ETHIOPIAN NATURAL ZEOLITES FOR PHOTOCATALYSIS

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ABSTRACT. The combination of zeolites and photochemistry has recently shown excellent results due to the special structure of the zeolites that helps a better use of the solar energy improving the selectivity of the chemical reactions carried out. There are several reports on the preparation of TiO_2 confined nanoparticles in synthetic zeolites. However, very few reports are found on the use of natural zeolites. Zeolites are a vast natural resource in Ethiopia that remains unexploited. Their microporous structure can accommodate a wide variety of cations such as sodium, potassium and magnesium among others. The main objective of our work was to test the potential use of the naturally occurring zeolites, with high content in titanium, as photocatalysts. The samples have been characterized by X-ray diffraction (XRD), chemical analysis (ICP-OES), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (UV-Vis) and photocatalytic activities of the samples were tested in photocatalytic degradation of methyl orange (MO).

KEY WORDS: Natural zeolite, Photocatalysis, Band gap energy, Methyl orange, TiO_2 loading

INTRODUCTION

Due to the increasingly polluted environment and the gradual depletion of fossil fuel reserves, the development of renewable technologies for environmental remediation, environmental sustainability and energy production is highly desirable. Semiconductor based heterogeneous photocatalysis is a promising means to alleviate the problems [1]. The photocatalysis research area has been interesting to the scientific community since 1972 when Fujuma and Honda [2] observed electrochemical photolysis of water on TiO_2 semiconductor electrode. Since then, different developments have been witnessed and the arena of this research area became widespread among chemical engineers, materials scientists, physicists, chemists and environmental scientists. Its application nowadays includes photocatalytic environmental treatment, photochemical synthesis and water splitting for energy purpose. Of the many tested photocatalysts, TiO_2 is found to be superb owing to its higher photocatalytic activity, suitable band position, reasonable price and photostability [3-7]. However, TiO_2 shows drawbacks such as narrow excitation wavelength and/or large band gap [8-10], fast recombination rate of photogenerated electron-hole pairs [2, 8-10] relatively poor adsorption capacity [8, 11, 12], and difficulties in recycling (recovering) [11, 13]. In addition, recent researches are indicating that the TiO_2 in the nanosized regime can be toxic in high concentration [14]. Thus, efforts should be devoted to preventing the leakage of TiO_2 to the environment during application. Among the various supports that are potentially available, zeolites have been most favorable to be used in supporting TiO_2, due to their photochemical stability, transparency to UV–Visible radiation above 240 nm wavelength, unique structures, uniform pores and channels, which leads to large surface area and synergetic adsorption effects of organic matter [11, 12]. In the past few years, new attempts to locate zeolite deposits in Ethiopia have yielded several interesting phases [15]. Among them, there is at least one area with a natural zeolite (Mordenite) containing high

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concentration of titanium. This sample, called ET4, contains other non-zeolitic phases like celadonite and ilmenite, which may synergize the potential application of this high Ti-containingsample for photocatalysis.

EXPERIMENTAL

Sample preparation

Three different approaches were carried out: i) simple calcination of raw zeolite ET4 sample: 1 g of natural zeolite (ET4) was calcined in air for 3 h at 300, 400, 500 and 600 ^{o}C at a rate of 3 ^{o}C/min. The resulting samples were labeled as ET4-300, ET4-400, ET4-500 and ET4-600 respectively. ii) Loading of raw zeolite ET4 samplewith 20% TiO_2 followed by calcination at 500 ^{o}C, labeled 20TET4-500: 1.6 g of ET4 is suspended in a solution of 2.01 mL of titaniumbutoxide (Ti(OBut)$_4$) dissolved in a mixture of 2-propanol (CH$_3$CHOHCH$_3$) and water (H$_2$O) with volume ratio of 1:10:2 (Ti(OBut)$_4$:CH$_3$CHOHCH$_3$:H$_2$O). The suspension was stirred at room temperature for 24 h. The solvent was removed by rotary evaporator and dried at 110 ^{o}C. The sample was then calcined in a furnace at 500 ^{o}C for 3 h at 3 ^{o}C/min. iii) Raw zeolite ET4 sample was treated following a recipe previously optimized in our laboratory [16], then loaded with 20% TiO_2 as described in (ii) followed by calcination at 500 ^{o}C, labeled 20TET4t-500. For the treatment, 2 g of ET4 was stirred in 26 mL of 3 M CH$_3$COONH$_4$ (NH$_4$Ac) at room temperature for 30 min. Then 12 mL of aqueous solution of 2.4 M NH$_4$F was added drop wise at 80 ^{o}C under magnetic stirring. The suspension was stirred for 30 min. The sample is then filtered and washed with distilled water, dried at 100 ^{o}C for 12 h. After this it is calcined at 550 ^{o}C for 6 h at rate of 3 ^{o}C/min and then loaded with 20% TiO_2 followed by calcination at 500 ^{o}C.

Sample characterization

Powder X-ray diffraction (XRD) patterns were collected with X´Pert Pro PANalytical (CuKα radiation = 0.15406 nm). Inductively coupled plasma optical emission spectrometry (ICP-OES) Optima 3300 DV model, was used to determine the chemical composition. Digestion of the samples was obtained by alkaline fusion in an automatic fusion in Teflon vessels. Two different scanning electron microscopes were used: Hitachi TM-100 and a FEI NOVA NANO SEM 230, both with backscattered electrons detector and EDX analysis. The UV-Vis diffuse reflectance UV-Vis spectroscopy (DRS) measurements were done using a Varian Cary 5000 double-beam UV-Vis-NIR spectrophotometer. Collected spectra were converted to Kubelka–Munk function, F(R) versus wavelength. The band gap of the samples was estimated using the Tauc plots.

Photocatalytic test

For a particular photocatalytic test, 0.5 g of sample was suspended in a ca. 10 ppm aqueous solution of methyl orange (MO) in a 1 L borosilicate glass reactor equipped with borosilicate glass cooling pipe and ports for sample withdrawing and oxygen purging. The mixture was stirred for 15 min in continuous purging of air to maintain adsorption-desorption equilibrium of MO with the powder photocatalyst material. Then, the suspension was irradiated with a 150 W UV lamp (Heraeus medium pressure mercury lamp) and samples were withdrawn in time intervals for analysis after filtering out the photocatalyst.

RESULTS AND DISCUSSION

In our attempt to locate and analyze deposits of natural zeolites in Ethiopia [16], we have identified some phases that possess interesting chemical compositions that may lead to direct photocatalysis with very little modifications. Among the natural zeolites identified, sample ET4, a mixture of celadonite, ilmenite and mordenite (Figure 1) was selected for further photocatalytic applications due to the high content of Ti and Fe (Table 1).
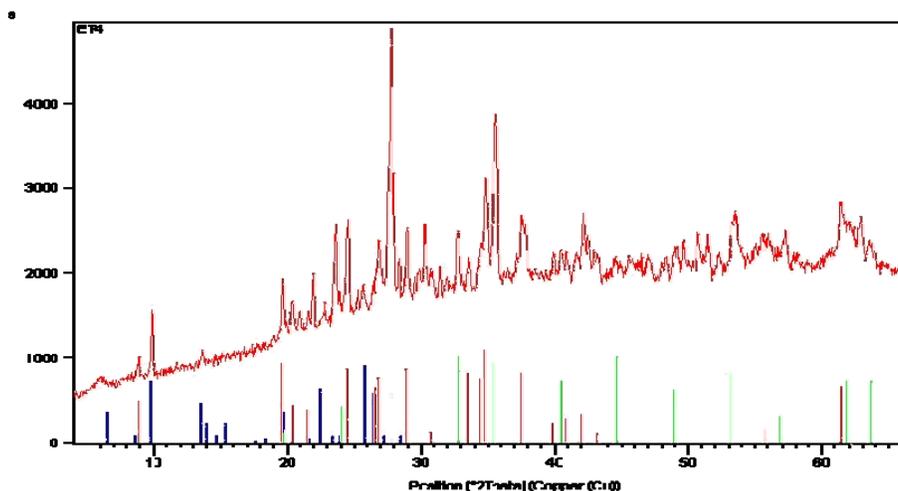
Figure 1. XRD profile where ET4 sample is identified as a mixture of Celadonite in red (00-017-0521), Mordenite in blue (00-038-0318) and Ilmenite in green.

Table 1. ICP elemental analysis of Ethiopian natural zeolite ET4.

Sample	Al (%wt)	Si (%wt)	Na (%wt)	K (%wt)	Ca (%wt)	Mg (%wt)	Fe (%wt)	Ti (%wt)
ET4	3.6	22.9	1.3	3.6	1.8	1.1	10.2	3.5

Figure 2. SEM micrographs of sample ET4 showing A) Mordenite, B) Celadonite and C) Ilmenite phases, identified by EDX.

The elemental composition reported in Table 1 yields a Si/Al molar ratio of 6.11, a bit higher than that of natural mordenites, which varies between 4 and 6 ($Na_{1.1}Ca_{0.5}K_{0.1}Al_{2.2}Si_{9.8}O_{24} \cdot 5.9(H_2O)$) [17]. This difference must be due to a significant contribution of silicon provided by Celadonite ($KMg_{0.8}Fe^{2+}_{0.2}Fe^{3+}_{0.9}Al_{0.1}Si_4O_{10}(OH)_2$), which is also responsible of larger amounts of K, Mg and Fe. Finally, the surprisingly high content on Ti is expected to be related to the Ilmenite phase ($FeTiO_3$), although the coexistence of Ti in the zeolitic Mordenite phase should not be discarded.
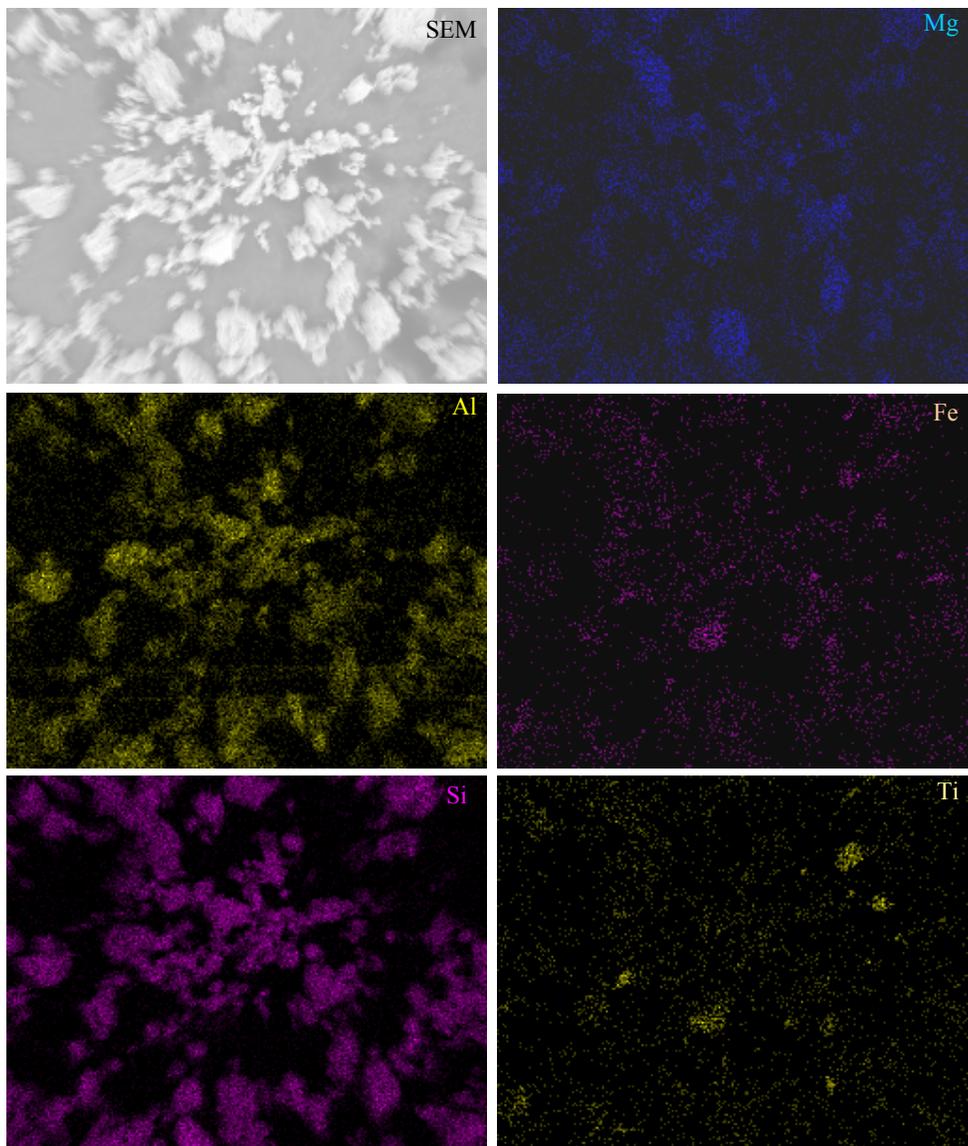
Figure 3. SEM/EDX Mapping of sample ET4.

   In order to corroborate this distribution of elemental composition, ET4 sample was studied by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX). Figure 2 collects representative SEM micrographs of ET4 where the nice hexagonally shaped crystals of Mordenite could be observed (Figure 2A) along with larger shapeless particles identified as Celadonite (Figure 2B), and brighter particles (due to the higher atomic number) identified as Ilmenite (Figure 2C).
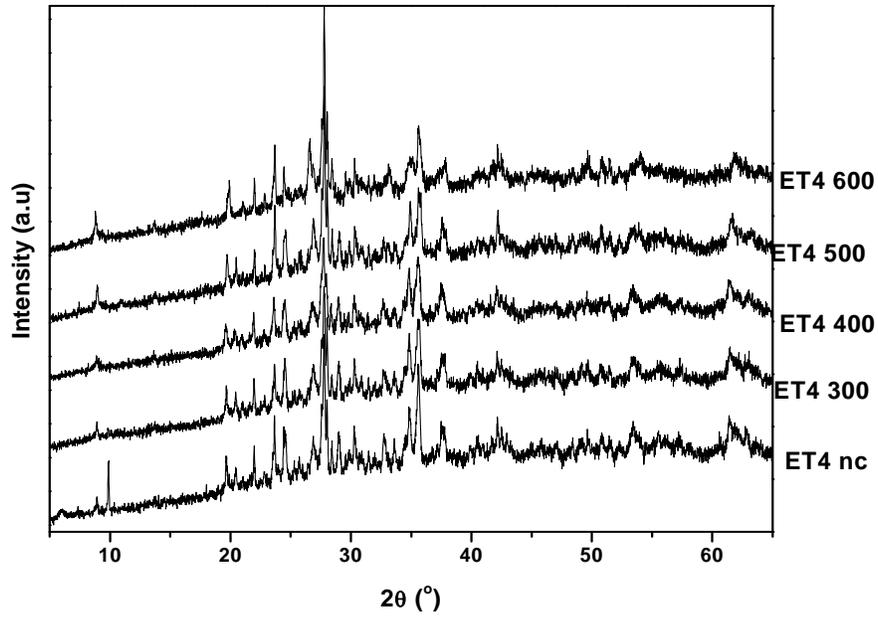
Figure 4. XRD patterns of ET4 not calcined (nc) and calcined at 300, 400, 500 and 600 °C.
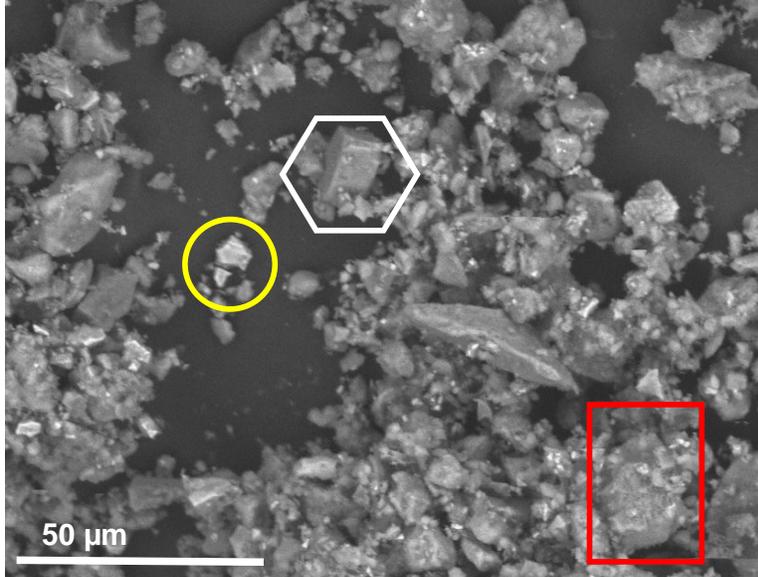

Figure 5. SEM micrograph of sample ET4 500 showing crystals of Mordenite (hexagon), Celadonite (rectangle) and Ilmenite (circle) phases, identified by their shape and EDX.

There seems to be higher ratio of Celadonite than the rest of the phases, and more Ilmenite than in other zeolites samples collected in the same region. Nevertheless, what makes this sample interesting is that the phases with Ti also seem to be associated to some Si.

The exhaustive SEM study coupled with EDX mapping (Figure 3) show that the particles with a higher amount of Na found by EDX could be richer in MOR and those with Mg could be richer in Celadonite. On the other hand, there are clearly Ilmenite particles always showing brighter contrast due to the higher atomic number with Fe/Ti = 1 by EDX, although the presence of Ti is also observed in Si-related particles as mentioned before.

Thus a range of calcination temperatures were tested to obtain the desired phases. The XRD pattern in Figure 4 confirm that the zeolite structure remains stable after calcination up to 600 °C showing no diffraction peaks of either rutile or anatase phases. This could be due to the small particle sizes obtained, in case the desired phases are obtained. The SEM analysis (Figure 5) of sample ET4 500 shows no presence of segregated phases of TiO_2, while the three main phases of parent ET4 could be clearly observed concluding that the calcinations process has not inferred any morphological change to the natural zeolites.

As can be seen from the diffuse reflectance spectra of the samples calcined at different temperature (Figure 6) the absorption edge has been extended to wider wavelength with increasing calcination temperature. The absorption edge of ET4nc and ET4-300 were around 450 nm. Upon further calcination the absorption edge for ET4-400 and ET4-500 is shifted to 521 nm and 560 nm, respectively. However, further calcination to 600 °C does not bring a change in the absorption edge. Thus the shift of absorption edge from ET4nc to ET4-500 may be indicating that calcination within this temperature range provokes electronic modification on the samples. The band gap energy of these samples is estimated using Tauc plot by plotting theroot square ofthe product of the Kubelka–Munk function (F(R)) and photonenergy (hν) of diffuse-reflectance of each sample against energy. Accordingly, it was found that the band gap energy of the ET4nc, ET4-300, ET4-400, ET4-500 and ET4-600 become 2.63, 2.63, 2.21, 1.52, and 1.52 eV, respectively.
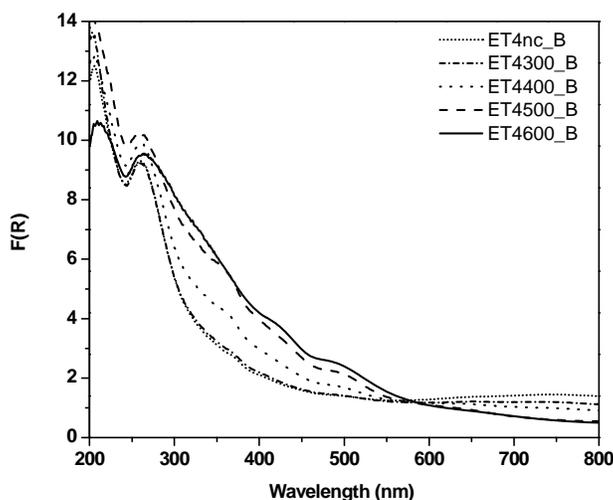

Figure 6. A) Diffuse reflectance spectra of ET4nc, and calcined at different temperatures.

From the diffuse reflectance spectra, this particular natural zeolite could be a promising photocatalyst by calcination at 500 °C. However, no significant photocatalytic activity was found, as it will be discussed later.

Further attempt was carried out in order to enhance the photocatalytic potential of the sample. Extra loading of 20% TiO_2 was included to ET4 yielding a material that contains Ti species potentially active for photocatalysis. However, the photocatalytic activity is very low. We presume that the reason behind this low activity is the presence of impurities that together to extra framework cations could deplete the path of the generated electrons and holes of the system, required for photocatalysis. Therefore, same 20% TiO_2 was loaded on ET4 sample that was previously treated to remove the impurities. The ICP results of these two samples (Table 2) indicate the exact same amount of Ti incorporated in both samples. However, the TiO_2 loading procedure has led to a remarkable decrease in the content of Si in sample 20TET4-500 with a final Si/Al ratio of 3.36. On the other hand, further treatment of ET4 sample with NH_4Ac + NH_4F yields further decrease in the Si content with a final Si/Al ratio 2.44.

Table 2. ICP Elemental Analysis of loaded ET4 samples untreated, 20TET4, and previously treated, 20TET4t, both calcined at 500 °C.

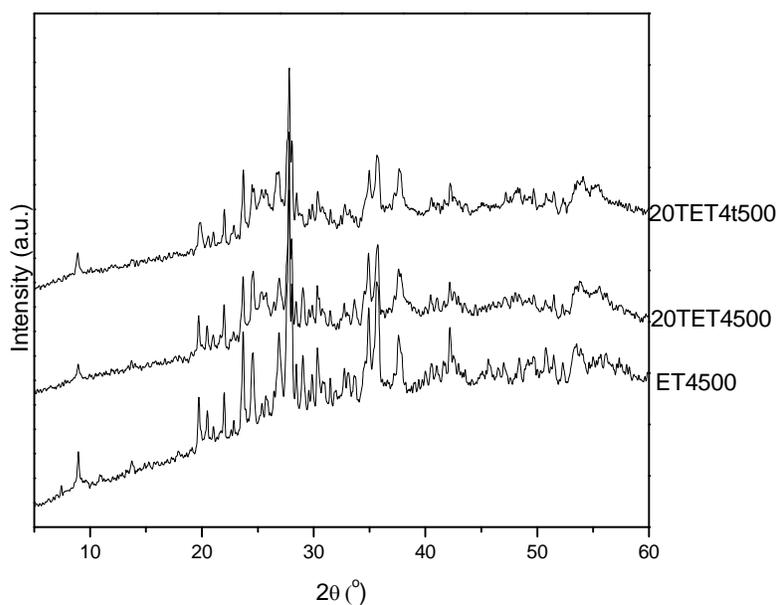| Sample	Al (%wt)	Si (%wt)	Na (%wt)	K (%wt)	Ca (%wt)	Mg (%wt)	Fe (%wt)	Ti (%wt)
20TET4-500	5.65	19.76	1.28	3.47	2.80	1.53	9.90	17.50
20TET4t-500	8.22	20.90	1.40	3.78	2.99	1.67	9.84	17.00

Figure 7. XRD profile of 20TET4t-500, 20TET4-500 and ET4-500.

The XRD profiles of these samples are plotted in Figure 7. The XRD patterns confirm that zeolite structure remains stable after treatment, loading 20% TiO_2 and calcination up to 500 °C.

Deeper search for evidences of the presence of TiO_2 independent particles is difficult, since most of the diffraction intensities overlap with those of the natural zeolite.

The diffuse reflectance spectra (DRS) of these samples are plotted in Figure 8. It is evident that, as expected, incorporation of TiO_2 led to a shift of the absorption edge and an increase of the area of absorption band for 20TET4-500 and 20TET4t-500 samples.
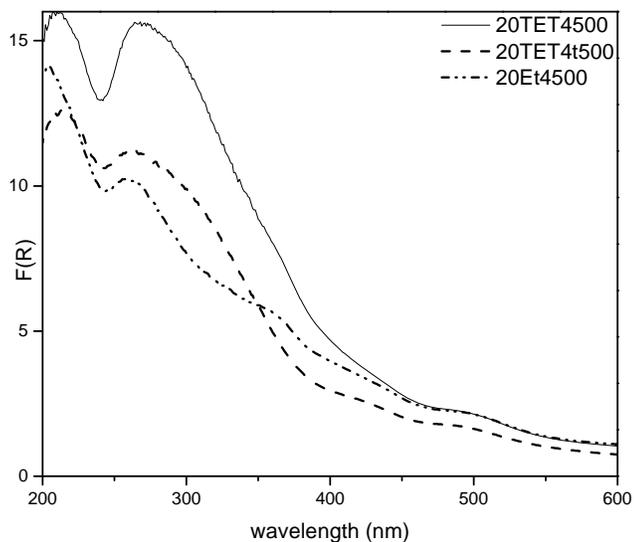

Figure 8. DRS of 20TET4t-500, 20TET4-500 and ET4-500.
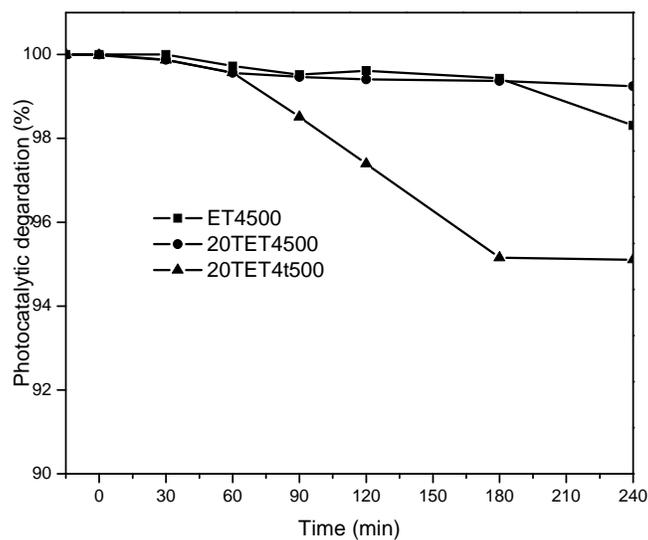

Figure 9. Photocatalytic degradation of 10 ppm MO 20TET4t-500, 20TET4-500 and ET4-500.

The photocatalytic activity test of 20TET4t-500, 20TET4-500 and ET4-500 materials is summarized in Figure 9. The sample that has been treated before TiO_2 loading (20TET4t-500) shows higher activity than 20TET4-500 and ET4-500 although it is still very low compared with that reported for pure TiO_2 using the same experimental device as in the present work [18]. Despite the small improvement given by the treatment, there are still a number of factors that hinder the photocatalytic efficiency of the tested natural zeolites, most likely related to specific impurities. Therefore, better techniques of removal of these cations must be studied.

CONCLUSIONS

The Ethiopian natural zeolite sample (ET4) can be potentially used for photocatalytic applications. This sample contains other non-zeolitic phases like celadonite and ilmenite, which may synergize the potential application of this high Ti-content sample for photocatalysis. However, since it has large number of cations with appreciable amounts, complete removal of these cations is required to customize it to a photocatalyst.

ACKNOWLEDGEMENTS

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