Synthesis, Characterization and Photocatalytic Application of Copper-Modified Zeolite

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Abstract

The copper-modified zeolite (Z-Cu) prepared by an ion-exchange process was characterized by X-ray diffraction, DRS spectroscopy, SEM microscopy and EDX analysis. The XRD analysis indicated the reduction of the peak intensity corresponding to Na^+ presence as a consequence of ion exchange process between Na^+ and Cu^{2+}. The presence of copper into Z-Cu was confirmed by EDX analysis. The DRS spectra showed that Z-Cu exhibited an intense absorption maximum at ~280 nm, which can be associated with the presence of Cu^{2+} ions within the zeolite. The photocatalytic activity of Z-Cu was proved through comparative studies of photolysis, photocatalysis on Z-Na and photocatalysis on Z-Cu.

Introduction

Copper, silver and zinc presents a great interest for different fields, such as catalysis, water treatment and medicine, due to their oligodynamic properties and catalytic properties The catalytic activity of these metals can be improved by encapsulating in any support matrix, like zeolite or some mesoporous materials.

Among all zeolites, the natural ones have aroused interest due to their low cost, availability and selectivity for a large number of cations. Natural clinoptilolite is one of the most used due to high availability and excellent adsorption and ion exchange properties [1, 2].

In the present study, the copper-modified zeolite was synthesized by ion-exchange process. X-ray diffraction, DRS spectroscopy and SEM/EDX analysis were used for the characterization of this material. The photocatalytic activity of the copper-modified zeolite was assessed for the degradation of cationic dye Methylene blue (MB) from aqueous solution by photocatalysis under UV irradiation.

Materials and Methods

The clinoptilolitic mineral from Mirsid, used as support for Cu^{2+} loading, was supplied by Cemacon Company, Romania. The mineral was powdered and sieved with a Multilab sieve shaker. 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, 0.28% TiO_2.

The chemicals used for this study, *i.e.,* hydrochloric acid (HCl), sodium chloride (NaCl) and cupric nitrate ($Cu(NO_3)\cdot 3H_2O$) were purchased from Merck Company. Methylene Blue (MB - analytical grade), was supplied by Pekin Chemical Works Peking (China). MB ($C_{16}H_{18}N_3SCl\cdot 3H_2O$) is a basic blue dyestuff with a molecular weight 373.9 $g\cdot mol^{-1}$. The preparation of the chemically modified zeolite presumes three stages:

(1) The first step to reach acid form (H form) by using 1M HCl solution, under magnetic stirring, with a S/L weight ratio of 1/10, for 8 h at 25° C. The resulted H form zeolite (Z-H) was washed with distilled water, till reach the pH of distillated water.

(2) In the second step, the acid form of zeolite was treated with 1M NaCl solution, at a S/L ratio of 1/5, for 8 h at 25° C, to achieve the monocationic form (Z-Na). This process was repeated three times with the replacing NaCl solution after each step, to improve the cation exchange capacity. Finally, the Z-Na material was separated by vacuum filtration and washed with deionized water until free of chloride ions and dried at 100°C over night.

(3) Therefore, Na form of zeolite was treated with 0.1M $Cu(NO_3)$ solution, at a S/L weight ratio = 1/100, under continuous stirring for 8 h at 25° C. The modified zeolite was washed with distilled water and dried at 100° C for 8 h.

The crystallinity of the samples was measured by X-Ray diffraction (XRD) using PANalytical X'PertPRO MPD Difractometer with Cu tube. A scanning electron microscopy (SEM) using Inspect S PANalytical model coupled with the energy dispersive X-ray analysis detector (EDX) was used to characterize the external surfaces of the hybrid materials, using catalyst powder supported on carbon tape. The light absorption properties of the materials were studied by diffuse reflectance spectroscopy (DRS), performed under ambient conditions using Lambda 950 Perkin Elmer in the wavelength range of 250-450 nm.

The photocatalytic activity of the prepared catalyst was assessed through degradation of 50 $mg \cdot L^{-1}$ MB in an RS-1 photocatalytic reactor (Heraeus, Germany). UV irradiation was provided by a medium-pressure Hg lamp (300 W). The concentration of MB was measured in terms of absorbance at 291 nm and 663 nm with a Carry 100 Varian spectrophotometer.

Results and Discussion

Structural characterization

XRD analysis

The XRD pattern of obtained material is illustrated in Fig. 1. For comparison, the XRD pattern of the natural zeolite in Na form is also shown (Fig.1, spectrum b). The presented results revealed that the natural zeolite used is mostly clinoptilolite (2 theta: 10°; 22.5°; 30°) [3]. The peak corresponding to 2 theta ~ 26.6° is attributed to Na^+ presence within zeolite lattice. XRD spectrum of Z-Cu revealed a diminution of this peak due to the ion exchange process between Na^+ and Cu^{2+}.

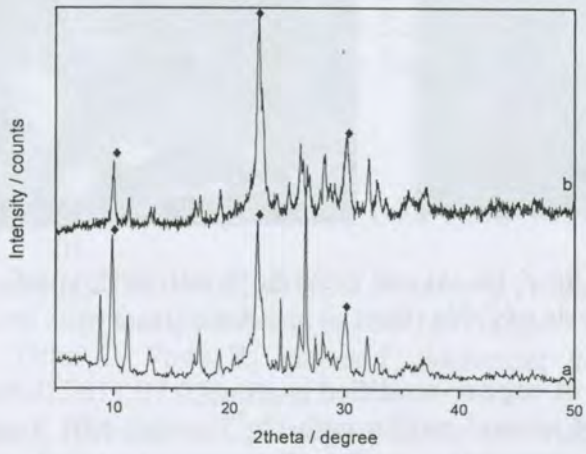


Fig.1. XRD patterns for a) Z-Na and b) Z-Cu (♦ – clinoptilolite)

DRS spectroscopy

DRS 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 ~280 nm, which can be associated with presence within the zeolite matrix of any new copper products (Fig. 2, spectra b) [4].

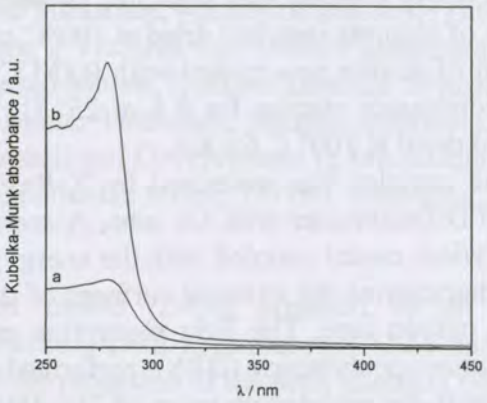
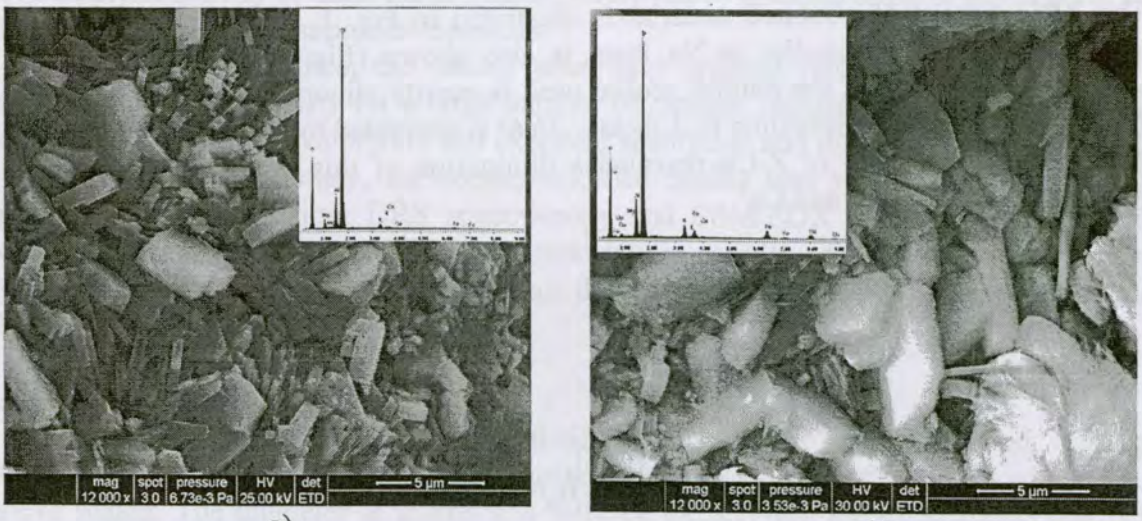


Fig. 2. DRS spectra of (a) Z-Na and (b) Z-Cu

Scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) results

The SEM images (Figs. 3a and b) present the lamellar texture of clinoptilolite, according to the literature data [5]. EDX microprobe provided a semiquantitative elemental analysis of the surface indicating that Cu is present in the zeolite structure (Inset Fig. 3b). Also, this natural zeolite contain the major elements such as Na, Si, Al, Ca, K, Mg as can be seen from the EDX spectra (Inset Fig. 3a).



a) b)

Fig. 3. SEM morphology for Z-Na (a) and Z-Cu (b); Inset: EDX spectra for elemental analysis of Z-Na (inset a) and Z-Cu (inset b)

Photocatalytic application of copper-modified zeolite

The doping effect of natural zeolite with Cu^{2+} on the MB photocatalytic oxidation efficiency was revealed by comparative studies of photolysis, photocatalysis onto Z-Na and photocatalysis onto Z-Cu (Fig. 4). It can be observed that the shape of spectra recorded for all three processes are similarly with the spectrum of initial dye solution, underlying that the

peaks corresponding to 291 nm and 663 nm wavelengths are smaller and decrease in the following order: photolysis> photocatalysis onto Z-Na > photocatalysis onto Z-Cu.

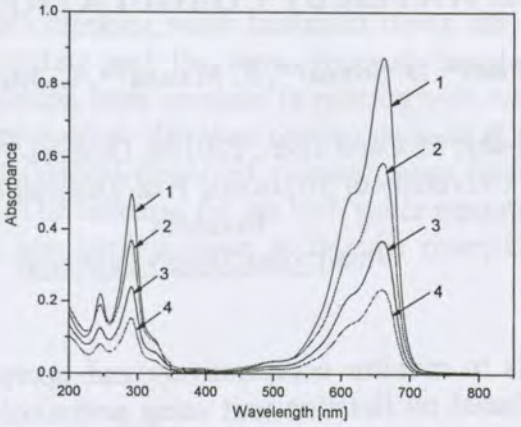


Fig. 4. UV-VIS spectra profile of MB dye solution after 240 min irradiation: **1** – initial MB dye solution; **2** – photolysis; **3** – photocatalysis onto Z-Na; **4** – photocatalysis onto Z-Cu. Conditions: 50 mg·L^{-1} MB dye solution; 1 g·L^{-1} catalyst loading; pH 9.

Conclusions

The XRD results revealed that the natural zeolite used was mostly clinoptilolite. From XRD spectra of Z-Cu, it can be observed that the main peak positions of natural zeolite (clinoptilolite) are unchanged, indicating that the crystalline structure of natural zeolite exhibited a good stability at the chemical treatment. Cu^{2+} presence was confirmed by EDX analysis. The DRS spectra indicated that modification of zeolite with copper led to a stronger UV light response than undoped zeolite. The shape of spectra recorded for the photolysis, photocatalysis onto Z-Na and photocatalysis onto Z-Cu were similarly with the spectrum of initial dye solution, but the peaks corresponding to 291 nm and 663 nm wavelengths were smaller and decreased in the following order: photolysis> photocatalysis onto Z-Na > photocatalysis onto Z-Cu.

Acknowledgements

This work was supported by the strategic grant POSDRU 2009 project ID 50783 of the Ministry of Labour, Family and Social Protection, Romania, co-financed by the European Social Fund – Investing in People, and by the Sectorial Operational Programme Human resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the contract number POSDRU/89/1.5/S/63700.

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