On an adsorption/photocatalytic performance of nanotubular Mg$_3$Si$_2$O$_5$(OH)$_4$/TiO$_2$ composite

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Here, we study a performance of nanotubular Mg$_3$Si$_2$O$_5$(OH)$_4$/TiO$_2$ hybrid adsorbent/photocatalyst in the process of decolorizing an aqueous solution of crystal violet. The composite material was produced by hydrothermal treatment with one or more subsequent cycles of TiCl$_4$ treatment and vapor-phase hydrolysis according to the molecular layering technique. Decolorization was observed in situ by UV-VIS spectroscopy. It was found that TiO$_2$ deposition yields 2 to 3 times improvement of decolorization performance. Depending on TiO$_2$ phase type – amorphous or crystalline – this rise is related with either enhancement of adsorption rate either appearance of photocatalytic activity. Finally, fitting procedure issues in case of complex decolorization process were discussed.

Keywords: chrysotile nanotubes, titanium tetrachloride, titanium oxide, crystal violet dye, adsorption, photocatalysis, water remediation.

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1. Introduction

In the last few decades, wastewater remediation becomes an important problem, the disregard of which accelerates depletion of fresh water resources and ocean contamination. Heavy and textile industries provide various contaminants like heavy metal ions, organic dyes, and diverse organics [1–3]. In order to prevent the overspread of hazardous materials, a number of techniques based on adsorption (separation) [4–7] and catalytic alteration [8–12] can be applied. The problem is that several pollutants can be present in the wastewater simultaneously, and a remediating agent which possesses only one instrument for purification, will not always be capable of handling them simultaneously.

Here, we study a combination of adsorption performance of synthetic Mg$_3$Si$_2$O$_5$(OH)$_4$ chrysotile nanotubes with photocatalytic action of TiO$_2$. The nanotubes can be synthesized by hydrothermal method using various crystalline and amorphous initial components [13–17]. Flexible capabilities of chemical composition tuning – for example, by introducing various d-elements like Ni [18–20], Co [21], Fe [22–24] – and synthesis conditions allows to control surface properties (active sites) and area [25]. Hydroxyl groups reached surface together with the inner channel make chrysotile nanotubes favorable for adsorption and immobilization of various molecules [26–28] and heavy metal ions of Pb, Cd, Sr, and Nd [29–32].

In turn, TiO$_2$ is a well-known and widely used photocatalysis for water purification and splitting [33–35]. Its photocatalytic activity can be further enhanced by creating various types of composite materials with metals [12,34], sulfides [36–39], oxides and clays [40–42], or by varying the shape of TiO$_2$ nanoparticles [43–45]. In our present study, we used molecular layer deposition technique [46,47] with subsequent hydrolysis to obtain TiO$_2$ phase on Mg$_3$Si$_2$O$_5$(OH)$_4$ nanotubes.

2. Experimental

Chrysotile nanotubes were synthesized hydrothermally using a procedure described in detail elsewhere [48,49]. Stoichiometric (with Mg:Si molar ratio as 3:2) mixture of MgO and SiO$_2$ were taken as initial compounds. Hydrothermal treatment was carried out in stainless-steel high-pressure vessels at 350 °C, 70 MPa during 24 h using 1 wt.% NaOH water solution as hydrothermal medium.
Mg$_3$Si$_2$O$_5$(OH)$_4$/TiO$_2$ composite synthesis was carried by sequential treatment of the nanotubes by TiCl$_4$ and H$_2$O vapors in a flow-through reactor equipped with a McBain balance (see [49] for details). Initially, as-synthesized nanotubes were annealed at 400 °C for 5 h on air and then exposed to dry N$_2$ for 2 hours in order to remove adsorbed water molecules and stabilize surface hydroxyl content. On a chemisorption step, chrysotile nanotubes were treated by TiCl$_4$ at 150 °C and 400 °C during 5 – 6 h. Generally, this time is enough to saturate the nanotubes by TiCl$_4$, what was controlled by McBain balance. After that, the reaction zone was purged with dry nitrogen. For the hydrolysis step, the sample was exposed to a stream of air passed at 20 °C through a bubbler filled with distilled water and at temperature in the reactor starting from 150 °C to 400 °C. A final step was purging the reactor with dry N$_2$ at 400 °C. Four full cycles (chemisorption–purge–hydrolysis–purge) were carried out for the sample treated by TiCl$_4$ at 150 °C in order to increase TiO$_2$ content.

Thus, 3 samples were prepared for further study: as-synthesized chrysotile nanotubes; nanotubes treated with TiCl$_4$ and H$_2$O for 4 times (cycles) at the chemisorption temperature of 150 °C; and nanotubes treated once at 400 °C.

X-ray powder diffraction (XRPD) patterns of as-synthesized chrysotile nanotubes and the products of their treatment were acquired by a Rigaku Smartlab SE powder diffractometer with a Cu anode (λ$_{Cu}$=0.15406 nm) in the 5 – 70 ° 2θ range with 0.01 ° steps A PDF-2 database was used for phase identification and peak indexing.

Specific surface area was calculated involving the Braunauer–Emmett–Teller theory. 9-points N$_2$ adsorption isotherms were acquired using Micromeritics ASAP 2020 analyzer. Prior the measurement, the samples were annealed at 400° until a constant weight was obtained.

Scanning electron microscopy (SEM) was performed on A Carl Zeiss NVision 40 SEM/EDS workstation.

In situ studies of decolorization performance were carried out on a modular system consisting of a Xe light source (Mikropack HPX-2000), temperature-controlled cuvette holder with magnetic stirrer (Quantum Northwest TC 125), attenuator, optical fiber connectors (Ocean Optics QP600-1-SR), and a UV-VIS spectrometer (Ocean Optics QE 65000). 1.5 ± 0.1 mg of the sample was mixed with 1.9 ml of deionized water in 4 ml PMMA cuvettes. The suspensions obtained were magnetically stirred at 25 °C throughout the experiment. First, the spectrum of each suspension was recorded in the 300 – 800 nm range and stored as the reference. Then, 0.1 ml of 400 mg/l crystal violet aqueous solution was added to the suspension. Absorbance spectra were recorded for every minute during more than 4 hours starting right after the dye addition. Here and subsequently, this regime is called measurement “on light”. To exclude action of light, the same batch of kinetics experiment were performed “in dark” by blocking off the beam. The cuvette with the sample was lighted up for 1 – 2 seconds only to acquire the spectra. For 4 hours run, 9 to 10 measurements were made.

Solution decolorization $P_t$ at time $t$ was calculated as follows:

$$P_t = \frac{I_0 - I_t}{I_0} \times 100 \%,$$

where $I_0$ is initial (maximal) absorbance intensity, and $I_t$ is intensity at time $t$.

3. Results and discussion

Figure 1a shows XRPD patterns of initial sample and its treatment products. According to phase analysis, hydrothermal synthesis yields chrysotile (card #10-381) nanotubes together with some amount of platy lizardite (#82-1837). Principal reflections of chrysotile and lizardite overlap, so only specific lizardite reflections are marked on the XRPD pattern. The presence of the platy lizardite phase could be caused by Al cations presence in starting hydrothermal synthesis yields chrysotile (card #10-381) nanotubes together with some amount of platy lizardite (#82-1837). Principal reflections of chrysotile and lizardite overlap, so only specific lizardite reflections are marked on the XRPD pattern. The presence of the platy lizardite phase could be caused by Al cations presence in starting material. The fact that the intensities of reflections at around 35° 2θ are comparable means that the lizardite phase content is negligibly low.

Low-temperature (150 °C) treatment with TiCl$_4$ and H$_2$O vapors does not lead to formation of new essential crystalline phases except NaCl as a byproduct. Ti element presence with concentration around 0.3 mmol per 1 g of Mg$_3$Si$_2$O$_5$(OH)$_4$ in case of low-temperature treatment was confirmed in [49] by SEM/EDS and chemical analysis, so we can assume that TiO$_2$ stays mostly in amorphous phase bounded with the chrysotile nanotube surface. High-temperature treatment with TiCl$_4$ and H$_2$O (400 °C) results in the formation of a mixture of anatase and rutile with predomination of the latter (Ti content around 2.9 mmol/g [49]). Chrysotile phase, in general, withstands the heat exposure, and its XRPD pattern remains the same.

Figure 1b demonstrates specific surface area decrease during the treatment of chrysotile nanotubes with TiCl$_4$ and H$_2$O vapors. The observable drop is caused both by heat effect (partial chrysotile dehydroxylation and shrinkage of its interlayer space) and, mainly, by mass increase due to TiCl$_4$ deposition and hydrolysis.
Figure 1. XRPD patterns of initial sample and samples after treatment with TiCl$_4$ and H$_2$O vapors (see experimental part for details). Cards numbers are given according to the PDF-2 database; b) Specific (BET) surface area of initial sample and its treatment products.

Figure 2 shows SEM-images of the samples obtained in SE (morphological contrast) and BSE modes (phase contrast). As-synthesized chrysotile nanotubes have diameters in the range of 30 – 50 nm and length varying from hundreds of nm up to 1 – 2 µm (Fig. 2a). Chrysotile nanotubes form various morphologies including cylinder, cylinder-in-cylinder, and cone. General nanotubular form preserves during TiCl$_4$ and H$_2$O vapors treatment, that correlates with the XRPD data. In particular, SEM-images on Fig. 2b (low-temperature treatment) reveal the absence morphology and phase which would differ from the nanotubular one. In contrast, high-temperature treatment (Fig. 2c) leads to the formation of highly crystalline – and more atomically dense in comparison to chrysotile nanotubes – particles which are obviously consist of TiO$_2$. The average size of the particle is around 100 nm, but there is also a fraction of them with the sizes under tens of nm.

Figure 3a demonstrates an example of change in crystal violet solution absorbance spectra during Mg$_3$Si$_2$O$_5$(OH)$_4$/TiO$_2$ composite-promoted decolorization. A common situation for all samples studied is that the majority of the decolorization effect is achieved during the first hour of solution contact with the solid phase. After that time, the decolorization rate decreases gradually. In accordance with Fig. 3, none of the samples was able...
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To reach 100% decolorization degree, which could be related both with general solid/liquid ratio and the sample’s individual performance. And the latter changes drastically.

Comparative analysis of decolorization kinetic curves reveals several following features: 1) decolorization performance of untreated sample (as-synthesized chrysotile nanotubes) is the lowest among the samples tested; 2) there is an increase in decolorization depending on how the measurements were carried out (on light or in dark, see experimental part for details); 3) there is a divergence (at the initial time of the experiment) and then convergence of kinetic curves on Fig. 3c. The initial sample, as we suppose, possesses only adsorption performance, whereas the samples treated by TiCl₄ and H₂O vapors can have both adsorption and photocatalytic potential, so it should be primarily compared with the samples investigated in dark. This comparison shows that the chrysotile nanotubes treated by 4 cycles at 150 °C have the highest adsorption performance. Assuming equal measurement conditions (temperature, pH, dye concentration, solid phase mass, stirring), two key factors govern adsorption performance: specific surface area and surface properties. Treatment with TiCl₄ and H₂O vapors leads to decrease of the former (Fig. 1b), so the increase of adsorption performance is caused by advantageous change of surface properties, in other words, a number and/or a type (force) of active sites. It is most probably that after low-temperature treatment TiO₂, while it does not form crystalline phase, distributes in an optimal way on the nanotube’s surface and forms a large number of active sites, thus increasing total adsorption performance. High-temperature treatment strongly decreases the surface area and forces TiO₂ to form autonomous crystalline phase. Note that the general forms of the kinetic curves on Fig. 3b and Fig. 3d (measured in dark) are highly similar. This fact can be related to partial reduction of chrysotile nanotubes surface properties after crystalline TiO₂ phase formation.

![Fig. 3.](image)

The most probable origin of the second feature (Fig. 3c,d) is photocatalytic action of TiO₂. A common condition for the photocatalysis is an existence of sufficiently wide bandgap, which can be realized in crystalline solid. According to that, there is an essential increase of decolorization performance when measured on light...
only in case crystalline TiO$_2$ is present in the system. Interaction with light grants 2 – 3 times increase of decolorization performance (Fig. 3d). After 4 hours of the experiment, the divergence of the curves decreases slightly. In case of amorphous TiO$_2$ there is also a light-induced decolorization, which can be seen at the very initial time of the process (Fig. 3c), the effect of which vanishes during the experiment. After 4 hours, the two curves become very similar. It is interesting to note that the maximum difference between the curves obtained on light and in dark for both samples achieves after around 15 – 20 minutes of exposure, but crystalline TiO$_2$ phase provide long-term constant shift of decolorization performance. Most likely this contribution should be related to photocatalytic activity. The Mg$_2$Si$_2$O$_5$(OH)$_4$/TiO$_2$ composite material obtained by 1 treatment cycle at 400 °C is the most appropriate one in the case of combined adsorption and interaction with light is utilized for water remediation. Considering complex interaction process of pollutant with decontaminating agent, there is often a problem of choosing the appropriate kinetic model. Here, we tried to adopt so-called double-exponential model used for description of heavy metal ions adsorption kinetics [51, 52]. The main reason for the use of this model is that it accounts for two ongoing processes, which, in our case, are adsorption and light-induced decolorization. Model equation is written as follows:

$$P_t = P_\infty - A_1 \exp (-k_1 t) - A_2 \exp (-k_2 t),$$

where $P_t$ is decolorization at time $t$, $P_\infty$ is decolorization at infinitely long time of the experiment, $A_1$, $k_1$, $A_2$, $k_2$ are model parameters. The main objective of this fit is to estimate the $P_\infty$ value which determines the performance of the studied material. Nonlinear fitting procedure was applied.

Text insets on Fig. 3b,c,d demonstrate fitting results for the decolorization curves. All cases show high value of adjacent $R^2$ criterion, which is, does not speak well for applicability and physical consistency of the chosen model. However, we can consider a number of features regarding $P_\infty$ value obtained.

First, for some samples (measured on light) the $P_\infty$ value can be underestimated by the fitting procedure. This is a typical situation for the case of kinetic data approximation [53]. In our case, it especially can be seen on Fig. 3d: there is deviation of the fitted curve at the end of the experiment. In addition, adsorption phenomena are considered to be equilibrium processes (in terms of adsorption and desorption speeds), whereas photocatalysis either occurs continuously either fades out because of photocatalyst degradation, and this can bring additional error to the $P_\infty$ value.

Second, double-exponential model was originally applied solely to the adsorption process, and the parts of the model equation (2) were rather related to certain adsorption stages. This complicates discussion of model parameter values in the case when adsorption is combined with other types of processes promoting decolorization. Nevertheless, we should note the proximity of model parameters for the samples obtained by low- and high-temperature treatment and measured in dark (Fig. 3c,d): treatment regime influences on adsorption rate stronger than on an adsorption capacity (proportional to observed decolorization). Finally, according to fitting results on Fig. 3d, the light-induced process which granted the highest performance of the composite with crystalline TiO$_2$ will lose its influence at long-term exposure lying beyond the current experiment time.

4. Conclusion

Here, we report on the application of Mg$_2$Si$_2$O$_5$(OH)$_4$ chrysotile nanotubes / TiO$_2$ composite as an adsorbent and photocatalyst for the process of decolorization of crystal violet. The composite material was obtained by hydrothermal synthesis of nanotubes with subsequent treatment with TiCl$_4$ and H$_2$O vapors according to the molecular layering technique. This treatment allows control of the TiO$_2$ content and phase state. Chrysotile nanotube treatment results in a 2- to 3-fold increase of their decolorization potential, depending on TiO$_2$ phase type. If it forms amorphous phase on the nanotubes surface, then the increase is caused mostly by favorable change of the active sites type. If it forms crystal phase, then decolorization is a combined action of adsorption and photocatalysis. The latter affords the highest decolorization rates.

Although the proposed composites are promising for the cases where combined remediation action is needed, there is still a number of hindrances regarding quantitative description (modeling) of the overall process kinetics. This is crucial for both in-depth understanding of relations between adsorption and photocatalysis, and design of an appropriate apparatus.

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