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EFFICIENCY EVALUATION OF NaY ZEOLITE AND TiO_2/NaY ZEOLITE IN REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTIONS

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ABSTRACT

In this study titanium dioxide cluster was incorporated onto NaY zeolite and characterized with X-Ray diffractometer and X-ray spectroscopy. These composites have many advantages such as high stability and high porosity. The adsorption behavior of methylene blue was investigated for NaY zeolite and TiO_2/NaY zeolite. The efficiency of time, pH, temperature and initial concentration of methylene blue (MB) on removal effect 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 absorbent. With increasing of temperature, the removal efficiency of NaY zeolite and TiO_2/NaY increased. Results showed that 92% and 85% of methylene blue was absorbed by synthesized NaY zeolite and TiO_2/zeolite, respectively. Adsorption isotherm as studied by fitting data to Langmuir and Freundlich isotherms models, showed monolayer adsorption and Langmuir equilibrium model to be more relevant.

Key words: Methylene blue; Removal; NaY zeolite; TiO_2/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 *et al*., 2006; Uddin *et al*., 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 *et al*. ,2011) , TiO_2 (Ehrampoush *et al*., 2010), carbon (McKay *et al.*, 1998), tea waste (Almedia *et al.,* 2009), clay (Hun *et al.,* 2009), zeolite (Wang and Zhu, 2006 Ghadiri *et al.*2010), MCM-22 (Wang *et al.,* 2006), waste wood (Bestani *et al.,* 2008), biomaterials (Vijayaraghavan *et al.,* 2008), polymer (Baldez *et al.,* 2008) and composite membrane (Lin *et al.,* 2009), have been developed for dye removal.

TiO_2 is by far the most important semiconductor with wide application as a photocatalyst for the degradation of pollutants in systems for the photochemical

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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 (Cabrera *et al.,* 1997; Cermenati *et al.,* 2000; Cosa *et al.,* 2002; Rezaee, 2008). 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 photoactivity 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 (Chen *et al.,* 1999; Anandan and Yoon, 2003; M U˘gurlu et al., 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_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 (Corrent *et al.,* 2001; Carolina *et al*., 2008) 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 (Yamashita *et al.,* 1998). The incorporation of TiO_2 clusters into zeolites should allow one to prepare photocatalysts with a range of distinctive activities.

In this study, a series of TiO_2/zeolite samples were prepared in which the TiO_2 incorporated onto zeolite and the efficiency of these nanocomposite materials was found for adsorption of methylene blue.

MATERIALS AND METHODS

Materials

Aluminum hydroxide, silica gel, sodium hydroxide, calcium chloride and methylene blue (MB) dye (Fig. 1) was supplied by Merck; and MB was the analytical reagent grade and used as received.

Synthesis of NaY zeolite

NaY zeolite with molar ratio of: 16 NaOH: 1 Al $(OH)_3$: 15 SiO_2: 320 H_2O was synthesized (Breck and Tonawanda, 1964) and characterized with X-ray diffraction.

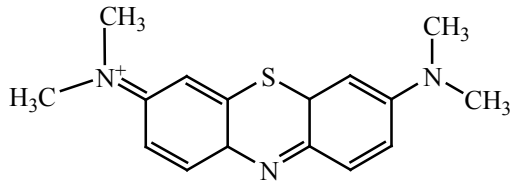

Fig. 1: The structure of methylene blue dye

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 $(Ti{=}O)K_2(C_2O_4)^{2-}.2H_2O$ or $(NH_4)_2(Ti{=}O)(C_2O_4)^{2-}.H_2O$ 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 diffractmeter (Philips 8440) with radiation at room temperature *Cu−Kα*. The elemental analyses were carried out by X-ray fluorescence spectroscopy using a Phillips MiniPal 25 fm that resulted the same as proceeded work (Chen *et al.,* 1999).

Adsorption of methylene blue

A weighed quantity of dry zeolite and TiO_2/zeolite (0.2 g) with different compositions were immersed in enough methylene blue (50 mg/L); the temperature was kept at 37°C. The amount of MB adsorbed was measured spectrophotometrically

(λ= 661.6 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) :

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

Where C_o and C are the initial and equilibrium concentrations of MB dye solution, respectively.

RESULTS

Characterization of NaY *zeolite and TiO_2/zeolite*

Fig. 2 shows X-ray diffraction for NaY zeolite and TiO_2/zeolite. XRD patterns indicated that the NaY zeolite and TiO_2/zeolite are almost similar to the parent. Also no crystalline pattern was observed for TiO_2/zeolite; this might be because of their fine distribution in the lattice. It appears that incorporation of TiO_2 had little effect on the crystalline structure of the host zeolite.

Effect of contact time on MB adsorption by zeolite and TiO_2/zeolite

The result of contact time shown in Fig.3 describes that about 40% absorption of methylene blue in first five minutes for both zeolite and TiO_2/zeolite. The adsorption increases up to 8 hours for both zeolite and TiO_2/zeolite and equilibrium time is 8h.

Effect of pH on MB adsorption by zeolite and TiO_2/zeolite

Fig. 4 shows the effect of pH on the removal efficiency of MB by NaY zeolite and TiO_2/zeolite in optimum time. pH of the solutions was changed in the range of 1 to 11. Result showed that adsorption of MB increased with increasing pH about 80 % and 100 % for TiO_2/zeolite and NaY zeolite, respectively and remained constant after pH 9. 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

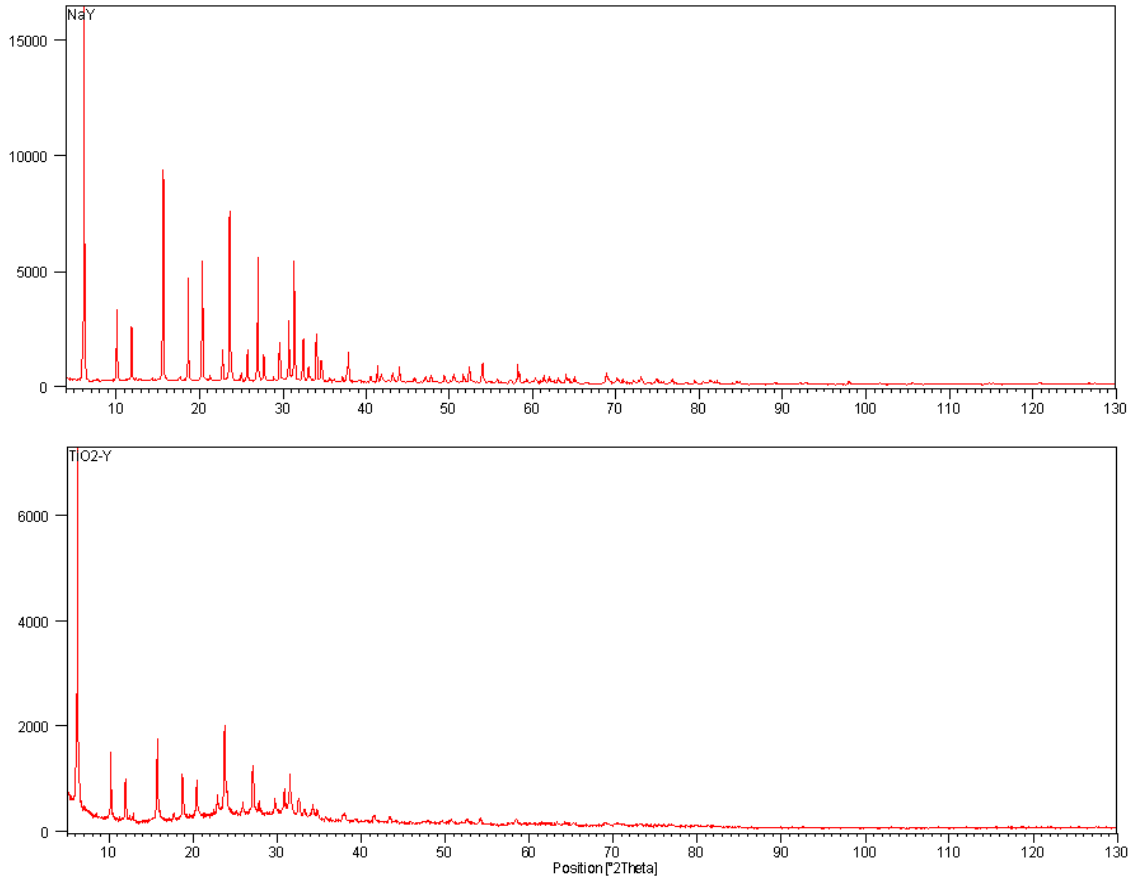

Fig. 2: X-ray diffraction patterns of NaY zeolite (a) and TiO_2/zeolite (b)

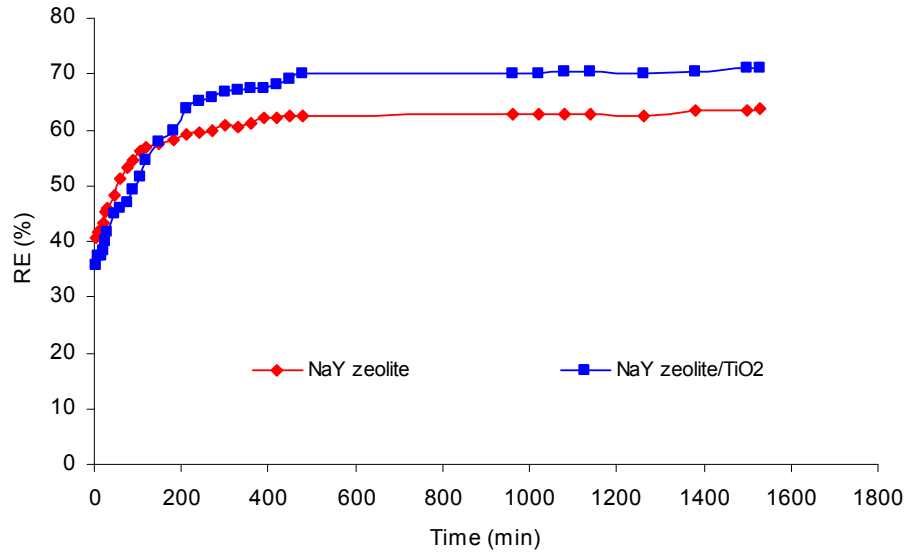

Fig.3: RE(%) of methylene blue by zeolite and TiO_2/NaY zeolite vs. time

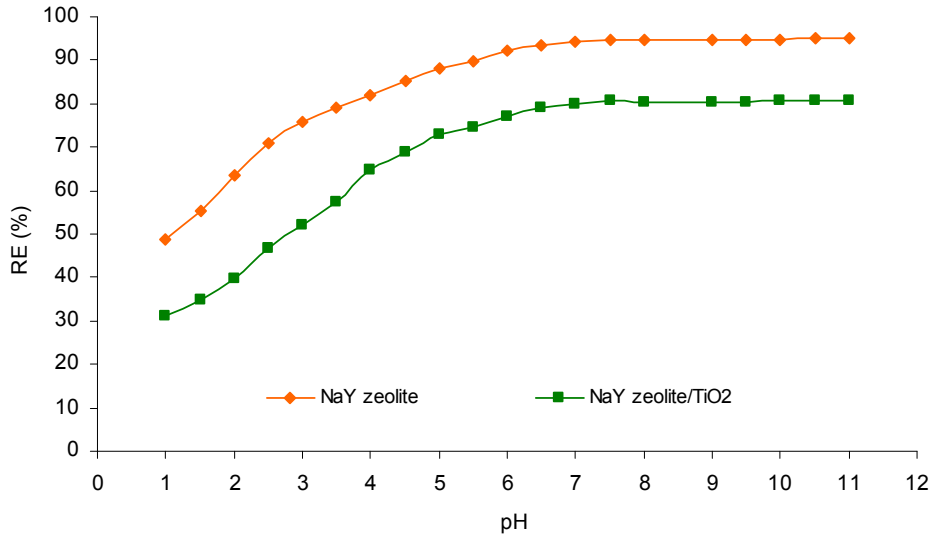

Fig.4: Effect of pH (1-11) on the removal efficiency of MB in zeolite and TiO_2/zeolite

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

Figs. 5, 6 show the removal efficiency of MB as a function of time and initial concentration in contact with zeolite and TiO_2/zeolite, respectively. The amount of MB adsorbed per unit mass of zeolite and TiO_2/zeolite increased with increasing MB concentration. Removal

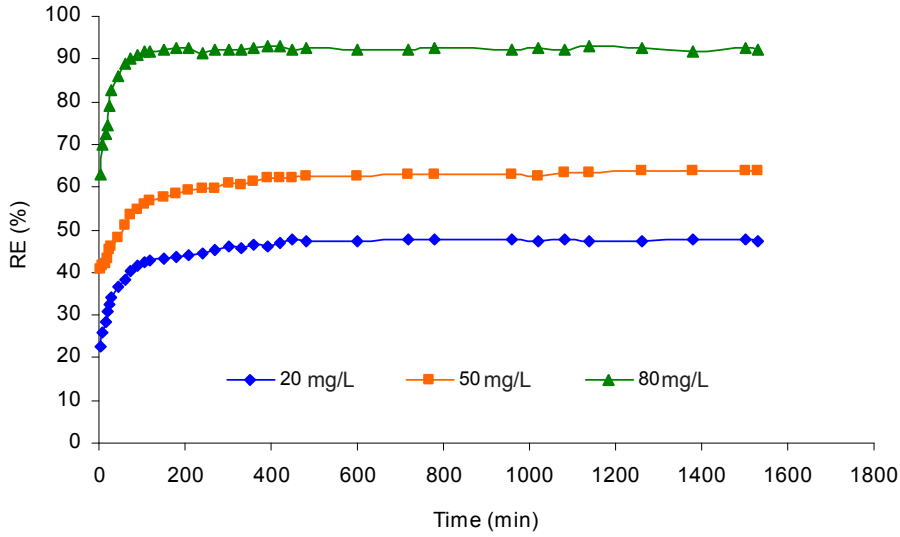

Fig.5: Effect of MB initial concentration on the removal efficiency in NaY zeolite

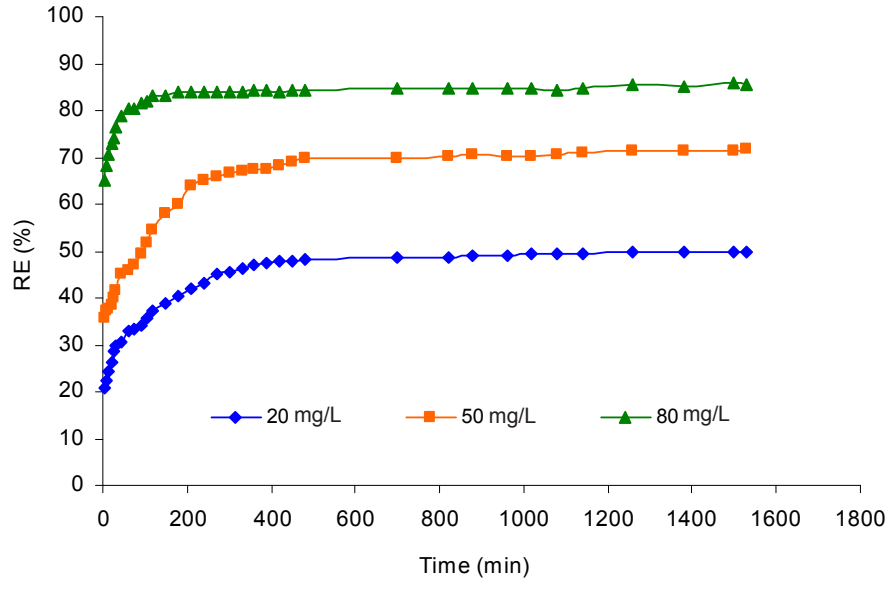

Fig.6: Effect of MB initial concentration on the removal efficiency in TiO_2/zeolite

efficiency of MB increased from 47% to 92% in NaY zeolite and 50% to 85% in TiO_2/zeolite when the concentration of MB was increased from 20 to 80 mg/L. The structure of NaY zeolite and TiO_2/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 NaY zeolite and 76% uptake of it in contact with TiO_2/zeolite were found to occur in the first period of time (30 min) and then the adsorption rate remained constant.

Effect of temperature

The effect of temperature on the adsorption of MB contacted with zeolite and TiO_2/zeolite is shown in Figs. 7 and 8, respectively. The temperature was changed from 20 to 40°C. The results showed that the removal effect of MB increased from 15% to 64% with temperature increasing from 20 to 40°C in NaY zeolite. Also, the removal effect of MB increased from 27% to 71% with temperature increasing from 20 °C to 40°C in TiO_2/zeolite. Hence, the system was considered to be endothermic.

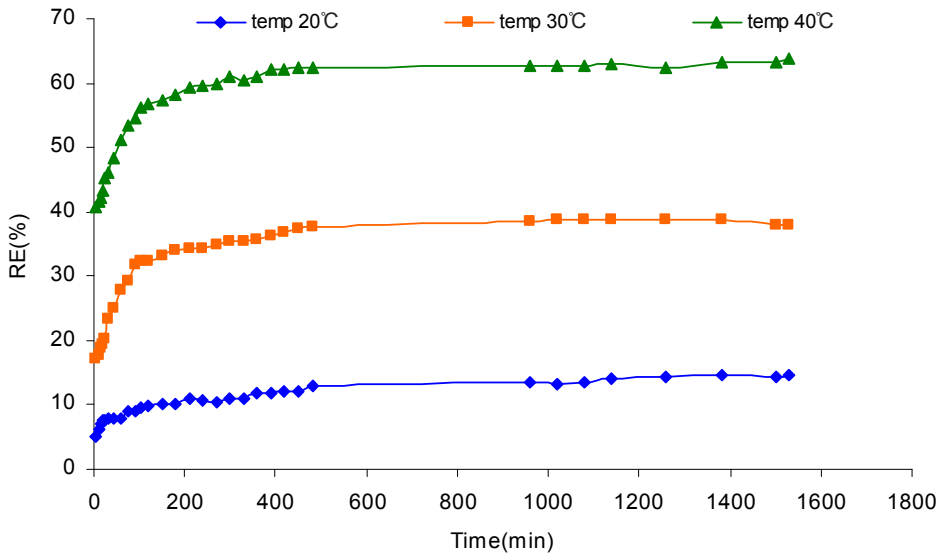

Fig.7: Effect of temperature changes from 20 °C to 40°C on the removal of MB in NaY zeolite

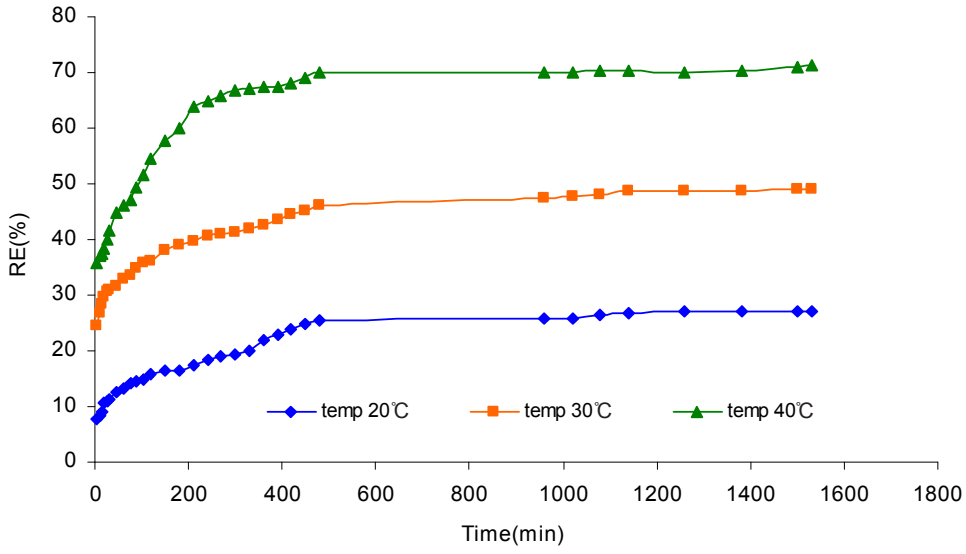

Fig.8. Effect of temperature from 20 to 40°C on the removal effect of MB in TiO_2/zeolite

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)

$$C_e/q_e = 1/bq_{max} + C_e/q_{max} \quad (2)$$

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 NaY zeolite and TiO_2/zeolite from aqueous solutions are shown in Figs. 9 and 10, respectively.

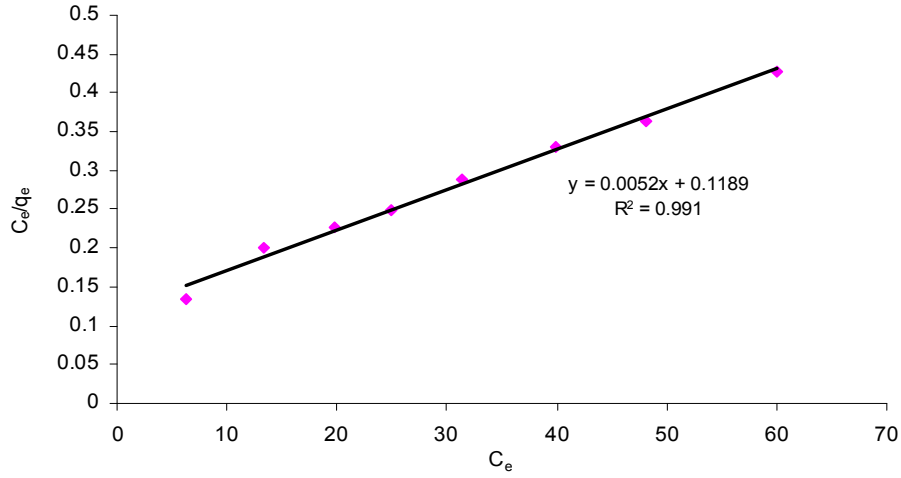

Fig. 9. Langmuir isotherm plot for the adsorption of MB on NaY zeolite in aqueous solutions

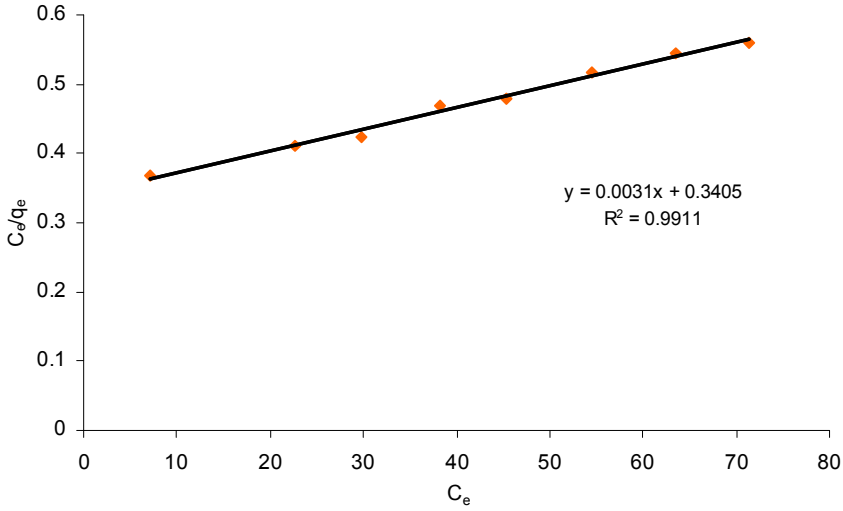

Fig. 10. Langmuir isotherm plot for the adsorption of MB on NaY zeolite/TiO_2 in aqueous solutions

DISCUSSION

In this work, TiO_2 was incorporated onto NaY zeolite without any change in its crystalline structure. NaY zeolite and TiO_2/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_2/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 92% and 85% of MB were adsorbed by synthesized NaY zeolite and TiO_2/zeolite, respectively. It seems that TiO_2 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_2/ 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.

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