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Synthesis Characterization and Investigation of Photocatalytic Activity of $H_3PMO_{12}O_{40}/TiO_2$/HY Nanocomposite for Degradation of Methyl Orange in Aqueous Media

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Abstract

Molybdophosphoric acid encapsulated into dealuminated zeolite Y (DAZY) was prepared by template synthesis method. Incorporation of TiO_2 into nanocage of DAZY was performed by impregnation method. The obtained photo catalyst (HPA/TiO_2/DAZY) was characterized by FT-IR, UV–Vis, FESEM, XRD, EDS and ICP technique. This catalytic system was investigated in the photodegradation of methyl orange. The obtained results reveal that the photo catalyst performance depends to photo catalyst loading and TiO_2/(HPA/HY) ratio. The photocatalytic activity of molybdophosphoric acid encapsulated into zeolite cage enhanced with impregnation of TiO_2 into nanocage of dealuminated Y zeolite so that complete removal of methyl orange was occurred.

Keywords: Heterogeneous catalyst; Methyl orange; Photodegradation; Molybdophosphoric acid; Dealuminated zeolite

Introduction

The photocatalytic degradation of organic compounds present in wastewater has attracted a great deal of attention from the viewpoint of green chemistry [1-3]. There are several methods for the removal of organic pollutants from wastewater including chemical and biological oxidation [4] adsorption [5] electrochemical [6] ion exchange [7] and membrane separation [8]. However, all these methods have many drawbacks such as expensive, commercially unattractive, and generate secondary contamination [9]. Meanwhile, photocatalytic degradation is another alternative method for removal of inorganic and organic contaminations in both water and air. TiO_2 is one of the best candidates for this purpose. However, photocatalytic activity is restricted because of high band-gap energy, difficulty in filtering and costly. Therefore, immobilization on inorganic support is good manner to overcome these advantages. On the other hand, the combination of TiO_2 and various supports such as silica, carbon materials and zeolites gives the unique properties extremely small size semiconducting particles lead to catalytic reactions which very different from photo electrochemical reactions observed on bulk TiO_2 semiconducting powders [10-19]. However, in order to improve the efficiency, the usage of photosensitive molecules is a good manner. Heteropoly acids are known to be active, exhibit the unique property of structural stability and redox activity which facilitate photocatalytic activity because of suitable HOMO-LUMO gap [20-24]. Meanwhile, by encapsulating of hetero poly acid, the specific surface area increased which in turn, affected on catalytic activity [20]. observed enhanced photocatalytic activity in the conversion of organic molecules in the presence of hetero polyacid $(PW_{12}O_{40})^{3-}$ (HPA) encaged into SBA-15 [25]. Anandan et al. also investigated increased photocatalytic activity heteropolytungstic acid-encapsulated TiSBA-15 in the degradation of methyl orange [24]. Motivated by the above work, we first modified Y zeolite by post-synthesis method with EDTA treatment in order to improve the surface hydrophilic–hydrophobic properties of support materials. This, in turn, increases the ability of absorption of dye contaminant on zeolite surface and improved the photocatalytic activity. Then molybdophosphoric acid was synthesized into nanocage of dealuminated Y zeolite by ship-in-a-bottle method. Finally, TiO_2 incorporate into zeolite cage by impregnation method. The photocatalytic activity of prepared catalyst was investigated in the degradation of methyl orange.

Experimental

Materials and reagents

All materials were of the commercial reagent grade and were used without any purification. NaY zeolite was purchased from Sigma Aldrich and was dealuminated by post-synthesis method with EDTA treatment. In this case, the controlling of the rate of EDTA addition, EDTA amount and reaction temperature is critical to prevention amorphization [26].

Preparation of zeolite-encapsulated HPA/TiO_2/DAZY

Synthesis of HPA/DAZY: In a typical procedure, NaY zeolite was dealuminated by chemical operation with EDTA treatment. This not only increased the zeolite structure stability in the presence of acidic HPA, but also modified surface hydrophilic–hydrophobic properties and therefore, absorption of organic dye on support is facilitated. 12-molybdophosphoric acid was prepared by ship-in-a-bottle method to the reported procedure [27].

Preparation of HPA/TiO_2/ DAZY: This catalytic system was prepared by impregnation method. In a typical procedure, 0.1 g HPA/DAZY was added to the suspension containing 0.01 g TiO_2 in 50 mL distilled water and was stirred for 24 h. Then the solvent was evaporated under vacuum and dried at 100 °C for 12 h. Then the samples were calcinated at 473 K for 3 h.

General procedure for the photodegradation of methyl orange

In a typical run, the suspension containing 0.02 g catalyst and 50 mL aqueous solution of methyl orange (5×10^{-5} g/L) was stirred

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first in the dark to establish adsorption/desorption equilibrium to eliminate the error due to any initial adsorption effect. Then irradiation experiments were carried out in a homemade reactor. The suspension was magnetically stirred throughout irradiation. To monitor the organic pollutants methyl orange degradation process, about 3 mL of the suspension was withdrawn and the photo catalysts were separated from the suspensions by 0.45 μm disc. The photodegradation process was monitored by its characteristic absorption band at 465 nm using a double-beam UV-Visible spectrometer.

Results and Discussion

Preparation and characterization of HPA/TiO_2/DAZY

NaY was dealuminated by post-synthesis method with EDTA treatment. In this case, not only mesoporous structure was formed, but also hydrophobicity of surface increased and therefore, the absorption of organic dye on zeolite surface enhanced [13]. Synthesis of HPA/ DAZY was carried out by template synthesis method. In this method, HPA act as a template and zeolite was formed around it. TiO_2 inserted into nanocage of zeolite by impregnation method. The prepared catalyst was characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and ion couple plasma (ICP) technique. The content of Mo and Ti in the synthesized samples was obtained using ICP analysis which equal with 0.0056 g and 0.0055 g /g of the supported catalyst for Mo and Ti respectively. The FT-IR spectra confirm the existence of MPA into nanocage of dealuminated Y zeolite. In the FT-IR spectra of HPA six characteristic peaks are observed at 1617, 1065, 966, 870, 787, 599 cm^{-1}. When the HPA encapsulated into DAZY, these peaks are observed at 1631, 1084 (P–O), 946 (Mo-O_t), 795 (Mo–O_e–Mo) (O_t: terminal oxygen, O_e: edge-sharing oxygen) 710, 559, 465 cm^{-1} (Figure 1). Meanwhile, the presence of absorption bands at 920, 895 and 860 cm^{-1} is related to Ti-O, Ti=O stretching vibration and Ti–O–Ti linkage vibration, respectively (Figure 1) These peaks were disappeared in the spectrum because of overlapping with to that of zeolite and HPA peaks (Figure 1). The XRD pattern of catalyst is brought in Figure 2. In this case, appearance of peaks in 2θ=28 is related to TiO_2 in anatase form which proved TiO_2 inserted on zeolite support. In addition, the XRD pattern of catalyst is identical to that of Y zeolite except with appearance peaks in the region which related to the HPA compound [28,29]. This proved Y zeolite act as support and can be involved HPA and TiO_2. The EDS results proved this claims. The field emission scanning electron micrograph (FESEM) of the HPA/TiO_2/ DAZY indicated the cubo-octahedral units that proved zeolite structure was preserved after the insertion of HPA and TiO_2 in the nanocage of zeolite. In addition the presence of species in nanometer size proved the insertion of TiO_2 into zeolite nanocage (Figure 3). FESEM-EDX spectrum of HPA/TiO_2/ DAZY showed the presence of component of photocatalyst. It proved the formation of metallo complexes into cages of zeolite (Figure 4). In order to detect the photocatalytic activity of HPA/TiO_2/ DAZY, degradation of methyl orange was tested as a function of different experimental parameters which are presented in Figures 5-7.

Effect of catalyst amount: The effect of catalyst amount on removal of methyl orange was investigated by varying the catalyst amount from 0.02 to 0.07 g and the result is brought in Figure 3. It can be seen that with increasing in amount of the catalyst, degradation of methyl orange increased because of increasing in absorbed of dye molecule. Optimum degradation was obtained with 0.03 g catalyst because of high removal of dye contaminant. At high catalyst loading the removal of dye is not significantly great. In higher loading catalyst, light absorption has been

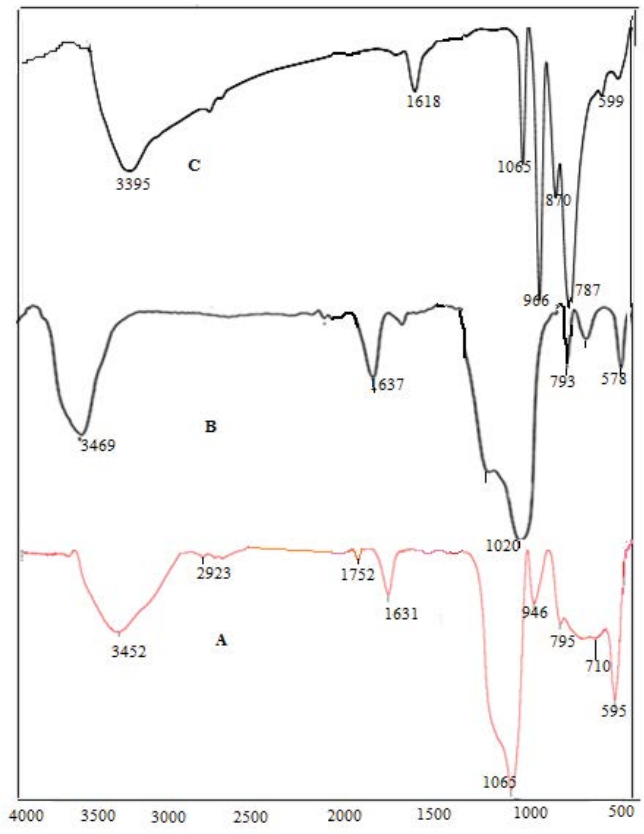

Figure 1: FT-IR spectra of A) HPA/TiO_2/DAZY B) HY C) $H_3PMo_{12}O_{40}$.

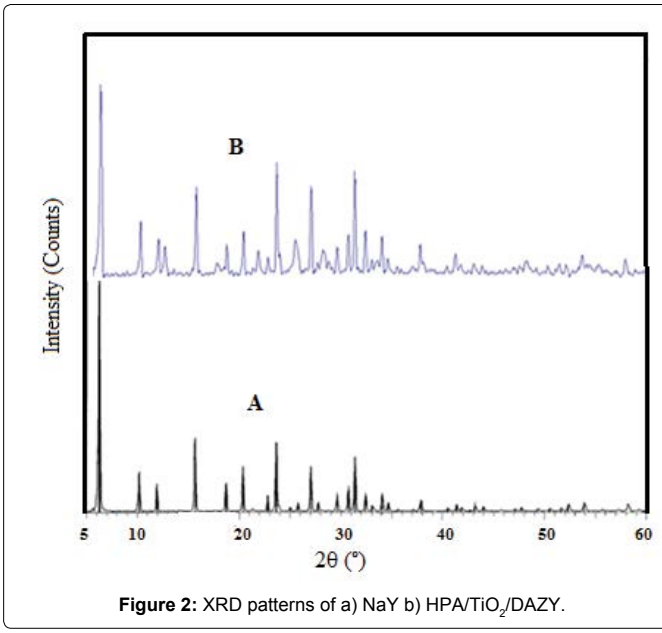

Figure 2: XRD patterns of a) NaY b) HPA/TiO_2/DAZY.

increased that can be related to light scattering which was occurred by the catalyst particle and the absorption phenomena was happened with catalyst instead organic dye. Therefore, the photocatalytic activity is reduces and the absorption band increased.

Effect of TiO_2/(HPA/DAZY) ratio: For this purpose variety of TiO_2/(HPA/DAZY) ratio including 1:5, 1:10 and 1:16 was tested in the

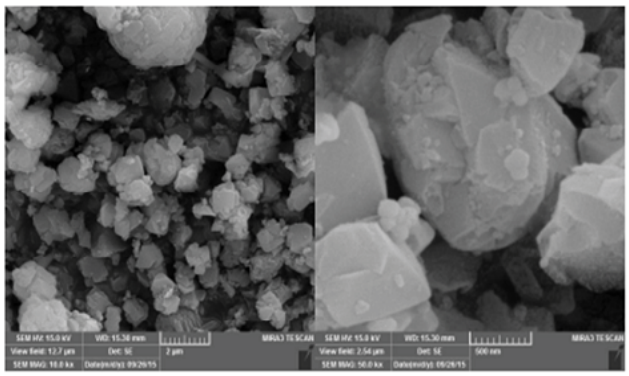

Figure 3: FESEM micrograph of HPA/TiO_2/DAZY.

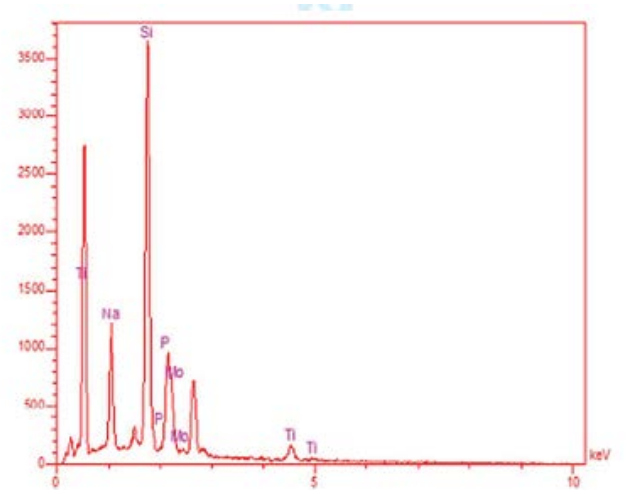

Figure 4: EDS analysis of HPA/TiO_2/DAZY.

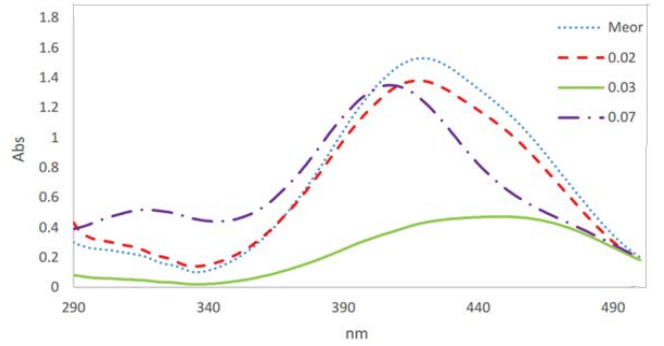

Figure 5: Effect of TiO_2/(HPA/DAZY) ratio on the photodegradation of MO. Concentration of methyl orange was 5.0 × 10^{-5} M.

photodegradation of dye molecules. The results was showed maximum photocatalytic activity was obtained with 1:10 ratio due to high removal of dye molecules. It seems at high TiO_2/(HPA/DAZY) ratio, the contact between photosensitizer and dye molecules reduces which related to decreasing in the interfacial area between the reaction solution and the photo catalyst. Therefore, the removal of dye is reducing [30]. Under the optimum conditions, decolorization of MO was investigated with HPA/TiO_2/DAZY as a function of irradiation time. Figure 4 shows the UV–Vis spectra of methyl orange before and after irradiation in the presence of HPA/TiO_2/DAZY. Methyl orange itself in the absence of HPA/TiO_2/DAZY was photochemically inert as observed by no change in the absorption spectrum. However, in the presence of photo catalyst, the absorption spectrum of methyl orange significantly reduces and after 1 hour, the decolorization of MO is completed.

Mechanism of reaction: The photodegradation of Methyl Orange was initiated by the illumination from a photosensitizer with radiation of energy which it provides the band gap energy of the semiconductor and therefore, separated the photo generated electrons (e-) and holes (h+) in the conduction band (CB) and valence band (VB), respectively. The photoinduced interfacial electron leads to photoreduction of MeOr and converted to photo decoloration product (Figure 8).

Conclusion

In this study, the preparation of HPA/TiO_2/DAZY catalyst was performed using template synthesis and impregnation methods respectively. The physicochemical properties of composites characterized by XRD, FT-IR, FESEM, ICP and EDS technique. XRD studies showed that the appearance of peaks in the regions of TiO_2 and HPA which indicated incorporation of TiO_2 and HPA in nanopores of zeolite. The catalyst displays an efficient photoactivity for the degradation methyl orange under UV illumination. Results indicated HPA/ DAZY hasn't high efficiency in the discoloration of MO and the presence of TiO_2 is necessary for removal of dye molecules. This catalytic system could be successfully recovered by filtration and reused for several times. Therefore, this system would be useful for the cleaning of wastewater containing organic dye using UV-light.

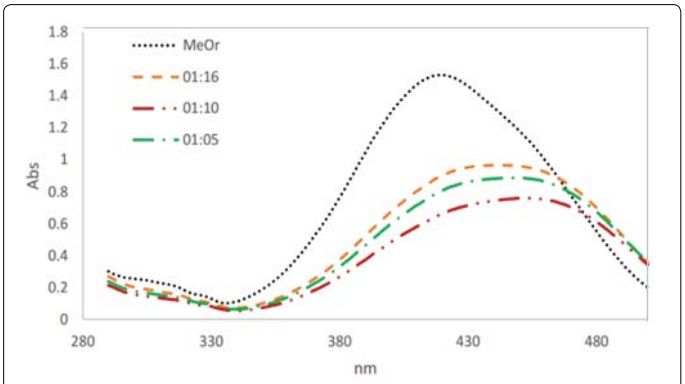

Figure 6: Effect of catalyst amount on the photodegradation of MO. Concentration of methyl orange was 5.0 × 10^{-5} M.

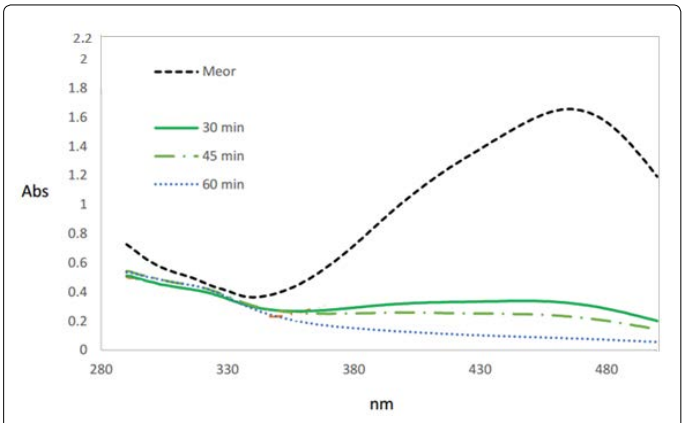

Figure 7: Absorption spectral changes of the filtered solution of methyl orange after irradiation in the presence of HPA/TiO_2/HY. Concentration of methyl orange was 5.0 × 10^{-5} M.

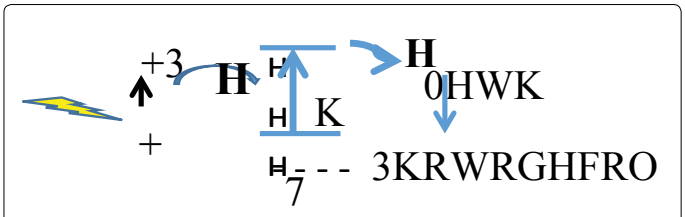

Figure 8: The proposed mechanism for photo decoloration of methyl orange.

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