

PHOTOCATALYTIC ACTIVITY OF Fe(III)-LOADED-CLINOPTILOLITE IN THE DEGRADATION OF METHYLENE BLUE AS A MODEL POLLUTANT

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ABSTRACT

Due to structural complexity and toxicity of organic dyes their presence in water body causes usually serious environmental problems. Advanced Oxidation Processes (AOPs) have been recognized as effective methods for a complete degradation of organic dyes. In this study, Serbian natural zeolite (clinoptilolite) loaded with Fe(III) was used for the preparation of a photocatalyst and its catalytic activity was tested in the photodegradation of methylene blue (MB) as a model cationic dye under visible light at room temperature and atmospheric pressure. It is showed that the prepared Fe(III)-containing clinoptilolite (FeZ) can be used as active and recyclable photocatalyst in degradation of MB.

Keywords: photocatalysis, zeolite, organic dyes, AOP, methylene blue.

INTRODUCTION

Organic dyes possess complex structures and their degradation in water solution is usually complicated. Effectiveness of AOPs, which enable a complete degradation of many organic pollutants, has mainly been ascribed to the formation of highly reactive hydroxyl radicals exhibiting a crucial role in the degradation.

Metal oxides such as TiO₂, ZnO, SnO₂, or Fe₂O₃ have been reported to show photocatalytic activity [1,2]. Since immobilization of the oxide particles on suitable carriers significantly improved catalytic activity and reusability of these oxides [3,4], we modified natural clinoptilolite with Fe(III) oxide and tested catalytic activity and reusability of the prepared product in photodegradation of MB as a model pollutant.

Natural clinoptilolite is the most abundant natural zeolite in Serbia and in previous detailed investigations it has been found that clinoptilolite can be transformed into novel materials for different purposes such as applications in catalysis for esterification processes [5], phenol preparation by lignin pyrolysis [6] as well as in adsorption of toxic cation and anion species present in water solution [7,8].

EXPERIMENTAL

Synthesis. Clinoptilolite-rich zeolitic tuff (Z) was obtained from Slanci deposit (Belgrade, Serbia) and used as a starting material. A qualitative Rietveld analysis (using the Rietveld refinement and the Topas-Academic v.4 software) [9] showed that Z contains clinoptilolite as the major mineral phase (> 80 mas.%), whereas quartz (< 7.5 mas.%) and feldspars (< 13 mas.%) are major mineral impurities. Particles between 63 and 100 µm mesh were used in experiments, the choice being based on the results of previous studies [5-8] that found for this fraction the highest adsorption ability. Fe(III)-loading was performed using a water solution of 0.05 mol dm⁻³ Fe(NO₃)₃·9H₂O (using solid:liquid ratio 1:40) in an acetate buffer (pH = 3.6) and then by an addition of 0.1 M NaOH until pH of the suspension was

adjusted to 7. After stirring at 70 °C for 24 h, the product (FeZ) was washed several times with deionized water, centrifuged and dried at 80 °C to a constant mass.

Characterization. The crystallinity was tested by a powder X-ray diffraction method (PXD) using an APD2000 Ital Structure diffractometer (CuK_α radiation, $\lambda=0.15418$ 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. Textural properties were studied by N₂ adsorption at -196 °C using a Micromeritics Instrument (ASAP 2020). Fe(III)-loading was analyzed by Transition Electron Microscopy (TEM) using a 200-kV TEM (JEM-2100 UHR, Jeol Inc., Tokyo, Japan) equipped with an ultra-high-resolution, objective-lens pole-piece having a point-to-point resolution of 0.19 nm. Electron diffraction patterns (EDP) and TEM images of the sample were recorded by 2k CCD camera using DigitalMicrograph™ (Gatan Inc.) as a user interface.

Photocatalytic tests. The tests were performed in a batch 50 cm³ reactor. The suspension contained a water solution of MB (10 ppm) and FeZ (10 or 20 mg) was firstly left in the dark for 30 min in order to achieve adsorption-desorption equilibrium, and then irradiated during 360 min with a visible-light lamp (Osram Ultra Vitalux 300 W). The concentration of MB was measured colorimetrically at $\lambda = 664$ nm using Hach DR 2800 spectrophotometer.

For recycling test, the catalyst was separated from suspension by filtration, left to dry at room temperature, and then calcined at 500 °C during 1 h prior to be reused.

RESULTS AND DISCUSSION

PXD analysis showed that crystallinity of the clinoptilolite phase remains intact after the conversion of Z to FeZ (data not shown). Also, the pattern of FeZ does not exhibit any novel phase indicating that Fe(III) phase presence onto clinoptilolite surface (*vide infra*) is amorphous. Chemical composition of the clinoptilolite phase of Z and FeZ obtained by EDS analysis as well as water content of the samples obtained by TG analysis are shown in Table 1.

Table 1. Chemical composition (wt.%) of the zeolite samples.

| | Al | Si | Na | K | Ca | Fe | H ₂ O* |
|-----|------|------|------|------|------|------|-------------------|
| Z | 7.13 | 33.2 | 2.09 | 1.33 | 0.76 | 0.20 | 13.0 |
| FeZ | 5.12 | 23.8 | 0.19 | 0.31 | 0.45 | 18.1 | 15.8 |

*Loss of ignition at 600 °C

Z and FeZ have similar Si/Al molar ratio (about 4.5) confirming that the clinoptilolite lattice was not affected by the Fe(III) loading. Increasing of the Fe content is following with significant decrease of the content of exchangeable cations. However, high Fe content (18.1 wt.%) suggests that the modification proceeded not only through an ion exchange but also through precipitation of Fe(III) species. This is confirmed by TEM analysis (Figure 1). At a typical TEM image of FeZ (Figure 1a) amorphous Fe(III)-precipitate is evident on the crystalline clinoptilolite pseudo-hexagonal sheets. The electron diffraction pattern (EDP) shows two diffraction rings ($D_1=0.27$ nm and $D_2=0.15$ nm) that appear in the sample areas with higher density of the Fe-rich precipitate (Figure 1b). There are no distinct spots within the rings that would suggest its crystallinity.

The accumulated Fe(III)-precipitate caused an increase of the specific surface area of Z from about 30 m² g⁻¹ to 140 m² g⁻¹ (FeZ).

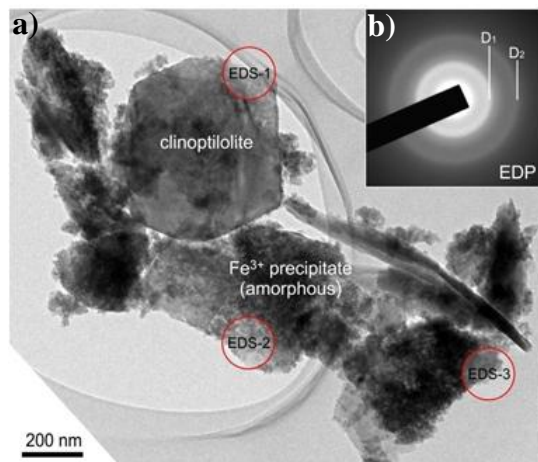


Figure 1. a) Bright-field TEM image of clinoptilolite sheets covered with flaky Fe-rich precipitate. EDP (b) confirms that the precipitate is amorphous.

Photocatalytic tests (Figure 2) showed that the FeZ exhibits promising photocatalytic performance. The activity of FeZ slightly increased with increasing amount of FeZ reaching the MB degradation rate of 78 % with 20 mg FeZ after 360 min. Moreover, the adsorption of MB onto FeZ during dark period is more affected by the amount of FeZ than the degradation of MB under illumination with visible-light.

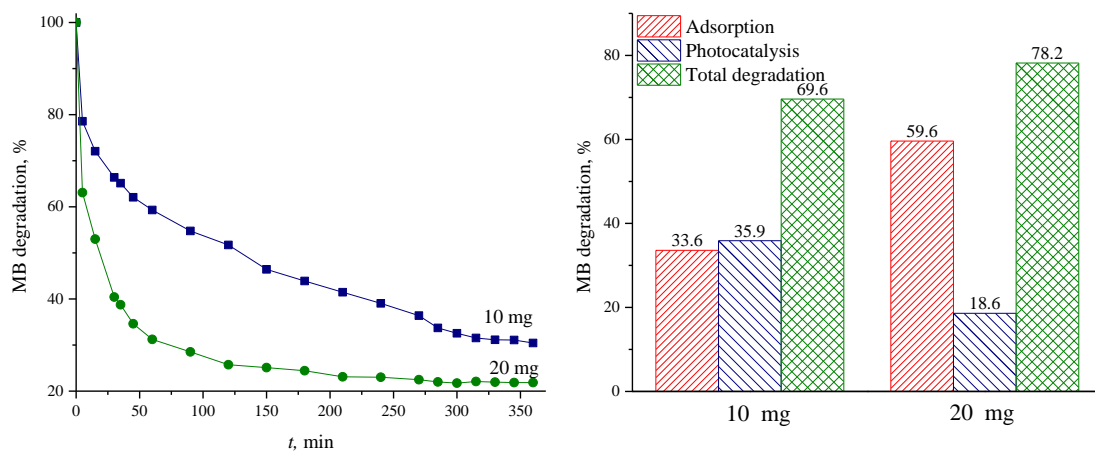


Figure 2. Photodegradation of MB in the presence of 10 and 20 mg of FeZ.

The recycling experiments (Figure 3) showed that during three reaction cycles the photocatalytic activity of FeZ slightly decreased (from 70 to 65 %) suggesting stability of the catalytic performance of FeZ.

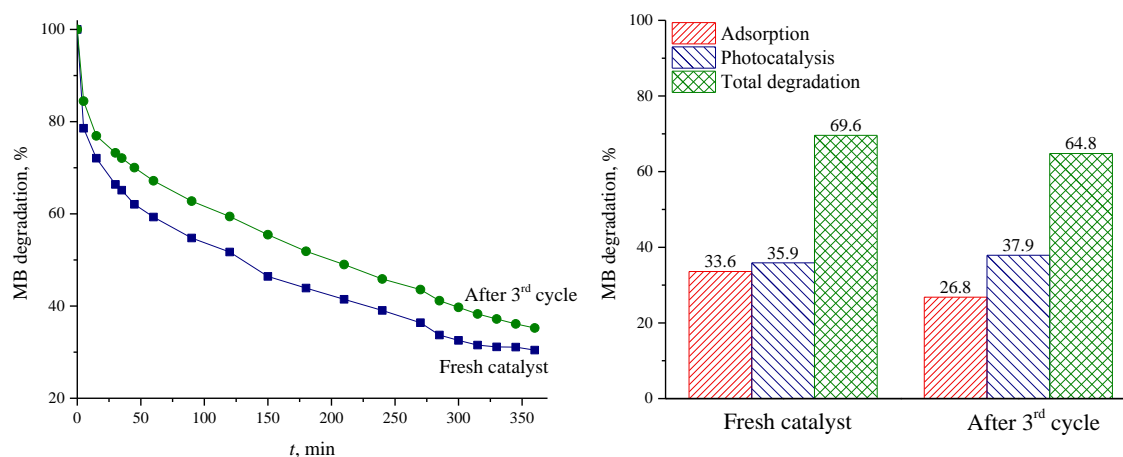


Figure 3. Recycling of the FeZ in photodegradation of MB.

CONCLUSION

A simple modification of clinoptilolite-rich zeolitic tuff with Fe(III) yielded the catalyst exhibited photocatalytic activity in the degradation of methylene blue under irradiation with visible light at 25 °C and atmospheric pressure. The catalytic performance is preserved during 3 cycles suggesting that Fe(III)-loaded clinoptilolite can be perspective as a cost-effective and environmentally friendly catalyst.

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