

# PHOTOCATALYTIC REMOVAL OF DYES FROM WASTEWATER UNDER SOLAR LIGHTS BY NATURAL CLINOPTILOLITE FROM DIFFERENT REGIONS

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## ABSTRACT

Due to their structural complexity, chemical stability, and toxicity, organic dyes mostly used in the textile industry, cause serious environmental problems. Advanced Oxidation Processes (AOPs) currently appear to offer a high potential for complete degradation of organic dyes. The present work is focused on natural clinoptilolite (CLI) and its unusual photocatalytic activity. CLI from different regions were studied as photocatalysts in the photodegradation of methylene blue (MB) as a model cationic dye under visible light at room temperature and atmospheric pressure at different pH. For all CLI samples at pH = 6, the total degradation degree of MB varied from 74 to 88 %, thus indicating a high photocatalytic activity of CLI.

Keywords: clinoptilolite, natural zeolites, organic dyes, photocatalyst, photocatalytic degradation.

## INTRODUCTION

Removal of the harmful organic dyes from wastewater is an important task for environmental protection. AOPs have been found as an effective and suitable method which enables a complete degradation of organic dyes by converting them into less harmful CO<sub>2</sub>, H<sub>2</sub>O, and inorganic salts. Catalytic degradation has mainly been ascribed to the formation of highly reactive hydroxyl radicals.

Natural clinoptilolite is the most abundant natural zeolite in many regions around the world. According to various studies, CLI can be used for different purposes, due to its unique structural features and possibility to be modified without loss of crystallinity. Although the catalytic activity of CLI has been reported in different reactions [1,2], however the use of unmodified CLI in photocatalysis has not been studied so far to the best of our knowledge.

In this study, we explored the photocatalytic performance of CLI from different regions for the degradation of MB, frequently used in the textile industry. Photocatalytic tests were performed under a visible-light lamp irradiation.

## EXPERIMENTAL

Natural clinoptilolite-rich tuffs, used in this study, were provided from different regions: a) Serbia (Slanci deposit, SCLI), b) Turkey (Gördes deposit, TCLI) c) Iran (Semnam deposit, ICLI), d) Romania (Baia Mare deposit, RCLI) and e) Slovakia (Nižný Hrabovec deposit, SKCLI).

Prior to all experiments, the samples were sieved to obtain the a particles population having the size in the range from within 63 and 125 µm mesh, washed with deionized water, and dried at 105 °C overnight. Such samples were then used in photocatalytic tests, without any additional modification.

The mineral composition of the zeolitic tuffs was determined by a powder X-ray diffraction method (PXRD) using an APD2000 Ital Structure diffractometer (CuK<sub>α</sub> radiation,

$\lambda=0.15418$  nm), generated at 38 kV and 28 mA. Scans were performed in the  $2\theta$  range  $5\text{--}50^\circ$  with a step of  $0.02^\circ$  per 1 s. Semi-quantitative PXRD analysis was conducted using the Rietveld refinement and the Topas-Academic v.4 software package [3].

**Photocatalytic tests:** The tests were performed using a photocatalytic reactor system shown in Fig. 1. In a typical experiment, suspension contained water solution of MB ( $C_0 = 10$  mg dm<sup>-3</sup>) and CLI in the concentration of  $0.2$  g dm<sup>-3</sup> at different pH (pH= 3, 6, or 9), was stirred by magnetic stirrer for 30 min to reach an adsorption/desorption equilibrium. Then the suspension was irradiated for 300 min under visible light by using the Osram Ultra Vitalux lamp (300 W), positioned 10 cm above the reactor. The photocatalytic pathway of the MB degradation was followed colorimetrically at  $\lambda = 664$  nm by using UV/VIS spectroscopy (Lambda 365 spectrophotometer, Perkin Elmer).

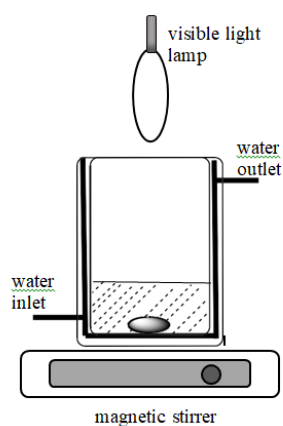


Figure 1. The schematic presentation of the reactor system used in photocatalytic tests.

## RESULTS AND DISCUSSION

Fig. 2 shows a representative PXRD diffraction pattern. In all samples, CLI is the major phase with the diffraction peaks at  $2\theta = 9.8; 11.7; 12.8; 17.2; 19.1; 22.4; 26.0; 29.9$  and  $32.3^\circ$  [4]. Results of a quantitative analysis performed by the Rietveld method showed that the tuffs have a high content of CLI which is in the range from 73 to 82 wt.%. The analysis revealed also the presence of a) feldspar and quartz (SCLI); b) anorthite and quartz (TCLI); c) quartz, anorthite and calcite (ICLI); d) biotite and calcite (RCLI), and e) anorthite and quartz (SKCLI).

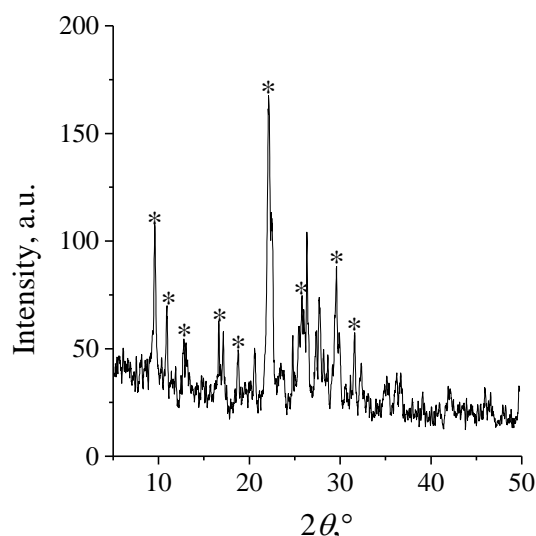


Figure 2. Representative PXRD pattern of the zeolitic tuff (\*clinoptilolite phase).

The degradation degree of MB in the absence of catalyst was found to be very low (approx. 10%, not shown). On the other hand, the photocatalytic tests showed that all CLI samples exhibit a high photocatalytic performance (Fig. 3).

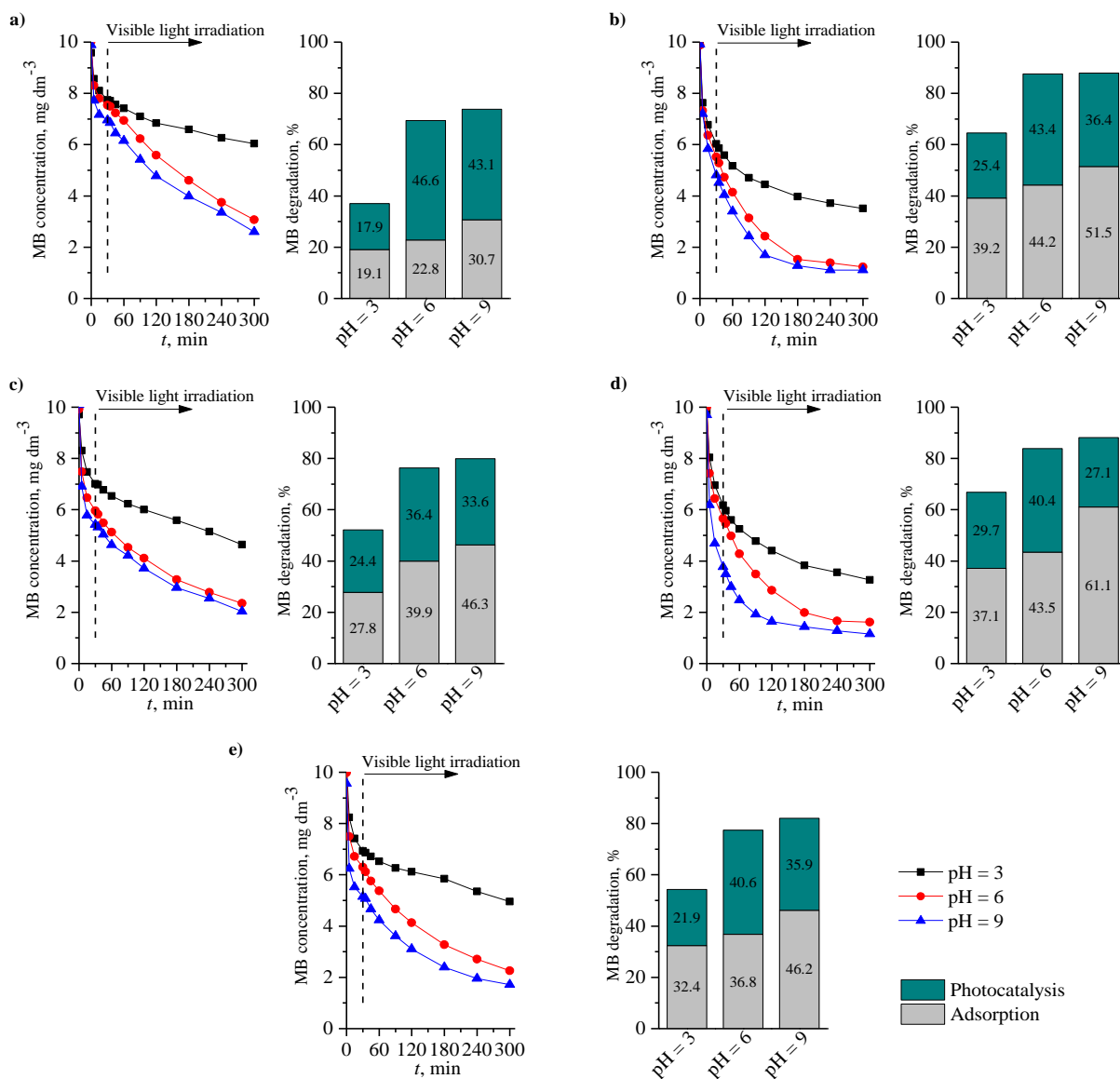


Figure 3. MB photodegradation using as catalyst: a) SCLI, b) TCLI, c) ICLI, d) RCLI and e) SKCLI. The reaction conditions are as follows:  $C_0 = 10 \text{ mg dm}^{-3}$ ,  $m_{\text{cat}} = 10 \text{ mg}$ ,  $V = 50 \text{ cm}^3$ ,  $t = 22 \text{ }^\circ\text{C}$ .

The total degradation degree of MB varies from 74% (SCLI) to 88% (RCLI) within 300 min. For all tested CLI samples, MB adsorption increases with pH. For cationic dyes such as MB, a competition between hydrogen ions and MB cations for adsorption sites occurs resulting in a lower adsorption efficiency in acidic media. Total degradation of MB notably increases by increasing pH from 3 to 6. A slowdown is evident at pH = 9. The best photocatalytic activity for all tested CLI samples was found at pH= 6 (up to 46.6%).

The photocatalytic performance of native CLI samples could be most probably explained by the presence of low content of Fe. The Fe species can photoinduce the species which are responsible for photocatalytic activity [4]. Although Al–O species can also originate active photocatalytic sites, Fe species induce more active photocatalytic species under the applied experimental conditions [4].

MB photodegradation follows the Langmuir–Hinshelwood model, the most commonly used kinetic model for the description of the kinetics of heterogeneous photocatalytic processes. The pseudo-first-order rate constant ( $k_{app}$ ), calculated from the slopes of the plots  $\ln(C_0/C_t)$  vs irradiation time ( $t$ ), are listed in Table 1. It can be seen that the constant significantly increased by increasing pH from 3 to 6. There are no noticeable changes with further increasing of pH up to 9 confirming favorable MB photodegradation at pH= 6.

Table 1. The rate constant ( $k_{app}$ ) calculated by Langmuir-Hinshelwood model at 22°C.

Sample	pH = 3	pH = 6	pH = 9
SCLI			
$k_{app}, \text{min}^{-1}$	0.0011	0.0035	0.0036
$R^2$	0.9613	0.9996	0.9980
TCLI			
$k_{app}, \text{min}^{-1}$	0.0024	0.0064	0.0066
$R^2$	0.9344	0.9686	0.9404
ICLI			
$k_{app}, \text{min}^{-1}$	0.0017	0.0037	0.0038
$R^2$	0.9678	0.9879	0.9894
RCLI			
$k_{app}, \text{min}^{-1}$	0.0027	0.0052	0.0054
$R^2$	0.9451	0.9683	0.9066
SKCLI			
$k_{app}, \text{min}^{-1}$	0.0014	0.0040	0.0044
$R^2$	0.9487	0.9937	0.9877

## CONCLUSION

Present results show that CLI obtained from different regions can be used as an efficient and environmentally safe photocatalytic material for the photodegradation of organic dyes such as MB under environmentally friendly visible light. Further research will be directed to a detailed study of the photocatalytic decomposition.

## ACKNOWLEDGEMENT

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