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Production and Investigation of Natural Zeolite-TiO₂/CuO Nanoparticles Composite

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KEYWORDS

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ABSTRACT

With the progress of various industries, the ever-increasing production of polluting wastewater has faced mankind with the concern of preserving the environment and providing clean water. The simultaneous use of adsorbents such as natural zeolite and nanophotocatalysts is one of the attractive methods. By doing this, while eliminating the limitations of each, synergy in properties occurs and the performance of pollution removal is improved. In this article, TiO₂/CuO nanocomposite was deposited on natural zeolite particles. The produced samples were evaluated and compared with different analyses. The results showed that the presence of the TiO₂-7.5% CuO (TC) nanoparticles has improved the ability to absorb UV light despite reducing the specific surface area. The performance of the zeolite-TC combination on the removal of methyl orange (MeO) showed acceptable results. The zeolite sample containing 15%TC with a specific surface area of 29 m²/g and band gap of 3.08 eV removed 93% of MeO dye after 120 min.

1. Introduction

Today, with the rapid development of the industry, large amounts of waste containing various pollutants are produced in many industries. These pollutions severely endanger the environment and the lives of living organisms. Therefore, considering the reduction of water in the world, it is very significant to treat polluted water and return it to the consumption cycle [1, 2].

One of the conventional methods is the use of mineral adsorbents. One of these adsorbents is zeolite, which has received a lot of attention. Zeolite is a combination of alumina-silica with a high specific surface area and small pores [3, 4]. The characteristic of ion exchange in zeolite, followed by its high absorption characteristic, has led to its use in the removal of different water pollutants. In addition, zeolite has many applications in agriculture, medicine, and other industries. Zeolite has been used and studied in two natural and artificial forms. Among these unique properties, the use of zeolite is associated with problems. One of the problems of zeolite is the reduction of its absorption capacity due to its

saturation with pollutants, therefore it is necessary to recycle them. On the other hand, the efficiency of absorption and removal of pollutants by zeolite needs to be improved to reach the optimal value. There are ways to solve these problems, each of which has specific conditions. One of the useful methods is the use of photocatalysts and their deposition on the surface of zeolite particles [5, 6].

The most widely used photocatalysts are Pt-TiO₂, SnO₂, NiS-TiO₂, and ZnO [7, 8]. Titanium dioxide (TiO₂) has attracted a lot of attention due to its unique properties such as cheapness, non-toxicity, optical and chemical stability, etc. One of the drawbacks of using photocatalysts is the high rate of electron-hole recombination in them. This problem limits their application as photocatalysts. In fact, by reducing the recombination rate, the efficiency of the photocatalyst can be improved. In these conditions, making a composite of TiO₂ with other semiconductors and thus transferring charge carriers between them can be effective [8, 9]. The presence of copper oxide (CuO) with a band gap of 1.2 eV together with TiO₂ with a band gap of about 3.2 eV, in addition to reducing the

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recombination rate of charge carriers, causes a decrease in the band gap of the composite and a shift of the absorption edge towards visible light [10-13].

The composition of absorbers such as zeolite with photocatalysts improves absorption and condensation properties by creating a synergistic effect. Zeolite as a support material can reduce hole-electron recombination by trapping the photo-induced electrons in the photocatalyst [5, 14]. So far, there has been no research on the deposition of TiO₂/CuO nanoparticles on natural zeolite and investigating the performance of the resulting composition. Therefore, in this research, first, the surface of zeolite particles is covered with TiO₂/CuO nanoparticles and then the effect of this action on the performance of zeolite is studied with different analyses.

2. Methodology

For the production of zeolite/TiO₂/CuO nanocomposite, natural zeolite prepared from the After mine located in Bakhtar, Semnan province, Iran, with the chemical composition listed in Table 1, was used. Si/Al ratio for zeolite is equal to 5.35, which indicates that the main mineral of zeolite is clinoptilolite [5].

Table 1. Chemical composition of natural zeolite used

compound	SiO ₂	Al ₂ O ₃	CaO	MgO
wt%	77.20	12.80	1.96	0.60
compound	K ₂ O	TiO ₂	Fe ₂ O ₃	Na ₂ O
wt%	2.55	0.18	0.75	3.60

2.1. Synthesis of Zeolite-TiO₂/CuO composite:

Based on previous research [12, 15, 16], the zeolite/TiO₂/CuO synthesis process was carried out as follows:

Solution A: First, 85 ml of deionized water, 6 ml of HCl, and 6 ml of 2-propanol were mixed by a stirrer. Then 5 ml of titanium isopropoxide was added drop by drop to the solution. The temperature of the solution slowly reached 60°C in a water bath within 2 h.

Solution B: First, 0.4 g of CuSO₄.5H₂O was poured into 100 ml of deionized water and stirred for 20 min. Then, 30 ml of 0.05M NaOH was added drop by drop to the solution. After stirring for 30 min, a dark blue solution was obtained, to which 30 ml of 0.05 M ascorbic acid was droply added.

Based on the results of previous works [12], the combination of TiO₂-7.5%CuO had the best efficiency. Therefore, solution B was mixed with solution A to synthesize a 7.5%CuO compound. Coarse zeolite particles were crushed by a ball mill for 12 h until particles <100 μm were obtained. Then the resulting powder was washed

three times with ethanol and deionized water and finally dried. A certain amount of zeolite powder was added to produce composites containing 5, 10, 15, and 20% TiO₂/7.5%CuO with the abbreviation Z5TC, Z10TC, Z15TC, and Z20TC respectively. After stirring for 1 h, the solution was kept overnight at room temperature. Then the precipitation obtained was filtered, dried for 1 h at 80°C, and calcined at 450 °C for 2 h.

2.2. Characterization:

The phases in the produced samples were detected with an X-ray diffractometer (XRD, Bruker D8, Germany) with monochromated Cu-K_α radiation (λ=1.54056 Å). The morphology of the particles was studied with a scanning electron microscope (SEM, XL 30-Philips, Netherlands).

To determine the molecular structure and functional groups on the surface of the particles, infrared spectroscopic analysis (FTIR) was used in the frequency range of 400-14000 cm by ABB-Bomem MB-100 device. The specific surface area of the produced samples was investigated with a BET surface analyzer (Belsorp mini II; Bel, Japan). The band gap value (E_g, eV) of the samples was measured by a UV spectrophotometer at room temperature and was obtained from the starting wavelength (λ_g, nm) using the following formula [15]:

$$E_g = \frac{1240}{\lambda_g} \quad (1)$$

To evaluate the photocatalytic activity of the samples, the removal of methyl orange (MeO) was performed. 1 g/l sample was added to 50 ml of methyl orange solution (with an initial concentration of 5 ppm and pH=6) at room temperature. Before the start of UV light irradiation (by two 6W lamps-Philips, China), the solution was stirred for 60 min to reach absorption-desorption equilibrium in darkness. The distance of the lamps from the surface of the MeO solution was kept at 10 cm. After 120 min, changes in MeO concentration were determined by a UV-vis spectrophotometer.

3. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of natural zeolite and Z-15TC composite. According to the peaks of pattern Figure 1a, the zeolite sample is completely crystalline. Investigating its peaks shows the structures of clinoptilolite, aluminum oxide, quartz, and aluminum silicate. The zeolite phases are consistent with the results in Table 1.

In Figure 2b, the pattern of the Z-15TC sample, in addition to various peaks of zeolite-forming

compounds, anatase, and CuO peaks are also observed. In the sample synthesis conditions, the main phase of TiO₂ was anatase. Rutile peaks have not been detected, which could be due to the detection power of the XRD device, which cannot find phases with small amounts. Another reason is the presence of zeolite, which causes the phase transformation of anatase to rutile to be delayed. This behavior has also been reported in similar studies [15]. The diffraction peaks of the CuO phase are related to the monoclinic crystal structure formed at 450°C [12].

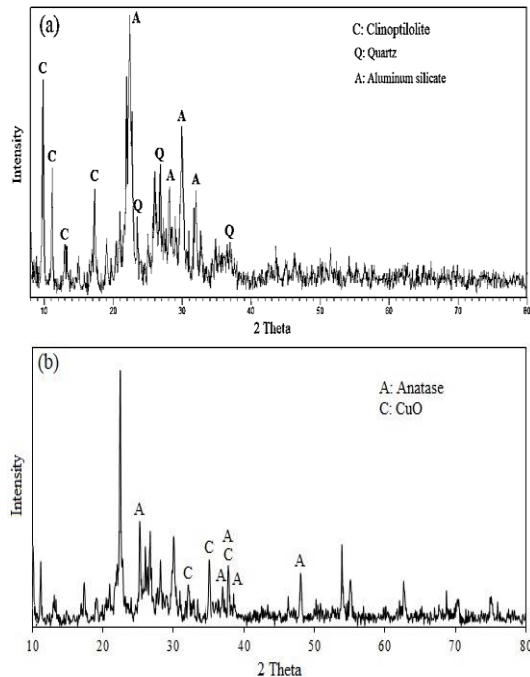


Fig. 1. XRD patterns of a) natural zeolite and b) Z-15TC composite

SEM images of the morphology of natural zeolite samples and Z-15TC composite are presented in Figure 2. Zeolite particles with a non-uniform shape and an approximate size of 0.5-4 μm are observed. After the deposition of TiO₂ and CuO nanoparticles on natural zeolite, there is no change in the shape of zeolite particles. Of course, nanoparticles have caused agglomeration to some extent by creating bonds and joins between zeolite particles and creating larger bulks. On the other hand, it has been proven that the addition of nanoparticles to zeolite reduces the pore size of zeolite and thus increases the active sites in the catalyst [15, 16].

In Figure 3, the infrared spectrum shows the type of surface and molecular bonds of the Z-15TC sample. In the range of 400-800 cm^{-1} , the peaks related to the stretching vibrations of the metal-oxygen bond (Ti-O, Cu-O, etc.) and compounds found in natural zeolite have appeared [17, 18]. The peak at 1060 cm^{-1} is related to vibrations of the Al-O bond and Si-O-Si asymmetric stretching [19]. The peak observed in

the range of 1629 cm^{-1} to 3624 cm^{-1} indicates the stretching vibration of the H-O-H bond and the stretching vibrations of the hydroxyl O-H bond, respectively [19, 20].

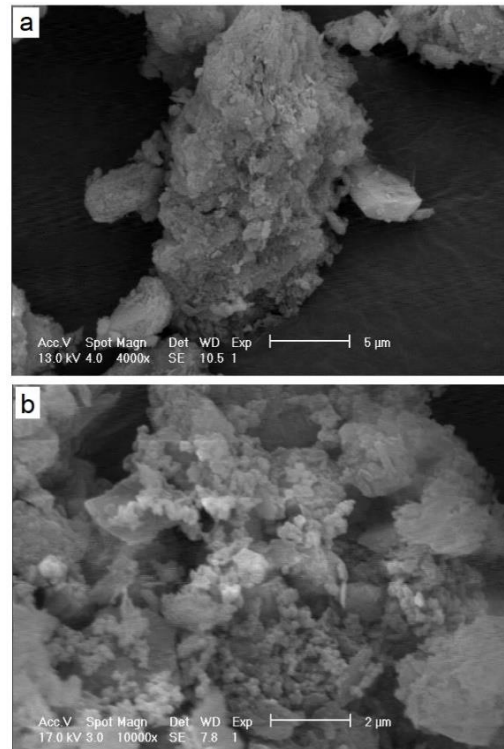


Fig. 2. SEM Images of a) natural zeolite and b) Z-15TC composite

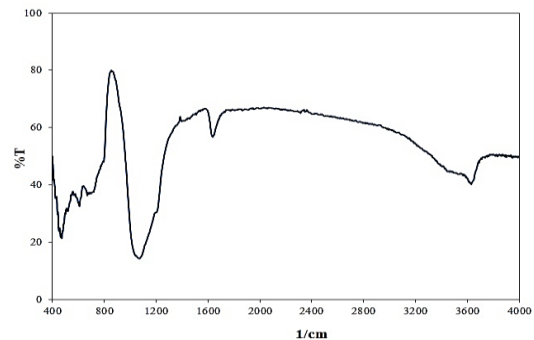


Fig. 3. FTIR spectrum of zeolite containing 15% TiO₂/7.5%CuO

The specific surface of catalysts and absorbent materials is one of their most important features. Table 2 illustrates the specific surface of different produced samples by the BET method. Natural zeolite has a higher specific surface and by depositing nanoparticles on it, the specific surface decreases [15, 16]. It can be seen here that with the increase in the number of deposited nanoparticles, due to the filling of the surface pores of the zeolite, the specific surface area of the sample decreases. Of course, it was also shown in the SEM images that the deposition of nanoparticles on the zeolite particles caused agglomeration and coarsening of the particles. In

research, it was shown that depositing ZnO nanoparticles on the surface of zeolite particles causes the specific surface area to decrease from 52 m²/g to 24 m²/g [21].

Table 2. Specific surface area and absorption properties of different samples

Sample	specific surface area, m ² /g	Absorption edge wavelength, nm	Band gap, eV
Zeolite	35	-	-
Z-5TC	34	370	3.35
Z-10TC	32	384	3.23
Z-15TC	29	403	3.08
Z-20TC	28	418	2.97

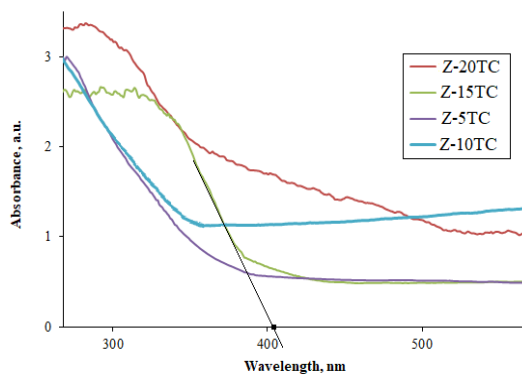


Fig. 4. Diffuse UV-vis absorbance spectra of various samples

One of the most important factors in the evaluation of photocatalytic performance is the evaluation of their optical properties. Figure 4 shows the UV absorption spectrum of different samples. In Table 2, the wavelength of the absorption edge and the value of the band gap of each sample extracted from Figure 4 are shown. Pure zeolite showed no absorption. But with the addition of TC nanoparticles, the absorption edge of the sample has a red shift and has been transferred to longer wavelength rays. Finally, the absorption edge of the sample containing 20% TC occurred at 418 nm. As the value of TC increases, the energy of the band gap has decreased. So that the energy of the band gap in the Z20TC sample is about 2.97 eV. The band gap reduction is due to the presence of TiO₂ nanoparticles with a band gap of 2.95 eV [12] and CuO nanoparticles with a band gap of 1.37 eV [22]. The band gap of TiO₂/7.5% CuO nanoparticles in the absence of zeolite is reported to be 2.53 eV [12]. Therefore, the presence of more nanoparticles on the surface of zeolite particles reduces the band gap.

The removal efficiency of MeO dye by different samples under UV light irradiation is shown in Figure 5. Zeolite has low efficiency due to a lack of photocatalytic properties. The presence of nanoparticles has improved the

efficiency because, in addition to the absorption properties of zeolite, the photocatalytic properties of nanoparticles also play an important role. Due to differences in particle surface charge, specific surface area, and band gap energy, the ability of samples to remove MeO varies. The highest efficiency corresponds to the sample Z-15TC (93%).

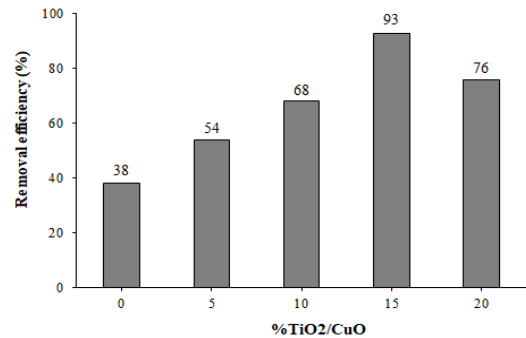


Fig. 5. MeO removal efficiency by different samples (time: 120 min, pH=5)

The incorporation of CuO and TiO₂ into zeolite particles has a significant effect on light absorption. The increased absorption of the samples in the visible light region is due to the formation of a p-n junction between the p-type CuO semiconductor and the n-type TiO₂ semiconductor. In the pure state, the conduction band edge and valence band edge of TiO₂ are higher than CuO, and the fermi level of CuO is lower than TiO₂. By combining, the fermi level of CuO moves up and the fermi level of TiO₂ moves down [10, 11, 23]. Under visible light irradiation, both CuO and TiO₂ can be excited to produce electron-hole pairs. Of course, at higher amounts of nanoparticles, because a larger surface area is covered by the zeolite particles, dye absorption is relatively reduced.

4. Conclusions

In this article, TiO₂/CuO nanoparticles were deposited on particles of natural zeolite to simultaneously use the surface adsorption ability of the zeolite and photocatalytic properties of nanoparticles. Deposition of nanoparticles on zeolite, despite the reduction of the specific surface area, causes the reduction of the energy of the band gap. The performance of the samples in the degradation of methyl orange under UV light showed that adding the optimal amount of TiO₂/7.5%CuO nanoparticles on the zeolite particles had the best photocatalytic performance. The improvement of photocatalytic efficiency is due to the effective separation of electrons and holes photo-induced in nanoparticles. The p-n junction in TiO₂/CuO-zeolite is a strong reason for the enhanced photocatalytic activities.

Conflicts of Interest

No potential conflict of interest was reported by the authors.

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