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HYBRID MATERIALS FOR THE REMOVAL OF ORGANIC COMPOUNDS FROM WATER

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Abstract

Water quality is an inportant concern for the ecosystem state from a particular region. Since the continuous urban and economic development induces a negative impact on entire hydrological cycle, this study investigates the water quality of a Romanian lake, located in the Surduc area - Timis County. This perimeter has undergone significant economic development in the past two decades due to increased tourism potential and the number of holiday residences.
We proposed hybrid materias for the degradation of organic pollutants from the lake water. Particle size, morphology and properties of the hybrid materials are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), DRUV-VIS spectroscopy and TOC determinations.

Key words: catalytic material, hypertrophication, photocatalytic activity, Z-Na

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1. Introduction

Water quality became an integral part of environmental quality management in today's world, when clean water is essential for humans, animals and plants. The demand for clean water and sanitation (including wastewater treatment) has been steadily rising with the rapid increasing in urbanization and population within civil habitats. That fact denotes the importance of water resources in the environment and its impact on humans, animals and plants under conditions of ever increasing anthropogenic activities linked to over population (Balica et al., 2012; Dinh et al., 2012; Van et al., 2012).

Streams, rivers and lakes located in areas of urban development are often associated with increased sediment load, trash, degraded water quality, and increased flooding (Jonoski et al., 2012a,b; Moya Quiroga et al., 2013; Muste et al., 2010; Quinn et al., 2010; Popescu et al., 2010, 2012a, b, c; Sonal et al., 2012).

Most often, accelerated development of tourist areas represent the main pollution causes for rivers and lakes in those regions. Untreated domestic wastewater, the increase of sewage quantity all contribute to water quality deterioration. The main effect is hypertrophication, since the over-enrichment of lakes and rivers with nutrients, causes toxic algae blooms, deoxygenating, foul odors, fish kills, and heavy economic losses to communities that depend on clean water for drinking, recreation or industrial use. Although there are many studies over photocatalytic methods applied in water treatment, this type of techniques continues to play an important role in water decontamination processes due to the fact that are environmental friendly (Corma et al., 2004; Ignat et al., 2011; Zhang et al., 2011). However, to increase the photonic efficiency is necessary to develop hybrid photocatalysts (Dubey et

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al., 2006; Farnandez et al., 1995; Konstantinou et al., 2004).

The aim of this study was to identify a simple and efficient method for the degradation of organic compounds from water using materials based on Z-Na-TiO_2. Also, it will establish the levels of water pollution and used materials for treat it.

2. Material and methods

Water samples were colected from three different zones of the Surduc Lake denoted by P1, P2 and P3 These individual water samples was taken and deposited in the same collection bottle and was kept at 4°C for 24 hours. Before analysis the water samples were homogenized by ultrasonic treatment and then water samples were filtered through a 0.45 um filter.

Chemicals

Romanian zeolitic mineral from Mirsid, used as support for doped TiO_2 loading, was supplied by CEMACON Company, Romania. The diameter of grains size selected to carry out the experiments was between 315-500 μm with the mass composition 62.20% SiO_2, 11.65% Al_2O_3, 1.30% Fe_2O_3, 3.74%CaO, 0.67% MgO, 3.30% K_2O, 0.72% Na_2O and 0.28% TiO_2.

3. Experimental

3.1. Total organic carbon content

The TOC analyzer used in this study was a SHIMADZU TOC-V_{CPN} equipped with a 94 – position auto sampler. The TC principle analysis was catalytic combustion at high temperature (900°C) and for IC –acidification at 200°C (Akpan et al., 2009). The amount of water samples used for TOC analysis was 25mL and reagent used was phosphoric acid, 1:1 v/v.

3.2. Atomic Absorption Spectrometry (AAS)

The tests for determination of heavy metals contents from water samples were conducted under international standard ISO 15586:2003 (E), with equipment: Analytik Jena novAA 400G - apparatus, with a graphite furnace, equipped with autosampler MPE60 and software WinAAS 3.17.0. Examined materials: samples of water (2mL) Substances: nitric acid, ultrapure water.

The samples were treated with 5.5 mL HNO3 65% and subjected to digestion in a Berghof microwave oven MWS 2, using a three stages program: T1=160°C, t1= 15 min, p1= 80%. T2=210 °C, t2=15 min, p2=90% and T3, t3=15 min, p3=0%. After digestion, the sample is brought to a volume of 100 mL with ultrapure water.

3.3. Preparation of photocatalyst

The catalytic material based on natural zeolite modified with undoped TiO_2 nanocrystals was obtained by microwave-assisted hydrothermal conditions (Kitano et al., 2007). Titanium dioxide photocatalyst was previous obtained by classical sol-gel method, pure anatase phase.

The preparation of the chemically modified zeolite presumes two stages to reach acid form (H form) by using a 2M HCl solution and sodium form (Na form) with 2M $NaNO_3$ solution for a more efficient ion exchange. Consequently, Na forms of natural zeoliteare expected to remove other cations easily in ion-exchange applications. The microwave synthesis was performed in a microwave reaction system, Multiwave 3000, produced by Anton Paar at 2.45 GHz for a continuous power of 1000 W. The temperature measurements were recorded with an IR sensor depending on solution content from autoclave. Therefore, an amount of Z-Na was mixed with 40 mL distilled water and undoped TiO_2 (2wt%), in aqueous solution under continuous stirring for 4 hours. The obtained solutions were introduced into a Teflon autoclave with a 50% degree of fullness, for 30 min to 180°C, under microwave radiations. After autoclaving, the catalytic materials (Z-Na-TiO_2) was washed with distilled water and dried at 60°C for 5 hours.

3.4. Characterization of catalytic material

The crystallinity of the prepared samples was investigated by X-Ray diffraction (XRD) using PANalytical X'PertPRO MPD Difractometer with Cu Cu $K\alpha$ radiation λ = 1.5406Å, 2θ-step of 0.01° from 10 to 100. Scherrer equation, $d = 0.9\lambda / (B \cos \theta)$ was used to estimate grain average sizes of crystallites, where B is the half height width of the reflection peak at 2θ and λ is the wavelength of the radiation. Scherrer equation, $d = 0.9\lambda / (B \cos \theta)$ was used to estimate grain average sizes of crystallites, where B is the half height width of the reflection peak at 2θ and λ is the wavelength of the radiation. The morphology of hybrid materials was observed using an Inspect S PANalytical model scanning electron microscopy (SEM) using coupled with the energy dispersive X-ray analysis detector (EDX). The semiquantitative elemental analysis was analyzed through EDAX facility of SEM.

The light absorption properties of catalytic materials were studied by UV–VIS diffuse reflectance spectroscopy (DRUV-VIS), performed under ambient conditions using Lambda 950 Perkin Elmer with the wavelength range of 200–430 nm. The blank sample was used as the reference.

3.5. Photocatalytic degradation procedure

The photocatalytic activities of the prepared catalytic materials were assessed by application of 6W UV irradiation at room temperature for 2 hours. The volume of the reaction solution was 50mL, into which 0.05 g of photocatalyst (Z-Na and Z-Na-TiO_2)

was added. After an irradiation time of 2 h, the suspension was sampled and filtered through a 0.2 μm membrane filter. Also, the mineralization degree was assessed by monitoring total organic carbon (TOC) parameter using a SHIMADZU TOC-V_{CPN}.

4. Results and discussion

Catalytic materials based on natural zeolite modified with undoped TiO_2 (Z-Na-TiO_2) was synthesized in microwave-assisted hydrothermal conditions. X-ray diffraction, DRUV-VIS spectroscopy and SEM/EDX and TOC analysis were used for the characterization of catalytic materials. Morphological and structural analysis of the catalytic material was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX).

4.1. Water analysis

Establisment of water pollution level was acomplish by two different analytic methods: TOC detection and atomic absorption spectrometry.

4.2. TOC analysis

Measurement of TOC is a much more fast method to determine the organic matter content in water and wastewater, which is directly related to total organic content. Organic, inorganic and total carbon content was measure from the water samples. The results are shown in the Table 1.

From TOC analysis results can be determinate the average of organic content of the lake water which is 21.31 mg/L. According to the date base values of TOC higher than 20 mg/L corresponds to poluted water (Table 2).

4.3. Atomic absorption spectrometry (AAS)

The evaluation of the metals contents (As, Cu, Pb, Zn, Cd, Fe and Ni) from water samples was performed through atomic absorption spectroscopy. The results of the analysis are presented in Table 3.

From the results obtained in Table 2 it can be seen that in water samples was found only two metals: iron and zinc in concentrations much lower than national and international regulation for drinking water: 200 μg/L for Fe and 5000 μg/L (Clesceri, 1996; Law 458, 2002; Law 311, 2004; Statutory Instruments, 2007).

4.4. Characterization of catalytic material

4.4.1. X-ray diffraction analysis

Fig. 1a and b described XRD patterns of catalytic materials i.e., Z-Na and Z-Na-TiO_2. For comparison, the XRD pattern of the natural zeolite (Z-Na) is also shown in Fig. 1a. The presented results revealed that the natural zeolite used is mostly clinoptilolite (2theta: 10°; 22.5°; 30°) (Bowman, 2003; Kowalczyk et al., 2006; Korkuna et al., 2006).

It can be seen that the main peak positions of natural zeolite (clinoptilolite) are unchanged, indicating that the structure of natural zeolite has a good thermal stabilization, after the microwave-assisted hydrothermal treatment.

4.4.2. DRUV-VIS spectroscopy

DRUV-VIS patterns are examined to determine the light absorption quantification and absorption wavelength range correlated with band gap energy. Fig. 2 presents an intense absorption maximum at ~260 nm, which can be assigned to isolated titanium with tetrahedral coordination. Another absorption range found in the range of 300–370 nm indicates that some titanium is also in an octahedral environment (Dabici et al., 2011).

Table 1. Results of TOC analyses

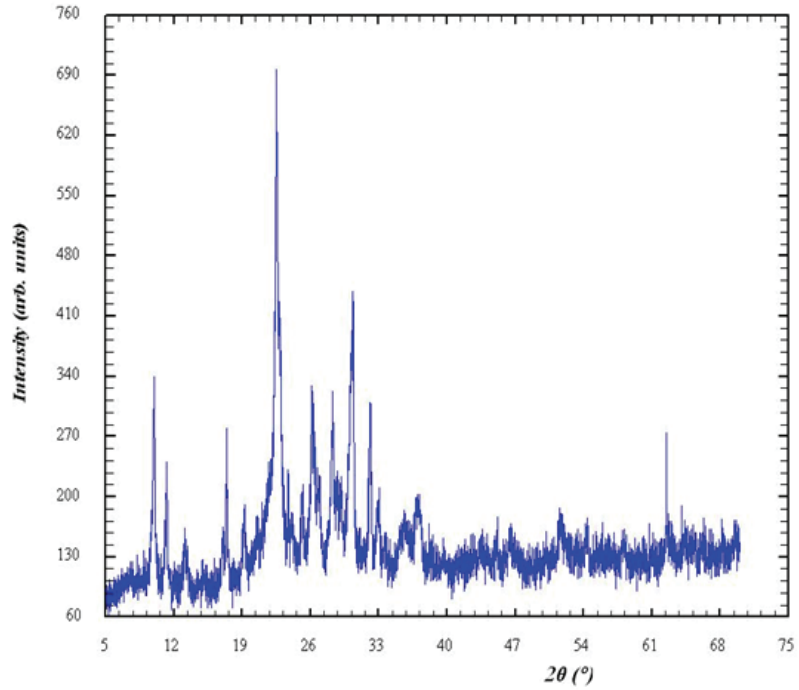
Water Sample	*TOC (mg/L)*	*TC (mg/L)*	*IC (mg/L)*
P1	20.78	21.56	0.7808
P2	21.27	21.81	0.5452
P3	21.89	22.27	0.3800

Table 2. Levels of TOC in various water streams (SIST ISO 8245, 1999; Clesceri et al., 1996)

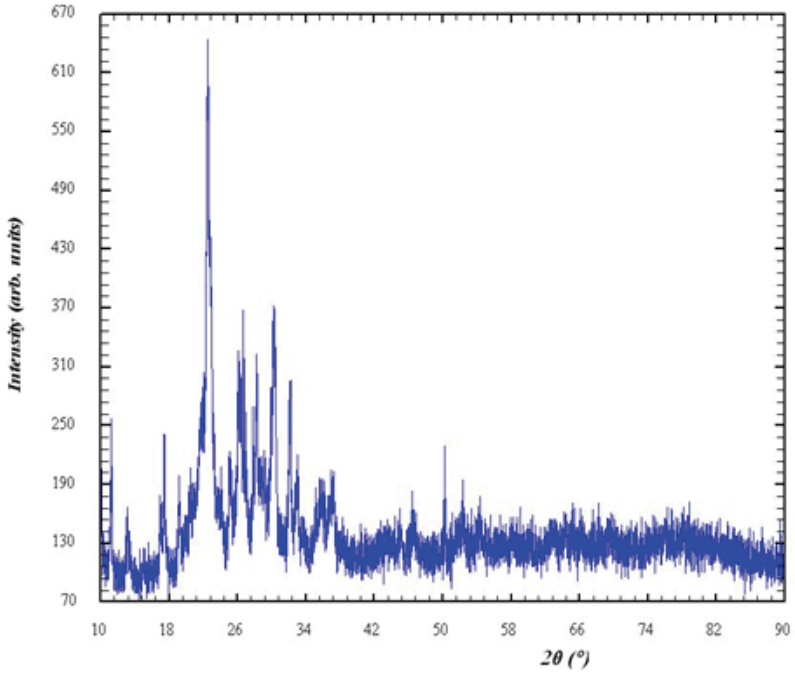
Type of water	*TOC (mg/L)*	*Type of water*	*TOC (mg/L)*	*Type of water*	*TOC (mg/L)*
High purity water	<0.01	Seawater	<1	Surface water	<10
Ground water	<1	Drinking water	<4	Wastewater	>20

Table 3. Concentration of metals detected by AAS analysis

Water Sample	*As (μg/L)*	*Cu (μg/L)*	*Ni (μg/L)*	*Pb(μg/L)*	*Cd (μg/L)*	*Fe (μg/L)*	*Zn (μg/L)*
P1	*	*	*	*	*	67.56	22.42
P2	*	*	*	*	*	52.64	24.24
P3	*	*	*	*	*	46.88	15.47



a)



b)

Fig. 1. a) XRD patterns of Z-Na material, b) XRD patterns of Z-Na-TiO_2 materials

For the catalytic material modified with undoped TiO_2 the absorption bands intensity is higher in UV domain, because the anatase form of undoped TiO_2 with the band gap energy about 3.2 eV strongly adsorbs in this domain. The SEM images (Fig. 3a, b) show the lamellar texture of clinoptilolite, according to the literature data (Kowalczyk et al., 2006).

The TiO_2 particles are distributed randomized and form cluster agglomerate groups on the surface and in site of zeolite channels. At a larger magnification (mag. 12.000X), it is obvious that the TiO_2 nanocrystals (spherical form) are non-uniformly distributed on the zeolite surface.

EDX results, that provided a semiquantitative elemental analysis of the surface, indicate that Ti was present on the zeolite surface. Also, this natural zeolite contains the major elements such as Na, Si, Al, Ca, K and Mg as can be seen from the EDX spectra (Figs. 3c, d).

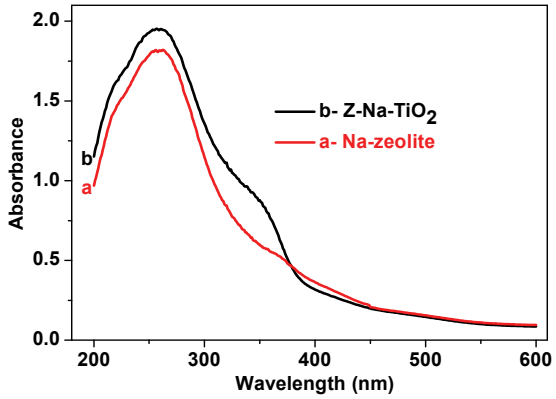


Fig. 2. DRUV-VIS spectra of catalytic materials (a) Na-Z- and (b) Z-Na-TiO_2

4.5. Photocatalytic activity

The prepared catalytic materials, Na-Z and Z-Na-TiO_2 were used to degrade and mineralize organic compounds under ultraviolet light irradiation for 2 h, and the results are presented in Figs. 4-6.

The performance of the photocatalytic activities of materials was determined comparatively for the degradation of organic compounds from water samples (P1-P3) by photocatalysis and photolysis under 6W UV irradiation at wavelengths of 254-365 nm at room temperature, after 2 hours of illumination. In comparison the Z-Na material was tested for degradation of pollutants from water.

The volume of the reaction solution was 50mL, into which 0.05 g of photocatalyst (Z-Na and Z-Na-TiO_2) was added. After irradiation time of 2 h, the suspension was sampled and filtered through a 0.2 μm membrane filter. Also, the mineralization degree was assessed by monitoring the removal efficiency expressed by total organic carbon (TOC) parameter reduction. It can be observed from the Figs. 4-6 that by comparison with other catalytic material tested (Z-Na), the hybrid material based on TiO_2 presents a good photocatalytic activity.

5. Conclusions

This study has demonstrated the photocatalytic efficiency of hybrid materials obtained through microwave-assisted hydrothermal synthesis. The performance of the photocatalytic activities of materials was determined comparatively for the degradation of organic compounds from real water (Surduc Lake, Romania) from three different areas, by photocatalysis and photolysis under 6W UV irradiation at wavelengths of 254-365 nm at room temperature, after 2 hours of illumination. In comparison the Z-Na material was tested for degradation of pollutants from water.

Thus, materials based on Na-Z and Z-Na-TiO_2 was used to degrade and mineralize organic compounds from water samples under ultraviolet light. The performance of the photocatalytic activities of materials was determined comparatively by photocatalysis and photolysis.

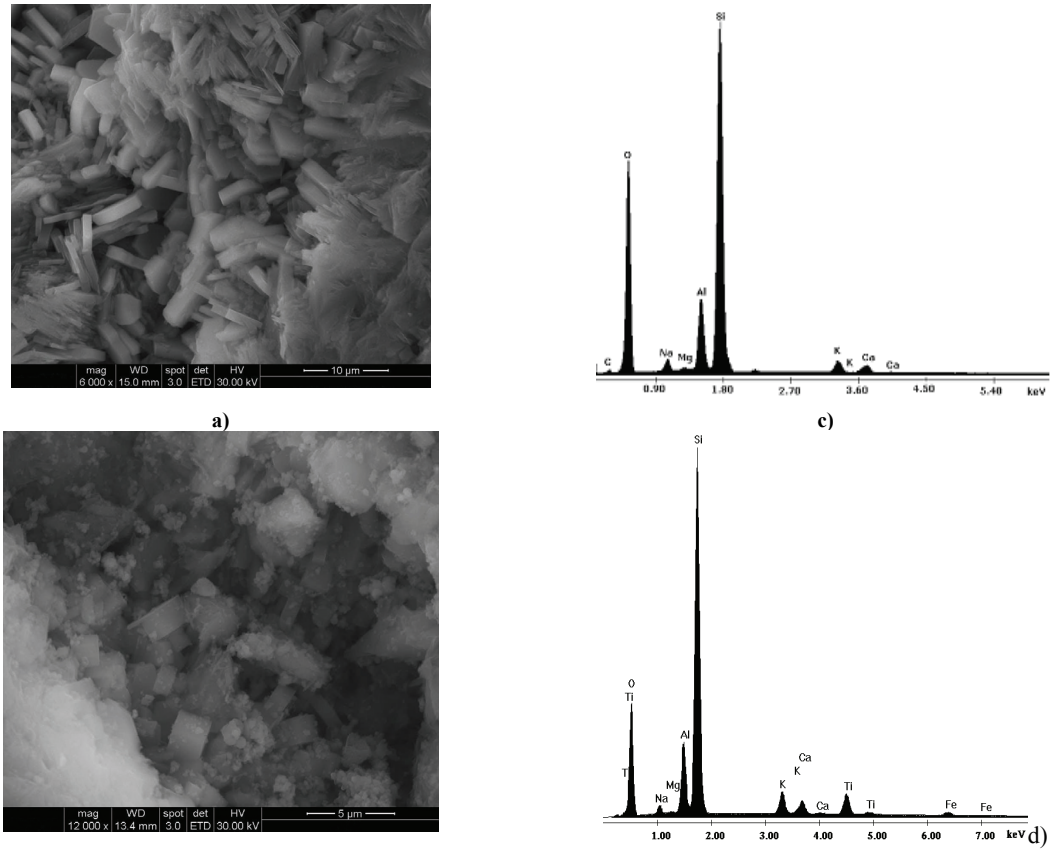


Fig. 3. SEM morphology for Z-Na-TiO_2 (a and b) and elemental analysis of Z-Na-TiO_2 (c and d)

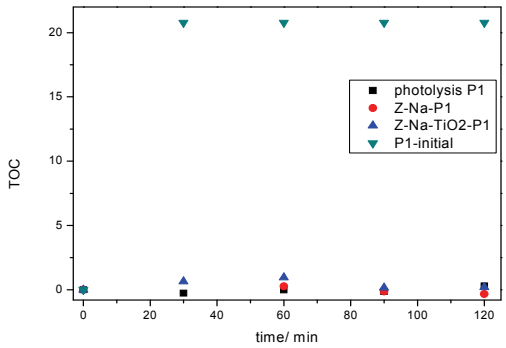


Fig. 4. Variation in time of removal efficiency expressed by total organic carbon (TOC) reduction for **P1**

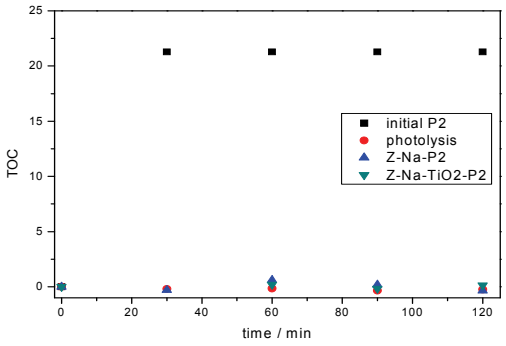


Fig. 5. Variation in time of removal efficiency expressed by total organic carbon (TOC) reduction for **P2**

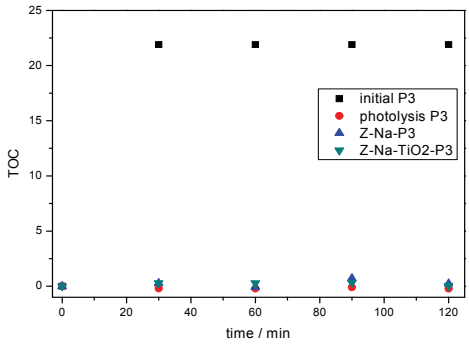


Fig. 6. Variation in time of removal efficiency expressed by total organic carbon (TOC) reduction for P3

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