

# Photocatalytic activity of the nano-sized TiO<sub>2</sub>/NaY zeolite for removal of methylene blue

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**ABSTRACT:** A preparation of TiO<sub>2</sub>-dispersed Y-zeolite has been attempted by a method comprising a substantial ion-exchange of ammonium titanyl oxalate (NH<sub>4</sub>)<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> 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 TiO<sub>2</sub>/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 TiO<sub>2</sub>/zeolite with UV irradiation.

**Keywords:** Methylene blue; Removal; UV irradiation; TiO<sub>2</sub>/zeolite.

## INTRODUCTION

Methylene blue is a cationic dye that can be widely used in medical science, coloring paper, dying 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 (Paulino, 2006; Uddin, 2009).

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 (Ehrampoush, 2011), TiO<sub>2</sub> (Ehrampoush, 2010), carbon (McKai, 1998), tea waste (Almedia, 2009), clay (Hun, 2009), zeolite (Wang and Zhu, 2006; Ghadiri, 2010), MCM-22 (Wang, 2006), waste wood (Bestani, 2008), biomaterials (Vijayaraghavan, 2008), polymer (Baldez, 2008) and composite membrane (Lin *et al.*, 2009), 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 TiO<sub>2</sub> in the treated solution [Colonna GM, *et al.* 1999]. TiO<sub>2</sub> is a cheap, readily available material, highly stable chemically and the photogenerated holes are highly oxidizing. In addition, TiO<sub>2</sub> is capable of oxidation of a wide range of organic compounds into harmless compounds such as CO<sub>2</sub> and H<sub>2</sub>O (D. Chatterjee, 2005).

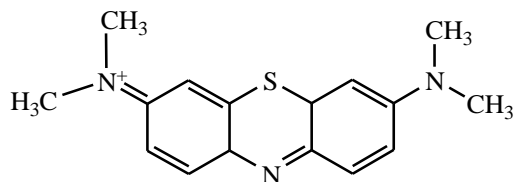
TiO<sub>2</sub> is by far the most important semiconductor with wide application as a photocatalyst for the degradation of pollutants in systems for the photochemical splitting of water and in photovoltaic solar cells. There is an enormous potential in controlling some of the photophysical and photochemical properties of bulk TiO<sub>2</sub> 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 (Cabrera, 1997; Cermenati, 2000; Cosa, 2002; Rezaee, 2008). Nanoparticles of TiO<sub>2</sub> have been reported to exhibit distinctive properties, different from those characteristic of bulk TiO<sub>2</sub> 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<sub>2</sub> photo activity and may help to circumvent the aggregation problem consists in the encapsulation of TiO<sub>2</sub> 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<sub>2</sub> clusters by choosing among the known zeolites, those with the appropriate pore dimension and topology (Chen , 1999; Anandan and Yoon, 2003; M U<sup>g</sup>urlu , 2010).

However, in spite of the promising advantages of the use of zeolites as organized media, the number of studies on the photoactivity of TiO<sub>2</sub> incorporated inside the pores of zeolites is still relatively small. Previous reports are limited to studies on the emission of zeolite-bound TiO<sub>2</sub> (Corrent , 2001; Carolina , 2008) intrazeolite electron transfer from TiO<sub>2</sub> to methyl viologen50, the photocatalytic activity of these materials for the decomposition of NO<sub>x</sub> and the photo reduction of CO<sub>2</sub> by H<sub>2</sub>O (Yamashita , 1998). The incorporation of TiO<sub>2</sub> clusters into zeolites should allow one to prepare photocatalysts with a range of distinctive activities.

## MATERIALS AND METHODS

Aluminum hydroxide, silica gel, sodium hydroxide, calcium chloride, (Ti=O) K<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup>.2H<sub>2</sub>O and methylene blue (MB) dye (Figureure. 1) was supplied by Merck; and MB was the analytical reagent grade and used as received.



Figureure. 1: The structure of methylene blue dye

### Synthesis of NaY zeolite

NaY zeolite with molar ratio of: 16 NaOH: 1 Al (OH)<sub>3</sub>: 15 SiO<sub>2</sub>: 320 H<sub>2</sub>O was synthesized (Breck and Tonawanda, 1964) and characterized with X-ray diffraction.

### Synthesis and characterization of TiO<sub>2</sub> /zeolite

The corresponding zeolite in its Na<sup>+</sup> form (10 g) was stirred at room temperature with a solution of (Ti=O) K<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup>.2H<sub>2</sub>O or (NH<sub>4</sub>)<sub>2</sub>(Ti=O)(C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup>.H<sub>2</sub>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<sub>2</sub>. 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 $\alpha$ . The elemental analyses were carried out by X-ray fluorescence spectroscopy using a Phillips MiniPal 25 fm that result the same as proceeded work (Chen *et al.*, 1999).

### Photo catalytic procedure

The degradations were carried out using the methylene blue dye (5 mg/L) solution was exposed to ultra-violet radiation in the presence of dry zeolite and TiO<sub>2</sub>/zeolite (0.04 g) ; the temperature was kept at 40 °C. The photocatalytic reactor used has a surface area ca.155 cm<sup>2</sup> 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 H<sub>2</sub>SO<sub>4</sub> .

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

$$RE (\%) = (C_0 - C/C_0) \times 10 \quad (1)$$

that C<sub>0</sub> and C are the initial and equilibrium concentrations of MB dye solution, respectively.

## RESULTS AND DISCUSSION

### RESULTS

#### *Characterization of NaY zeolite and TiO<sub>2</sub>/zeolite*

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

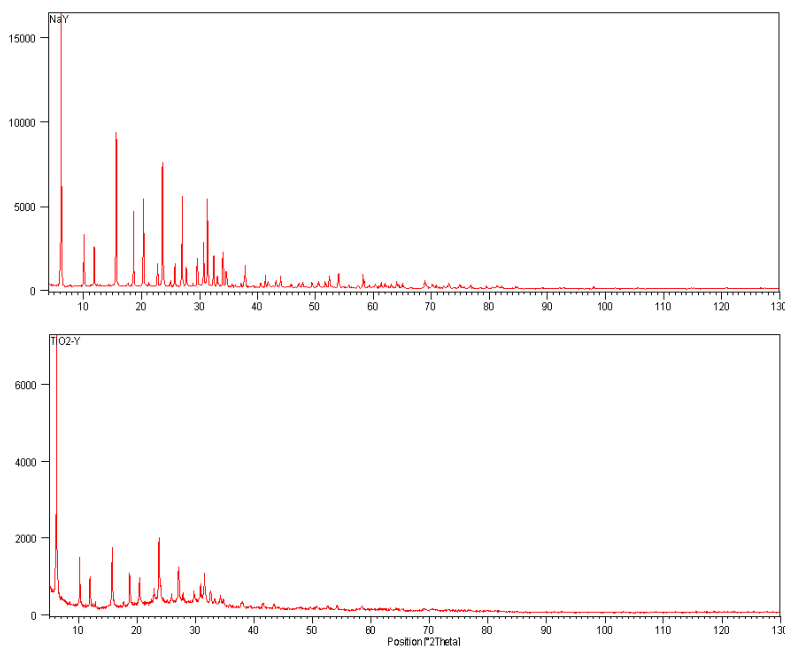


Figure 2. X-ray diffraction patterns of NaY zeolite (a) and TiO<sub>2</sub>/zeolite (b)

#### ***Effect of contact time on photo degradation of MB by zeolite and TiO<sub>2</sub> /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 TiO<sub>2</sub>/zeolite . The adsorption increases up to 8 hours for both zeolite and TiO<sub>2</sub>/zeolite and equilibrium time is 8 h. Result showed that the absorption of methylene blue by TiO<sub>2</sub>/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.

#### ***Effect of pH on photo degradation MB by zeolite and TiO<sub>2</sub> /zeolite***

Figure. 4 shows the effect of pH on the removal efficiency of MB by TiO<sub>2</sub>/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 TiO<sub>2</sub>/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.

#### ***Effect of initial concentration of MB on adsorption***

Figures. 5 show the removal efficiency of MB as a function of time and initial concentration in contact with TiO<sub>2</sub>/zeolite. The amount of MB adsorbed per unit mass of TiO<sub>2</sub>/zeolite increased with increasing MB concentration. Removal efficiency of MB increased from 91% to 99% in TiO<sub>2</sub>/zeolite when the concentration of MB was increased from 5 to 10 mg/L. The structure of TiO<sub>2</sub>/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 TiO<sub>2</sub>/zeolite was found to occur in the first period of time (30 min) and then the adsorption rate remained constant.

**Effect of amount of NaY/TiO<sub>2</sub> (adsorbant) for adsorption of MB**

Figures. 6 show the removal efficiency of MB as a function of time and different amount of TiO<sub>2</sub>/zeolite. The amount of MB adsorbed per unit mass of TiO<sub>2</sub>/zeolite increased with increasing amount NaY/TiO<sub>2</sub>. Removal efficiency of MB increased from 91% to 97% in TiO<sub>2</sub>/zeolite when amount NaY/TiO<sub>2</sub> was increased from 0.04 to 0.08 g. The structure of TiO<sub>2</sub>/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 (Basha and Murthy, 2007). 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) .  $C_e/q_e = 1/bq^{max} + C_e/q^{max}$

Where C<sub>e</sub> is the equilibrium concentration (mg/L) and q<sub>e</sub> is the amount of adsorbed ion at equilibrium (mg/g). The Langmuir constants q<sup>max</sup> (mg/g) represents the monolayer adsorption capacity and b (Lmg<sup>-1</sup>) is related to the heat of adsorption. The Langmuir isotherm plots for adsorption of MB by TiO<sub>2</sub>/zeolite from aqueous solutions are shown in Figure. 7.

**DISCUSSION**

In this work, TiO<sub>2</sub> was incorporated onto NaY zeolite without any change in its crystalline structure. NaY zeolite and TiO<sub>2</sub>/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 favorable for absorption of MB.

Also, high initial concentration and temperature were more favorable because of high porosity for NaY zeolite and TiO<sub>2</sub>/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 TiO<sub>2</sub>/zeolite in presence UV radiation. It seems that TiO<sub>2</sub> nanoparticles were anchored on the external surface as well as encapsulated in the cavities of porous zeolites (Easwaramoorthi and Natarajan, 2009). Hence, with using of TiO<sub>2</sub>/NaY zeolite, the removal efficiency of methylene blue dye decreased, triviality. The results of these adsorbents were better in composition with other adsorbents (Almedia *et al.*, 2009, Zendehdel *et al.*, 2011). Finally, the equilibrium removal performance of the composites fitted to langmuir model and have monolayer adsorption.

Photocatalytic activities of TiO<sub>2</sub>/Y-zeolite system explain by studying the photoreduction of methyl blue. According to them, in the UV irradiation of TiO<sub>2</sub>-zeolite, the conduction band electron can be removed quickly from the TiO<sub>2</sub> site before charge recombination, because the electron-rich zeolite surface functions as a hole scavenger (figure.7) .

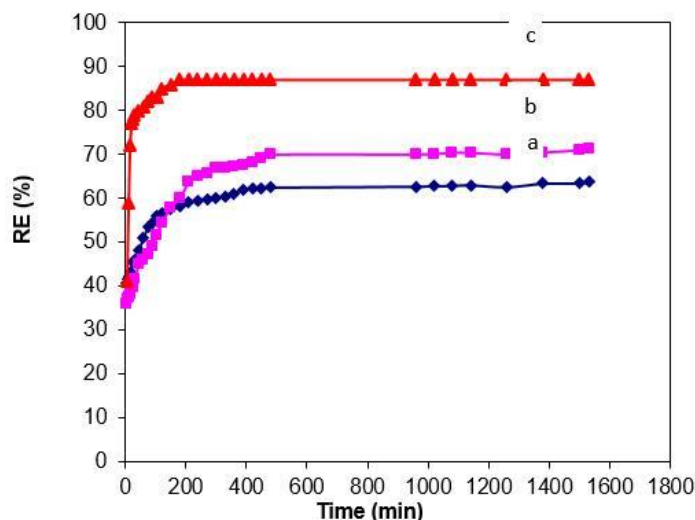


Figure 3. RE(%) of methylene blue by (a) zeolite NaY ,(b) TiO<sub>2</sub>/NaY zeolite without UV radiation and (c) TiO<sub>2</sub>/NaY zeolite in presence UV radiation vs time

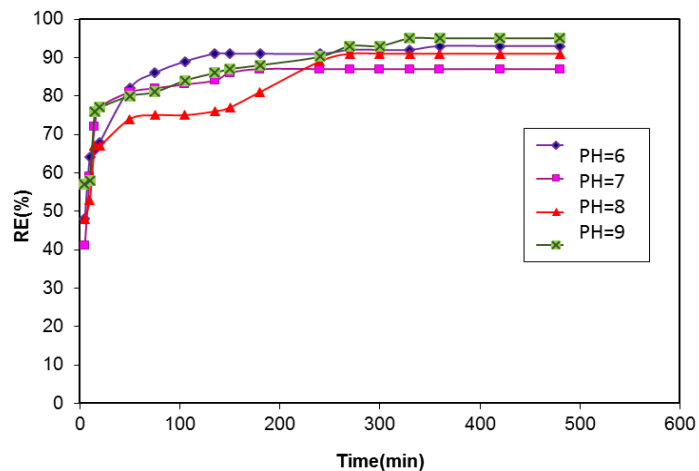


Figure 4. RE(%) of methylene blue by TiO<sub>2</sub>/NaY zeolite vs. time in different PH

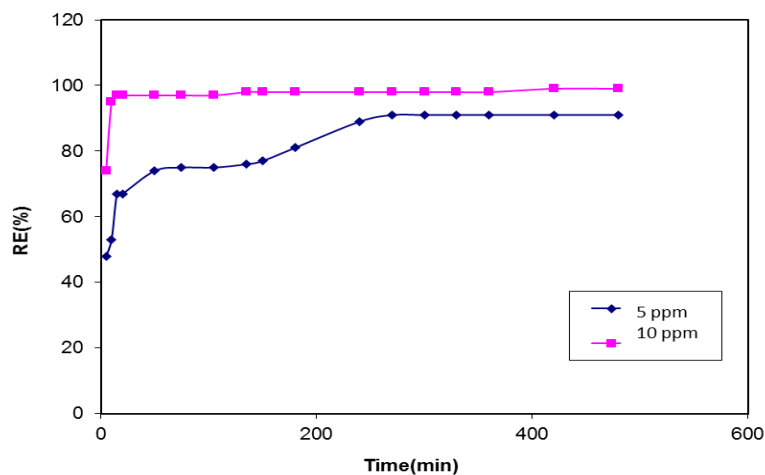


Figure 5. Effect of MB initial concentration on the removal efficiency in TiO<sub>2</sub>/zeolite

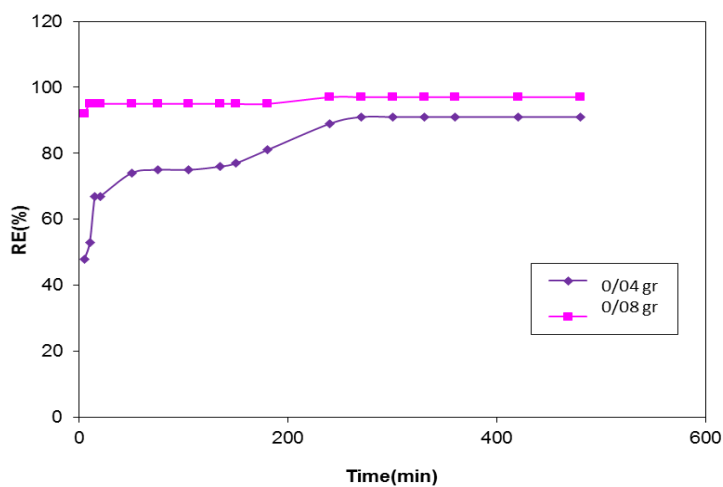


Figure 6. Effect of different amount NaY/TiO<sub>2</sub> such as absorbant for remove M

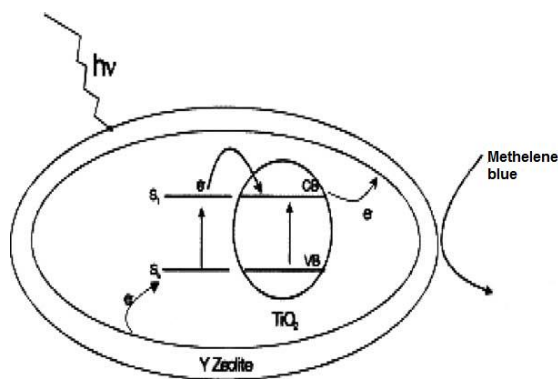


Figure 7. The proposed mechanism for photoreduction of MB

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