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Photocatalytic activity of the nano-sized TiO₂/NaY zeolite for removal of methylene blue

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ABSTRACT

A preparation of TiO₂-dispersed Y-zeolite has been attempted by a method comprising a substantial ion-exchange of ammonium titanyl oxalate (NH₄)₂TiO(C₂O₄)₂ and its decomposition. This composite characterized with X-Ray diffractometer and X-ray spectroscopy. These composites have many advantages such as high stability and high porosity. The photocatalytic degradation behavior of methylene blue was investigated for NaY zeolite and TiO₂/NaY zeolite. The efficiency of time, pH, temperature and initial concentration of methylene blue (MB) on degradation of methylene blue was investigated by UV-Vis spectroscopy. And, the optimum conditions were determined 8h time, basic pH and high initial concentrations of methylene blue and photocatalyst. Results showed that 90% of methylene blue was removal by synthesized TiO₂/zeolite with UV irradiation. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Methylene blue;
Removal;
UV irradiation;
TiO₂/zeolite.

INTRODUCTION

Methylene blue is a cationic dye that can be widely used in medical science, coloring paper, dyeing cottons, wools and etc. Although methylene blue is not strongly hazardous, but can cause harmful effects such as increased heart rate, vomiting, shock, Heinz body for motion, cyanosis, jaundice, quadriplegia and tissue necrosis in human. Also this dye in water can affect plant life and is aesthetically unpleasant^[23,24].

Adsorption study has attracted considerable interest as a feasible procedure for removing dyes from effluents. Literature review shows different methods and various adsorbents such as activated eggshell^[16], TiO₂^[17], carbon^[22], tea waste^[1], clay^[18], zeolite^[20,27],

MCM-22^[27], waste wood^[5], biomaterials^[26], polymer^[3] and composite membrane^[19], have been developed for dye removal.

Recently, advanced oxidation processes (AOP) have been widely investigated of which heterogenous photocatalysis has become the most popular. Most studies related to photocatalytic degradation of organic pollutants have been carried out using suspensions of powdered TiO₂ in the treated solution^[12]. TiO₂ is a cheap, readily available material, highly stable chemically and the photogenerated holes are highly oxidizing. In addition, TiO₂ is capable of oxidation of a wide range of organic compounds into harmless compounds such as CO₂ and H₂O^[10].

TiO₂ is by far the most important semiconductor

with wide application as a photocatalyst for the degradation of pollutants in systems for the photochemical splitting of water and in photovoltaic solar cells. There is an enormous potential in controlling some of the photophysical and photochemical properties of bulk TiO_2 such as the onset of the absorption band related to the semiconductor band gap and the efficiency and life time of photoinduced electron transfer processes. To achieve this control, a reduction of the particle size down to the nanometer range in which quantum size effects may operate has been pursued^[7,9,14,21]. Nanoparticles of TiO_2 have been reported to exhibit distinctive properties, different from those characteristic of bulk TiO_2 particles. However, this strategy is complicated by the instability inherent to nanoparticles and the tendency of the primary nanoparticles to undergo aggregation at neutral pH into grains of much larger size with a nonuniform distribution and to age changing the properties over the time.

A novel approach that should lead to the control of the TiO_2 photo activity and may help to circumvent the aggregation problem consists in the encapsulation of TiO_2 nanoclusters inside the rigid internal voids of zeolites that are on the nanometer scale. This strategy offers a simple way to control the size, geometry and accessibility of the TiO_2 clusters by choosing among the known zeolites, those with the appropriate pore dimension and topology^[2,11,25].

However, in spite of the promising advantages of the use of zeolites as organized media, the number of studies on the photoactivity of TiO_2 incorporated inside the pores of zeolites is still relatively small. Previous reports are limited to studies on the emission of zeolite-bound TiO_2 ^[8,13] intrazeolite electron transfer from TiO_2 to methyl viologen50, the photocatalytic activity of these materials for the decomposition of NO_x and the photo reduction of CO_2 by H_2O ^[29]. The incorporation of TiO_2 clusters into zeolites should allow one to prepare photocatalysts with a range of distinctive activities.

MATERIALS AND METHODS

Materials

Aluminum hydroxide, silica gel, sodium hydroxide, calcium chloride, $(\text{Ti}=\text{O})\text{K}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ and meth-

ylene blue (MB) dye (Figure 1) was supplied by Merck; and MB was the analytical reagent grade and used as received.

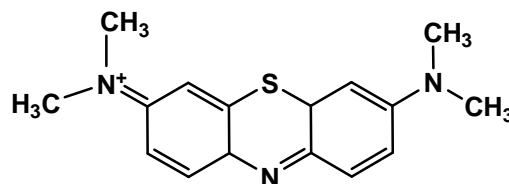


Figure 1: The structure of methylene blue dye

Synthesis of NaY zeolite

NaY zeolite with molar ratio of: 16 NaOH: 1 Al(OH)₃: 15 SiO₂: 320 H₂O was synthesized (Breck and Tonawanda, 1964) and characterized with X-ray diffraction.

Synthesis and characterization of TiO_2 /zeolite

The corresponding zeolite in its Na⁺ form (10 g) was stirred at room temperature with a solution of $(\text{Ti}=\text{O})\text{K}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ or $(\text{NH}_4)_2(\text{Ti}=\text{O})(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ at the required concentration (0.05, 0.4 and 0.8 M) for 4 h. After this time, the solid was filtered and washed exhaustively with distilled water until no oxalate anions were detectable in the washing waters using a freshly prepared 0.5 M aqueous solution of CaCl_2 . The solids were dried in an oven at 150°C for 5 h. All of them were used without further purification. Final product was characterized with X-ray diffractometer (Philips 8440) with radiation at room temperature *Cu-K α* . The elemental analyses were carried out by X-ray fluorescence spectroscopy using a Phillips MiniPal 25 fm that result the same as proceeded work^[11].

Photo catalytic procedure

The degradations were carried out using the methylene blue dye (5 mg/L) solution was exposed to ultraviolet radiation in the presence of dry zeolite and TiO_2 /zeolite (0.04 g); the temperature was kept at 40 °C. The photocatalytic reactor used has a surface area ca.155 cm² illuminated by low-pressure mercury lamp (output at 254 nm, 15 W) kept at 10 cm distance from solution. The solution of the dye was adjusted to the desired pH by addition of NaOH or H₂SO₄.

The amount of degradation MB was measured spectrophotometrically ($\lambda = 670$ nm) in periodically

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taken solution samples and again placed in the same vessel so that the liquid volume was kept constant. The removal efficiency (RE %) of the dye was calculated by Eq. (1)

$$\text{RE (\%)} = (C_0 - C/C_0) \times 100 \quad (1)$$

that C₀ and C are the initial and equilibrium concentrations of MB dye solution, respectively.

RESULTS

Characterization of NaY zeolite and TiO₂/zeolite

Figure 2 shows X-ray diffraction for NaY zeolite and TiO₂/zeolite. XRD patterns indicated that the NaY zeolite and TiO₂/zeolite are almost similar to the parent. Also no crystalline pattern was observed for TiO₂/zeolite; this might be because of their fine distribution in the lattice. It appears that incorporation of TiO₂ had little effect on the crystalline structure of the host zeolite.

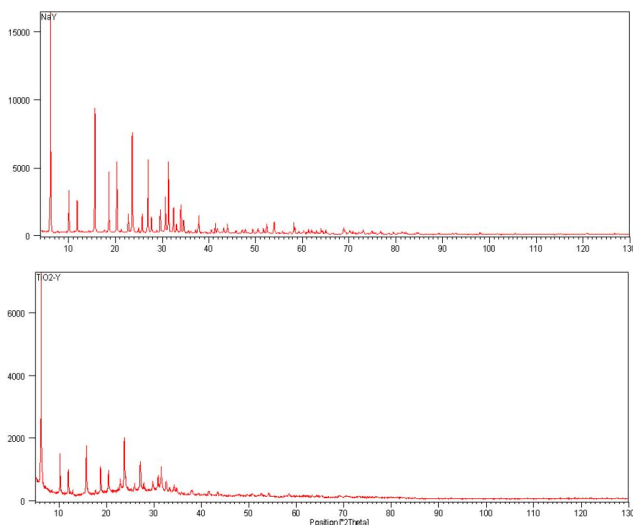


Figure 2 : X-ray diffraction patterns of NaY zeolite (a) and TiO₂/zeolite (b)

Effect of contact time on photo degradation of MB by zeolite and TiO₂/zeolite

The result of contact time shown in Figure 3 describes that about 40% absorption of methylene blue in first five minutes for both zeolite and TiO₂/zeolite. The adsorption increases up to 8 hours for both zeolite and TiO₂/zeolite and equilibrium time is 8 h. Result showed that the absorption of methylene blue by TiO₂/zeolite in presence UV radiation has more increased. These results clearly indicate that the presence of titanium oxide incorporated within the zeolite, as well as UV irradiation,

are indispensable for the photocatalytic reaction to take place.

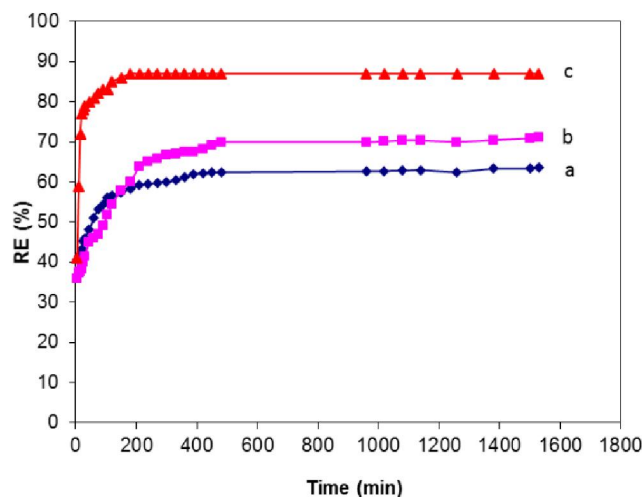


Figure 3 : RE (%) of methylene blue by (a) zeolite NaY, (b) TiO₂/NaY zeolite without UV radiation and (c) TiO₂/NaY zeolite in presence UV radiation vs. time

Effect of pH on photo degradation MB by zeolite and TiO₂/zeolite

Figure 4 shows the effect of pH on the removal efficiency of MB by TiO₂/zeolite in presence UV radiation and in optimum time. pH of the solutions was changed in the range of 6 to 9. Result showed that adsorption of MB increased with increasing pH about 100 % for TiO₂/zeolite. Methylene blue is a cationic dye which exists in aqueous solution in form of positively charged ions. Its adsorption onto the adsorbent surface is related to the surface charge on the adsorbent, which in turn is influenced by the solution pH. It seems that, proton ions compete with MB cations for vacant adsorption sites at lower pH, and that higher pH is favorable for absorption of MB.

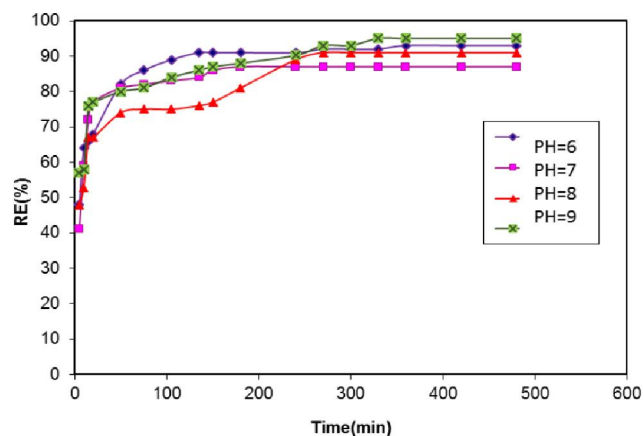


Figure 4 : RE (%) of methylene blue by TiO₂/NaY zeolite vs. time in different pH

Effect of initial concentration of MB on adsorption

Figure 5 show the removal efficiency of MB as a function of time and initial concentration in contact with TiO₂/zeolite. The amount of MB adsorbed per unit mass of TiO₂/zeolite increased with increasing MB concentration. Removal efficiency of MB increased from 91% to 99% in TiO₂/zeolite when the concentration of MB was increased from 5 to 10 mg/L. The structure of TiO₂/zeolite may contain a large number of active sites and MB cations can uptake to them. Also, almost 80% uptake of total amount of dye in contact with TiO₂/zeolite was found to occur in the first period of time (30 min) and then the adsorption rate remained constant.

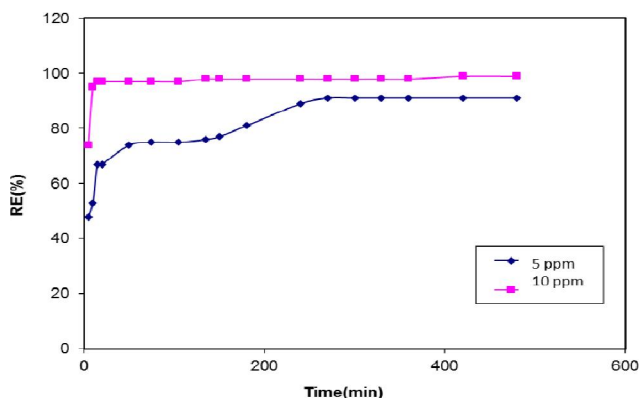


Figure 5 : Effect of MB initial concentration on the removal efficiency in TiO₂/zeolite

Effect of amount of NaY/TiO₂ (absorbant) for adsorption of MB

Figure 6 show the removal efficiency of MB as a function of time and different amount of TiO₂/zeolite. The amount of MB adsorbed per unit mass of TiO₂/zeolite increased with increasing amount NaY/TiO₂. Removal efficiency of MB increased from 91% to 97% in TiO₂/zeolite when amount NaY/TiO₂ was increased from 0.04 to 0.08 g. The structure of TiO₂/zeolite may contain a large number of active sites and MB cations can uptake to them.

Adsorption isotherm studies

Adsorption isotherm was studied fitting data to Langmuir and Freundlich isotherms which may show monolayer or multilayer sorption^[4]. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the

linear form as Eq.(2)

$$C_e/q_e = 1/bq^{max} + C_e/q^{max} \tag{2}$$

Where C_e is the equilibrium concentration (mg/L) and q_e is the amount of adsorbed ion at equilibrium (mg/g). The Langmuir constants q^{max} (mg/g) represents the monolayer adsorption capacity and b (Lmg⁻¹) is related to the heat of adsorption. The Langmuir isotherm plots for adsorption of MB by TiO₂/zeolite from aqueous solutions are shown in Figure 7.

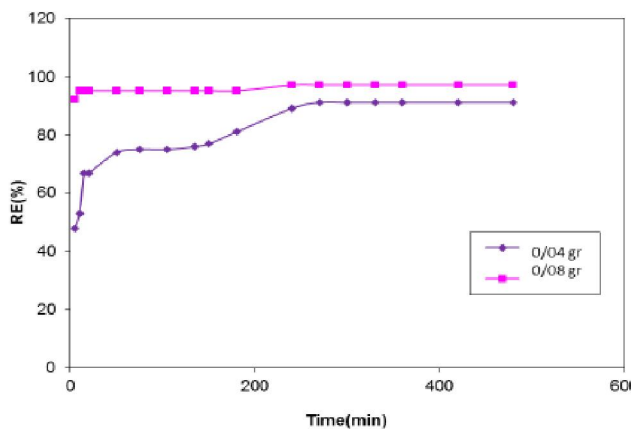


Figure 6 : Effect of different amount NaY/TiO₂ such as absorbant for remove MB

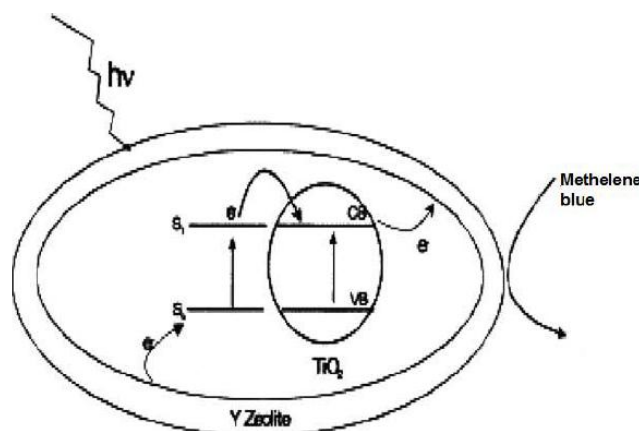


Figure 7 : The proposed mechanism for photoreduction of MB

DISCUSSION

In this work, TiO₂ was incorporated onto NaY zeolite without any change in its crystalline structure. NaY zeolite and TiO₂/zeolite were used for adsorption of methylene blue and the optimum conditions for the adsorption were determined as 8h contact time, basic pH, because proton ions compete with MB cations for vacant adsorption sites at lower pH and higher pH is fa-

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favorable for absorption of MB.

Also, high initial concentration and temperature were more favorable because of high porosity for NaY zeolite and TiO₂/zeolite and endothermic conditions for reaction. As it is demonstrated in experiments, at first the absorbance of MB increased with increasing time and then remained constant after 8h. It was also observed that almost 97% MB was adsorbed by synthesized TiO₂/zeolite in presence UV radiation. It seems that TiO₂ nanoparticles were anchored on the external surface as well as encapsulated in the cavities of porous zeolites^[15]. Hence, with using of TiO₂/NaY zeolite, the removal efficiency of methylene blue dye decreased, triviality. The results of these adsorbents were better in composition with other adsorbents^[1,30]. Finally, the equilibrium removal performance of the composites fitted to langmuir model and have monolayer adsorption.

Photocatalytic activities of TiO₂/Y-zeolite system explain by studying the photoreduction of methyl blue. According to them, in the UV irradiation of TiO₂-zeolite, the conduction band electron can be removed quickly from the TiO₂ site before charge recombination, because the electron-rich zeolite surface functions as a hole scavenger (figure 7).

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