Original Article

Investigation of TiO_2/zeolite photocatalytic activity for Safranin dye removal of aqueous solution

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ABSTRACT

Aims: This study was aimed to determine the TiO_2/zeolite photocatalytic activity for removing red Safranin dye form aqueous phase.

Materials and Methods: In this study, TiO_2 nanoparticles were produced using sol-gel method and 2.5 ml sol-gel was coated on 1.2222 g of zeolite. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were applied to specify the structure and morphology of TiO_2 nanoparticles. The effect of TiO_2 coating on zeolite, ultraviolet (UV) radiation intensity, initial concentration of dye and the type of photocatalyst substrate (fixed and moving) on photocatalytic process was investigated.

Results: According to XRD results, the TiO_2 nanoparticles had two phases including anatase (80.5%) and rutile (19.5%). The uniformity of nanoparticles was obvious in the SEM images. The removal efficiency of TiO_2 coated on zeolite was higher than TiO_2 photocatalysis with increasing UV radiation intensity from 2.4 w/m^2 to 3.9 w/m^2, the photocatalytic efficiency was also enhanced. The removal efficiency decreased from 91.61% to 77.91% by increasing the red Safranin dye concentration from 10 mg/L to 50 mg/L. The moving bed of TiO_2/zeolite photocatalyst had a higher efficiency than the fixed bed.

Conclusion: In over all, the TiO_2/zeolite photocatalyst was much more effective than TiO_2 photocatalyst for Safranin dye removal from the aqueous phase. With increasing UV radiation intensity and decreasing dye concentration photocatalytic efficiency, was improved. TiO_2/zeolite photocatalyst with fixed bed is recommended to be used in water treatment. The most important problem of using moving-bed TiO_2/zeolite photocatalyst in the water treatment is opacity.

Key words: Photocatalyst, red Safranin dye, TiO2 nanoparticles, ultraviolet radiation, zeolite

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INTRODUCTION

The organic dyes are considered as the most important group of pollutants in waste water produced from industrial processes such as textile. More than 15% of the textile dyes enter to wastewater drainage system during dyeing processes.[1-3] The textile industry produces large quantities

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of dyes released into the environment, which are mostly stable toxicants.[3] The photocatalyst reactions are used for removing different toxic compounds released from industries.[4-9]

The photocatalyst decomposition of the dye using both titanium dioxide catalyst and ultraviolet (UV) radiation are from advanced oxidation methods with an increasing trend of usage. TiO_2 nanoparticles are of the semi-conductors, which have been highly considered through the past decades due to their advantages such as high photocatalyst activity, self-cleaning and antibacterial properties, physical and chemical stability, non-toxicity, long life, high availability and low cost.[10-12] On the other hand, researchers have found that the combination of some absorbents with TiO_2 nanoparticles can increase the influence of the photocatalyst reactions in aqueous systems.[13-16]

Some problems such as the way of separating the TiO_2 nanoparticles and the low efficiency of photocatalyst reactions in aqueous solutions can limit the usefulness of TiO_2. Recently, many studies have been carried out in searching for an appropriate substrate for TiO_2 nanoparticles to be supported in order to improve the efficiency of TiO_2 recovery.[15,17-19] Out of several substrates, zeolite seems more appropriate due to their unique structure, uniformed pores and channels and excellent ability in attaching to TiO_2.[5,20,21] Many researches have firmly confirmed working with synthetic zeolites.[5,15,22] However, the high cost of synthetic zeolites typically restrict the extent appliance of them in industrial photocatalysts. In comparison with synthetic zeolites, natural zeolites are much cheaper, more abundant and more accessible.[23]

The purpose of this study was to determine TiO_2/zeolite photocatalyst activity in removing Safranin dye in the aqueous phase in order to specify the zeolite effects on TiO_2 photocatalyst activity where the red Safranin was used as a contaminant model.

MATERIALS AND METHODS

This study used titanium tetraisopropoxide, dry ethanol, triethanol amine, the red Safranin dye (Merck, Germany) and clinoptilolite natural zeolite (Semnan province mines). In this study, the UV-A light source was used with a wavelength peak of 400 nm. Properties of red Safranin dye are illustrated in Table 1.

Preparation of TiO_2 photocatalyst

The sol-gel method was used for the synthesis of TiO_2 nanoparticles. First, the dry ethanol and the triethanol amine were added to titanium tetraisopropoxide and were vigorously stirred for 1 h with magnetic stirrer (Hotplate and Stirrer Jenway 1000). Then, the dry ethanol and deionized water were added drop-wise into the solution, which was gently stirred for 20 h with magnetic stirring. After preparing the sol-gel, 2.5 ml of the prepared sol-gel was taken and poured into the plate and was dried for 2 h at 80°C.

Then, it was calcined in the electric oven (Wise Therm FP/FHP). The oven temperature was increased to 550°C with a thermal rate of 1°C/min and was remained constant for 2 h in this temperature.

TiO_2/zeolite photocatalyst preparation

40 and 150 mesh clinoptilolite zeolites were screened using laboratory sieve and were dried at a temperature range of 25-30°C after being washed with distilled water. The 1.2222 g of zeolite and 2.5 ml sol-gel (the zeolite ratio to TiO_2 was 5%) were mixed inside a laboratory plate and were dried at 80°C for 2 h and after that was calcinated in the electric oven. The oven temperature was increased to 550°C with a thermal rate of 1°C/min and was kept constant for 2 h in this temperature.

Preparation of dye stoke solution

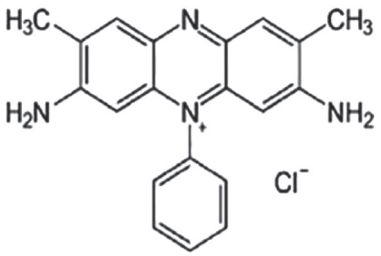
A total of 0.01 g of Safranin dye was dissolved in deionized water and was reached the volume of 100 ml (with a concentration of 100 mg/L) and was kept in a dark place.

Photocatalytic experiments

The factors to be examined in this study included the dye initial concentration (10 and 50 mg/L), the intensity of UV radiation (in intensity range of 2.4 and 3.9 w/m^2) and TiO_2/zeolite fixed and moving bed. The reaction was continued until the dye concentration was remained constant. To begin the experiment, the first photocatalyst to be investigated (TiO_2 and TiO_2/zeolite) and the dye with known concentrations (10 and 50 mg/L) were reached equilibrium in a dark place for 30 min. After reaching equilibrium, the UV lamp was switched (Ultalite Japan F15T10BLB) while the solution was continuously stirred by magnetic stirrer. All photocatalytic experiments were performed in a reactor with a volume of 75 ml. Schematic diagram of reactor is shown in Figure 1.

For turbidity removal caused by zeolite and TiO_2, the samples were centrifuged for 10 min (Hettich zentrifugen D-7200

Table 1: Characteristics of dye applied in the study

Chemical structure	
Molecular formula	$C_{20}H_{19}ClN_4$
Molar mass	350.84 g/mol
Application	Textile industry

Tuttlingen) and the changes the dye intensity were measured by spectrophotometer (spec UV-2100) at wavelength of 518 nm.

To investigate the morphology of TiO_2 surface coated on the zeolite the X-ray diffraction (XRD) analysis (Bruker, D8 ADVANCE, Germany, Wavelength: 1.5406 Å [CuK], Voltage: 40 kV, Current: 40 mA) with radiation CuK ∞ and scanning electron microscopy (SEM) (XL 30, Philips) were used.

In order to observe the effect of TiO_2 and zeolite catalyst in the removal and degradation of pollutants, the red Safranin dye was chosen as a pollutant model. Catalytic efficiency in two concentrations was investigated in different intensities of the UV radiation at room temperature condition.

Characteristics of TiO_2 nanoparticles

To determine the crystal structure of TiO_2 nanoparticles, the XRD was used and the results are shown in Figure 2.

According to XRD pattern, two phases of anatase (80.5%) and rutile (19.5%) was observed in the crystal structure phases and using Shrer equation, the average size of TiO_2 nanoparticles obtained 17 and 41 nm, respectively, in these two phases.

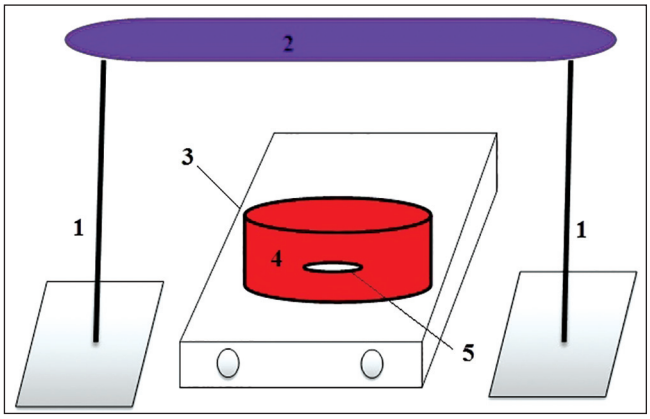


Figure 1: Schematic diagram of reactor for red Safranin dye photocatalytic Degradation. (1) Ultraviolet (UV) lamp holder; (2) UV lamp; (3) Magnetic stirrer; (4) Container containing photocatalytic and dye; (5) Magnet

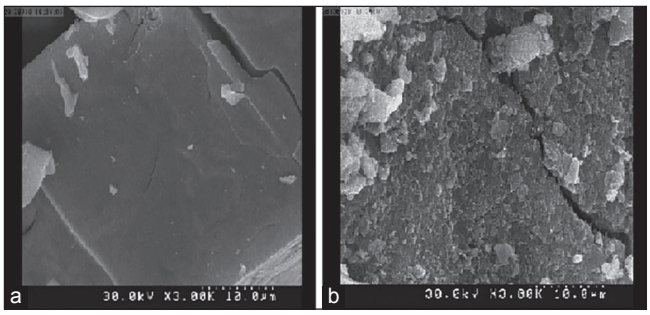


Figure 3: (a) Scanning electron microscopy (SEM) pattern of TiO2. (b) SEM pattern of TiO2/zeolite

Figure 3a shows the SEM pattern of TiO_2 nanoparticles and Figure 3b represents the SEM pattern of TiO_2/zeolite. The uniform distribution of TiO_2 is quite evident in Figure 3a and Figure 3b shows an increase in the surface area and porosity caused by coating TiO_2 nanoparticles on zeolite.

Effect of TiO_2 coating on zeolites

In this study, the concentration of 10 and 50 mg\L red Safranin dye solutions were prepared from stoke solution of 100 mg/L and the catalytic efficiency of TiO_2 and TiO_2/zeolite was investigated in order to determine the effect TiO_2-coating on the zeolite. Based on the results, the decomposition efficiency in the concentration of 10 mg/L were 15.75% and 75.88% for TiO_2, and TiO_2/zeolite, respectively. However, these values were 10.49% for TiO_2 and 69.63% for TiO_2/zeolite in the concentration of 50 mg\L. In fact, the TiO_2 coated on zeolite showed a higher efficiency than the TiO_2 without zeolite coating. The decomposition efficiency of red Safranin dye in the presence of TiO_2 and TiO_2/zeolite is illustrated in Figure 4.

Effects of ultraviolet radiation intensity in photocatalytic process

The UV-A irradiance effects on Safranin dye concentrations of 10 mg/L and 50 mg\L were examined at two intensities of

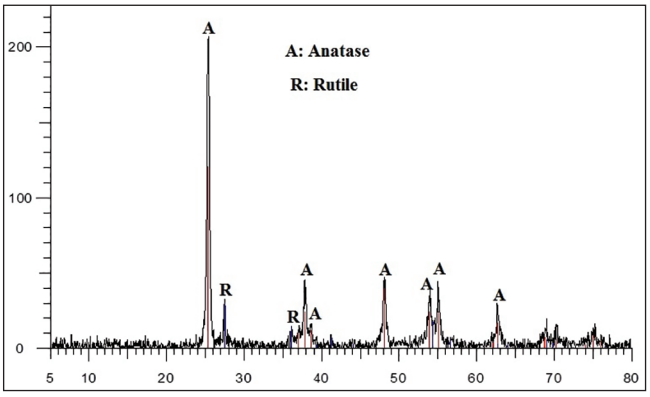


Figure 2: TiO2 nanoparticle XRD pattern

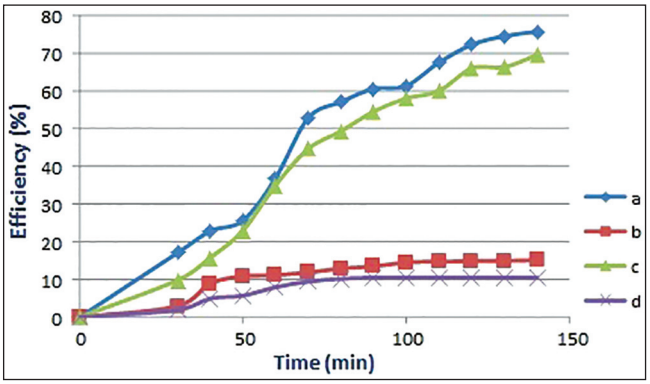


Figure 4: The photocatalytic removal efficiency of (a) TiO2/zeolite with concentration of 10 mg/L; (b) TiO2 with concentration of 10 mg/L; (c) TiO2/zeolite with concentration of 50 mg/L; (d) TiO2 with concentration of 50 mg/L

2.4 and 3.9 w/m^2. In concentration of 10 mg/L red Safranin dye, the UV-A intensity of 3.9 w/m^2 had a removal efficiency of 91.61% and 19.8% for TiO_2/zeolite, respectively, while the removal efficiency was obtained 75.88% for TiO_2/zeolite and 15.21% for TiO_2 at an intensity of 2.4 w/m^2 in the same concentration level. Furthermore, in the radiation intensity of 3.9 w/m^2, the removal efficiency of Safranin dye with the concentration of 50 mg/L was 78.01% in TiO_2/zeolite, which was higher than that for TiO_2 (15.21%) in the radiation intensity 3.9 w/m^2. Figure 5 represents TiO_2 and TiO_2/zeolite removal efficiency with concentration of 10 mg\L, and Figure 6 shows TiO_2 and TiO_2/zeolite removal efficiency with concentration of 50 mg\L in terms of time duration.

Effect of the pollutants concentration in photocatalytic process

In order to study the effect of dye initial concentration in the catalyst removal efficiency the two concentration (10 and 50 mg/L) of Safranin dye with UV-A radiation intensity of 3.9 w/m^2 was used. The photocatalyst activity of target material in concentration of 10 mg/L was more than that for the concentration of 50 mg/L and hence that the photocatalyst activity had the removal efficiency of 91.61% and 19.8% in TiO_2/zeolite and TiO_2 photocatalyst, respectively, in a concentration of 10 mg/L, while in the concentration of 50 mg/L, lower photocatalyst efficiency obtained for TiO2/zeolite and TiO_2 that were 77.91% and 12.75%, respectively. Figure 7 illustrates the effect of the pollutants concentration in photocatalytic process.

Effect of photocatalyst bed type

The TiO_2/zeolite photocatalyst with concentrations of 10 and 50 mg/L red Safranin dye was studied inside the reactor in two states of fixed and moving bed. TiO_2/zeolite photocatalyst was calcined at the bottom of the reactor and was considered as fixed bed. To prepare the moving bed, the TiO_2/zeolite photocatalyst was precisely removed after being calcined, and was poured into the reactor in a powder form. The prepared powder, then, was stirred continuously by a magnetic stirrer in order to provide a homogeneous mixture in the reactor.

In an equal time, the removal efficiency of target photocatalyst with the concentration of 10 mg/L was 97.96% and 91.61% in moving and fixed beds, respectively and with the concentration of 50 mg/L; it was 95.68% and 76.28% for moving and fixed beds. The moving bed had higher removal efficiency than the fixed bed in both concentrations of 10 mg/L and 50 mg/L. Figure 8 represents the catalytic removal efficiency for TiO_2/zeolite in both fixed and moving beds.

DISCUSSION

TiO_2 coating on zeolites

This study results indicated that the TiO_2 photocatalyst activity coated with zeolite (TiO_2/zeolite) was much higher than the TiO_2 photocatalyst without coating. These findings were similar to the results of other studies.[24-26] In a study carried out by Ichiura *et al*., the TiO_2/zeolite cover was used for removing gaseous toluene and formaldehyde. They concluded that the TiO_2/zeolite cover was much more effective than just the TiO_2 cover, and its efficiency even might reach 100% and hence that the cover can be used in removing contaminants from walls and ceilings.[27] In another similar study by Li *et al*. the effects of two types of photocatalysts including TiO_2 and TiO_2 hybrid with clinoptilolite natural zeolite were evaluated in removing the orange methyl and it was proved that the TiO_2 particle growth was controlled by the surface of zeolite. On the other hand, the TiO_2 colloidal particles made a compound with the active sites of clinoptilolite by the very durable link between Ti-O-Al and Ti-O-Si. The TiO_2 photocatalyst activity coated with clinoptilolite was more than that of the photocatalyst made up of TiO_2 nano-powders.[23]

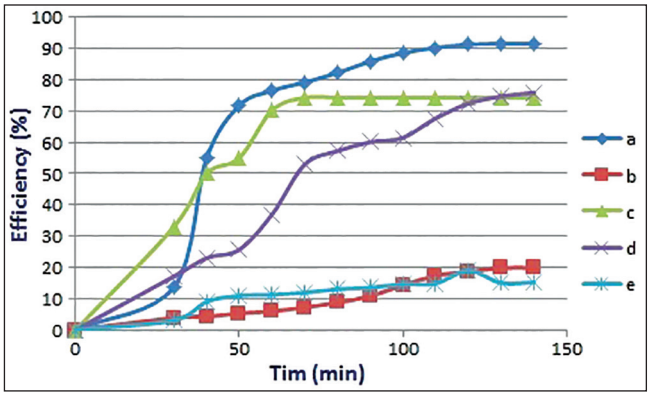


Figure 5: The photocatalytic removal efficiency in concentration of 10 mg\L: (a) TiO2/zeolite with radiation intensity of 3.9 w/m^2; (b) TiO2 with radiation intensity of 3.9 w/m^2; (c) Only the zeolite; (d) TiO2/zeolite with radiation intensity of 2.4 w/m^2; (e) TiO2 with radiation intensity of 2.4 w/m^2

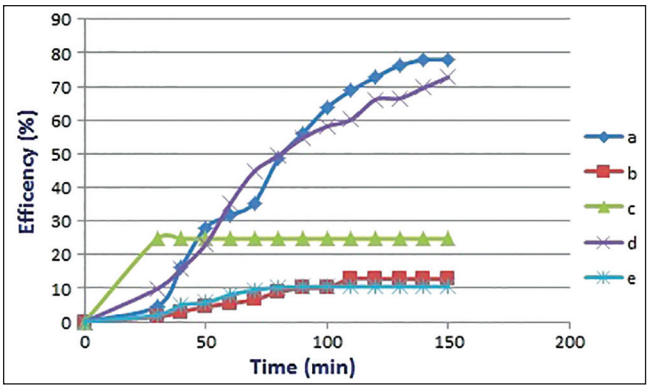


Figure 6: The photocatalytic removal efficiency in concentration of 50 mg\L (a) TiO2/zeolite with radiation intensity of 3.9 w/m^2; (b) TiO2 with radiation intensity of 3.9 w/m^2; (c) Only the zeolite; (d) TiO2/zeolite with radiation intensity of 2.4 w/m^2; (e) TiO2 with radiation intensity of 2.4 w/m^2

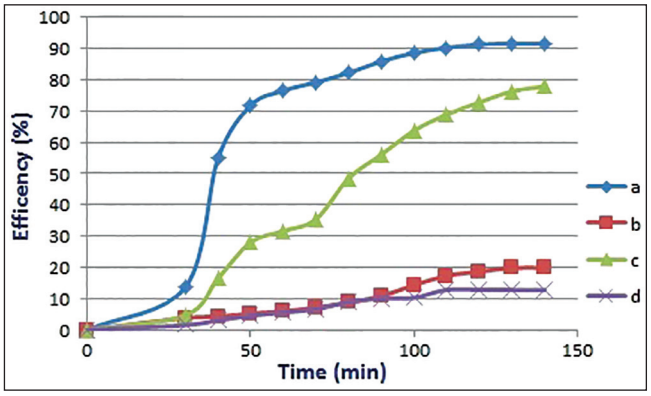


Figure 7: Catalytic removal efficiency with 3.9 w/m² UV radiation intensity (a) TiO2/zeolite with concentration of 10 mg/L; (b) TiO2 with concentration of 10 mg/L; (c) TiO2/zeolite with concentration of 50 mg/L; (d) TiO2 with concentration of 50 mg/L

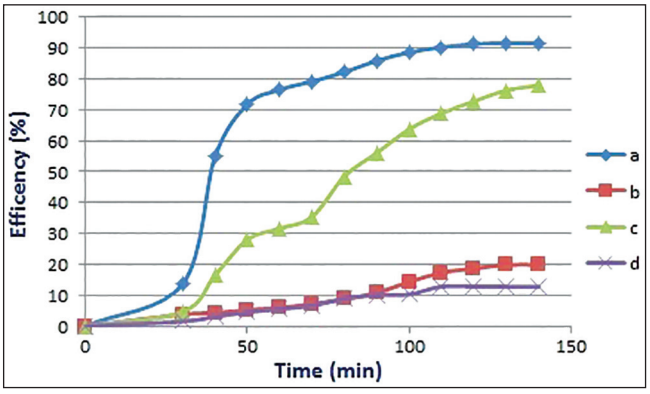


Figure 8: The catalytic removal efficiency with UV radiation intensity of 3.9 w/m² (a) TiO2/zeolite fixed bed with concentration of 10 mg/L; (b) TiO2/zeolite fixed bed with concentration of 50 mg/L; (c) TiO2/zeolite moving bed with concentration of 10 mg/L (d) TiO2/zeolite moving bed with concentration of 50 mg/L

In fact, the supported adsorbent such as zeolite on photocatalysts, can absorb pollutants and the pollutant, then, are exposed to the TiO_2 at high concentrations leading to materials removal process. This remarkable function due to the combination of zeolite and TiO_2 can enhance the removal efficiency compared to the time that the TiO_2 without coating eliminates harmful compounds.

Ultraviolet radiation intensity in photocatalytic process

In this study, the removal efficiency for both TiO_2 and TiO_2/zeolite photocatalysts in the UV-A radiation intensity of 3.9 w/m² was higher than the radiation intensity of 2.4 w/m² for both Safranin dye given concentrations. The results of this study were similar with many other studies in which an increase in radiation intensity caused the photocatalytic reaction to being increased.[28-30] Shiraishi *et al*. assigned that the increasing of the UV radiation intensity would contribute to an increase in active sections in a given photocatalyst area, therefore, the molecules of formaldehyde have more chances to encounter with the active sections following by promoting the removal efficiency.[31] The UV radiation to the photocatalyst surface results in producing electron-hole pairs in titanium atoms that consequently may cause electron-hole pairs to be spreaded at the photocatalyst surface and react with their surrounding Safranin dye. The electron pairs lead the formation of hydroxyl ion and radicals that will oxidize the dye Safranin. Thus, the higher intensity of the UV radiation contributes to the further electron-hole pairs that increase removal efficiency.

Pollutants concentration in photocatalytic process

The photocatalyst had a higher removal efficiency in lower concentration of Safranin dye so that the removal efficiency of TiO_2/zeolite photocatalyst reduced from 91.61% to 77.91% when the concentration of the red Safranin dye increased from 10 mg/L to 50 mg/L. These results were consistent with the results of other studies.[6,32-34] Hayat *et al*. used the WO_3 nanoparticles to remove the Safranin dye. It was demonstrated in his study that the removal rate was decreased as the dye initial concentration increased from 2.85×10^{-4} M to 1.425×10^{-3} M.[35] In addition, Jing *et al*. investigated different concentrations of quinoline in a range of 0.15-0.95 mmol/L on the TiO_2 catalyst and reported a considerable reduce in decomposition efficiency of the material from 99.3% to 53.1%.[36] Based on the results of this study, a large amount of high concentration dye would be adsorbed on the TiO_2 surface which may lead to preventing the dye reaction with free radicals. In other words, with increasing the dye concentration, a large amount of dye materials was adsorbed on the photocatalyst surface, and the number of photons reached on the photocatalyst surface was decreased. Thus, the fewer OH radicals were produced resulting in lower removal efficiencies in higher concentrations.[37]

Photocatalyst bed type

The removal efficiency of moving bed was higher than the fixed type in both concentrations of Safranin dye (10 mg/L and 50 mg/L). This result is probably due to the powder form of TiO_2/zeolite photocatalyst in moving-bed that causes more contact surface between the dye and the UV radiation. On the other hand, due to increasing the contact surface of the photocatalyst with the UV radiation, a greater number of electron-hole pairs would be produced following by making more OH radicals by the released electrons which may contribute to promote photocatalyst activity in the dye removal and degradation. On the other hand, the photocatalyst contact surface with dye was increased to make more chance for Safranin dye to be encountered with all surfaces of the photocatalyst leading to a higher Safranin dye oxidation by the surfaces that leading to increased oxidation of Safranin dye by the photocatalyst. The reason of achieving a lower removal efficiency in fixed bed referred to the fact that both Safranin dye and UV radiation were in contact with only the photocatalyst surface but not with any other lower layers.

The advantage of a fixed bed was making no opacity in aqueous solution so that there was not any precipitation after the centrifugation of the aqueous solution but in the moving-bed photocatalyst caused high opacity in the aqueous solution. Thus, in water treatment, where the opacity seems the main problem of using TiO_2/zeolite photocatalyst, the same kind of photocatalyst can be used with the fixed-bed.

CONCLUSION

In this study, the TiO_2/zeolite photocatalyst activity in the removal of red Safranin dye was investigated after coating TiO_2 nanoparticles on zeolite. In the TiO2/zeolite catalytic, zeolite absorbing pollutants then contaminant at high concentrations being placed around TiO_2 may cause an increase in the removal efficiency. Lower concentration of dye was found to have higher efficiency because the dye was absorbed on the photocatalyst surface in high concentration, and the number of photons reaching the photocatalyst surface was decreased. Thus, fewer OH radicals were produced leading to decreasing the removal efficiency. High UV-A intensity played a more important role in removing the pollutants due to increasing the number of electron-hole pairs that can effectively remove contaminants. Since the fixed bed had no opacity in aqueous solution and using the moving-bed TiO_2/zeolite photocatalyst in the water treatment seems like a major barrier where the opacity seems like a major. The same photocatalyst with the fixed bed is recommended to be used in water treatment.

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