

Research Article

Durability of Ag-TiO₂ Photocatalysts Assessed for the Degradation of Dichloroacetic Acid

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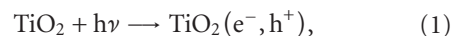
The stability of Ag-TiO₂ photocatalysts was examined for the photocatalytic degradation of dichloroacetic acid (DCA) as a function of the recycling times. The photocatalytic activity was investigated by measuring the rate of H⁺ ions released during the photodegradation of DCA and confirmed by measuring the total organic carbon removal. The photodegradation reactions were studied at pH 3 and pH 10 for a series of Ag-TiO₂ photocatalysts as different with Ag loadings. All the Ag-TiO₂ and bare TiO₂ photocatalysts showed a decrease in photocatalytic activity on recycling for the DCA photodegradation reaction. The decrease in activity can be attributed to poisoning of active sites by Cl⁻ anions formed during the photocatalytic DCA degradation. The photocatalytic activity was, however, easily recovered by a simple washing technique. The reversibility of the poisoning is taken as evidence to support the idea that the recycling of Ag-P25 TiO₂ photocatalysts does not have a permanent negative effect on their photocatalytic performance for the degradation of DCA. The choice of the preparation procedure for the Ag-TiO₂ photocatalysts is shown to be of significant importance for the observed changes in the photocatalytic activity of the Ag-TiO₂ particles.

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1. INTRODUCTION

The presence of cocatalytic noble metal deposits on metal oxide particles is often employed to enhance the photocatalytic oxidation efficiency of processes through achieving a more efficient charge separation [1]. Considerable work has been done on Ag-TiO₂ modified photocatalysts and their potential applications as enhanced photocatalysts. The presence of Ag deposits on the TiO₂ surface can help to efficiently separate the electron hole pairs by attracting the conduction band photoelectrons. This process has been shown to improve the overall efficiency for a number of photocatalytic reactions [2]. Ag-TiO₂ particles are typically prepared by photodeposition with the titanium dioxide particles being suspended in an aqueous solution containing the metal salt. When the suspension is illuminated, metal ions are reduced by conduction band electrons to form the metal deposits on the TiO₂ surface. This process is described by the series of reactions (1)–(3). Depending on the preparation conditions, this photodeposition procedure

typically yields small metal deposits ranging from a few nanometers to tens of nanometers [2]



The size and dispersion of metal deposits on TiO₂ particles are critical in controlling their photocatalytic activity. Given the strong effect of deposit size and dispersion, the development of preparation methods which provide such close control over deposit size is essential [3, 4]. An issue that is not often addressed is the stability of these metal-doped particles and hence the effects, if any, on the longer-term application potential and shelf-life stability of these particles. This is particularly true for applications as photocatalysts, where these particles are subjected to irradiation with UV(A) light. Reformation of surficial metal clusters when the semiconductor particles are exposed to ultrabandgap irradiation has often been reported [5, 6]. For example, while

cluster stabilization can be achieved by adsorption of metal clusters onto a solid surface, it has been shown that the rate of cluster growth on a quartz surface is accelerated by UV light [5].

The stability of metal deposits on photocatalysts under illumination may depend on a number of factors, such as, for example, the type of metal, the deposit size, the photocatalytic reactions taking place, and the reaction conditions such as solution pH. Additionally, the redox potential can affect the reduction state of the supporting oxide. For example, the efficiency of the cluster-oxide coupling has been found to strongly depend on the band bending in TiO_2 after silver deposition which in turn varies with the reduction state of the oxide [7].

Despite the large volume of studies focusing on metal-deposited TiO_2 photocatalysts, particularly Ag- TiO_2 , the photocatalyst stability and recycling has been addressed only in a few studies. Reproducibility tests were carried out on Ag-doped TiO_2 films prepared through a 2-step dipping and illumination process using Degussa P25 as the photocatalyst. These tests proved that the photocatalytic activity of the silver-modified films for the degradation of methyl orange remains unchanged even after six consecutive experiments with newly added pollutant quantities [8]. Xu et al. [9] have studied recycled 0.5 atom% Ag-deposited magnetic $\text{TiO}_2\text{-SiO}_2\text{-Fe}_3\text{O}_4$ photocatalysts and have also found that the photoreactivity for the degradation of orange (II) was maintained after 3 recycles. However, the total irradiation time was only 20 minutes which is relatively short.

In a study by Zhang, Ag- TiO_2 photocatalysts were in fact deactivated during the photocatalytic degradation of acetone in air [10], with a 73% reduction in activity during the fourth hour of reaction. The deactivation was explained as being due to interactions between partially oxidized organics and the Ag deposits, and possibly by the aggregation of the silver nanoparticles, which was reflected in changes in the absorption spectra of these particles. Regeneration was achieved by visible light illumination and was attributed to the oxidation of Ag deposits to Ag^+ ions, in the form of Ag_2O , which were reduced to Ag^0 upon UV illumination. This study raised the issue of the nanometre level control of feature size and interfeature spacing and the long-term stability of such structures, hindering their full exploitation for device applications [11].

Apart from photocatalytic applications, Sun et al. [12] have studied Ag- TiO_2 cyanide sensors prepared by the photodeposition method which were tested under mild conditions and found to give good results using $0.1\text{--}10\text{ }\mu\text{mol/L}$ cyanide at pH 9–12. The Ag- TiO_2 sensors were found to be effective, without the need for regeneration for up to one month. It must be said that the available silver content was greater than the amount of cyanide to be detected.

In this study, we have examined the durability of Ag- TiO_2 photocatalysts under practically relevant conditions. The model reaction was the photodegradation of dichloroacetic acid (DCA). DCA is a known industrial pollutant the photodegradation of which has been studied extensively, for example, by Bahnemann et al. [13]. Important parameters selected for an initial exploration were the duration of

illumination and the silver content. The poisoning of the photocatalyst surface by chloride ions was explored and reactivation was investigated using a simple washing technique. The deactivation of self-prepared colloidal TiO_2 was compared to that of the commercially available P25 TiO_2 photocatalysts.

2. EXPERIMENTAL

2.1. Preparation of Ag- TiO_2 and colloidal TiO_2 photocatalysts

The Ag- TiO_2 photocatalysts were prepared by a photodeposition process. Degussa P25 was used as the TiO_2 photocatalyst. P25 TiO_2 consists of 70% anatase and 30% rutile with an average primary particle diameter of $55 \pm 5\text{ nm}$ and a BET surface area of $48\text{ m}^2/\text{g}$. The photochemical experiments were performed in a reactor (50 mL) with a plain quartz window on which the light beam ($\lambda \geq 320\text{ nm}$) was focused. Figure 1 provides a schematic of the photocatalytic reactor setup. The reactor was equipped with a magnetic stirring bar, a water-circulating jacket and three openings for pH electrode, gas supply, and sample withdrawing. The photoreactor was filled with 50 mL of the aqueous suspension containing the TiO_2 photocatalyst at a loading of 0.5 g/L . The photocatalyst slurry was illuminated with UV(A) light for 20 minutes to oxidize any possible organic carbon impurities on the TiO_2 surface.

Silver ions in the form of AgClO_4 were then added to the TiO_2 slurry at an initial pH of approximately 6 to obtain the desired $\text{Ag}^+:\text{Ti}$ ratio. The suspension was illuminated for 24 hours. A series of Ag- TiO_2 photocatalysts with a respective Ag loading of 0.1, 0.2, 0.35, 0.5, 1, and 2 atom% was prepared. The samples were labelled as $x\text{Ag-TiO}_2$, where x is the amount of Ag^+ added given in atom%.

The prepared particles were characterized by electron microscopy (emission transmission electron microscope JEOL JEM-2100F-UHR and emission scanning electron microscope JEOL JSM-6700F). The STEM was supported by an energy dispersive spectroscopic analysis (EDX) and elemental X-ray mapping images provided information regarding the distribution of the various components (TiO_2 and Ag) and ions (Ti, Ag, Cl) before and after the photoreaction.

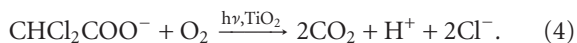
Colloidal TiO_2 was prepared by a method described by Bahnemann [14] that involved the dropwise addition of titanium tetraisopropoxide dissolved in 99.99% 2-propanol to an aqueous hydrochloric acid solution of pH 1.5. The final concentrations of TiO_2 and 2-propanol were 1.5×10^{-2} and 1.2 M, respectively. The reaction volume was 1 L. This mixture was stirred overnight employing a magnetic stirrer. The final solution was optically transparent. Evaporation under vacuum was used to collect the TiO_2 powder which can be resuspended in water and other polar solvents (e.g., alcohols) to form transparent colloidal suspensions. UV-Vis absorbance measurements in the wavelength range 200–700 nm showed the steep increase in absorption below approximately 350 nm which is typical for nanosized TiO_2 . The final TiO_2 solution, whose photoactivity was tested, was

prepared by suspending 500 mg of this powder in 1 L of water.

2.2. Photocatalytic degradation of DCA

After the photodeposition reaction, the Ag-TiO₂ photocatalysts were collected and sonicated for 15 minutes before the addition of 1 mM DCA into the slurry. The pH was then adjusted to either 3 or 10, by addition of 0.1 M HClO₄ or 0.1 M NaOH, respectively. The temperature of the suspension was maintained at 25°C. The suspension was vigorously stirred without illumination for 30 minutes to attain adsorption equilibrium of the DCA molecules on the photocatalyst surface and continuously purged with air to ensure a constant O₂ concentration throughout the experiment. After this adsorption period, UV illumination was provided by a high-pressure Xe-lamp (OSRAM HBO-500W). A UV(A)/Vis illumination was achieved employing a band-pass filter (WG 320) which eliminates UV-radiation below $\lambda = 320$ nm. The intensity of UV(A) illumination was 20 mW/cm² at the entrance window of the photoreactor as measured by a UV light meter (ultraviolet radiometer LT Lutron UVA-365).

The pK_a of DCA is 1.29 [15] and it thus exists in its anionic form in aqueous solutions at pH > 2. The photocatalytic oxidation of one DCA anion results in the formation of one proton, two CO₂ molecules, and 2 Cl⁻ ions (4). The reaction pH was maintained constant using a pH-stat setup with the addition of HClO₄ or NaOH as needed.



The rate of the photodegradation of DCA was followed by measuring the amount of OH⁻ added to keep the pH constant and thus the amount of H⁺ formed using the pH-stat technique as described by Bahnemann et al., 1993 [16]. Samples were taken at the beginning and at the end of each run for total organic carbon (TOC) analysis. The reaction time was 4 hours for each run. In total, 3 consecutive runs were performed with the same photocatalyst. 1 mM of DCA was injected at the beginning of each run. For the third run, 4 mM Cl⁻ was also added to selected experiments in order to compare and investigate the effect of chloride ions on the photocatalytic reaction rate.

3. RESULTS AND DISCUSSION

For the preparation of the Ag-TiO₂ photocatalysts, the first indication of the deposition of metallic silver onto the TiO₂ surface upon irradiation of the TiO₂ and Ag⁺ suspensions was a color change of the particles from white to brown. A higher concentration of silver ions corresponded to a higher intensity of this brownish color. According to the literature, the photodeposited Ag should be present in metallic form, based on XRD analysis of Ag/TiO₂ particles prepared using 20.0 atom% Ag⁺ loading which confirmed the presence of metallic silver [17]. At lower Ag content, metallic silver could not be detected since the mass of silver in the sample was below the detection limit of the employed instrument [17].

In Figure 2(a), the degradation of 1 mM DCA within each run (followed as release of H⁺ ions during the degradation process) using pure Degussa P25 as the photocatalyst is shown. Three runs were consecutively carried out and a third run from a second series of experiments is also presented here with 4 mM Cl⁻ added before the illumination to evaluate a possible poisoning effect of the photocatalyst's active sites by chloride ions. It can be clearly seen that both the reaction rate and yield are reduced during each consecutive run with the most obvious inhibition being observed upon the addition of chloride ions.

As shown in Figure 2(b), the photocatalytic activity of Degussa P25 toward the degradation of DCA is almost completely recovered once the catalyst is simply washed with pure water before the next activity test. This clearly indicates the inhibitory effect of Cl⁻ ions that was already obvious from the results presented in Figure 2(a).

The effect of recycling the 0.35 Ag-TiO₂ photocatalyst on the photocatalytic degradation rate of DCA is shown in Figure 3(a) and once again employing the washing technique in Figure 3(b). The reaction conditions were the same as described previously for the experiment with pure P25 TiO₂. As can be seen from Figure 3(a), the reaction rate is found to be lowered after the first run, and is lowered even more during the 3rd run. Once again, the reaction rate is further reduced when this third run is carried out after the addition of 4 mM Cl⁻. Moreover, the reaction seems to stop in this case after about 20% of the initially present DCA has been degraded. This is consistent with the respective TOC results shown in Figure 6 (*vide infra*).

In the next set of experiments, the aim was to investigate whether the negative effect of recycling the Ag-TiO₂ photocatalyst can also be avoided by a simple washing technique. Washing of the photocatalysts was carried out by recovering the material by centrifugation of the reaction slurry after each run and resuspending it in distilled water, followed by the appropriate adjustment of pH. The results are shown in Figure 3(b). As in the case of pure Degussa P25, it is obvious that this simple intermittent washing technique between each reaction run leads to a remarkable improvement in activity following the first and second recycles.

The results shown in Figures 2 and 3 clearly show that a "clean" surface is a prerequisite for the photocatalyst to exhibit its full activity independent of the absence or presence of cocatalysts such as Ag-deposits. The detrimental effect of codissolved ions such as Cl⁻ is known since they are likely to adsorb onto the TiO₂ surface and can disturb the adsorption of the organic compounds [18].

The self-prepared colloidal TiO₂ photocatalyst was tested with the same intention as pure Degussa P25 and P25-Ag under the identical experimental conditions. Figure 4 shows the results of these experiments. Obviously, the reaction rate and yield also decrease in subsequent runs. However, this poisoning effect appears to be much less pronounced for the colloidal particles as compared with pure or Ag-deposited Degussa P25. Even with the further addition of 4 mM of Cl⁻ ions before the third run, no substantial difference is observed as compared with a third run without the addition of chloride ions. Thus the capacity of the self-prepared

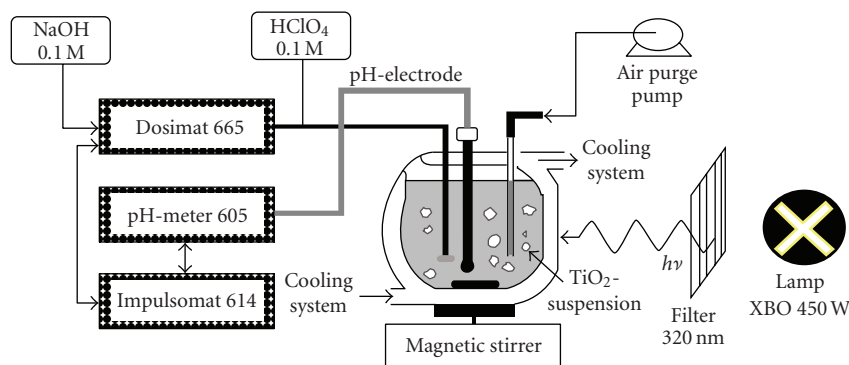


FIGURE 1: Schematic presentation of the photocatalytic reactor setup.

colloidal particles to accommodate chloride ions without any loss in photocatalytic activity appears to be very high.

The results of the TOC analysis performed at the end of each experimental run, that is after 4 hours of illumination, and the H^+ production efficiency in percent increase at the same time are presented in Figures 5–7. These figures provide a summary of the effect of recycling and washing of the photocatalysts with respect to the mineralization of DCA. The TOC removal results are in fact in good agreement with the results obtained following the release of H^+ , evincing that the simple stoichiometry given in (4) is indeed correct.

In Figure 5, the results for pure Degussa P25 are shown. The gradual decline in photoactivity following each recycle can be seen from set A for the consecutive runs. In set B, the strong detrimental effect of chloride ion addition before run 3 can be clearly seen. In set C, the photocatalyst was collected after each run by centrifugation, resuspended in distilled water at the correct pH and placed back in the reactor. However, for the pure P25 photocatalyst, the recovery of the photoactivity was not complete. Comparing the results obtained from set A with those of set C, however, it is obvious that the photoactivity after the washing technique is slightly higher than that observed without washing.

The results for the TOC removal using the 0.35 Ag-TiO₂ photocatalyst are presented in Figure 6. These are also in agreement with the DCA degradation results shown in Figures 3(a) and 3(b). The results of set C show the successful application of this simple washing technique resulting in an almost complete recovery of the photocatalytic activity. While the amount of DCA degraded after 4 hours of illumination even seems to slightly increase after each illumination/washing cycle (Figure 6, set C), the initial rate of degradation is found to decrease (Figure 3(b)), in particular, for the second run. In comparison with the results obtained for pure Degussa P25, however, it is obvious that the photocatalytic activity of Ag-TiO₂ can be recovered much more rapidly by this simple washing procedure. As will be shown below (in Figures 13 and 14), this might be due to the fact that the chloride ions show a strong tendency to adsorb at the silver clusters from where they can obviously be removed much easily than from the bare TiO₂ surface.

For the colloidal TiO₂ particles, the analysis of the TOC removal after 4 hours of illumination also showed

the durability of this photocatalyst (the results are shown in Figure 7). In fact, this photocatalyst showed a greater resilience to deactivation compared to pure Degussa P25 and to the Ag-TiO₂ photocatalysts. This is believed to be due to the greater number of active sites provided by this photocatalyst for the photocatalytic reaction, hence minimizing the observed poisoning by the chloride ions. It is important to note that due to its colloidal nature, this photocatalyst could not be separated by centrifugation and hence it could not be washed between the recycles. Both its advantages and drawbacks need to be taken into account when considering its application under real conditions.

In the next set of experiments, the effect of catalyst recycling on the photocatalytic DCA-degradation rates was examined for a series of Ag-TiO₂ photocatalysts varying the amount of deposited Ag. These degradation experiments were carried out both under acidic (pH 3) and under basic (pH 10) conditions. The aim was to identify reaction conditions or photocatalyst composition, where the observed reduction in photonic efficiency due to recycling can be minimized. Figure 8 provides a summary for the results obtained for the measured photonic efficiencies (based on the initial degradation rate of DCA as measured by the release of H^+).

The photonic efficiency ζ is defined as the ratio of the initial degradation rate and the incident photon flux (see (5)), where the initial photocatalytic rate is calculated from the slope of the individual concentration versus time profiles. This definition of the photonic efficiency was first suggested by Serpone and Salinaro [19]. The incident photon flow per volumetric unit (I varied between 3.39×10^{-2} Einstein $L^{-1}h^{-1}$ and 3.74×10^{-2} Einstein $L^{-1}h^{-1}$) was calculated based upon the UV-A light meter measurements [20], the irradiated surface area of 8.042 cm², and the volume of the suspension (5×10^{-2} L).

$$J_0 = \frac{I \cdot \lambda}{N_A \cdot h \cdot c}, \quad (5)$$

$$\zeta(\%) = \frac{k \cdot c_0 \cdot V}{J_0 \cdot A} \cdot 100$$

with J_0 = light flux [$mol \cdot s^{-1} cm^{-2}$]; I = light intensity [$J \cdot s^{-1} cm^{-2}$]; N_A = Avogadro's number [$6.022 \cdot 10^{23} mol^{-1}$];

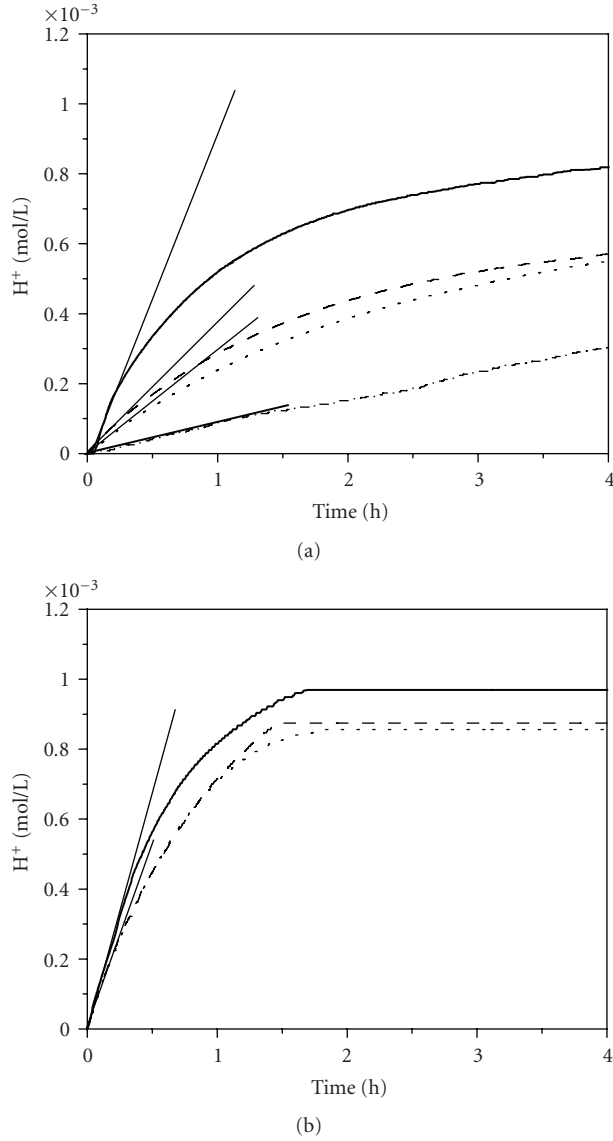


FIGURE 2: (a) Degradation of DCA (shown as release of H^+) using the photocatalyst Degussa P25 at pH 3 in 3 consecutive runs, 1st run (—), 2nd run (---), 3rd run (···), a 3rd run (---) with addition of 4 mM Cl^- before the run started, and slope (—) used for the determination of the photonic efficiency of each run with $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$. The photocatalyst loading was 0.5 g/L. (b) Degradation of DCA (shown as release of H^+) using the photocatalyst Degussa P25 at pH 3 in 3 consecutive runs with intermittent washing between the runs, 1st run (—), 2nd run (---), 3rd run (···), and slope (—) used for the determination of the photonic efficiency of each run with $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$. The photocatalyst loading was 0.5 g/L.

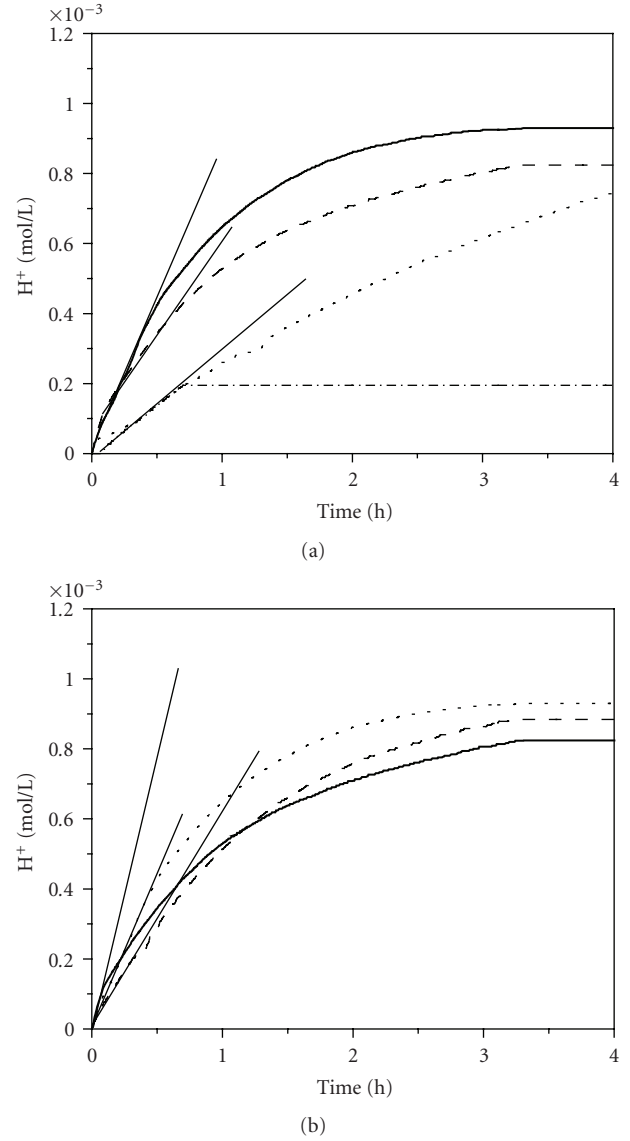


FIGURE 3: (a) Degradation of DCA (shown as release of H^+) using the photocatalyst 0.35 Ag- TiO_2 at pH 3 in 3 consecutive runs, 1st run (—), 2nd run (---), 3rd run (···), a 3rd run (---) with addition of 4 mM Cl^- before the run started, and slope (—) used for the determination of the photonic efficiency of each run with $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$. The photocatalyst loading was 0.5 g/L. (b) Degradation of DCA (shown as release of H^+) using the photocatalyst 0.35 Ag- TiO_2 at pH 3 in 3 consecutive runs with intermittent washing between the runs, 1st run (—), 2nd run (---), 3rd run (···), and slope (—) used for the determination of the photonic efficiency with $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$. The photocatalyst loading was 0.5 g/L.

h = Planck constant [$6.63 \cdot 10^{-34}$ J s]; c = light velocity [$3 \cdot 10^8$ m s^{-1}]; k = initial rate constant [s^{-1}]; A = area [cm^2]; C_0 = initial DCA concentration [$mol \cdot L^{-1}$]; λ = wavelength [nm]; V = volume [L].

In Figure 8, the photonic efficiency measured for each run is presented, comparing the fresh photocatalyst with the recycled ones after the second and third runs. Figure 8 shows

overall higher rates during the first run at pH 3 compared to pH 10 both, for pure Degussa P25 and when silver is photodeposited. This DCA degradation trend, although performed with a different photocatalyst, is in agreement with earlier studies reported by Bahnemann et al. [13], who attributed the faster rates observed under acidic conditions (pH 2.6) to the favorable DCA coordination through the

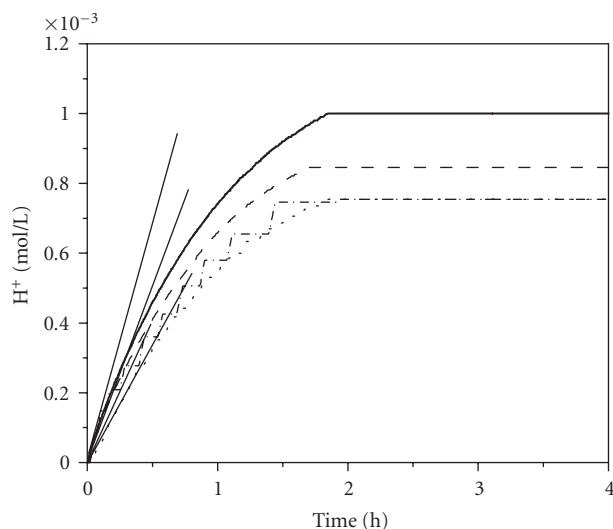


FIGURE 4: Degradation of DCA (shown as release of H^+) using the prepared colloidal TiO_2 photocatalyst at pH 3 in 3 consecutive runs without intermittent washing between runs, 1st run (—), 2nd run (---), 3rd run (···), a 3rd run (---) with addition of 4 mM Cl^- before the run started, and slope (—) used for the determination of the photonic efficiency of each run with $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$. The photocatalyst loading was 0.5 g/L.

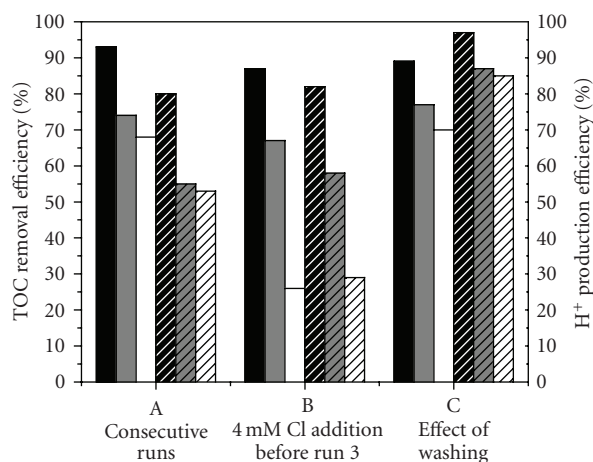


FIGURE 5: Removal of DCA (TOC removal) after 4 hours of illumination using the photocatalyst P25- TiO_2 at pH 3 in 3 consecutive runs (1st run ■, 2nd run ■, and 3rd run □), the H^+ production efficiency after 4 hours of illumination is also shown (1st run ■, 2nd run ■, and 3rd run □) in set A, with chloride ion addition before the third run (set B), and with intermittent washing between runs (set C). The photocatalyst loading was 0.5 g/L and the light intensity $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$.

formation of bidentate complexes that could not be formed in alkaline medium at pH 11.3. The absolute value of the photonic efficiency for the pure P25 photocatalyst obtained here is slightly lower than that reported previously [21], where a photonic efficiency $\zeta = 3.9\%$ was measured at pH 3 under similar conditions. This could, for example, be explained by a variation of the activity of such a commercial

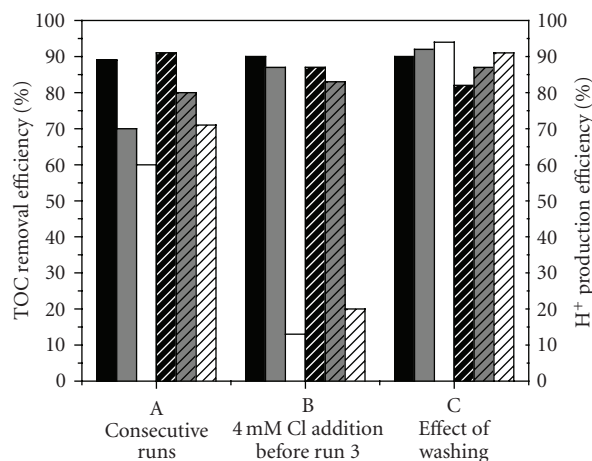


FIGURE 6: Removal of DCA (TOC removal) after 4 hours of illumination using the photocatalyst 0.35 Ag- TiO_2 at pH 3 in 3 consecutive runs (1st run ■, 2nd run ■, and 3rd run □), the H^+ production efficiency after 4 hours of illumination is also shown (1st run ■, 2nd run ■, and 3rd run □) in set A, with chloride ion addition in set B before the third run and with intermittent washing between runs (set C). The photocatalyst loading was 0.5 g/L and the light intensity $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$.

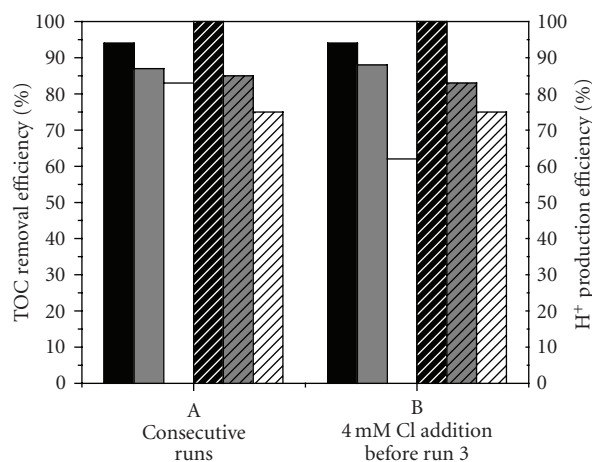


FIGURE 7: Removal DCA (TOC removal) after 4 hours of illumination using the colloidal- TiO_2 photocatalyst at pH 3 in 3 consecutive runs (1st run ■, 2nd run ■, and 3rd run □) the H^+ production efficiency after 4 hours of illumination is also shown (1st run ■, 2nd run ■, and 3rd run □) in set A and with chloride ion addition before the third run (set B). The photocatalyst loading was 0.5 g/L and the light intensity $I \approx 3.39 \times 10^{-2}$ Einstein $L^{-1}h^{-1}$.

product between different production batches which are well known for most catalysts. It is interesting to note the influence of the presence of chloride ions in the suspension. With the presence of 8 mM NaCl (2×2 mM for runs 1 and 2 plus 4 mM added before run 3) prior to run 3 the efficiency decreases by approximately 50%, that is, the photocatalytic activity can be considerably inhibited by the presence of

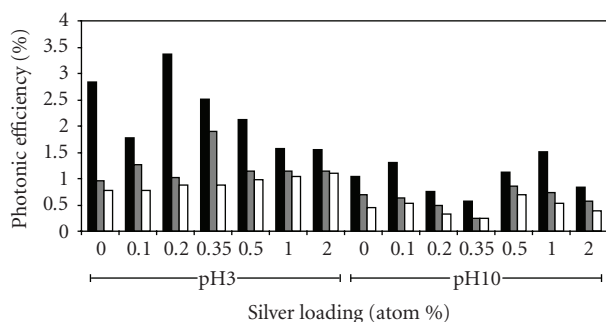


FIGURE 8: Effect of recycling Ag-TiO₂ photocatalysts on observed photonic efficiencies at pH 3 and pH 10 (1st run ■, 2nd run ■, and 3rd run □), degradation of 1 mM DCA without any extra addition of chloride ions or washing technique performed. The photocatalyst concentration was 0.5 g/L with different silver loadings (atom%). The light intensity at pH 3 was $I \approx 3.39 \times 10^{-2}$ Einstein L⁻¹h⁻¹ and at pH 10 was $I \approx 3.74 \times 10^{-2}$ Einstein L⁻¹h⁻¹.

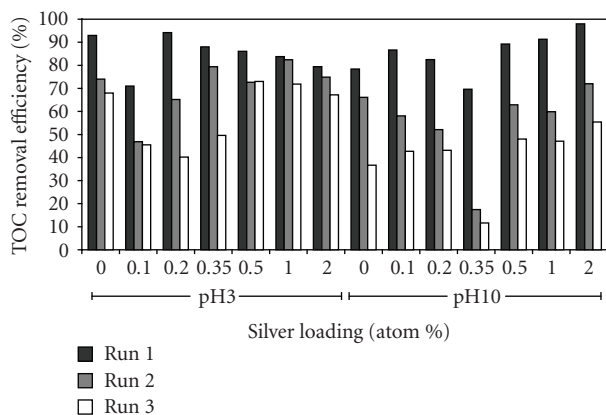


FIGURE 9: Effect of recycling Ag-TiO₂ photocatalysts on observed TOC removal at pH 3 and pH 10 (1st run ■, 2nd run ■, and 3rd run □), degradation of 1 mM DCA without any extra addition of chloride ions or washing technique performed. The light intensity at pH 3 was $I \approx 3.39 \times 10^{-2}$ Einstein L⁻¹h⁻¹ and at pH 10 was $I \approx 3.74 \times 10^{-2}$ Einstein L⁻¹h⁻¹.

anions such as chloride. A similar yet less pronounced effect has been reported previously [21].

In Table 1, all photonic efficiency values are presented that have been calculated using (5) for each experiment. Previous reports ([21], Figure 4), concerning the photonic efficiency of the degradation of DCA in the presence of P25, are consistent with the photonic efficiency values obtained in this work. Here, the photonic efficiency was found to be between 2.83 and 3.69% at pH 3 (cf. $\zeta = 3.9\%$ at pH 3 [21]). Also, a decrease of the photonic efficiency was previously noted at pH 10 (cf. $\zeta = 0.6\%$ at pH 10 [21]). The results obtained here concerning the influence of Cl⁻ can be compared with a set of experiments carried out previously also [21], where the efficiency was reported to decrease from $\zeta = 3.8\%$ with the number of subsequent experiments to $\zeta = 2.0\%$ during run 3 and $\zeta = 0.9\%$ during run 6. Once

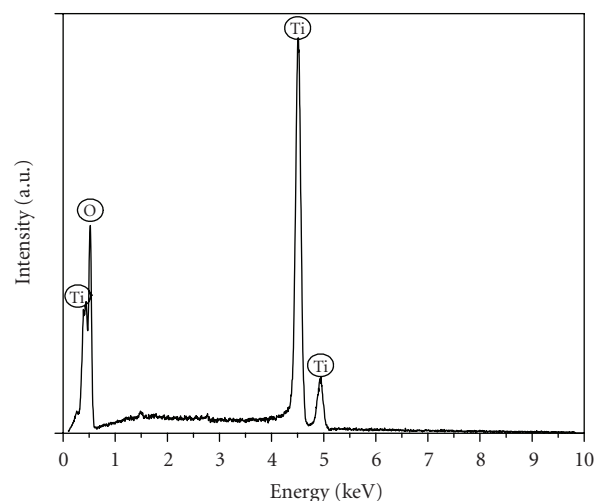


FIGURE 10: EDXS-spectrum of Degussa P25 prior to the photodeposition of silver or the photodegradation of DCA.

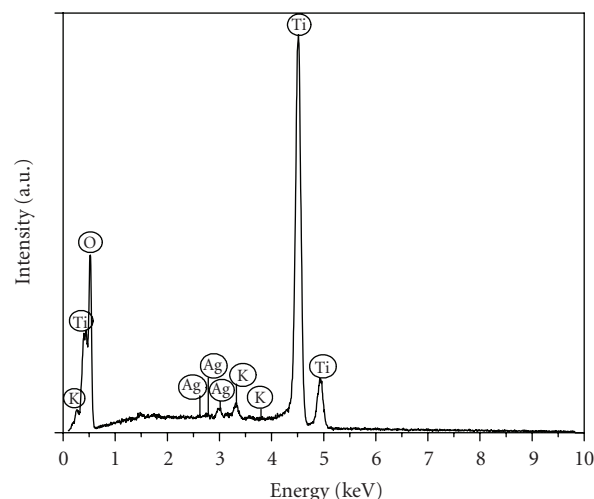


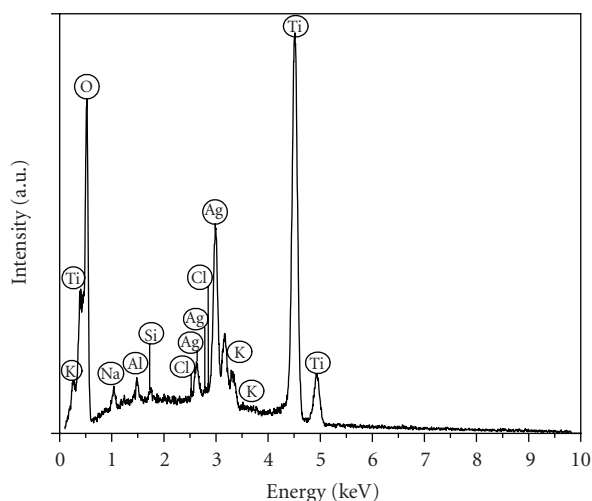
FIGURE 11: EDXS spectrum of 0.2 Ag-TiO₂ photocatalyst prior to the photodegradation of DCA.

again, the photonic efficiency recovered after washing of the photocatalyst (reaching $\zeta = 2.2\%$ [21]) as confirmed in the present results.

A closer inspection of the results shown in Figure 8 reveals that while at pH 10 there is no clear relationship between the observed photonic efficiency and the absence or presence of Ag on the photocatalyst, at pH 3, the fresh 0.2 Ag-TiO₂ photocatalyst slightly outperforms pure Degussa P25. For the second run, however, the situation has changed with 0.35 Ag-TiO₂ now being the best photocatalyst for the DCA degradation. Finally, in the third run all tested catalysts exhibit almost the same photocatalytic activity ($\zeta \leq 1\%$). Apparently, the Cl⁻ ions formed during the photocatalytic oxidation of dichloroacetate are able to completely “neutralize” any enhancement in activity induced by the Ag clusters. Based on the experimental evidence given in Figures 13 and

TABLE 1: Photonic efficiency values of the employed photocatalysts (e.g., as given in Figures 2 and 3).

Photocatalyst [0.5 g/L]	pH 3								pH 10						
	Rate			Intensity	Photonic			Rate			Intensity	Photonic			
	[mol/Lh]			[mol/Lh]	Efficiency (%)			[mol/Lh]			[mol/Lh]	Efficiency (%)			
	1.00E-04							1.00E-04							
	Run 1	Run 2	Run 3		Run 1	Run 2	Run 3	Run 1	Run 2	Run 3		Run 1	Run 2	Run 3	
P25	9.58	3.26	2.65	3.39E-02	2.83	0.96	0.78	3.90	2.60	1.70	3.74E-02	1.04	0.70	0.45	
0.1	6.00	4.30	2.60	3.39E-02	1.77	1.27	0.77	4.86	2.39	1.95	3.74E-02	1.30	0.64	0.52	
0.2	11.42	3.48	3.00	3.39E-02	3.37	1.03	0.89	2.84	1.84	1.24	3.74E-02	0.76	0.49	0.33	
0.35	8.50	6.40	3.00	3.39E-02	2.51	1.89	0.89	2.16	0.95	0.95	3.74E-02	0.58	0.25	0.25	
0.5	7.22	3.88	3.33	3.39E-02	2.13	1.15	1.98	4.20	3.20	2.59	3.74E-02	1.12	0.85	0.69	
P25-Ag%	1	5.35	3.90	3.53	3.39E-02	1.58	1.15	1.04	5.61	2.78	2.00	3.74E-02	1.50	0.74	0.53
2	5.26	3.84	3.74	3.39E-02	1.55	1.13	1.10	3.12	2.16	1.48	3.74E-02	0.83	0.58	0.40	
0.35	8.03	5.45	2.35	3.39E-02	2.37	1.61	0.69								
(4 mM Cl)															
0.35	12.50	6.17	8.54	3.39E-02	3.69	1.82	2.52								
Washed															
P25															
before 3rd run	9.32	3.14	0.75	3.39E-02	2.75	0.93	0.22								
(4 mM Cl)															
P25	12.30	9.37	9.31	3.39E-02	3.63	2.77	2.75								
Washed															
TiO ₂	11.40	9.07	6.73	3.39E-02	3.37	2.68	1.99								
colloid															
TiO ₂ colloid															
before 3rd run	11.20	8.92	6.44	3.39E-02	3.31	2.63	1.90								
(4 mM Cl)															

FIGURE 12: EDXS spectrum of 0.2 Ag-TiO₂ photocatalyst after photodegradation of DCA in three consecutive runs.

14 below, this is explained by the preferred adsorption of chloride ions at these silver clusters.

In Figure 9, a summary is provided of the results obtained for the measured TOC removal after 4 hours of

illumination for the same experiments shown in Figure 8. Figure 9 shows the TOC removal measured for each run, comparing the fresh catalysts with the recycled photocatalysts after the third run. Again, the results show the decline in activity on recycling, with no particular trend with regard to the amount of silver deposited or to the reaction pH. It is clear from both, the results in Figures 8 and 9, that while there is an optimum silver loading at 0.2 atom% at pH 3, this 0.2 Ag-TiO₂ photocatalyst has no clear advantage compared to the other Ag-TiO₂ samples after recycling. Finally, it should be noted that while the initial degradation rate (used to calculate the ζ -values presented in Figure 8) seems to be rather sensitive to the presence of the Ag-clusters (at least at pH 3), there is no such dependence observed for the overall reaction yield after 4 hours of illumination (cf. Figure 9).

At pH 10, all the Ag-TiO₂ photocatalysts showed a similar performance regardless of silver content. Given that P25 TiO₂ and Ag-TiO₂ photocatalysts had a similar photoactivity after recycling, this study demonstrates that at least for the photodegradation of DCA, there was no advantage in depositing Ag on the TiO₂ surface if the intention is to recycle the photocatalyst with no intermittent washing. For practical applications, where recycling is part of a normal assumed procedure [22], this finding is of great consequence.

TEM analysis of the photocatalysts was carried out with the aim to examine if any visible morphological changes

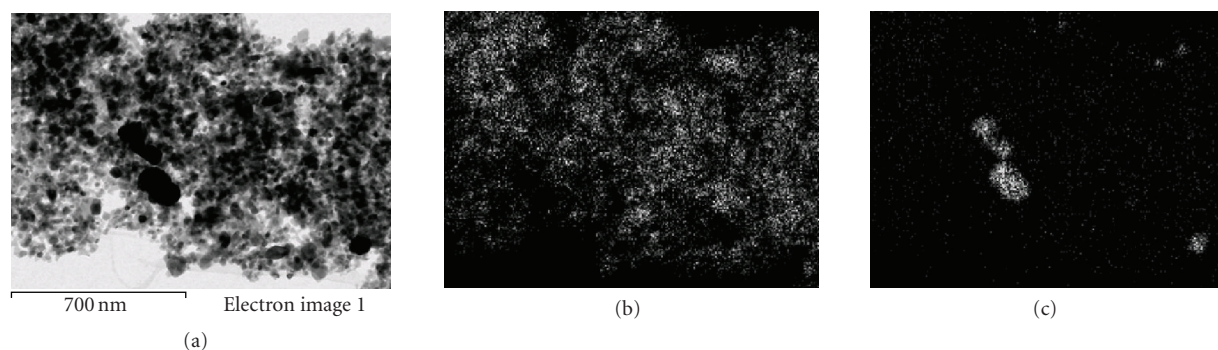


FIGURE 13: Electron microscopy analysis of 0.2 Ag-TiO₂ photocatalyst particles before the DCA photodegradation reaction. (a) STEM image of particles, (b) corresponding Ti X-ray map, and (c) corresponding Ag X-ray map.

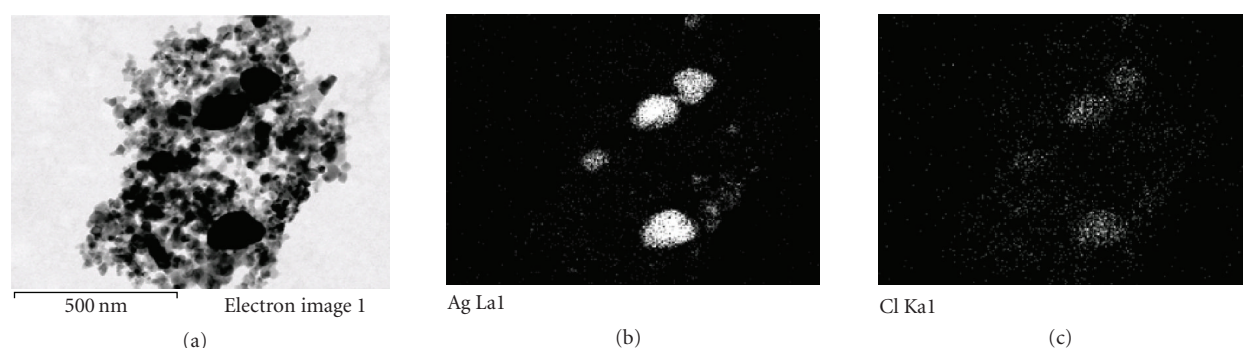


FIGURE 14: Electron microscopy analysis of 0.2 Ag-TiO₂ photocatalyst particles after the DCA photodegradation reaction. (a) STEM image of particles, (b) corresponding Ag X-ray map, and (c) corresponding Cl X-ray map.

had occurred to the photocatalyst samples after the second recycle. The TEM analysis was combined with an EDX-REM from which elemental maps of Ti, Ag, and Cl were obtained to observe their distribution in the samples. As a blank comparison, Figure 10 presents an EDX spectrum of Degussa P25 before the photodeposition of silver or the photodegradation of DCA. Figure 11 shows the same sample after Ag was deposited on the surface. The results are presented for the 0.2 Ag-TiO₂ sample which showed the highest initial activity at pH 3 and the greatest decline in performance after 2 recycles. Figure 12 shows the EDX spectrum after the photodegradation of DCA in three consecutive runs. The presence of Cl⁻ ions detected, indicative of the poisoning of the photocatalyst surface.

In Figure 13, the STEM image and the elemental maps of Ti and Ag in the 0.2 Ag-TiO₂ are shown. These show the distinct silver deposits present in the samples. The size of the silver deposits in 0.2 Ag-TiO₂ sample is larger than that typically presented in the literature [2]. This is believed to be due to the comparatively long irradiation time of 24 hours during the photodeposition reaction. Figure 14 shows the STEM image of the same 0.2 Ag-TiO₂ photocatalyst sample after the DCA photodegradation reaction. The corresponding X-ray maps of Ag and Cl confirm the presence of the Cl⁻ ions and the close association of Ag with the Cl⁻ ions.

Based on the above electron microscopy results, it is clear that following the DCA degradation, there is a considerable amount of Cl⁻ ions on the photocatalysts surface.

It is believed that the chloride ions are merely physically adsorbed onto the surface of the photocatalyst rather than reacting with the silver deposits. This was supported by the fact that the photocatalysts were found to regain their activity by a simple washing procedure. When considering the preparation of the Ag-TiO₂ particles by photodeposition, the silver salt (AgClO₄) was added at slightly acidic pH (pH 6) and the titration to the reaction pH followed afterward. Hence at pH 10, the silver ions are expected to stay adsorbed on the surface and there will be hardly any external formation of AgOH precipitates. Similarly, at pH 3 the silver ions are expected to remain adsorbed onto the TiO₂ surface. This is believed to have minimized the reaction between Cl⁻ ions and Ag⁺ or AgOH as the photodegradation reaction proceeded.

If, on the other hand, the titration of the titania to pH 3 or pH 10 was to be done before the silver was added, different results would have been expected. At pH 3, there would have been a lower amount of silver adsorbed onto the titania surface since both Ag⁺ and the titania surface are positively charged. At pH 10, AgOH will most certainly form adjacent to the titania particles. When Cl⁻ anions are formed in solution, these are expected to react with the Ag⁺

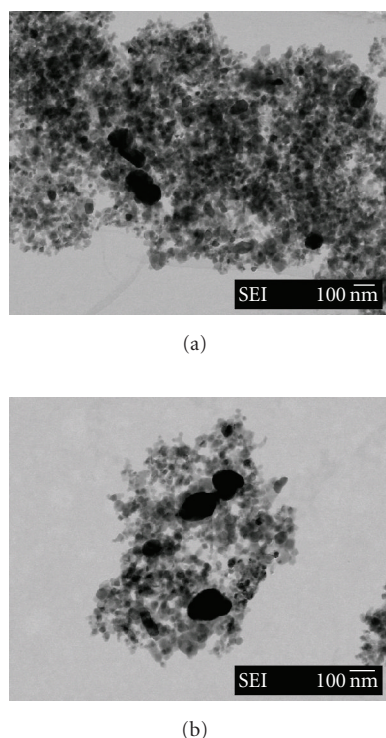


FIGURE 15: TEM images of 0.2 Ag-TiO₂ photocatalyst (a) before and (b) after recycle.

ions or AgOH to form the silver halides (silver chloride has a solubility of 0.8 ppm ($K_{sp}(\text{AgCl}) = 1.6 \times 10^{-10}$) which is pH independent, so most of the silver chloride would have precipitated). Upon UV exposure, the silver salts/compounds are expected to be reduced to silver atoms (as in the photographic process). This would have quite a significant impact on the photolytic formation of the silver deposits on the titania surfaces and the subsequent photocatalytic behavior of the material.

It is also often reported that small photodeposited Ag particles grow due to Oswald ripening as the photodeposition reaction proceeds. For example, at a silver loading of 0.39 wt%, after 60 seconds of irradiation, the size of the Ag deposits was 3 nm which increased as the irradiation time was doubled with some larger Ag deposits (23 nm) being formed [23]. TEM analysis was carried out on the 0.2 Ag-TiO₂ photocatalysts before and after recycling to check, if the silver deposits were in fact reforming after multiple exposures. The results presented in Figure 15 demonstrate that there was no observable change in the size of the Ag deposits. This was as expected since the preparation process allowed 24 hours of illumination for the deposition of the silver particles. As mentioned earlier, the initial Ag deposits were in fact much larger than Ag-TiO₂ photocatalysts which are typically studied. Such studies often employ much shorter irradiation times (30 minutes to few hours) [2]. For our case, the intention was to mimic real conditions which in fact can involve long periods of illumination as several pilot plant studies on photocatalysis have demonstrated [18, 22]. Hence

the procedure for preparing the Ag-TiO₂ photocatalyst particles is critical in determining the nature of the Ag-TiO₂ particles that are formed and the subsequent changes and/or interactions which may occur as the photocatalytic reaction proceeds under real conditions.

4. CONCLUSIONS

In this study, it was possible to demonstrate the drop in photocatalytic activity after 3 consecutive runs for the degradation of DCA, using Ag-TiO₂ photocatalysts under both acidic and basic conditions. The aim was to test these photocatalysts under realistic process conditions which may involve photocatalyst recycle, and extended periods of illumination (up to 12 hours). Interestingly, a minimal reduction in activity was observed for high-surface area, colloidal TiO₂. This is believed to be due to the greater number of active sites in this sample which made it more resilient to poisoning by the released chloride ions during the photodegradation of DCA.

The photocatalytic activity was easily recovered by a simple washing technique, which involved the collection of the photocatalyst particles by centrifugation and their resuspension in a chloride-free solution. The reversibility of the poisoning by the chloride ions provides evidence to the assumption that the recycling of Ag-P25 TiO₂ photocatalysts (for a total 12 hours of illumination) does not have a permanent negative effect on their photocatalytic performance for the degradation of DCA. This was clearly affected by the choice of preparation procedure which minimized the interaction of the chloride ions with free Ag⁺ ions or AgOH precipitates in solution, hence avoiding the formation of AgCl. The formation of AgCl in the system would have lead to complex photolytic reactions, whereby the overall performance for the photodegradation of DCA would have been difficult to predict.

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