NANOCRYSTALLINE TiO₂ AND HALLOYSITE CLAY MINERAL COMPOSITE FILMS PREPARED BY SOL-GEL METHOD: SYNERGISTIC EFFECT AND THE CASE OF SILVER MODIFICATION TO THE PHOTOCATALYTIC DEGRADATION OF BASIC BLUE-41 AZO DYE IN WATER

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ABSTRACT

Tubular halloysite clay mineral and nanocrystalline TiO₂ were incorporated in the preparation of nanocomposite films on glass substrates via sol-gel method at 450 °C. The synthesis involves a simple chemical method employing nonionic surfactant molecule as pore directing agent along with the acetic acid-based sol-gel route without addition of water molecules. Drying and thermal treatment of composite films ensure elimination of organic material and lead to the formation of TiO₂ nanoparticles homogeneously distributed on the surface of the halloysite. Nanocomposite films without cracks of active anatase crystal phase and small crystallite size on halloysite nanotubes are characterized by microscopy techniques and porosimetry methods in order to examine their structural properties. The composite halloysite-TiO₂ films with variable quantities of halloysite were examined as photocatalysts to the discoloration of Basic Blue 41 azo dye in water. These nanocomposite films proved to be very promising photocatalysts and highly effective to dye's discoloration in spite of small amount of halloysite/TiO₂ catalyst immobilized onto glass substrates. It also has been shown that the efficiency of the halloysite/TiO₂ films could be further improved when silver particles were deposited on their surface after successful adsorption from an aqueous solution of a silver salt and UV reduction of the adsorbed ions.

Keywords: Titanium dioxide; nanocrystalline; clay mineral; Halloysite; Photocatalysis; AOPs, Silver modification.

1. Introduction

Wastewater treatment is considered to be a procedure with outmost environmental implications, especially, in the case of industrial wastes. Disposition of colored effluents by textile, paper pulp and other related

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industries represents a technological issue affecting several countries around the world. In particular, wastewater pollution from textile industry is one of the major sources of environmental pollution introducing intense coloring and toxicity to the aquatic system. Azo dyes are synthetic colors that contain an azo group, -N=N-, as part of their structure. These dyes account for approximately 60-70% of all dyes used in food and textile manufacture. Most of the azo dyes are chemically stable and are common constituents of effluents in textile industries which demand an appropriate method to dispose them off. The removal of these azo dyes from effluents is difficult since, they are stable to light, heat and oxidizing agents (Robinson et al., 2003; Pearce et al., 2003). Advanced Oxidation Technologies (AOTs) are considered as alternative methods to the decontamination of polluted water. Basically, AOTs are highly efficient treatments to remove recalcitrant dyes from water based on the oxidative power of radical species created during these processes. Photocatalysis as a method belonging to AOTs, is one of the strategies that can be successfully applied to the oxidation and final removal of azo dyes to the formation of carbon dioxide as a latter product. Photodegradation of various organic pollutants by photocatalysis, using wide band gap semiconductors under UV or solar light, has been extensively studied (Chong et al., 2010; Choi et al., 2010; Ahmed et al., 2010). Among them, TiO$_2$ is a relatively inexpensive semiconductor which exhibits high photocatalytic activity, non-toxicity and stability in aqueous solutions, (Litter, 1999; Song et al., 2009) etc. Furthermore, the synthesis of mesoporous nanocrystalline anatase TiO$_2$ particles, films or membranes has extended their use in environmental remediation (Choi et al., 2007). Ultra fine TiO$_2$ powders with high particle surface area have good photocatalytic activity since reactions take place on the surface of the nanocatalyst. On the other hand, powders can easily agglomerate in larger particles and as a consequence adverse phenomena to their photocatalytic activity are observed. Nevertheless, TiO$_2$ powders cannot easily be recovered from aquatic systems when they are used for water treatment. Highly dispersed TiO$_2$ particles in suspension are difficult to handle and remove after their application in water and wastewater treatment. However, TiO$_2$ can also be used as mobilized catalyst exhibiting high catalytic surface area and activity (Choi et al., 2006). Many research studies have been carried out to immobilize TiO$_2$ catalyst onto various substrates as thin films and membranes. Despite of their lower catalytic surface area compared to powder, significant catalytic activity and utilization have been monitored expanding in this way the field of applications (Bizarro et al., 2009; Sakkas et al., 2010; Li et al., 2008). The specific surface area, particle morphology and possible aggregation, phase composition and number of -OH surface groups are among the most critical parameters for high photocatalytic activity of the as-prepared films. Another approach to enhance the photocatalytic properties of the catalysts is the promotion of their porous structures.

Several procedures have been applied to the immobilization of TiO$_2$ with enhanced properties and photocatalytic activity. Glass slides and fibers, membranes, activated carbon and zeolites are used as supports for TiO$_2$ particles (Wang et al., 2009; Rose et al., 2009; Wang et al., 2008). The efficiency of photocatalytic procedure is generally decreases with catalyst immobilization as the illuminated total surface area is lower than the case of pure TiO$_2$ powder. However, the use of highly porous materials such as clay minerals can be considered as alternative substrates for TiO$_2$ immobilized particles (Bouna et al., 2011; An et al., 2008). Halloysite clay mineral with tubular structure could be considered as suitable and also cheap material for TiO$_2$ particles immobilization (Papoulis et al., 2010; Papoulis et al., 2014). In this work we present the fabrication of thin mesoporous nanocrystalline TiO$_2$ films in presence of halloysite. The formation of the mesoporosity of the films ought to a template technique based on the sol-gel method with surfactant molecules. The enhanced photocatalytic activity of TiO$_2$ nanoparticles in combination with halloysite nanocomposite tubes was examined to the discoloration of azo-dye Basic Blue 41 in aqueous solutions. The synergistic effect between TiO$_2$ and clay mineral tubes was also examined in spite of small amount of TiO$_2$ catalyst immobilized onto glass substrate. Moreover, we modified the as-prepared composite films with silver in order to increase the photocatalytic efficiency of the films. To the best of our knowledge, it is the first time that halloysite/TiO$_2$ nanocomposite photocatalysts immobilized on glass...
substrates with or without the co-existence of silver particles are referred to the decomposition of azo dyes in water.

2. Experimental

2.1. Chemicals and Materials

Pure and well crystalline halloysite samples with tubular morphology were originated from Utah, USA and they were size fractionated by gravity sedimentation to obtain sizes less than 2 μm. Separation of the clay fraction was carried out by using centrifugation methods. The clay fractions of the most halloysite-rich samples were used for the preparation of TiO$_2$-halloysite nanocomposites. Commercially available Triton X-100 (X100, polyethylene glycol tert-octylphenyl ether), titanium tetraisopropoxide (TTIP), acetic acid (AcOH), Basic Blue 41 (BB41), silver nitrate (>99%) and all solvents were purchased from Sigma-Aldrich. Double distilled water with resistivity 18.2 MΩ (Millipore) was used in all experiments.

2.2. Sol synthesis

The X100 as a nonionic long chain surfactant organic molecule was selected as a pore directing agent in a sol. Such amphiphilic molecules may succeed the existence of ordered mesophase and the ability to adjust large inorganic clusters in aqueous condition at the same time. A suitable amount of X100 was homogeneously dissolved in ethanol (EtOH). Before adding alkoxide precursor, AcOH was added into the solution for the esterification reaction with EtOH. Then, TiO$_2$ precursor, TTIP was added at a time under vigorous stirring. The molar ratio of the materials was optimized at X100:EtOH:AcOH:TTIP = 1:69:6:1 in accordance to previous published results (Stathatos et al., 2004). Halloysite (HAL) powder was mixed with previous solution in various quantities following HAL 5%, 20%, 25% and 30% weight ratio compared to TiO$_2$. After several minutes, the dispersion was ready to be used on glass slides. Films prepared on glass slides for the four HAL weight ratios will be referred as HAL5, HAL20, HAL25 and HAL30 respectively while HAL0 represents pure TiO$_2$ films without the presence of halloysite.

2.3 Formation of HAL-TiO$_2$ Thin Films and powders. Silver modification

Borosilicate glass with a size of L75 mm (effective L60) × W25 mm × T1 mm was used as a substrate for fabricating immobilized HAL/TiO$_2$ thin films. Before coating, the substrate was thoroughly cleaned with detergent and washed with water and acetone and finally dried in a stream of nitrogen. A home-made dip-coating apparatus equipped with a speed controller to maintain a withdrawal rate of ~10 cm min$^{-1}$ was used to dip in and pull out the substrate from the sol. After coating, the films were dried at room temperature for 1 hr, calcined in a multi-segment programmable furnace (PLF 110/30, Protherm) at a ramp rate of 5 °C min$^{-1}$ to 450 °C for 15 min, and cooled down naturally. Only one layer of catalyst was formed for all HAL/TiO$_2$ ratios. In the case that powders of the above mentioned samples were prepared, the solutions were put in rotary evaporator in order to remove the solvent. Then the viscous sols were heat-treated for 2 hours at 450 °C instead of 15 min as in making thin films in order to remove all the organic content. In this case the heating ramp rate was 1 °C min$^{-1}$. In case that the as resulted films was chosen to be modified with silver, they were immersed in 1mM silver nitrate aqueous solution. The films were remained in the sol for 15 minutes and then they were rinsed with double distilled water and dried under nitrogen gas. Afterwards, they were exposed to black light (UV source) for 20 minutes while their color was turned to brown which means that adsorbed silver ions were reduced and they were converted to zero valence silver.

2.4. Materials characterization

A Bruker D8 Advance diffractometer with CuKα ($\lambda = 1.5406$ Å) radiation and Bragg-Brentano geometry was employed for X-ray diffraction (XRD) studies of the halloysite-TiO$_2$ catalyst. Nitrogen intrusion/extrusion curves were measured with a Micromeritics Tristar 3000 and the surface area, porosity, and pore size
distribution were derived by differentiating them according to BET method. The values were obtained from thick films after scratching the material due to the difficulty of sample collection from the thin films. For the visual morphology of HAL/TiO₂ nanostructure, an environmental scanning electron microscope (FESEM, Zeiss SUPRA 35VP) was used and inspect film homogeneity. Absorption measurements of BB-41 sols were carried out with a Hitachi U-2900 UV-Vis spectrophotometer.

2.5 Photocatalytic activity of HAL-TiO₂ composite films

A cylindrical reactor presented in a previous publication (Stathatos et al., 2012) was used in all experiments. Air was pumped through a gas inlet using a small pump to ensure continuous oxygen supply to the reaction solution while simultaneously agitating it. Four Black lights with 4 W nominal power were placed around the reactor for UV illumination. The whole construction was covered with a cylindrical aluminum reflector. Cooling was achieved by air flow from below the reactor using a ventilator. The catalyst was in the form of four borosilicate glasses, covered on one side with nanocrystalline HAL% TiO₂ films. The total surface of the photocatalyst films was approximately 60 cm² while the catalyst mass was approximately 50 mg. The reactor was filled with 80 ml of 2.5x10⁻⁵ mol l⁻¹ BB-41 aqueous solution. This dye is strongly adsorbed on pure or halloysite modified TiO₂ films. For this reason, we stored the solution in the presence of the photocatalyst in the dark for an hour and all of our photocatalytic results were obtained after equilibrium. The photocatalytic discoloration process for the dye was examined by monitoring the absorption maximum of the BB-41 solution (610 nm) at various irradiation times. Photocatalytic discoloration rate of BB-41 was calculated by the formula

\[ r = \frac{C_0 - C}{C_0} \]

as the concentration of the dye is proportional to the absorbance for low concentration values. Where C₀ is the initial concentration of BB-41 solution and C is the final concentration after irradiation with UV light. Discoloration efficiency is determined as

\[ \text{eff\%} = \frac{C_0 - C}{C_0} \times 100\% \]

For repeated use of the photocatalysts, the films were washed with distilled water and dried at 80 °C while no further treatment was followed for the films.

3. Results and discussion

3.1. Structural properties of HAL-TiO₂ nanocomposites

Composite halloysite-TiO₂ films prepared on borosilicate glass substrates for different HAL weight proportions as described in experimental section. Samples, abbreviated as HAL5, HAL20, HAL25 and HAL30 represent different weight proportions of halloysite in TiO₂ sol while HAL0 is referred to pure TiO₂. After calcination at relatively high temperature (450 °C) for removing the organic template all films were firmly attached on the glass because of TiO₂ without any cracks. Halloysite was finely dispersed in the films for any proportion was used. First, the crystallinity of the films was examined in order to detect any differences to the crystal structure of halloysite after heating and the crystal phase of resulting nanocomposite TiO₂. The XRD patterns of all films are presented in Fig.1. Strong reflection at 2θ=12.2° is corresponded to halloysite 7Å, while a less intensive reflection at 2θ equal to 8.80° corresponds to halloysite 10Å (Fig.1, curve a). The main peak of halloysite 7Å seems that is remaining after heating but it is much lower mainly to the low amount of the mineral in films proving the remaining crystallinity of the clay mineral. A second reason is probably the partial dehydration of halloysite due to the temperature applied for the synthesis of the films.
It should be noted that in this sample (Fig. 1, curve a) low amounts of quartz are also present (main reflections observed at 26.60° and 20.80°).

Figure 1. XRD patterns of Halloysite-TiO$_2$ nanocrystalline films: (a) powder of halloysite clay mineral as a reference (b) HAL5, (c) HAL20, (d) HAL25, (e) HAL30, (f) HAL0

Titania pure nanocrystalline film (HAL0) is also presented in Fig. 1 (curve f) where a reflection (101) of anatase form at 2θ=25.1° is observed. The two basic reflections at 2θ=12.2° and 2θ=25.1° for HAL and TiO$_2$ are maintained at the rest of samples with different intensity ratio because of the variable proportion between them. The grain size for TiO$_2$ has been calculated from XRD patterns using Scherrer’s equation: $D=0.9\lambda/(s \cos\theta)$, where $\lambda$ is the wavelength of the X-ray and $s$ is the full width (radians) at half maximum (FWHM) of the signal. The crystallite size for TiO$_2$ is calculated 7.5, 8.1, 11.3, 8.5 and 9.4 nm for samples HAL0, HAL5, HAL20, HAL25 and HAL30 respectively.

Table 1. Structural characteristics of Halloysite-TiO$_2$ films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total pore volume Vp (cm$^3$ g$^{-1}$)</th>
<th>Specific surface area S (m$^2$ g$^{-1}$)</th>
<th>Total porosity $\varphi$(%)</th>
<th>Mean pore diameter $D_{por}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halloysite</td>
<td>0.125</td>
<td>50.9</td>
<td>24.46</td>
<td>9.85</td>
</tr>
<tr>
<td>TiO$_2$ (HAL0)</td>
<td>0.133</td>
<td>121.3</td>
<td>33.58</td>
<td>4.78</td>
</tr>
<tr>
<td>5% Hal-TiO$_2$ (HAL5)</td>
<td>0.165</td>
<td>108.6</td>
<td>39.10</td>
<td>6.09</td>
</tr>
<tr>
<td>20% Hal-TiO$_2$ (HAL20)</td>
<td>0.155</td>
<td>77.5</td>
<td>37.62</td>
<td>7.98</td>
</tr>
<tr>
<td>25% Hal-TiO$_2$ (HAL25)</td>
<td>0.171</td>
<td>95.3</td>
<td>39.95</td>
<td>7.20</td>
</tr>
<tr>
<td>30% Hal-TiO$_2$ (HAL30)</td>
<td>0.159</td>
<td>106.2</td>
<td>38.21</td>
<td>6.01</td>
</tr>
</tbody>
</table>

All the peaks indicated that the crystal phase of the materials containing TiO$_2$ was anatase and the relatively large width of peaks indicated that the size of the nanocrystallite was less than 12 nm. It should be noted that it is evident from the XRD patterns that the calcination at 450 °C for 15 min did not completely destroy halloysite.
Because of the difficulty in directly characterizing the porosity of immobilized HAL-TiO$_2$ thin films, the characterizations were carried out on the corresponding particles. The structural characteristics of HAL-TiO$_2$ particles are shown in Table 1.

The specific surface area $S$, the total pore volume $V_p$, the mean pore diameter $D_{por}$, and the total porosity $\phi$ were calculated for all samples and they are presented in Table 1.

Pure halloysite has relatively large pore volume while similar result was obtained for pure TiO$_2$. On the other hand their mixtures possess slightly greater values. As it concerns the particle surface areas, in the case of pure TiO$_2$ a relatively high value of 121.3 m$^2$/g$^{-1}$ is measured and 50.9 m$^2$/g$^{-1}$ for halloysite. All other samples with different proportions of halloysite in TiO$_2$ matrix exhibit intermediate values for particle surface areas as they appear in Table 1. The nitrogen sorption-desorption curves of samples HAL5, HAL20 and HAL25 are presented in Fig.2 and the pore size distribution for HAL20 as an example appear as an inset of Fig.2b. This porosity is, also, apparent in SEM images shown in Fig.3. Halloysite samples are consisted of tubular particles as it can be seen in Fig.3a. The average diameter of the tubes, as they were observed before modification, is 40-70nm while the length is between 100-500nm. After modification, TiO$_2$ nanoparticles uniform in size overlay halloysite tubes.

Figure 2. Sorption-desorption isotherms and pore size distribution (20% in Halloysite) for several %wt of Halloysite in composite Halloysite-TiO$_2$ material

The specific surface area $S$, the total pore volume $V_p$, the mean pore diameter $D_{por}$, and the total porosity $\phi$ were calculated for all samples and they are presented in Table 1.
Besides, TiO$_2$ nanoparticles help to the stabilization of the composite material on the borosilicate glass substrate after calcination by forming stable Ti-O-Si bonds (Stathatos et al., 1997; Liu, 1999). In Fig.3c, d, e and f halloysite nanotubes seem to be completely covered with uniform layers of TiO$_2$ and uniform particle distribution. The thickness of TiO$_2$ film without halloysite tubular particles is around 180-200 nm with only one dipping layer according to cross sectional SEM image. The homogeneity of TiO$_2$ particles’ size and film can be seen in all images of Fig.3. According to images of Fig.3 the TiO$_2$ crystal grains have a spherical shape.

**Figure 3.** SEM images of: (a) Halloysite powder, (b) pure TiO$_2$, (c) HAL5, (d) HAL20, (e) HAL25 and (f) HAL30 films.
while they have an average size ranging from 12 to 16 nm. TiO$_2$ particles were also found to form aggregates on halloysite external surfaces but these were of uniform small size as it was also proved by porosimetry data. The dispersion of halloysite in TiO$_2$ films is obvious but it is firmly agglutinated. No cracks or peeling off traces around halloysite boundaries were observed. The film is permanently attached on the glass substrate with good adherence while halloysite cannot be rived from the composite material. The evidences of SEM images for the nanocomposite material may help us to schematic represent the film fabrication on glass substrates (scheme 1). It is assumed that the organophilic interphase, assured by X100 surfactant coating, acts like a templating medium which provides titanium dioxide nanoparticles with relatively monodispersed particle sizes on the surface. The initially amorphous TiO$_2$ phase was crystallized after calcination at 450°C for 15 min in air while X100 was completely burned out.

Scheme 1. Procedure of HAL-TiO$_2$ nanocomposite photocatalyst formation as films after calcination to promote TiO$_2$ nanoparticles

Silanol groups (Si-OH) of clay mineral can react with titanium alkoxide giving covalently bonded organic-inorganic derivatives, which could be useful for anchoring metal oxide nanoparticles on halloysite surface. From the SEM observations it is evident that halloysite tubes were not destroyed from the temperature involved in the synthesis.

3.2. Photocatalytic activity of composite halloysite and TiO$_2$ films

It is commonly known that titanium dioxide mediated photo-degradation involves the generation of electron-hole pairs (Litter, 1999), which migrate to the photocatalyst surface forming surface bound hydroxyl and superoxide radicals according to following equations:

\[
\text{TiO}_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \\
\text{O}_2 + e^-_{cb} \rightarrow \text{O}_2^- \\
\text{H}_2\text{O} + h^+_{vb} \rightarrow \cdot\text{OH} + \text{H}^+
\]

It is also commonly known that the hydroxyl and superoxide radicals are the primary oxidizing species in the photocatalytic process. These oxidative reactions result in the photodiscoloration of dyes as target pollutants in water. Photocatalytic experiments were undertaken on Basic Blue 41 to evaluate HAL-TiO$_2$ composite catalyst in films as shown in Fig. 4. The different weight percentages of halloysite in TiO$_2$ nanocrystalline films showed slight variations to the photocatalytic activities of the films. The rate of discolorization was monitored with respect to the change in intensity with time of the absorption peak at 610 nm. The absorption peak of the dye diminished with time and disappeared during the reaction indicating that it had been decomposed. Besides, the UV illumination was started after one hour of the photocatalyst presence in dye’s sol in order to be in equilibrium before illumination. The results also show that there was no direct photolysis of BB-41 in the absence of any photocatalyst. In the case of HAL20 a complete decolorization was reached within 140 min of illumination implied the synergistic effect between
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clay mineral and TiO$_2$ by preparing highly porous HAL-TiO$_2$ catalysts. However, the further addition of halloysite in films caused a slight decrease on the photocatalytic activity of films mainly at early stage of the procedure. The combination of clay mineral porous structure with uniform coverage of TiO$_2$ particles on the surface could provide more active sites for dye stuff discoloration. This is also proved by the higher values measured for the porosity and mean pore diameter of the composite HAL-TiO$_2$ compared to the pure TiO$_2$ and Halloysite. However, we may not guarantee that dipping procedure for the film formation succeeds a clear discrimination concerning the quantity of halloysite in films with variable HAL-TiO$_2$ percentage when the clay mineral is dispersed in high amounts in the sol. So, an error to the experimental data presented in Figure 4 cannot be excluded and we estimate it to be at the level of 2-3%.

![Figure 4. Photo-discoloration of BB-41 by TiO$_2$ films in presence of different weight percentages of halloysite under UV light](image)

Considering the small amount of TiO$_2$ catalyst immobilized onto the substrate, the HAL-TiO$_2$ films were highly efficient to degrade the azo dye. As a consequence, the tubular nanocomposite materials can be an alternative substrate for the growth of nanoparticle TiO$_2$ achieving an efficient photocatalyst. Decomposition kinetics of BB-41 has been observed to follow first-order kinetics and it is well established that photo-discoloration experiments follow Langmuir-Hinshelwood model, where the reaction rate, r, is proportional to the surface coverage, θ, according to the following equation (Ibhadon et al., 2008):

$$r = \frac{dC}{dt} = k_1 \theta = \frac{k_1 KC}{1 + KC}$$

where $k_1$ is the reaction rate constant, K is the adsorption coefficient of the reactant and C is the reactant concentration. In the case that C is very small, KC factor is negligible in respect to unity and the equation (1) describes first-order kinetics. The integration of eq.1 yields to the eq.2:

$$-\ln \left( \frac{C}{C_0} \right) = k_{app} t$$

With limit condition that on t=0 we have the initial concentration $C_0$. $k_{app}$ is the apparent first-order rate constant. Discoloration kinetics of BB-41 in presence of different HAL proportions in TiO$_2$ nanocrystalline films is presented in Fig.5. The maximum value for rate constant was calculated for sample HAL20 (29.8x10$^{-3}$ min$^{-1}$) while the value for pure TiO$_2$ film was estimated at 12.9x10$^{-3}$ min$^{-1}$ (Table 2). Furthermore, all the samples HAL-TiO$_2$ exhibited better performance than pure TiO$_2$. We mainly attribute this behavior to
the internal light scattering because of the presence of the halloysite. The poor photocatalytic performance observed for pure TiO$_2$ films after 100 min of irradiation is mainly due to the limited quantity of the material as the total thickness of the films was approximately 180nm (1 layer of TiO$_2$). However, the composite HAL-TiO$_2$ material with only one layer has substantial performance compared to pure TiO$_2$ which proves the effectiveness of the halloysite presence in the films.

![Figure 5. Ln(C$_0$/C) as a function of irradiation time for HAL-TiO$_2$ photocatalysts](image_url)

This is also could be attributed to better structural characteristics of the films compared to pure TiO$_2$ film mainly tabulated at porosity and total pore volume. However, the rate of dye discolorization depends on adsorption of the dye into the catalyst porous structure. Finally, it has been found that the same photocatalysts can be used in several photocatalytic cycles without remarkable loss to their efficiency.

**Table 2. Constant of BB-41 degradation rate in the presence of Halloysite-TiO$_2$ composite films modified with silver particles**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k_{app}$ (x10$^{-3}$ min$^{-1}$) without silver</th>
<th>$k_{app}$ (x10$^{-3}$ min$^{-1}$) with silver</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Hal-TiO$_2$</td>
<td>12.9</td>
<td>18.5</td>
</tr>
<tr>
<td>5% Hal-TiO$_2$</td>
<td>19.8</td>
<td>19.8</td>
</tr>
<tr>
<td>20% Hal-TiO$_2$</td>
<td>29.8</td>
<td>26.6</td>
</tr>
<tr>
<td>25% Hal-TiO$_2$</td>
<td>24.8</td>
<td>25.3</td>
</tr>
<tr>
<td>30% Hal-TiO$_2$</td>
<td>23.2</td>
<td>28.5</td>
</tr>
</tbody>
</table>

**3.3. Photocatalytic activity of silver modified halloysite-TiO$_2$ films**

As an alternative procedure to further increase the efficiency of the HAL-TiO$_2$ photocatalysts silver ions were deposited on the TiO$_2$ surface by submerging TiO$_2$ films in aqueous solutions of metal salt for several minutes. It generally believed that silver modified TiO$_2$ could cause a better separation of charge carriers on the oxide surface (Stathatos et al., 2000). Metal cations could be adsorbed onto TiO$_2$ films at substantial quantities because of the relatively high specific surface area of the films. In the case of silver ions and after
their adsorption only one electron is enough to reduce silver ions and create zero valence noble metal on the surface of TiO$_2$, according to the following equation:

$$\text{Ag}^{+1} + e^- \rightarrow \text{Ag}^0$$

This electron is easy to be generated, either by UV illumination under black light irradiation or by thermal heating of the films (Stathatos et al., 2000).

![Ag modified](image)

**Figure 6.** Photo-discoloration of BB-41 by silver particles modified TiO$_2$ films in presence of different weight percentages of halloysite under UV light

Indeed, the films after UV exposure were turned to light brownish colored attributed to the creation of zero valence silver due to plasmon resonance absorption (Gong et al., 2012). The corresponding photocatalytic experiments to evaluate the silver modified HAL-TiO$_2$ composite catalyst in films are shown in Fig. 6. However, the original salt concentration obviously affects the quantity of deposited metal, affected photo-discoloration efficiency. When the silver salt concentration was $10^{-3}$ mol l$^{-1}$ we obtained the highest photocatalytic efficiency.

![Ln(C$_0$/C)](image)

**Figure 7.** Ln(C$_0$/C) as a function of irradiation time for silver modified HAL-TiO$_2$ photocatalytic films
At higher metal load, efficiency dropped, possibly due to screening effects. Decomposition kinetics of BB-41 in presence of silver modified HAL-TiO$_2$ films, have been observed to follow first-order kinetics as in the case of bare HAL-TiO$_2$ films. The data are presented in Table 2 and Fig.7.

In the case of silver modification the most efficient films are proved to be HAL30 where a complete discoloration of the dye was achieved within 100 minutes.

For a direct comparison among HAL-TiO$_2$ films and silver modified ones to the photocatalytic decomposition of BB-41, we present the data of Fig.8.

**Figure 8.** Comparison between bare and silver modified HAL-TiO$_2$ films to the photo-discoloration of BB-41

It is obvious that silver modified films exhibit a slight better performance to the discoloration of BB-41 mainly due to the better separation of charge carriers on the oxide surface. Further experiments with several noble metals modified composite HAL-TiO$_2$ films are under way.

4. Conclusions

Highly porous nanostructured HAL-TiO$_2$ particles and films were synthesized via sol-gel method composed of ethanol, acetic acid, titanium tetraisopropoxide, halloysite nanotubes and nonionic surfactant molecules as organic template. Slow hydrolysis reaction and stable incorporation of inorganic network onto surfactant molecules made it possible to control the subsequent porous nanostructure. The HAL-TiO$_2$ films exhibited enhanced structural properties including crystallinity and active anatase phase while enhanced photocatalytic properties to the discoloration of BB-41 in water were succeeded. The experiments on photocatalytic discoloration of BB-41 implied the importance of synergistic effect between clay mineral nanotubes and TiO$_2$ nanoparticles. In addition, the presence of silver particles on the surface of the
composite photocatalyst could further increase the efficiency of the catalyst due to better separation of charge carriers on the TiO$_2$.

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