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SnO_2-CONTAINING CLINOPTILOLITE AS A COMPOSITE PHOTOCATALYST FOR DYES REMOVAL FROM WASTEWATER UNDER SOLAR LIGHTS

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Photocatalysis has attracted great attention as an environmentally friendly and cost-effective method for the degradation of complex organic dyes in water media. Its mechanism is generally based on a light-induced redox process driven by species formed on the surface of the photoactivated catalyst. Semiconductors such as TiO_2, CuO, ZnO, or SnO_2 are photocatalytically active. Their catalytic performance can be enhanced by different methods including their immobilization onto suitable supports (Han et al., 2018; Rimoldi et al., 2017). Thus, immobilization of ZnO onto natural zeolite - clinoptilolite significantly increased its efficiency in the photodecolorization of bromothymol blue (Bahrami and Nezamzadeh-Ejhieh, 2015). Also, immobilization of TiO_2 onto porous silica enhanced photocatalytic performance of TiO_2 in the decomposition of toluene and formaldehyde (Suligoj, 2016).

Here we present photocatalytic activity of SnO_2-containing clinoptilolite (Sn-Z) in the degradation of methylene blue (MB) as a model pollutant under visible light at room temperature. For the preparation of Sn-Z a clinoptilolite-rich zeolitic tuff (with about 80 wt % of zeolite phase) from the Serbian deposit Slanci (near Belgrade) was used. The tuff sample was modified by a three-step procedure which includes: 1) conversion of the sample to H-form by an acid treatment, 2) ion exchange using a solution of $SnCl_2$ followed by a pH adjustment to 10, and 3) calcination at 400 °C under air. The Sn-Z samples with 3-15 wt. % of Sn were prepared. Their crystallinity checked by a powder X-ray analysis was unaffected by the modification. Diffuse reflectance UV/VIS spectra of the samples confirmed the presence of SnO_2 (an intense absorption peak at λ=263 nm, characteristic for pure SnO_2 is evident in spectra of all Sn-Z) and X-Ray Absorption Spectroscopic studies suggested that SnO_2 particles are not only at the surface of the clinoptilolite phase but also inside the lattice.

Photocatalytic tests were performed in a batch 50 cm^3 reactor. The suspensions contained a water solution of MB (10 ppm) and catalyst (7.5-40 mg) were firstly left in the dark for 30 min in order to achieve adsorption-desorption equilibrium, and then irradiated during 240 min in a solar simulator cell with a visible-light lamp (8 mW cm^{-2}). From the bottom of the cell, the suspensions were mixed by bubbling O_2 at 25 cm^3 min^{-1}. The concentration of MB was measured colorimetrically at λ = 664 nm. In the recycling experiments the spent catalysts were filtered off, left to dry at room temperature, washed 3 times with 0.01 M HNO_3 and dried at 90 °C.

Photocatalytic tests showed that pure SnO_2 exhibits a negligible adsorption capacity towards MB (4 wt. %) in the dark, and after illumination total degradation is about 15 % indicating low catalytic performance of SnO_2. The Z showed higher adsorption capacity (10%) and better catalytic activity. Total degradation of MB in the presence of Z was about 30%. The presence of SnO_2 increased both adsorption capacity and catalytic performance. Total degradation of MB for the Sn-Z with the highest amount of Sn (15 wt. %) is about 45 % suggesting a synergetic activity of SnO_2 and clinoptilolite lattice (Fig. 1a). An interesting

phenomenon was evident in the visible spectra of suspensions: at longer irradiation the absorption maximum at 643 nm appears together with absorption at 610 nm which was ascribed to penetration and stabilization of MB inside the zeolite lattice (Awala et al., 2016).

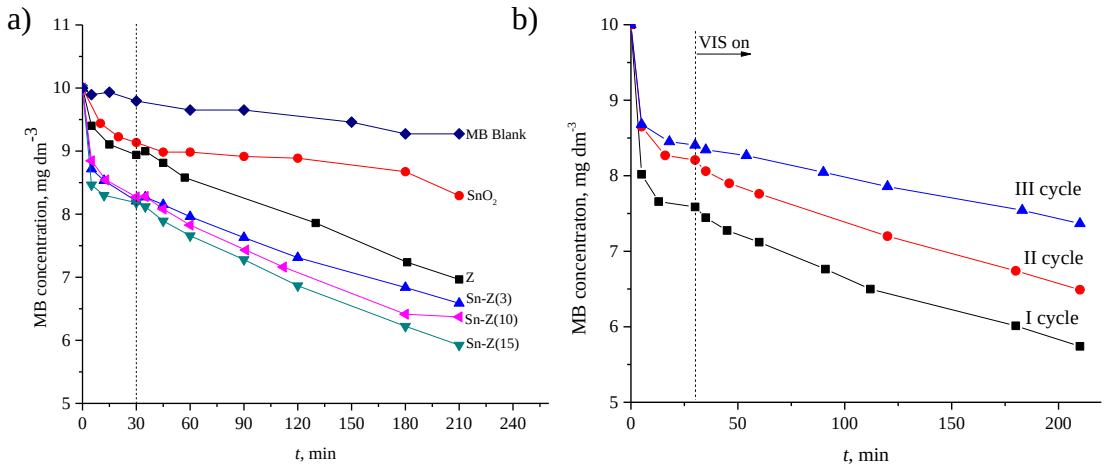

Figure 1. a) Photodegradation of MB in the presence of SnO_2, Z and Sn-Z with different amounts of Sn (3, 10 and 15 wt.%). The Sn amounts are written in parenthesis. The beginning of the illumination is marked by a dashed line; b) Reusability of Sn-Z (15 wt.%) during three cycles.

Reusability tests showed that in the dark period the adsorption capacity of the reused Sn-Z partially decreased most probably due to a partial blockage of the active sites caused by products of the MB degradation. The catalytical performance also decreased but Sn-Z retains the photocatalytic activity.

It can be concluded that the composite prepared by a simple modification of clinoptilolite-rich zeolitic tuff with SnO_2 showed photocatalytic activity in the degradation of methylene blue under irradiation with visible light at 25 °C and atmospheric pressure. The activity is ascribed to a synergetic effect of SnO_2 and the clinoptilolite lattice. Although the composite lost a part of the catalytic activity during 3 cycles its performance could be stabilized and improved by optimization of the regeneration process of the spent catalyst. The composite is perspective as cost-effective and environmentally friendly catalyst.

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