International scientific conference

Environmental impact of illegal construction, poor planning and design IMPEDE 2019

CONFERENCE PROCEEDINGS

10 – 11 October 2019, Belgrade, Serbia

CONFERENCE PROCEEDINGS

International scientific conference Environmental impact of illegal construction, poor planning and design IMPEDE 2019

Organizer / Publisher: Association of Chemists and Chemical Engineers of Serbia (UHTS)

Organizer: Academy of Engineering Sciences of Serbia (AESS)

Co – Organizers: Faculty of Forestry, University of Belgrade and Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade

IMPEDE 2019 conference is supported by Ministry of Education, Science and Technological Development, Republic of Serbia

Editor in Chief: Marina Mihajlović, Ph.D

For publisher: Zoran Popović, M. Sc.

Printing office: Čigoja štampa
Studentski Trg 1, Belgrade

Print run: 120

ISBN: 978-86-901238-0-3

SCIENTIFIC COMMITTEE

- Emeritus Professor Miroljub Adžić, University of Belgrade - Faculty of Mechanical Engineering, AESS Vice President
- Emeritus Professor Slobodan Petrović, University of Belgrade - Faculty of Technology and Metallurgy, AESS full member
- Emeritus Professor Čedo Maksimović, Imperial College, London, England
- Prof. Branka Dimitrijević, FHEA, Director of Research and Knowledge Exchange Department of Architecture University of Strathclyde, Glasgow, Scotland
- Mila Pucar, Ph.D., Institute of Architecture and Urban and Spatial Planning of Serbia, AESS full member
- Prof. Florian Nepravishta, Faculty of Architecture and Urbanism, Dean, Polytechnic University of Tirana, Albania
- Prof. Ilija Ilić, AESS full member
- Prof. Aleksandra Smiljanić, University of Belgrade - Faculty of electrical engineering, AESS corresponding member
- Prof. Ratko Ristić, University of Belgrade – Faculty of Forestry Dean, AESS corresponding member
- Prof. Kiril Sotirovski, University Ss. Cyril and Methodius – Faculty of Forestry Dean, Skopje, North Macedonia
- Prof. Anita Grozdanov, University Ss. Cyril and Methodius – Faculty of Technology and Metallurgy, Skopje, North Macedonia
- Prof. Mirjana Drenovak Ivanović, University of Belgrade – Faculty of Law
- Prof. Nataša Tomić-Petrović, University of Belgrade – Faculty of Transport and Traffic Engineering
- Prof. Radmilo Pešić, University of Belgrade – Faculty of Agriculture, Associate Fellow of the World Academy of Art and Science, Vice-President of the Club of Rome Serbian Chapter
- Sanja Šaban, MSc Architecture, Ministry of Construction and Physical Planning – Assistant Minister, Zagreb, Croatia
- Miroslav Sokić, Ph.D., Director Institute for Technology of Nuclear and other Mineral Raw Materials director, Belgrade, Serbia
- Prof. Dušan Vuksanović, University of Montenegro – Faculty of Architecture, Podgorica, Montenegro
- Marina Mihajlović, Ph.D., Scientific Committee Secretary, Innovation center Faculty of Technology and Metallurgy, Belgrade
- Prof. Mića Jovanović, Scientific Committee General Chair, University of Belgrade - Faculty of Technology and Metallurgy, AESS full member, UHTS Board member

ORGANIZING COMMITTEE

- Zoran Popović, M.Sc., Organizing Committee General Chair UHTS Board President
- Gordana Nešić, M.Sc. UHTS Board member
- Branislav Tanasić, Ph.D., UHTS Board member
- Marina Mihajlović Ph.D., Innovation center Faculty of Technology and Metallurgy, Belgrade
- Ana Dajić, M.Sc., Innovation center Faculty of Technology and Metallurgy, Belgrade
- Julijana Tadić, M.Sc., Innovation center Faculty of Technology and Metallurgy, Belgrade
- Milica Svetozarević, M.Sc., Innovation center Faculty of Technology and Metallurgy, Belgrade
- Prof. Mića Jovanović, University of Belgrade - Faculty of Technology and Metallurgy, AESS full member, UHTS Board member

Table of contents

Photocatalytic Degradation of Methylene Blue by Catalysts Prepared from Serbian Clinoptilolite and SnO_2

Fotokatalitička degradacija metilensko plavog u prisustvu katalizatora na bazi klinoptilolita sa područja Srbije i SnO_2

***Jelena Pavlović*[1], *Aleksandra Popović*[2], *Nevenka Rajić*[2,*]**

[1]Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia, [2]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

In this work, clinoptilolite-rich zeolitic tuff from the deposit Slanci (near Blegrade) was used for the preparation of a photocatalyst. Clinoptilolite surface was modified by Sn(IV) oxide in different amounts (3-15 wt.% Sn) using a simple procedure consisted of three steps: a) ion exchange, b) precipitation of Sn hydroxide and c) calcination under air at 400 ^{o}C. Photocatalytic activity was studied in water solution of methylene blue (MB) as a model pollutant with initial concentration of 10 ppm at room temperature, using different amounts of the prepared catalyst. The suspension was irradiated for 180 min in a solar simulator chamber with a visible-light lamp (8 mW cm^{-2}). The prepared catalysts exhibited catalytic activity higher than pure SnO_2 indicating a significant role of the clinoptilolite lattice in the photodegradation of MB. It is showed that the initial concentration of MB decreased for 45-75 % depending of the catalyst amount. Reusability of the catalyst was tested in three catalytic cycles showing that photocatalytic activity partially decreases which is ascribed to partial blockage of catalytically active sites.

Keywords: photocatalysis, zeolite, organic dyes

* nena@tmf.bg.ac.rs

1. Introduction

Different organic dyes are discharged in water body mainly from textile and leather industries. These organics are generally toxic and carcinogenic and their presence in water even in low concentrations causes serious environmental problems. Although still important, traditional water purification methods such as mechanical separation, filtration, flocculation, coagulation or chemical treatments need to be invented as well as novel water treatment technologies more efficient than the traditional ones should be developed.

Organic dyes possess complex structures and their degradation is usually complicate. Advanced Oxidation Processes (AOPs) have been recognized as effective methods for a complete degradation of organic dyes. Effectiveness of

AOPs has mainly been ascribed to the formation of highly reactive hydroxyl radicals formed by an activated catalyst.

Photocatalysis is one of the AOPs considered as an environmental friendly and efficient method. Metal oxides such as TiO_2, ZnO, SnO_2, or Fe_2O_3 have been reported to exhibit significant photocatalytic performance [Kim et al., 2015; Dariani et al., 2016]. It has been reported that the catalytic activity and reusability of these oxides can be significantly improved by immobilization of the oxide particles onto suitable supports [Bahrami and Nezamzadeh-Ejhieh, 2015; Maučec et al., 2018].

Due to their unique structural properties as well as due to low cost and environmental compatibility, in this work we used for the preparation of a photocatalyst zeolite – clinoptilolite which is the most abundant natural zeolite in Serbia. Clinoptilolite 3D structure is characterized with an open-framework lattice which enables an easy access to the channel system with nanometric apertures.

Catalytic activity was tested in the photodegradation of methylene blue (MB) as a model cationic dye under visible light.

2. Experimental

2.1 Synthesis

Zeolitic tuff (Z) obtained from Slanci deposit (near Belgrade) was used in this study. Semiquantitative X-ray diffraction analysis performed by Rietveld refinement method (Topas-Academic v.4) showed that zeolite – clinoptilolite is the major mineral phase (about 80 wt.%) whereas quartz (~ 4 wt.%) and feldspars (~ 16 wt.%) are accompanying mineral phases.

The grain size used in all experiments was in the range of 0.063-0.1 mm for which previous experiments showed to be optimal ones for the modification process.

The modification consisted of two phases. In the first one, the tuff sample was treated with HCl (1 mol dm^{-3}) and then with NH_4OH (0.2 mol dm^{-3}). The treatment resulted in the preparation of NH_4-containing clinoptilolite (NH_4-Z). The calcination of the NH_4-Z at 600 °C resulted in conversion of NH_4-Z to HZ.

In the second phase the HZ was loaded by SnO_2 as follows. HZ was suspended in the ethanol solution of $SnCl_2$ containing different amounts of $SnCl_2$ and pH was adjusted to 10 using NH_4OH. The dried products were calcined at 400 °C under air yielding SnO_2-Z (with 3-15 wt.% Sn).

2.2 Characterization

The crystallinity of the samples was tested by a powder X-ray diffraction method (PXD) using an APD2000 Ital Structure diffractometer (CuK_α radiation, λ=0.15418 nm).

Elemental analyses were performed using a Carl Zeiss Supra™ 3VP field-emission gun scanning electron microscope (FEG-SEM) equipped with EDS detector (Oxford Analysis) with INCA Energy system for quantification of elements.

Porosity characteristics were determined by N_2 adsorption at –196 °C using a Micromeritics Instrument (ASAP 2020). The specific surface area (S_{BET}) was calculated according to the Brunauer, Emmett, Teller (BET) method up to relative pressures $p/p_0 = 0.15$.

The presence of SnO_2 onto samples was revealed from diffuse reflectance spectra (DRS) measured in the range 200-600 nm using V-650, JASCO UV-VIS spectrometer.

2.3 Photocatalytic tests

The photocatalytic experiments were performed in a batch 50 cm^3 reactor. The reaction mixture, contained a solution of MB (10 ppm) and catalyst (7.5-40 mg) was illuminated with a visible-light lamp (8 mW cm^{-2}) and mixed by bubbling O_2 at 25 cm^3 min^{-1} from the bottom of the chamber during 180 min. The concentration of MB was measured colorimetrically at λ = 664 nm using Hach DR 2800 spectrophotometer.

The spent catalyst for which the photocatalytic experiments gave the best performance was chosen for recycling experiments. The catalyst was separated from suspension by filtration, left to dry at room temperature, washed 3 times with 0.01 M HNO_3 and dried at 90 °C for 1h prior to be reused.

3. Results and discussion

PXD analysis showed that crystallinity of the zeolite - clinoptilolite remains intact after the conversion of Z to SnO_2-Z (Fig. 1). The pattern of SnO_2-Z does not exhibit any novel phase even at the highest amount of Sn which suggests that the formed SnO_2 (*vide infra*) is amorphous.

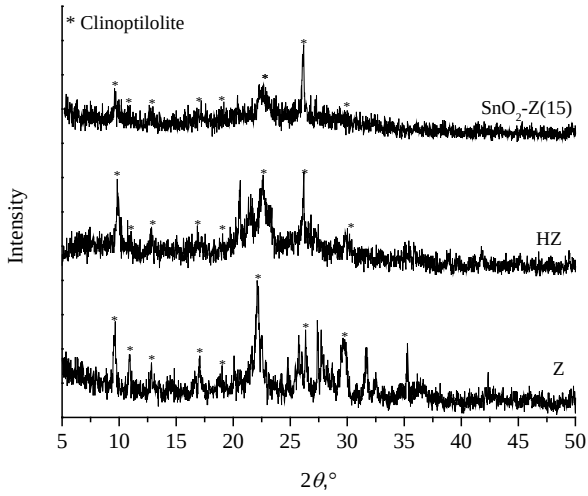


Figure 1. PXD patterns of Z, HZ and SnO_2-Z (with 15 wt.% Sn).

EDS analysis of the clinoptilolite phase of all the studied samples showed that conversion of the Z to HZ caused: a) a partial dealumination of the clinoptilolite lattice which results in increase of Si/Al molar ratio from 4.9 to 7.2, b) significant decrease of Na content (from 0.2 to 0.02 wt.%), c) removal of K, Ca and Mg present in the Z before its modification and d) the content of Sn varied from 3 to 15 wt.% in SnO_2-Z samples

The conversion of Z into HZ increased the specific surface area from 32 to 198 m^2 g^{-1}. The SnO_2 loading slightly influenced the specific surface area and decreased it to 170 m^2 g^{-1}. This could be ascribed to a partial pore blockage of the clinoptilolite lattice by formation of SnO_2 particles.

DRS revealed that the second phase of the modification process resulted in the formation of SnO_2. Fig. 2 clearly shows that the absorption maximum centered at 263 nm present in the spectrum of pure SnO_2 is also evident in the spectrum of SnO_2-Z. This maximum is not evident in the spectrum of HZ.

Photocatalytic tests showed that all SnO_2-Z samples are catalytically active. The activity increased with increasing of the Sn content (Fig. 3a) in SnO_2-Z as well as with increasing of applied catalyst amount. The highest degradation rate of MB (75 %) was achieved with 40 mg of the SnO_2-Z (Fig. 3b).

Fig. 3a shows an interesting phenomenon: all SnO_2-Z samples exhibited better catalytic performance than pure SnO_2. It indicates that the clinoptilolite lattice has a significant role in the photocatalytic degradation of MB.

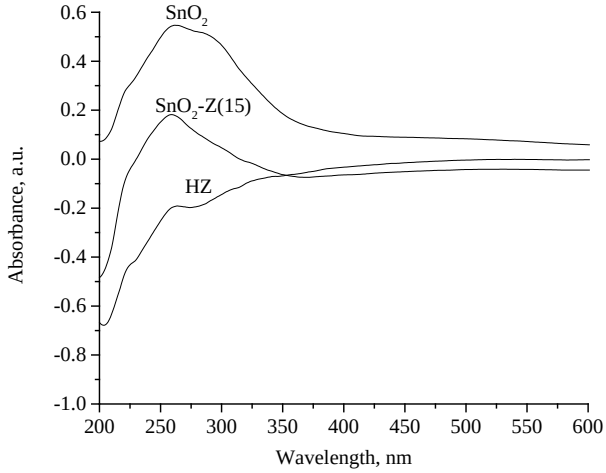
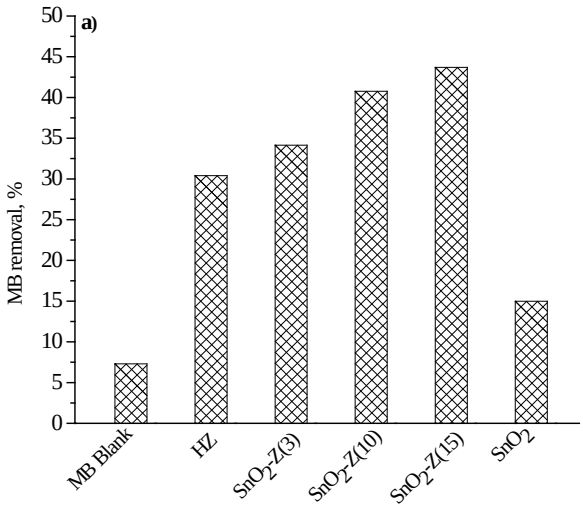


Figure 2. DR spectra of SnO_2, HZ and SnO_2-Z with 15 wt.% Sn.

The recycling experiment was performed using the highest amount of the SnO_2-Z (Fig. 4). During three cycles the photocatalytic activity of SnO_2-Z decreased to about 30 %. The effect could be ascribed to a partial blockage of the active sites on the catalyst surface by the degradation products of MB. This shows that future work should be directed towards preservation on active sites on the catalyst as well as to optimization of recovering process.



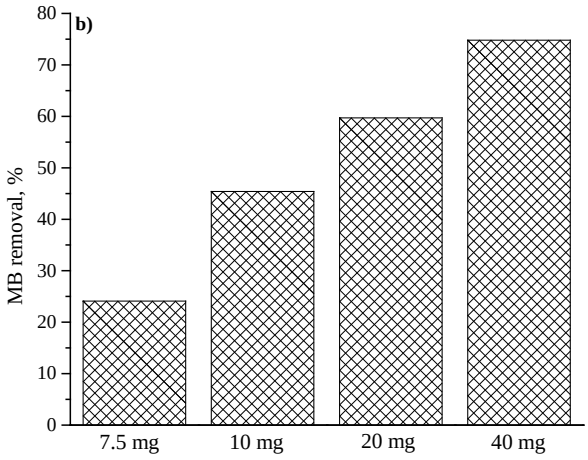


Figure 3. Results of photocatalitical degradation of MB: a) in the presence of 10 mg catalyst. Different amounts of Sn (in wt.%) are in parentheses; b) by using a different amount of SnO_2-Z(15).

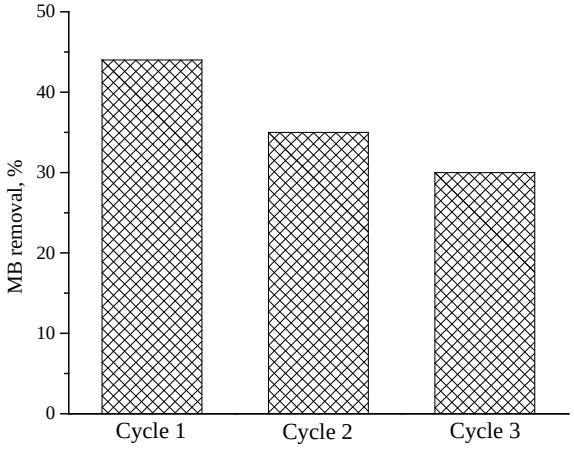


Figure 4. Reusability of SnO_2-Z(15) in photocatalitical degradation of MB.

4. Conclusion

Present results show that the clinoptilolite-rich zeolitic tuff from a Serbian deposit can be used in the preparation of catalysts active in the photodegradation of organic dyes under visible light. By a simple procedure sample of the tuff was converted in the catalyst with a high catalytic activity in the photodegradation of methylene blue. Since the photocatalytic activity partially decreased during reuse experiments future investigation will be directed towards the preservation of its activity.

Acknowledgement

This research was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. 172018).

References

Bahrami M, A Nezamzadeh-Ejhieh, Effect of the supported ZnO on clinoptilolite nano-particles in the photodecolorization of semi-real sample bromothymol blue aqueous solution, *Materials Science in Semiconductor Processing*, 30 (2015) 275-284, DOI 10.1016/j.mssp.2014.10.006

Dariani R S, A Esmaeili, A Morteyaali, S Dehghanpour, Photocatalytic reaction and degradation of methylene blue on TiO_2 nano-sized particles, *Optik*, 74 (2016) 7143-7154, DOI 10.1016./j.ijleo.2016.04.026

Kim S P, M Y Choi, H C Choi, Photocatalytic activity of SnO_2 nanoparticles in methylene blue degradation, *Materials Research Bulletin*, 74 (2016) 85-89, DOI 10.1016./j.materresbull.2015.10.024

Maučec D, A Šuligoj, A Ristić, G Dražić, A Pintar, N N Tušar, Titania versus zinc oxide nanoparticles on mesoporous silica supports as photocatalysts for removal of dyes from wastewater at neutral pH, *Catalysis Today*, 310 (2018) 32–41, DOI 10.1016/j.cattod.2017.05.061