TOXICITY ASSESSMENT OF VERMICULITE/TiO₂ AND BENTONITE/TiO₂ COMPOSITES USING GREEN ALGAE DESMODESMUS SUBSPICATUS

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Abstract

Vermiculite and bentonite belong to clay minerals, which thanks to their properties have broad industrial applications. Their structure may additionally serve as a suitable matrix for anchoring metal oxide nanoparticles, e.g. titanium dioxide (TiO₂). Due to the photocatalytic properties of TiO₂ induced by UV irradiation, the composites could be used for industrial purposes, such as additives to paints and construction materials, removal of organic pollutants from air and water, etc. Generally, nanoparticles may bring number of advantages related to their nano-dimension, however when released into environment they may pose several risks. Diminishing the environmental risks of nanoparticles can be achieved by their anchoring onto the surface of a suitable matrix. “Eco – friendly” character of developed nanocomposites is an important attribute and one of the tested parameters is acute toxicity to freshwater species of phytoplankton – green algae Desmodesmus subspicatus. The planctonic algae are important primary producers and play significant role in aquatic environment.

The work deals with acute toxicity assessment of the prepared vermiculite/TiO₂ and bentonite/TiO₂ composites according to the OECD 201 on algal growth inhibition test. The composites were prepared by hydrolysis of titanyl sulfate and analyzed using combination of analytical techniques (XRFS, Raman spectroscopy) allowing for chemical and phase characterization of the samples. Based on experimental toxicity data can say that the composites assessed not showed of inhibition of algal growth.

Keywords: vermiculite, bentonite, TiO₂, aquatic toxicity, Desmodesmus subspicatus.

1. INTRODUCTION

Titanium dioxide (TiO₂) is considered as the most suitable photocatalyst for decomposition of many organic pollutants in water and air. It can be used in various processes such as the degradation of oil spills in surface water systems and degradation of harmful organic contaminants as herbicides and pesticides [1]. The photocatalytic activity of TiO₂ is influenced by its crystal structure, particle size, specific surface area and porosity. It was found, that TiO₂ nanoparticles have a large specific surface area, and good photocatalytic properties because the reactions catalyzed proceed on the TiO₂ surface [2, 3]. However, TiO₂ nanoparticles are of considerable concern in relation to their potential toxicity. Several studies have shown that isolated TiO₂ nanoparticles have several toxic effects and therefore may pose environmental risk. Decrease of environmental risks of nanoparticles can be achieved by their anchoring to a suitable solid clay matrix [4]. Clay minerals, because of their low permeability, play an important role, as physical barriers, for the isolation of metal – rich wastes; but chemical barrier too, as a consequence of the ability of some types of clay minerals to adsorb heavy metals and to avoid their environmental dispersion. In this sense, the adsorption of heavy metals by clay minerals is quite well documented in the specialized literature. The fixing of the TiO₂ nanoparticles on the surface of clay matrix enables to obtain nanocomposites, which have photocatalytic properties after exposure of UV light. These properties are given by photodegradation processes on surface of nanoparticles (on which nanoparticles of TiO₂ are securely anchored) [5].

The goal of the study was to assess the acute toxicity of two prepared composites on model aquatic organism. Determination of acute toxicity was performed according to the OECD 201 on algal growth
inhibition test. Two clay minerals – vermiculite (VE) and bentonite (BE), were selected as a matrix for anchoring of TiO$_2$ nanoparticles. The vermiculite/TiO$_2$ (VETI) and bentonite/TiO$_2$ (BETI) composites were prepared by a simple synthesis method using titanyl sulfate (TiOSO$_4$). These composites were further characterized using X-ray fluorescence spectroscopy (XRFS) and Raman microscopy.

### 1.1 Samples preparation and characterization

The vermiculite used in this work was achieved from Letovice (Czech Republic) and the bentonite was obtained from Ankerpoort NV (Maastricht, Netherland). For the preparation of VETI and BETI a simple synthesis was used. Firstly, 30g of VE (BE) clays was mixed with appropriate volume of TiOSO$_4$ Precheza a.s. Přerov (Czech Republic) to give 20 wt.% of TiO$_2$ in the final composite. Prepared suspension was stirred for 24 hour at a constant temperature of 23 ± 2°C. After this period the mixture was heated to 80°C and stirred for 5 hour, and then the 90 min long hydrolysis using 150 ml of distilled water accomplished the synthesis of the VETI and BETI composites. The prepared composites were washed several times with distilled water. The obtained samples were dried at 105°C.

Chemical composition of studied samples was determined using XRFS SPECTRO XEPOS (SPECTRO Analytical Instruments, Germany) equipped with 50 W Pd X-ray tube. The samples were prepared in form of fusions for this measurement.

Raman spectroscopy provides information about molecular vibrations, which allows determining phase composition as well as identification of the sample. This technique is nowadays used in many applications. Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France) was used for this measurement. Raman spectra were acquired with 532 nm excitation laser source, 50x objective and using 1800 gr./mm grating in the range from 100 to 1000 cm$^{-1}$.

### 1.2 Determination of acute toxicity of VETI and BETI composites

Algal toxicity tests on aquatic autotrophic organisms have an essential a role in evaluating newly developed materials introduced into practice. These tests especially serve for testing of potential effects to aquatic organisms.

The determination of acute toxicity of aqueous suspensions of VETI and BETI composites were performed in accordance with the OECD 201. Freshwater green algae (Desmodesmus subspicatus) were used as detection organism. According to the OECD 201 the pH value of prepared aqueous suspension of VETI and BETI (both 10 wt.%) has to fall within the physiological range of 8.1 ± 0.2 and was adjusted using NaOH (1 mol/dm$^3$). These experiments were conducted in duplicate and run in parallel with two controls (algae medium and algal cells without tested samples). Samples were incubated for 72 hour at constant temperature 23°C ± 2°C and under constant aeration and light conditions [6]. Algal cells density was measured using light microscope Olympus CX31 and Bürker counting chamber. The obtained data were processed using Microsoft Office Excel 2003.

### 2. RESULTS AND DISCUSSION

Chemical composition of VE and BE clays and the prepared VETI, BETI composites was determined by XRFS and the results are presented in Table 1. Chemical analysis of the VE and BE clays revealed that the dominant oxides are MgO, Al$_2$O$_3$, SiO$_2$. The VETI and BETI composites were prepared with presumed final TiO$_2$ content 20wt.%. Although the proportion of both matrices (VE and BE) was set to give 20 wt.% of TiO$_2$ in final composite, this value was not achieved especially at composite VETI12. This could be caused by the fact that not all TiO$_2$ particles were anchored on the matrix and were washed out at composite preparation during the decantation step.
Table 1 Chemical composition of VE, BE and VETI, BETI composites

<table>
<thead>
<tr>
<th>Analyte (wt.%)</th>
<th>VE</th>
<th>BE</th>
<th>VETI12</th>
<th>BETI12</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>24.220</td>
<td>3.108</td>
<td>10.990</td>
<td>2.232</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.090</td>
<td>18.430</td>
<td>7.222</td>
<td>13.950</td>
</tr>
<tr>
<td>SiO₂</td>
<td>33.730</td>
<td>54.890</td>
<td>40.350</td>
<td>46.290</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.022</td>
<td>0.309</td>
<td>3.875</td>
<td>3.675</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.028</td>
<td>0.588</td>
<td>0.015</td>
<td>0.354</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.235</td>
<td>0.141</td>
<td>13.660</td>
<td>18.280</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.522</td>
<td>3.625</td>
<td>4.912</td>
<td>2.298</td>
</tr>
<tr>
<td>LOI (%)*</td>
<td>20.100</td>
<td>14.000</td>
<td>17.000</td>
<td>10.700</td>
</tr>
</tbody>
</table>

* Loss on Ignition

Raman spectra of the composites BETI12 and VETI12 are shown in Fig.1. Only one characteristic band of anatase is clearly detectable at 161 cm⁻¹ for BETI12 and 168 cm⁻¹ for VETI12 as is evident on Fig. 1 [7]. Other three characteristic bands are not clearly visible because of fluorescence background of the clay [8].

Table 2 shows the experimental results of acute toxicity testing of samples using Desmodesmus subspicatus. Growth inhibition of green algae was not proved for prepared VETI and BETI composites. Both composites stimulated the growth of the Desmodesmus subspicatus. Stimulatory effects for composites VETI and BETI were: 13.39 % for VETI12, 7.78 % for BETI12, therefore all the samples may be considered as inert to the freshwater green algae. Due to this finding we can assume that these materials should not pose risk to freshwater phytoplankton when used for applications such as water treatment. Nonetheless, further toxicity assessment on other water organisms from different trophic levels should be performed.

Table 2 Toxicity results of the VETI and BETI composites to green algae Desmodesmus subspicatus

<table>
<thead>
<tr>
<th>Algae</th>
<th>Sample</th>
<th>Average stimulation of algae growth [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desmodesmus subspicatus</td>
<td>VETI12</td>
<td>13.39</td>
</tr>
<tr>
<td></td>
<td>BETI12</td>
<td>11.78</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Peaks centered at positions 161 cm\(^{-1}\) for BETI12 and 168 cm\(^{-1}\) for VETI12 observed using Raman microscopy demonstrated the presence of anatase phase of TiO\(_2\) in the studied samples. It was found, that both VETI and BETI composites did not have any inhibitory effects on *Desmodesmus subspicatus* growth. The extent of stimulation effect obtained for both composites are comparable, 13.39% for VETI composite and 11.78% for BETI composite.

ACKNOWLEDGMENTS

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LITERATURE


