

Original Article

The photocatalytic removal of azo dye by nickel-doped titanium dioxide nanoparticles coated on Iranian natural zeolite clinoptilolite fixed substrate

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ABSTRACT

Aims: The purpose of this study was to remove azonium compound using the photocatalytic property of nickel (Ni)-doped titanium dioxide (TiO₂) nanoparticles coated on Iranian natural zeolite.

Materials and Methods: Nickel-doped TiO₂ nanoparticles with the molar ratios of 0, 0.17, 2, 9% Ni/TiO₂ were prepared via the sol-gel process and coated on Iranian natural zeolite clinoptilolite (CLI). Afterward, X-ray diffraction, scanning electron microscopy and inductively coupled plasma studies were conducted to describe Ni and titanium. Photocatalytic removal of azo dye in concentrations of 25 and 50 mg/L was performed by fixing the composite under ultraviolet irradiation.

Results: TiO₂ nanoparticles in both the anatase and rutile phases were obtained via the sol-gel method with the ratios of 86.33%, (34.44 nm particle size) and 13.67% (18 nm particle size) and were then coated on Iranian natural CLI zeolite.

The results indicated that the photocatalytic removal efficiency of the 9% Ni/TiO₂-CLI samples, in which the azo dye concentrations were 25 and 50 mg/L, was 93% and 79% at 160 min. In addition, the composition of the 9% Ni/TiO₂-CLI possessed the greatest removal rate difference of azo dye at the concentrations of 25 and 50 mg/L.

Conclusion: Application of Iranian CLI as a substrate is the most cost-effective way to increase the photocatalytic activity. Furthermore, adding Ni to TiO₂ can increase the photocatalyst removal efficiency of azonium compound.

Key words: Dye, nickel-titanium dioxide, photocatalytic removal, zeolite

INTRODUCTION

When it comes to the environment, pollutants such as hazardous wastewater are of more interest to researchers. In addition, organic dyes are one of the most important polluters groups in wastewater, industrial processes and textile industries. Among the various techniques of physical, chemical and biological wastewater treatment, heterogeneous

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photocatalyst has been proposed as a cost-effective way to improve water.^[1] Titanium dioxide (TiO₂) is widely used in photocatalysts due to advantages such as high photocatalytic activity, chemical and physical stability, zero toxicity, long life, high availability and low cost.^[2,3]

There are three different forms of crystal structure: Anatase, rutile, and brookite while most of the studies already conducted have been done on anatase and rutile. Anatase is more effective than brookite in removing organic contaminants. The excitation of TiO₂ with an Anatase phase takes place using ultraviolet (UV) radiation (380 nm wavelength) because the band gap of anatase phase is 3.2eV. Brookite, on the other hand, with a 3-eV band gap, is excited in the 410 nm wavelength.^[4]

Studies have shown that, doping metals with TiO₂ can lead to TiO₂ response in visible light or increase photocatalytic activity under UV irradiation.^[2,3] The metals play a role of trapping and transferring photo-excited electrons to the photocatalyst surface, reducing the recombination of hole-electron pairs. In fact, it increases the photocatalytic properties of TiO₂. Generally, a heterogeneous photocatalytic process generates electrons and holes when absorbing semiconductor photo energy equal to or greater than the band gap energy. This leads to the production of free radicals in the system, and the result is an effective oxidization for organic dyes.^[5]

Semiconductor materials, such as TiO₂ are supported by a solid surface which can change the chemical properties, the absorption ability and the ability to perform oxidation-reduction or red-ox reaction in the presence of light.^[3,6,7] Among the different substrates, zeolites are considered due to their unique and highly uniform pores.^[8] Zeolites are crystalline materials which contain micron pores and vary in size. In addition, the shape and framework of zeolites lead to interesting properties and high performance.^[8] In many works of research, using synthetic zeolites has been stressed. However, in comparison with synthetic zeolites, natural zeolites are much cheaper, more plentiful and more available.^[9,10] Furthermore, the deposition of TiO₂ on zeolites and the combination of zeolite adsorption with the photocatalytic properties of TiO₂ cause a dramatic increase in photocatalytic efficiency.^[9,11] Due to these reasons, the use of nanomaterials such as catalysts in environmental technologies has been in the focus of attention in recent years for the purpose of removing pollutants and sensors. Size, surface structure and absorption capacity can improve performance and create exceptional properties in these materials. The present study investigates the effects of adding nickel (Ni) on the TiO₂ photocatalytic activity as a model for removing azo dye (safranin-O [SO]) which is an environmental pollutant [Figure 1]. SO is a phenazine dye (azonium compound) which is used extensively in the textile industry.^[1,5]

MATERIALS AND METHODS

Experimental procedures

Materials and apparatus

In order to make samples via the sol-gel method, tetrabutyl orthotitanate (MERK), ethanol absolute (MERK), Ni (II) nitrate hexahydrate (MERK), triethanolamine (MERK) and deionized water were used. In addition, SO (C.I. name: Basic Red 2, C₂₀H₁₉ClN₄) was used as the contaminant for the purpose of testing the photocatalytic activity.

Scanning electron microscopy (SEM) and inductively coupled plasma (varian model) were used in order to characterize the morphology, the structure of the catalyst and to find the qualitative determination of Ni and titanium (Ti) present in the crystal, respectively. The crystallographic structure of the samples and particle size of the anatase were analyzed using an X-ray diffraction (XRD) (X'Pert MPD, cobalt tube, Philips Company, radiation $\lambda = 1.78897 \text{ \AA}$). Concentration changes were determined by a UNICO spectrophotometer, model 2100UV.

Synthesis of nickel-titanium dioxide nanoparticles

Tetrabutyl orthotitanate 4 ml was dissolved in a solution containing 1 ml of triethanolamine and 16 ml of ethanol and was considered as the (A) solution. Then, the appropriate amount of Ni nitrate (molar ratio of Ni to Ti is 0.17%, 2%, 9%) was added to 16 ml of ethanol and considered as the (B) solution. Solution (B) was added slowly to the solution (A), and the two were mixed strongly for 1 h at room temperature. About 2 ml of deionized water was added to 5 ml of ethanol and was dissolved. Subsequently, droplets were added to the final solution^[13] and were stirred for 20 h.

Fabrication of nickel-titanium dioxide/clinoptilolite photocatalyst

Iranian natural clinoptilolite zeolites (CLI) were sieved by a grade-40 mesh and washed and were then exposed to a suitable temperature for activation. An appropriate amount of sol was added to CLI zeolites in a way that the TiO₂-natural zeolite weight ratio was 5%, and the sample's macroscopic level was 23 cm². In order to prepare the sample, 8 samples with four different mole ratios of Ni to TiO₂ and fixed weights of TiO₂-CLI namely Ni9%-TiO₂/CLI (N9TC code), Ni2%-TiO₂/CLI (N2TC code), Ni0.17%-TiO₂/CLI (No. 17TC), Ni0%-TiO₂/CLI (TC), Ni2%-TiO₂ (N2T), TiO₂ (T code), Ni9%-TiO₂ (N9T) and CLI (Code C) with fixed substrate were prepared and the mixture of zeolite and sol was placed at 80°C for 2 h for the solvent to evaporate. Finally, the sample was calcinated at the temperature of 550°C for 2 h to form crystals of TiO₂.^[12]

Photocatalyst testing

In this experiment, a UV-ultralite 220-volt lamp (made in Japan) with an intensity of 2/2 watt/m² and a maximum wavelength of 360 nm was used. Four ratios of Ni to Ti (0,

0.17, 2, 9%) for removing SO soluble-water based on the two concentrations of 25 and 50 mg/L with a fixed substrate of Ni-TiO₂/CLI were investigated. To maintain a constant concentration in all parts, a magnetic stirrer was used. After the fixation of adsorption by the sample photocatalyst, the UV lamp illuminated and the absorption rate of solution SO etch was monitored at 10-min intervals using a UNICO spectrophotometer (made in the United States of America) at a 520 nm wavelength and the results, according to the color removal rate and efficiency of photocatalytic performance, were reported.

RESULTS

Description of titanium dioxide and nickel-titanium dioxide

The XRD patterns of the pure TiO₂ and the TiO₂ containing Ni are shown in Figure 2. As can be seen, the peaks at the 2θ angles of 38.68, 41.99 and 58.10 are related to the crystal planes of NiTiO₃ with a rhombohedral crystal structure.^[5] Furthermore, a strong peak occurs at 29.48 and confirms the presence of anatase and rutile crystal structures [Figure 2]. Furthermore, the peaks of anatase on TC are separated from the peaks of Na, Ca, Al and Si Zeolite CLI. According to the peak of N2T and T, and also with respect to the presence of a large number of anatase and rutile crystals [Figure 2], it seems that adding Ni to the TiO₂ has not significantly changed the TiO₂ anatase phase. However, it appears that, as pure anatase TiO₂ is larger than anatase TiO₂ samples containing zeolite CLI; the microporosity of the zeolite prevents the enlargement of TiO₂ crystals.^[10,13,14] It seems that the N2T pattern is similar to the pure TiO₂ pattern but increasing the amount of Ni in the N9T sample has possibly led to reducing the size of anatase to 22 nm and decreasing the amount of anatase to 66.98%. Table 1 shows the calculated crystallite sizes for the samples using the Scherrer equation.^[15]

The surface morphology of the samples is presented in Figure 3. In the SEM image, compared with the XRD graph,

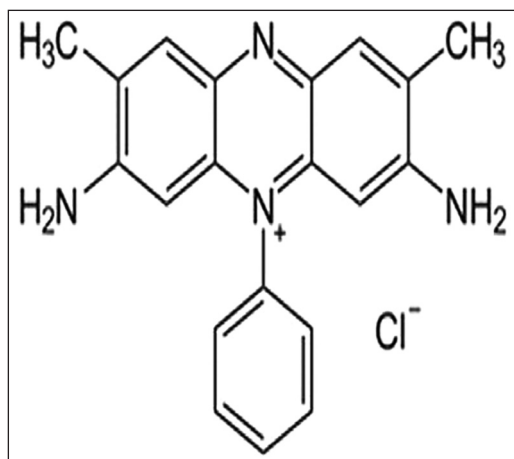


Figure 1: The molecular structure of safranin-O (SO) (3,7-diamino-2,8-dimethyl-5-phenylphenaziniumchloride)

it can be seen that the particle sizes of (N2TC) and (T) are <80 and 40 nm, respectively [Figure 3]. This confirms the results from the Schrodinger equation. In addition, it is clear that changes in the surface morphology of the samples occurred in the presence of Ti crystals.

Inductively coupled plasma elemental analysis is used to find the actual amount of mole ratio of Ni to Ti present in the crystals. This technique, with R² = 0.999, confirms the molar ratios used in the samples.

Photocatalytic removal of safranin

The concentration changes through time for the photocatalytic samples are shown in Figures 4 and 5. According to the curve, in the samples containing Ni-doped and zeolite substrates, the concentrations of 25 and 50 mg of SO reduced to 5 and 10 mg, respectively, at 160 min of time. In addition, the N9TC sample shows the highest concentration gradient. As a result, it shows the highest decrease of concentration in the sample. The graph shows that the photocatalytic activity of the samples containing the 9%Ni is slightly more than that of the 2%Ni and in the 2%Ni it is more than the 0.17% Ni.

As can be seen in Figure 5, the N9TC sample possesses the highest, and the TC sample possesses the lowest concentration gradients among the specimens containing zeolites. Furthermore, among the zeolite-free samples, the N9T sample has the greatest concentration gradient. Therefore, by comparing the N9T and N9TC samples, it becomes clear that adding zeolite has caused a dramatic increase in the concentration gradient and thus,

Table 1: Crystallite sizes of the samples using the Scherrer equation

Sample code	Crystallite size (nm)		Degree of phase TiO ₂ (%)		CT (°C)
	Anatase	Rutile	Anatase	Rutile	
T	34.44	18	86.33	13.67	550
N9T	22	13.1	66.98	13.98	550
N2T	34.96	31.64	86.61	10.13	550
N2TC	22.5	4.7	49	13.7	550

N2T: Ni/TiO₂ 2%-None clinoptilolite, N2TC: Ni/TiO₂ 2%-Clinoptilolite, T: Undoped TiO₂, N9T: Ni/TiO₂ 9%-None clinoptilolite, CT: Calcination temperature, Ni: Nickel

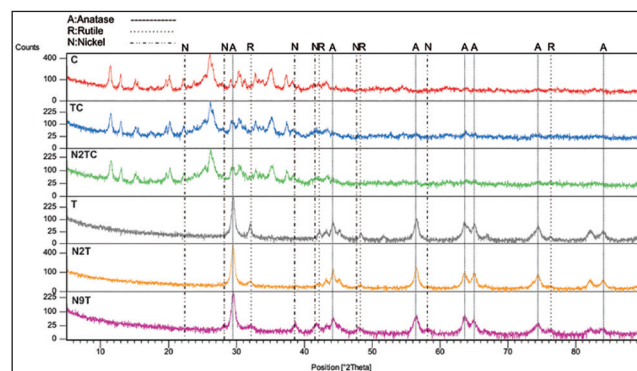


Figure 2: X-ray diffraction patterns of pure clinoptilolite (C) (red), TC (Blue), N2TC (Green), Pure TiO₂ (T) (Grey), N2T (orange) and N9T (Purple)

it has increased the photocatalytic efficiency. Figures 6 and 7 show the photocatalytic removal rate of SO which is calculated using Eq. 1:^[4,13]

$$\ln[C] = -kt + \ln[C - 0]$$

The rate of the photocatalytic removal reaction of SO was estimated to obey pseudo-first-order kinetics and thus, the rate

constant for the photocatalytic removal (K), was determined according to Eq. 1 where C₀ is the initial concentration, C is the concentration after a time (t) of SO removal [Figures 6 and 7].

As can be seen, the N9TC sample has shown the highest photocatalytic removal efficiency at the concentrations of 25 and 50 mg of SO.

According to the above equation, the diagram in Figure 6 indicates the photocatalytic conversion rate of safranin at the initial concentration of 25 mg/L where the values of R² calculated for (N9TC) (N2TC) (No. 17TC) and (TC) were 0.9404, 0.9926, 0.9853 and 0.9481, respectively. In addition, the constant K was 0.020, 0.013, 0.0137 and 0.012 min⁻¹, respectively.

Figure 7 indicates the photocatalytic conversion rate of SO at the initial concentration of 50 mg/L where the values of R² calculated for (N9TC) (N2TC) (No. 17TC) and (TC) were 0.9915, 0.9856, 0.9515, and 0.9975, respectively. Furthermore, the constant K was 0.0074, 0.0067, 0.0064, and 0.0060 min⁻¹, respectively.

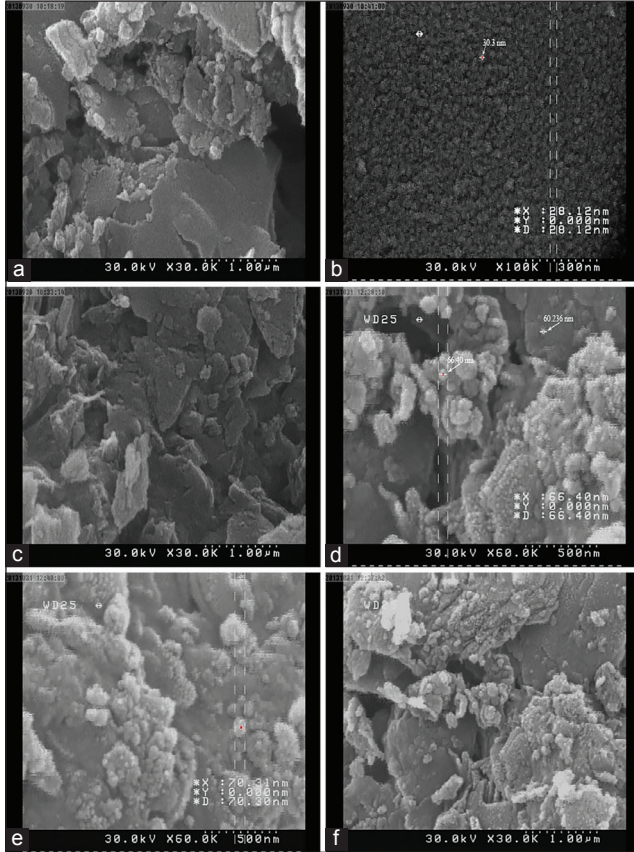


Figure 3: Scanning electron microscopy image of samples, (a) C (clinoptilolite), (b) T (TiO₂), (c) TC (TiO₂/CLI), and (d-f) N2TC

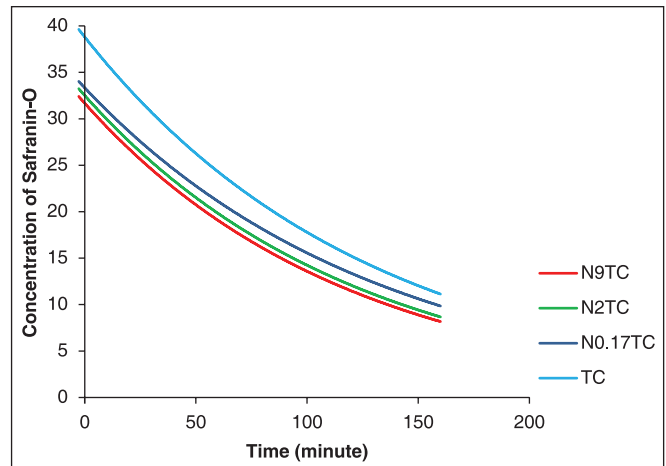


Figure 4: Changes in concentration of safranin-O (50 mg/L) with respect to time

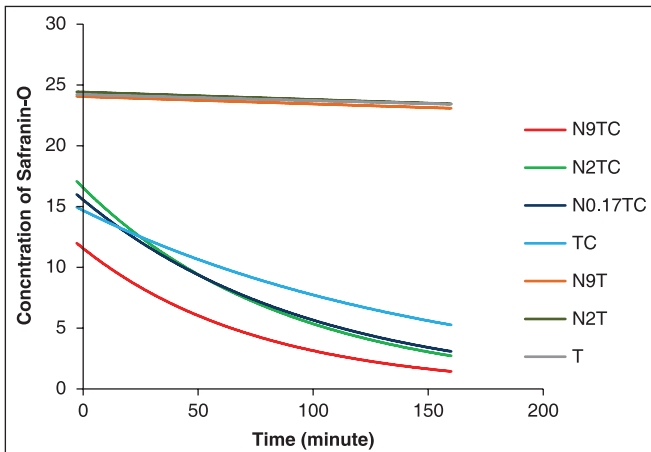


Figure 5: Changes in concentration of safranin-O (25 mg/L) with respect to time

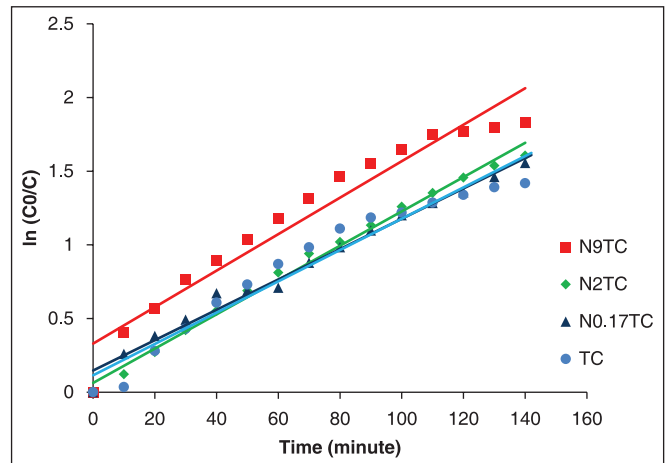


Figure 6: The photocatalytic removal rate of safranin-O at a concentration of 25 mg/L

Photocatalytic removal efficiency

The removal efficiency of SO (E%), calculated from the absorbance decrease of the dye solution at a wavelength of 520 nm was as follows:^[16]

$$E\% = \left[1 - \frac{A}{A_0} \right] \times 100$$

In this equation (Eq. 2), A₀ and A_i are the absorbance values of the dye solution before and after irradiation, respectively.

Figure 8 shows the samples' photocatalytic removal efficiency. As can be seen, N9TC with an efficiency of 93% and 79% has the highest photocatalytic removal activity when the concentrations of SO are 25 mg/L and 50 mg/L. Furthermore, by adding Ni, the photocatalytic removal efficiency of safranin has also increased; this indicates that adding Ni-doped increases the photocatalytic activity.

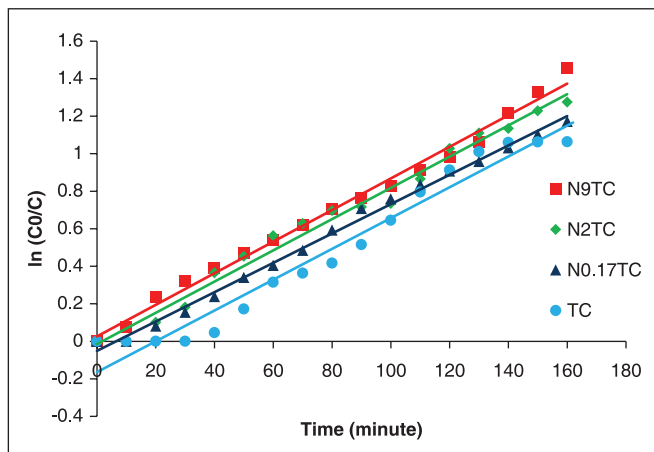


Figure 7: The photocatalytic removal rate of safranin-O at a concentration of 50 mg/L

Effects of safranin dye concentration on the photocatalytic removal efficiency

In Figure 9, it can be seen that the photocatalytic removal efficiency of SO has decreased by increasing the concentration. In addition, the effect of increasing the concentration on the photocatalytic removal rate of SO is quite tangible. In all samples, the reaction constant rate has decreased to <0.008 min⁻¹ in the concentration of 50 mg/L of SO in a way that the N9TC and N2TC samples possess the highest and lowest photocatalytic removal rate of SO, respectively [Figure 10].

DISCUSSION

The results of the rate constants have also confirmed the photocatalytic removal efficiency of the N9TC sample [Figure 8]. As observed, increasing Ni in the sample has led to an increased photocatalytic removal activity in SO so that, with an excessive increase of Ni, it can be the center

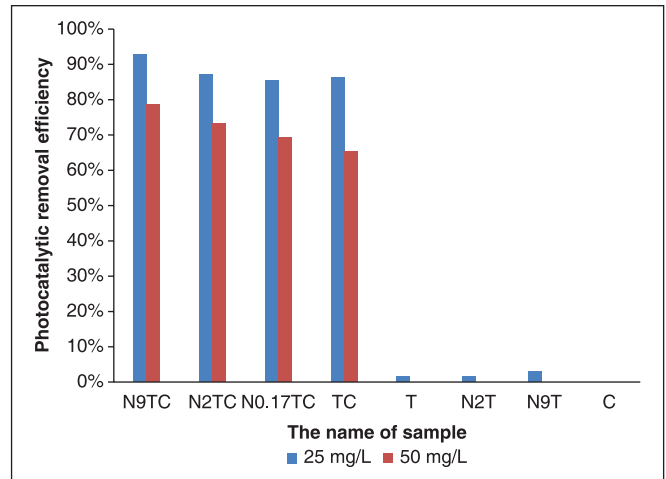


Figure 8: The photocatalytic removal efficiency of the samples at a concentration of 25 mg/L (blue) and 50 mg/L (red)

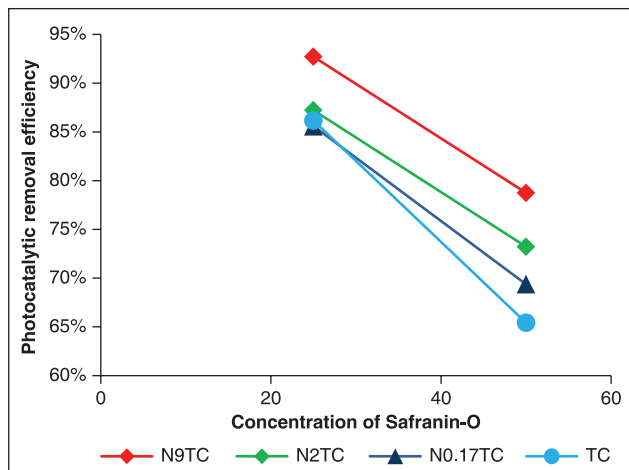


Figure 9: The photocatalytic removal safranin-O efficiency at a concentration of 25 and 50 mg/L of safranin-O

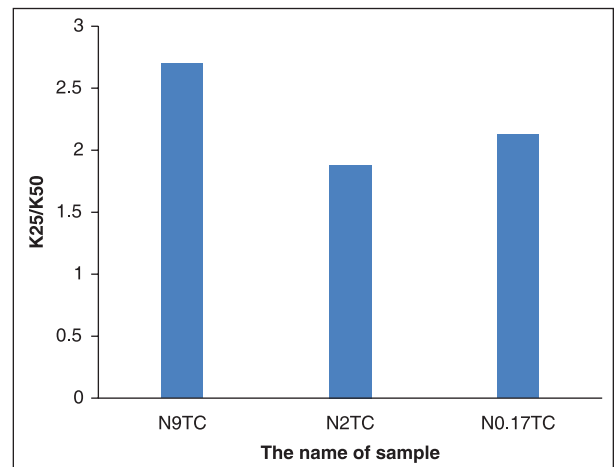


Figure 10: The constant ratio of K at a concentration of 25 and 50 mg/L of safranin-O

of electron-hole pairs and lead to facilitating the transfer of electrons. Thus, it increases the recombination of electron-holes^[13,17] and reduces the photocatalytic activity. Furthermore, the results related to the photocatalytic removal rate of SO and Figures 6, and 7 confirmed the hypothesis of the inverse relationship between higher concentration and the photocatalytic removal rate of SO, meaning that the photocatalytic removal rate of SO at a concentration of 25 mg/L is 2.2 times (on average) more than the photocatalytic removal rate at a concentration of 50 mg/L in all samples. As can be seen, a double increase in the reaction rate constants is proportional with a double reduction in the concentration of SO from 50 to 25 mg/L. Therefore, the results presented in Figure 9 confirm the results from Figure 8. This confirms the hypothesis of obtaining a higher photocatalyst deactivation rate by increasing the concentrations.^[5,18] Since the concentration of the catalyst is constant in both the 25 and 50 mg/L concentrations, it can be concluded that as concentration increases, the efficiency of safranin-dye removal ($E\%$) by the photocatalytic activity decreases [Figure 8]. Degradation rates are directly related to the possibility of the formation of hydroxyl radicals and the possibility of these radical reacting with SO molecules.^[19] Although the increase in the safranin-dye molecules increases the possibility of the reaction of hydroxyl radicals with SO molecules, these SO molecules cover the photocatalyst surface. In fact, this leads to a quicker saturation of the active sites of the photocatalyst. On the other hand, there is the phenomenon of the effect of UV screening, which leads to the UV absorption of the safranin solution (of course, by reducing the thickness of the solution on the fixed substrate of the photocatalyst to 0.5 cm, the effects of this phenomenon is minimized). These two factors lead to lower photocatalytic activity.^[5,18,19]

Finally, the results show that using the optimal amount of Ni and Iranian natural zeolite CLI as an adsorbent bed cheap has a significant impact on increasing the photocatalytic efficiency for decreasing the concentration of SO in water.

Furthermore, the study by Bhosale *et al.* was focused on the removal of Methylene blue dye using Ni-doped TiO₂ coated onto activated carbon using a sol-gel method. He reported an increase in the weight percentage of Ni and Ti on a substrate of activated carbon, which led to an increased efficiency in the photocatalytic removal of methylene blue dye.^[12] In another study by Nikazar *et al.*, the removal of red acid 114 from water was embarked upon using TiO₂ coated on Iranian natural zeolite CLI. It showed that the zeolite substrate leads to an increase in the photocatalytic removal efficiency of red acid from water.^[20] In addition, the removal of methylene blue with the molar percentages of 1, 2, 5, 10 of Ni/TiO₂ was conducted by Ahmed, (2012) using the sol-gel method, and by increasing the molar ratio to 5%, the highest photocatalytic removal efficiency of methylene blue was achieved, which confirms the results from this study.^[21]

CONCLUSIONS

Considering the photocatalytic samples which have been produced using the sol-gel method, it can be concluded that increasing the Ni/TiO₂ ratio up to 9% has caused an increase in the photocatalytic removal efficiency of the samples in comparison with the samples containing pure TiO₂. Moreover, using Iranian zeolite CLI as a porous substrate has led to a significant increase in the photocatalytic removal efficiency. This can also be realized by comparing the efficiency of the N9TC and N9T catalysts.

Eventually, the N9TC sample with the photocatalytic removal efficiencies of 93%, and 79% for the safranin concentrations of 25 mg/L and 50 mg/L has shown to possess the highest photocatalytic removal efficiency level among the other photocatalytic samples.

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