Novel micro- and nano- composite materials for water purification

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Considering industrialization and the rising amounts of wastewater, effective water treatment has become a matter of great importance. Adsorption and photocatalysis show superior results compared to conventional water purification methods. Since they are economical and environmentally friendly, many recent studies are focused on developing efficient materials for application in adsorption and photocatalysis. Zeolite is a good sorbent for many metal ions due to its specific porous structure, but it shows low adsorption capacity towards Ni^{2+} and Cr^{3+} ions [1]. In order to improve its adsorption efficiency, zeolite and hydroxyapatite-based composite was synthesized in this study. Hydroxyapatite shows a significantly higher adsorption capacity for Ni^{2+} ions compared to natural zeolite. On the other hand, titanium dioxide is a widely used photocatalyst, but it suffers from high recombination rate and possess low efficiency under solar light. These limitations can easily be overcome by coupling TiO_2 with a conducting polymer [2]. Among many conducting polymers, one of the most promising is polyaniline (PANI) since it is stable, economical, and easy to synthesize. In this work, TiO_2/PANI composites with different amount of PANI (0, 1, 3, 5 wt.%) were synthesized.

Zeolite/hydroxyapatite (Zeo/HAp) composite was obtained by the hydrothermal crystallization of calcium hydroxyapatite in the presence of natural zeolite clinoptilolite at 160°C for 4 hours. TiO_2/PANI composites were obtained by physical mixing of hydrothermally synthesized TiO_2 and PANI, produced using the chemical oxidative polymerization. X-ray powder diffraction (XRPD) analysis was used to determine the phase composition of the obtained composites using an Ital Structure APD2000 diffractometer. Particle size distribution analysis was performed using Mastersizer 2000 (Malvern Panalytical) and Zetasizer Nano S (Malvern Panalytical). The adsorption property of the obtained Zeo/HAp sample was examined towards Ni^{2+} and Cr^{3+} ions. Photocatalytic properties of the prepared TiO_2/PANI composites were investigated towards degradation of toxic textile azo dye Reactive Orange 16 (RO16).

XRPD analysis showed that the composites were successfully prepared. The diffractogram of Zeo/HAp adsorbent confirmed the presence of clinoptilolite and hydroxyapatite in microcrystalline form. All four photocatalysts crystalized in preserved anatase structure of TiO_2 with crystallites less than 50 nm, according to the XRPD analysis. Particle size analysis showed that all the prepared composites were stable in aquatic suspension without further tendency to agglomerate over time. Most of particles had size around 100 µm in the Zeo/HAp composite. Interestingly, it was revealed that the PANI had impact on particle size distribution in TiO_2/PANI composites: with an increase in PANI content, the average particle size increased from 213 nm for pure TiO_2 to 360 nm for TiO_2/5 % PANI. After 24 hours, Zeo/HAp composite adsorbed 42.4 % Ni^{2+} ions and 94.8% Cr^{3+} ions meaning that the adsorption capacity of Zeo/HAp composite is 2.7 times bigger for Ni^{2+} ions and 1.8 times bigger for Cr^{3+} ions compared to natural zeolite clinoptilolite. TiO_2/PANI composites demonstrated significantly better adsorption properties during process of photocatalysis comparing to pure TiO_2. The best photocatalytic activity was reached by TiO_2/1 % PANI which almost completely (99.8 %) degraded the dye after 120 min under simulated solar light.

In summary, micro-sized Zeo/HAp and nano-sized TiO_2/PANI composites were successfully obtained. Both, Zeo/HAp adsorbent and TiO_2/PANI photocatalysts showed better outcomes in water purification compared to the natural zeolite clinoptilolite and the pure TiO_2.

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