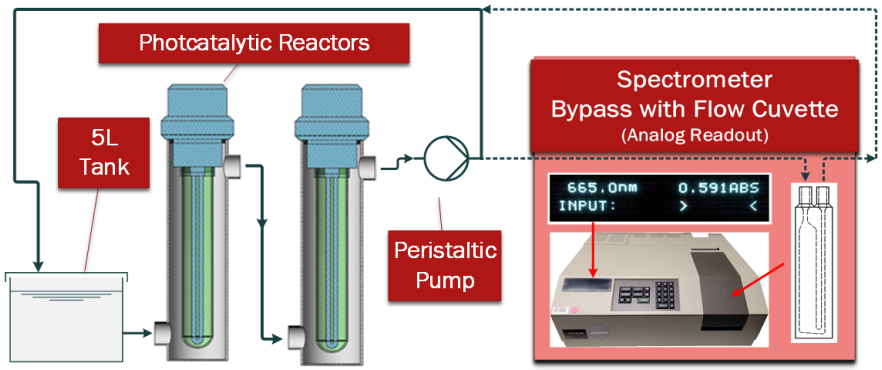


Figure 2: Schematic illustration of the photocatalytic reactor with spectrometer bypass

Figure 3 shows a schematic illustration of the cross-section of a photocatalytic reactor. For each experiment, two 11 W G23 light sources were used. The light sources were powered using a power supply that also held the coated and uncoated quartz glasses. In the case of the coated quartz glass, the TiO_2 coating was applied with a thickness of 100 nm. Between the TiO_2 coating and the quartz glass, a 20 nm pure titanium bond layer was applied. The volume of aqueous solution of methylene contained in a single photocatalytic reactor measured 410 ml. The inlet methylene blue solution was at the bottom of the reactor and the outlet was located at the top. Figure 3 (on the right) shows the coated quartz glass after use in the experiments. The light source used for the UV-C degradation experiments was a Philips TUV PL-S 11W/2P G23, EAN 8711500624888. For the UV-A experiments, the light source was a Philips Actinic BL UV-A PL-S 11W/10/2P G23 EAN 8711500952011. The third type of light source was an Osram Dulux S G23 EAN 4050300010618. In the case of the coated quartz glass, the coated and fully immersed glass surface area was 0.0225 m^2 for one reactor. When combined, the two reactors had a total of 0.045 m^2 of coated surface area and 22 W power of light intensity, resulting in a power density of approximately 488 W/m^2. The coating was illuminated from the back side of the quartz glass. The aqueous solution of methylene blue was freshly prepared with deionized water for every experiment. To obtain a volume of exactly 5 l of the solution, 25 mg of methylene blue was dissolved in deionized water prior to the start of all experiments and mixed for 5 minutes before the tank was filled. Once the tank was filled, the peristaltic pump was set at 2 l/min for 15 minutes before the light was turned on. After 15 minutes of pre-pumping, the absorbance was constant, the light was turned on, and the experiment commenced.

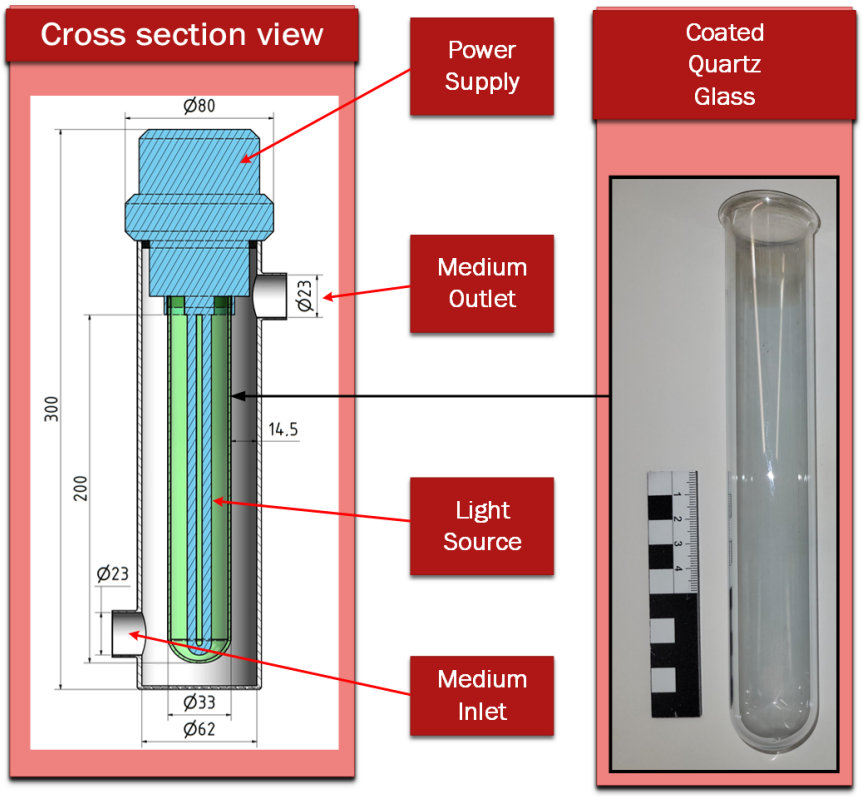
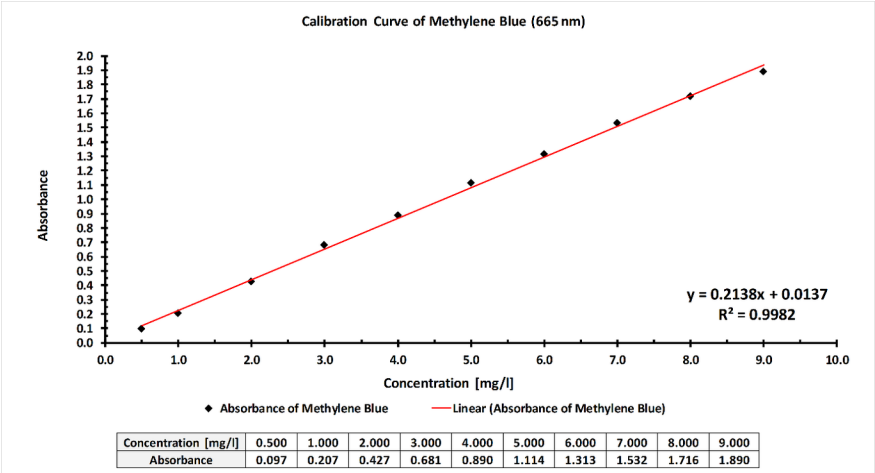


Figure 3: Detailed cross-section view of the photocatalytic reactor

When the light was turned on, the measuring of the absorbance was also started. Subsequently, the experiment was conducted in a room with no additional light turned on to keep the influence of unwanted light to a minimum. The formula of methylene blue used in this study was $C_{16}H_{18}ClN_3S \cdot 3H_2O$ and has a molecular weight of 373.9 g/mol. Prior to the experiments of photocatalytic methylene blue degradation, a calibration curve of methylene blue was prepared (Figure 4). In total, 10 different concentrations (0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 9.0 mg/l) of methylene blue were freshly prepared and every sample was measured in a clean glass cuvette using a spectrometer. The formula $y = 0.2138x + 0.0137$ was derived from the measured absorbances at different concentrations and the coefficient of determination (R^2) was 0.9982.



Concentration [mg/l]	0.500	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000
Absorbance	0.097	0.207	0.427	0.681	0.890	1.114	1.313	1.532	1.716	1.890

Figure 4: Calibration curve of methylene blue at 665 nm

4. Results

An anatase TiO_2 coating was used for the photocatalytic degradation of methylene blue dye. To determine the stability of methylene blue dye under different light sources, two coated and two uncoated quartz glasses were used. In the case of the coated quartz glass, the TiO_2 layer was almost completely transparent to the light source. As expected, when no photocatalytic coating was applied to the quartz glass surface, degradation of the methylene blue dye also occurred in all experiments. The comparison of the recorded concentration of methylene blue dye with the use of UV-C lamps is shown in Figure 5. As indicated in the graph, the degradation of methylene blue dye was much stronger without the photocatalytic coating. In addition, the degradation of methylene blue dye was non-linear in this case. The calculated relative concentration of methylene blue was 0.101 mg/l after 24 hours of treatment which corresponds to a degradation of 22.4 mg of methylene blue. Compared to the 24-hour degradation with the coating applied, the degradation behavior was more linear, and a relative concentration of 0.470 mg/l was measured at the end of the experiment. Calculated from the relative concentration, in this case, 13.1 mg was degraded during the experiment.

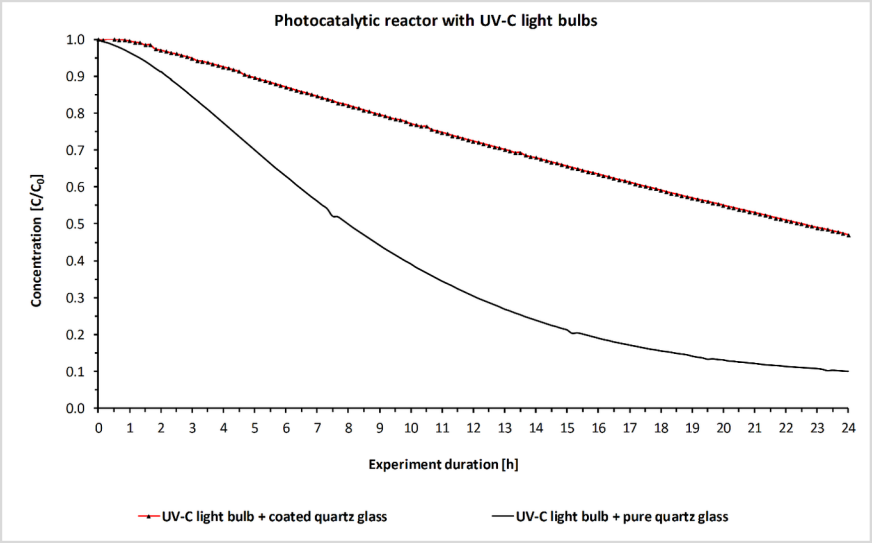


Figure 5: Reactor setup with a total of 22 W UV-C light, 24-hour experiment duration, showing a comparison between coated and pure quartz glass

Figure 6 shows the comparison of the recorded concentration of methylene blue dye with the use of UV-A light bulbs. In this experiment, in contrast to the experiments with UV-C light, the degradation behavior with coated quartz glass was much stronger than with pure quartz glass. For pure quartz glass, the degradation behavior was linear. The calculated relative concentration of methylene blue with the photocatalytic coating was 0.872 mg/l after 24 hours of running the experiment which corresponds to a degradation of 3.2 mg. In the case of pure quartz glass, the degradation behavior was still present and measured at a relative concentration of 0.961 mg/l after 24 hours, resulting in a total degradation of only 1.0 mg methylene blue dye.

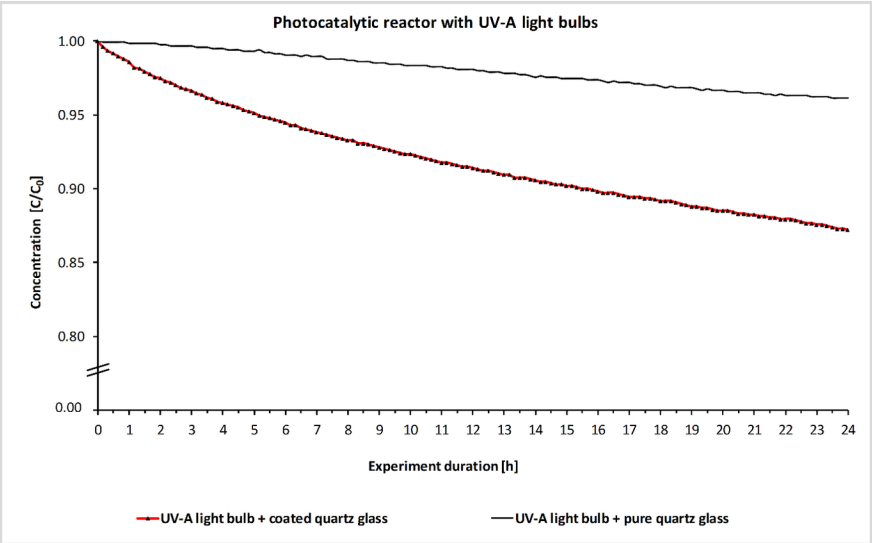


Figure 6: Reactor setup with a total of 22 W UV-C light, 24-hour experiment duration, showing a comparison between coated and pure quartz glass

Figure 7 shows the comparison of methylene blue degradation performance with the use of regular fluorescent

light bulbs. In this experiment, the degradation behavior was weak but still present and there is only a slight difference between the coated and uncoated quartz glass. Both experiments yielded a linear degradation behavior. After 24 hours, the coated quartz glass performed only slightly better than the uncoated quartz glass used in the experiment. However, degradation was still observed for the pure quartz glass. The calculated relative concentration of methylene blue with the photocatalyst coating was 0.877 mg/l after 24 hours, corresponding to a removal of 3.3 mg. In the case of pure quartz glass, the degradation behavior resulted in a relative concentration of 0.890 mg/l after 24 hours, corresponding to a total of only 2.9 mg methylene blue dye.

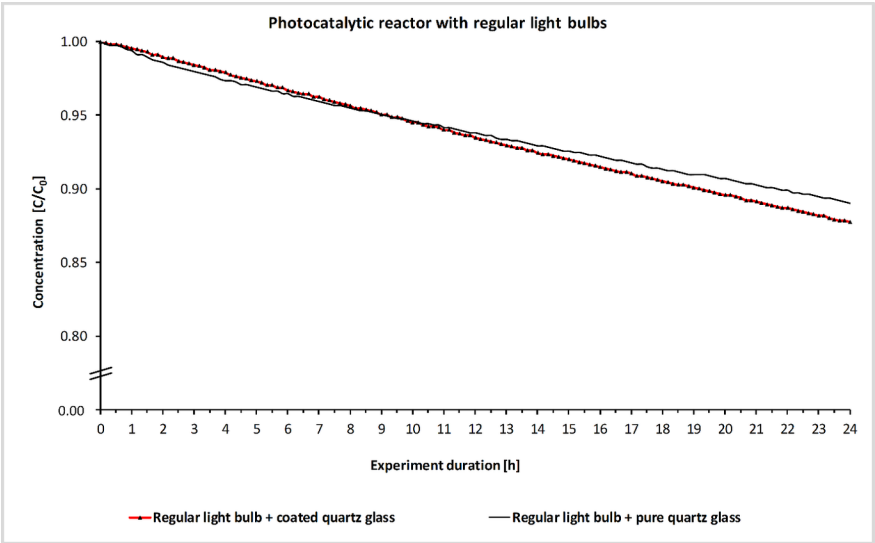


Figure 7: Reactor setup with a total of 22 W UV-C light, 24-hour experiment duration, showing a comparison between coated and pure quartz glass

5. Conclusion

The objective of this study was to analyze degradation of methylene blue under different light sources. As postulated, the stability of methylene blue is already affected by exposure to light in general and the total setup of six experiments, including the use of coated quartz glass and pure quartz glass, shows that by only analyzing a coated surface there is room for misinterpretation of the real efficiency of the coating used. In this study, we measured the highest methylene blue degradation with pure quartz glass under UV-C illumination. The lowest methylene blue dye removal was measured with pure quartz glass under illumination with regular fluorescent light bulbs. In all cases, the use of coated quartz glass resulted in an almost linear removal of methylene blue. These results indicate that generated data on the photocatalytic degradation of methylene blue should be critically reviewed and, in this case, the use of a different dye that is more resistant to light degradation is recommended. The use of a light degradation-resistant test solution with water could help to determine the real performance of the advanced oxidation process leading to the degradation of the analyzed chemical.

Conflict of Interest Statement

The authors declare no conflict of interest.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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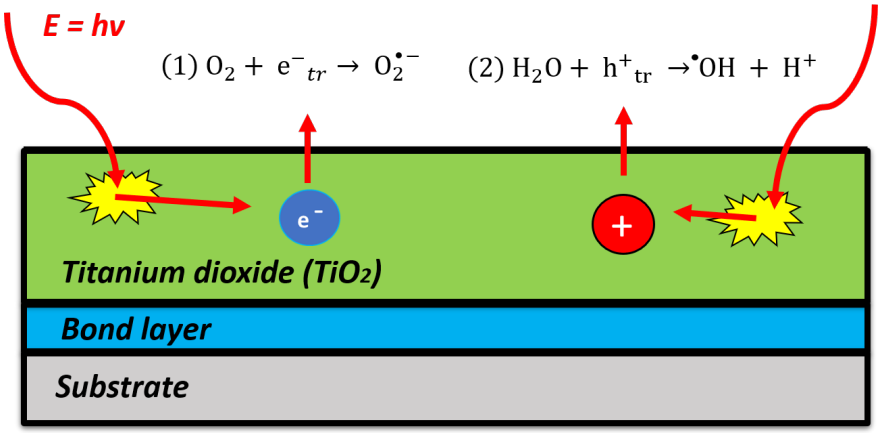

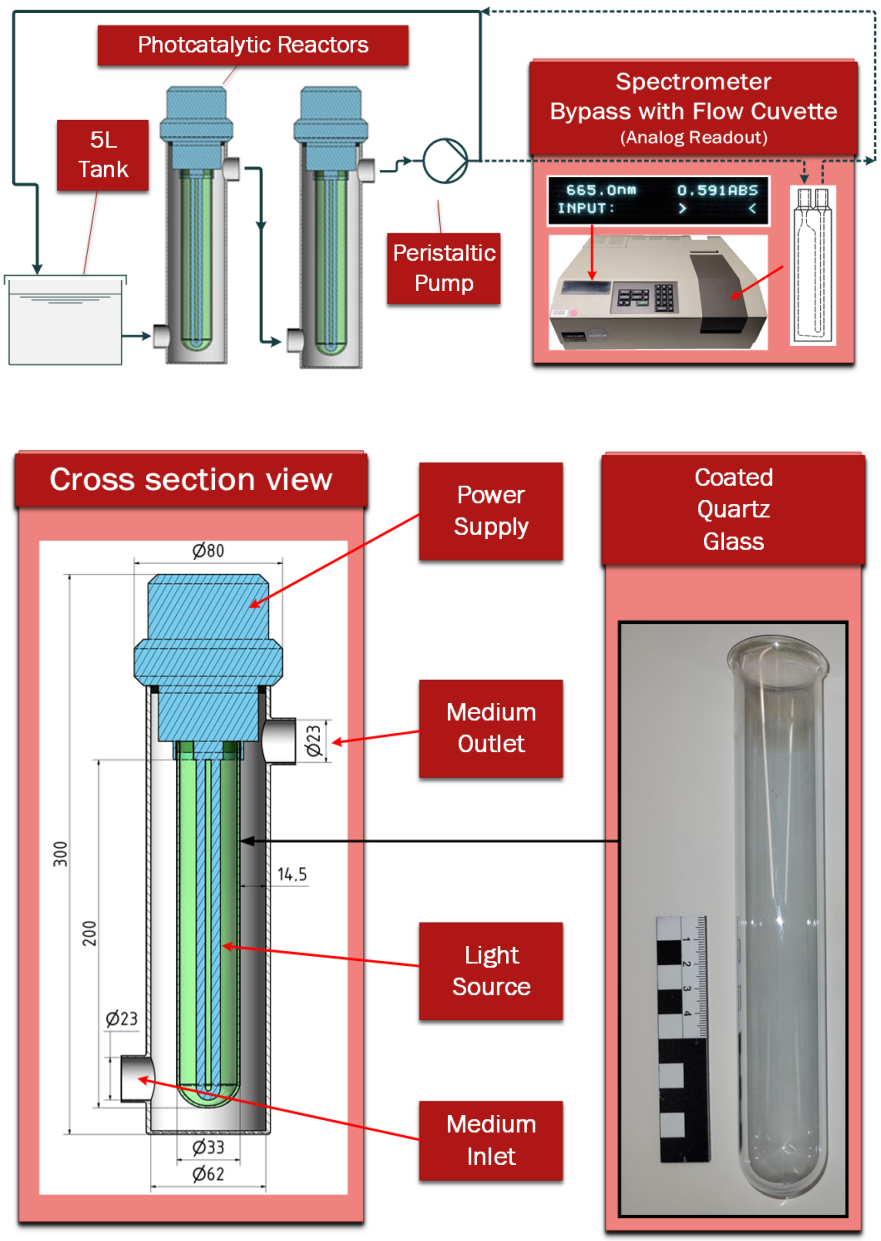

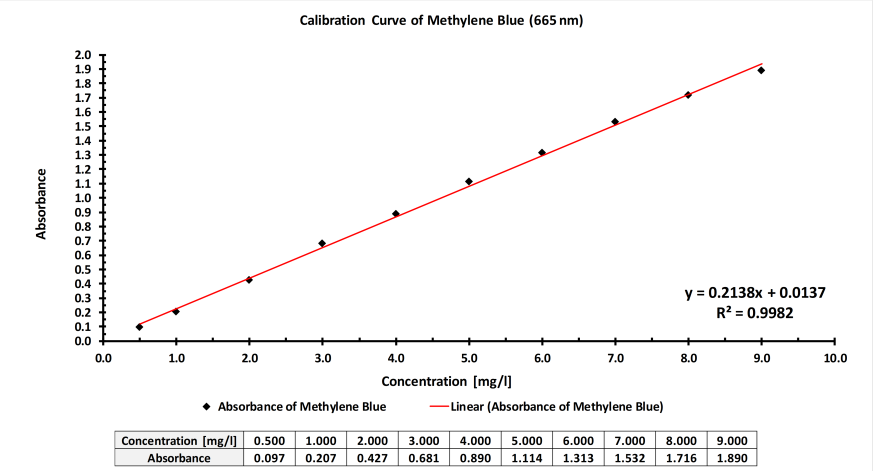

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