ORIGINAL RESEARCH PAPER

Methylene Blue Removal Using Surface-Modified TiO$_2$ Nanoparticles: A Comparative Study on Adsorption and Photocatalytic Degradation

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ABSTRACT

This study describes the adsorption and photocatalytic removal of methylene blue (MB) from aqueous solution by surface-modified TiO$_2$ nanoparticles under ultraviolet irradiation in a batch system. The 5-sulfosalicylic acid grafted TiO$_2$ (5-SA-TiO$_2$) as a photocatalyst was characterized by means of XRD, FTIR and SEM techniques. The surface of TiO$_2$ nanoparticles was modified by 5-sulfosalicylic acid (5-SA) to increase performance by altering surface properties. Notably, in contrast with the adsorption process, the remarkable removal enhancement of MB dye was observed by photocatalytic degradation process from aqueous solution. The adsorption and photocatalytic degradation kinetics of MB using 5-SA-TiO$_2$ nanoparticles have also been investigated. The results show that the photocatalytic degradation was good fit with the pseudo-first-order kinetic model (R^2 > 0.99). The adsorption isotherm of MB onto modified TiO$_2$ nanoparticles fitted into the Temkin equation. In addition, thermodynamic studies indicate the spontaneous behavior of adsorption and photocatalytic degradation processes.

Keywords: *Adsorption, Photocatalytic Degradation, Surface Modification, TiO$_2$ Nanoparticles*

INTRODUCTION

Organic and inorganic colorants are widely used in various industries, including the paper and food industries, textile dying, cosmetics, pigments and paints, and high technology materials, etc [1]. On the other hand, organic dyes that are used by different industries are now mostly synthetic. Organic dyes are regularly derived from the petroleum-based intermediates. Meanwhile, more than 10,000 types of synthetic organic colorants are used widely in the industrial processes. About 10-15% of these dyes may be found in industrial effluents [2]. Textile industries produce large amounts of liquid wastes that contain organic colorants. These wastes are rich in dyes, some of

which are carcinogenic and pose a major threat to health and the environment if not properly treated [3]. Methylene blue is one of them which have been shown to have harmful effects on living organisms on short periods of exposure [4].

In recent years, several treatment processes such as flocculation, chemical coagulation, simple sedimentation, aerated lagoons, aerobic activated sludge, trickling filters, reverse osmosis, photocatalytic oxidation, adsorption and electrodialysis have been developed to treat these wastes [5-11]. The adsorption process is desired as an environmentally friendly and cost effective procedure. It has high purification yield and the choice of adsorbent plays very essential role in

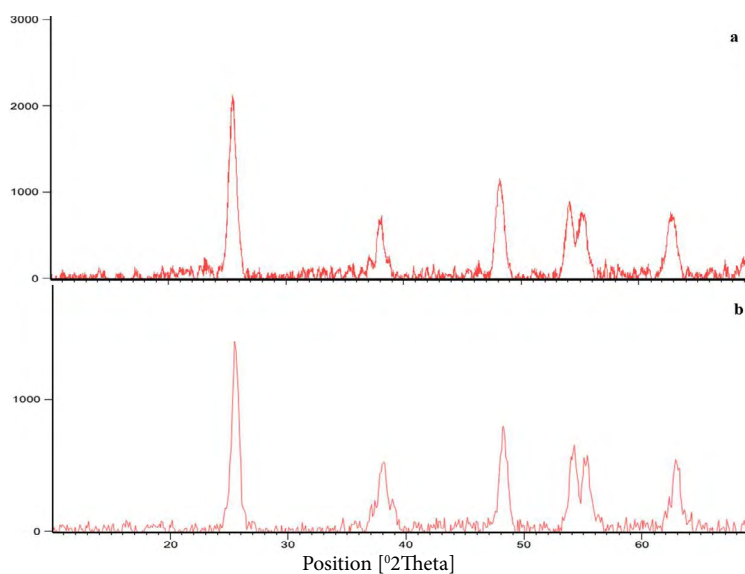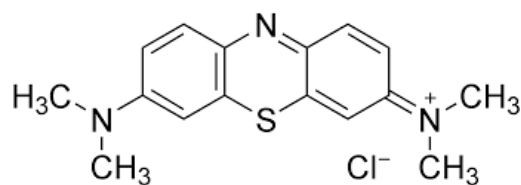* Corresponding Author Email: a_mohammadi@guilan.ac.ir

Fig. 1. XRD pattern of prepared samples: (a) TiO2; (b) 5-SA-TiO2.

determining its cost efficiency [12]. On the other hand, photocatalytic oxidation procedure was usually selected for its high yield, low energy use, simple process, mild reaction conditions, wide application range, and little secondary pollution [13].

In addition, photoactivity may be entitled as a photoinduced reaction that is enhanced using the presence of an adsorbent. Among the adsorbents having photocatalytic properties, nano-TiO_2 and surface-modified nano-TiO_2 particles have commercial benefits for their low cost, large specific surface area, nontoxicity, long service life, high efficiency and simple assemble technology [14-18]. Although TiO_2 photoactivity was found to be effective for the destruction of a wide variety of environmental contaminants present in water and wastewater, this knowledge has not yet been effectively commercialized since of the issues related to the separation of TiO_2 particles from the solution after treatment. In order to solve this problem, supported photoadsorbents have been developed [19-21]. Unfortunately, the surface area of adsorbent subjected to solution in supported systems is lower than in suspended systems [22].

In the present study, 5-sulfosalicylic acid grafted TiO_2 (5-SA-TiO_2) as a photoadsorbent for the removal of MB were synthesized and characterized by means of X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR) and scanning electron microscope (SEM). The effects of various parameters, such as contact time, adsorbent dose, pH, dye concentration, photocatalytic

Scheme 1. Molecular structure of MB.

activity and temperature were examined. Furthermore, the adsorption kinetics, isotherms and thermodynamics of MB dye onto synthetic adsorbent were studied.

MATERIALS AND METHODS
Chemicals
Methylene blue was supplied by Sigma–Aldrich Company, and used without further purification. The chemical structure of MB is shown in Scheme 1. Titanium isopropoxide (TIP) was obtained from Merck Chemical Company. 5-sulfosalicylic acid was obtained from Sigma Chemical Company and its solutions were used freshly in order to avoid oxidation by dissolved oxygen. All other chemicals were of the highest purity commercially available. De-ionized water was purified with a Milli-Q water ion-exchange system and was used in all experiments.

Preparation of TiO₂ and 5-SA-TiO₂ Nanoparticles
TiO_2 nanoparticles were synthesized using the titanium isopropoxide (TIP) according to a method described in the literature [23]. In situ surface
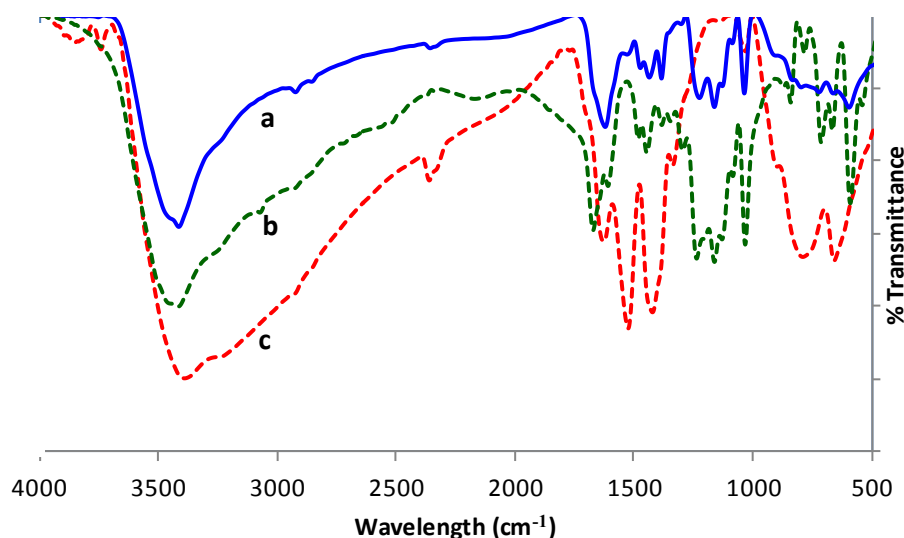
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Fig. 2. FTIR spectra of samples. (a) 5-SA-TiO2; (b) 5-SA; (C) TiO2.

modification was carried out through stirring TiO$_2$ nanoparticles for 60 min in the saturated solution of 5-sulfosalicylic acid. It was worth noting that the color of the TiO$_2$ surface changed into yellow, indicating that a chemical reaction took place (i.e., chemisorption) between 5-sulfosalicylic acid (surface modifier) and TiO$_2$. After filtration, the modified TiO$_2$ was washed with deionized water for three times and then heat-treated for 30 min at 105°C. The resulting powders were characterized by XRD, FTIR and SEM.

Adsorption and Photocatalytic Degradation Experiments

To achieve the equilibrium data, the adsorption and photocatalytic removal of MB from aqueous solutions onto nano 5-SA-TiO$_2$ was done using batch technique. The MB concentration changes over time with respect to several parameters such as pH, 5-SA-TiO$_2$ dosage, initial dye concentration and temperature were evaluated. The effect of pH on the adsorption of MB was examined by mixing 0.02 g of 5-SA-TiO$_2$ nanoparticle with 25 mL of MB solution (20 μM) with the pH ranging from 3.0 to 11.0. The pH of the samples was adjusted by adding of 0.5 M HCl or NaOH solutions.Photocatalytic degradiation were done in a beaker contains of MB solution and nano 5-SA-TiO$_2$ that exposed to UV light (400 W). After adsorption and and photocatalytic degradiation, the liquid and solid phases were separated by centrifuging at 300 rpm for 10 minutes. UV-vis spectrophotometer was employed for absorbance measurements of the

samples. The maximum wavelength (λ_{max}) used for determination of residual concentration of the MB in supernatant solution was 665 nm. Morever, the concentrations of MB in the liquor were determined using standard curve. The amount of MB adsorbed was determined by using the following equations:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

$$Removal\ (\%) = \frac{100\ (C_0 - C_e)}{C_0} \tag{2}$$

where q_e is the adsorption capacity of adsorbent, C_0 and C_e (mg L^{-1}) are concentration of MB at the initial and equilibrium states, respectively, V (L) is the volume of the solution and m is the weight of adsorbent (g).

RESULTS AND DISCUSSION

Characterization of TiO$_2$ and 5-SA-TiO$_2$ Nanoparticles

TiO$_2$ nanoparticles could be surface modified by organic and inorganic compounds [24-27]. Herein, TiO$_2$ nanoparticles are modified by chemisorption of 5-sulfosalicylic acid (5-SA) surface modification agent. The role of 5-SA on the improvement TiO$_2$ nanoparticles might be due to the enhancement of the affinity between dye and the 5-SA-TiO$_2$, larger surface areas by the reduction in particle size, and the increased formation of mobile OH radicals [28].

The XRD patterns of TiO$_2$ and 5-SA-TiO$_2$ nanoparticles are shown in Fig. 1. As shown in
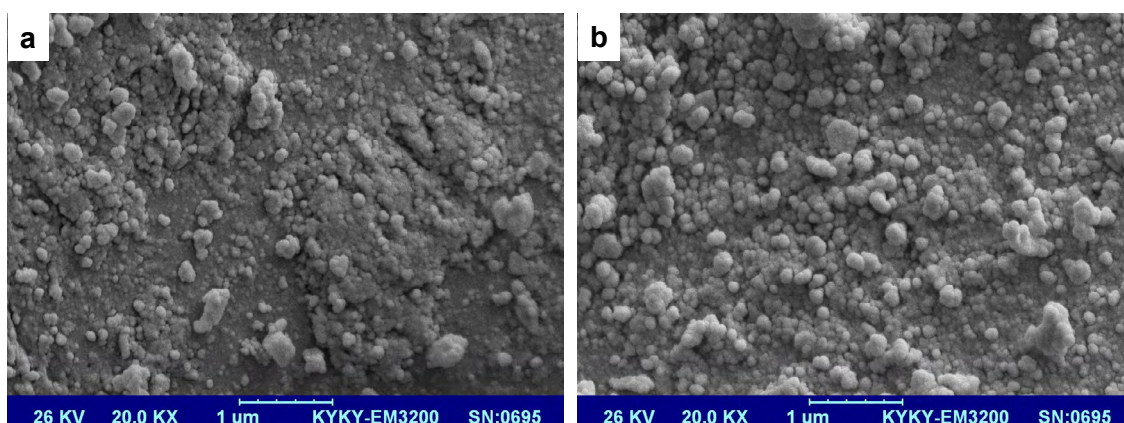
Fig. 3. SEM image of samples. (a) TiO2; (b) 5-SA-TiO2.

Fig. 1a, diffraction peaks for TiO_2 (2θ = 25°, 38°, 48°, 54°, 55° and 63°) are observed for both pure TiO_2 ananoparticles and surface-modified TiO_2. These diffraction peaks for TiO_2 can be attributed to anatase phase. As shown in Fig. 1b, the intensity of diffraction peaks in the surface-modified TiO_2 is decreased, which indicates that the surface modification of TiO_2 nanoparticles [29-30]. This confirms the existence of 5-sulfosaliccylic acid surface modifier in TiO_2 nanoparticles.

The functional groups present in the modified TiO_2 nanoparticles can be studied using FTIR spectroscopy. Fig. 2 shows the FTIR spectra of TiO_2, 5-SA and 5-SA-TiO_2 samples. From spectra of TiO_2, The stretching vibration of absorbed water as well as surface hydroxyl groups (OH) which presented in the TiO_2 nanoparticles were confirmed by the broad absorption band between 3200 and 3450 cm^{-1} and the low intensity peak at 1640 cm^{-1}. After surface modification by 5-SA, The absorption peaks from hydroxyl groups (OH) groups (3350-3350 cm^{-1}), phenyl (1442 and 1477 cm^{-1}), SO_3H (1164 and 1224 cm^{-1}), C=O (1672 cm^{-1}), and C-O (1470 cm^{-1}) were observed on 5-SA-TiO_2 surface. These functional groups indicate that the 5-sulfosaliccylic acid as modifier was chemically immobilized on the surface of nanoparticles. Thus, it can be concluded that the TiO_2 nanoparticle modified with 5-SA.

In addition, in order to investigate the morphology of the obtained adsorbent, the SEM image of TiO_2 and 5-SA-TiO_2 nanoparticles are illustrated in Fig. 3. It was found that the surface modifier could not only affect the dispersibility of the TiO_2 particles, but also change their morphology and size of the particles. Furthermore, SEM study of 5-SA-TiO_2 nanoparticle, indicate that

the particle size of the prepared sample is less than 60 nm.

Effect of pH Value on the Adsorption and Photocatalytic Degradation of MB

The effect of pH at a range of 3.0-11.0 on the adsorption and photocatalytic degradation of MB was shown in Fig. 4. As shown in Fig. 4, the removal capacity increased with increasing pH value from 3.0 to 6.0 and then decreased with the more increase of the pH from 6.0 to 11.0. Therefore, the optimum pH value for the adsorption and photocatalytic degradation of MB was 6.0. The isoelectric point of TiO_2 was 5.1. Consequently, at pH higher than 5.1, the TiO_2 surface would remain negatively charged. Hovever, the MB removel capacity was decreased at pH higher than 6.

Effect of the Photoadsorbent Dosage on MB Removal

The effect of adsorbent dosage on MB removal using adsorption and photocatalytic degradation from aqueous solution is shown in Fig. 5. As shown in Fig. 5, the MB removal efficiency increased with the addition of 5-SA-TiO_2 nanoparticle from 0.02 to 0.08 g in the adsorption process, because the adsorption surface and accessibility of more adsorption sites increased. However, if the adsorption capacity was expressed in mg adsorbed MB per gram of 5-SA-TiO_2 nanoparticle as adsorbent, the capacity decreased with the increasing amount of adsorbent. This may be attributed to association of adsorption sites resulting in a decrease in total surface area presented to the dye molecules and an increase in dispersion path length [31]. Meanwhile, from the Fig. 5, it was observed that the photocatalytic degradation of MB

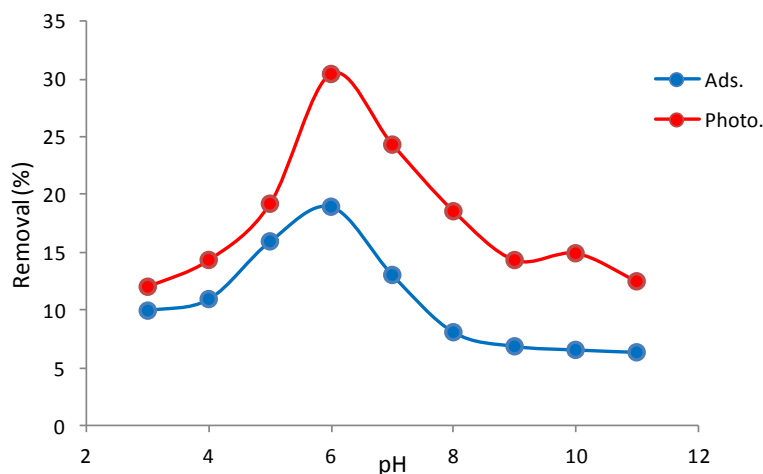*J. Water Environ. Nanotechnol., 2(2): 118-128, Spring 2017*

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Fig. 4. Effect of pH for the removal of MB; initial concentration of MB (200 mg/L), T= 298 K, contact time 180 min for adsorption process and irradiation time (40 min) for photocatalytic degradation.
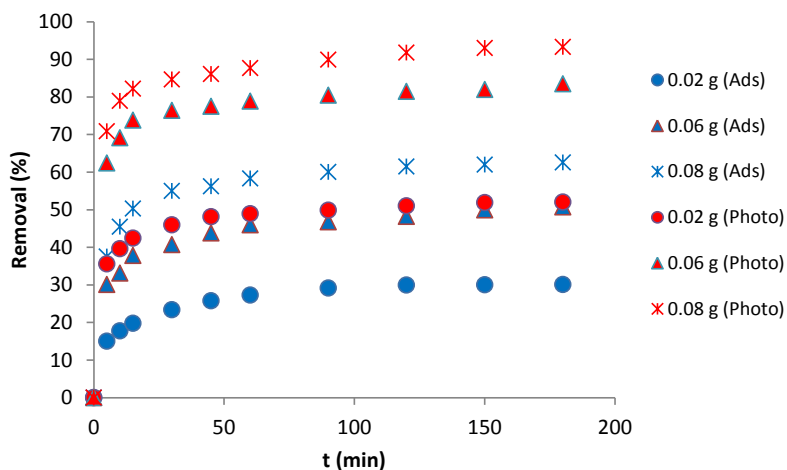

Fig. 5. The effect of adsorbent dosage on the adsorption and photodegradiation of MB on 5-SA-TiO2 (initial concentration 200 mg/L, pH = 6, T=298 K and contact time 180 min).

increased from 52% to 93.3% with increasing the dosage of 5-SA-TiO$_2$ photoadsorbent from 0.02 to 0.08 g. It is due to the active sites for the production of OH free radicals was increased. However, further increase of the 5-SA-TiO$_2$ photoadsorbent did not provide more increment in the percentage of the dye removed. This can be attributed to the fact that after a certain dosage of 5-SA-TiO$_2$, the maximum removal is achieved and the amount of dyes adsorbed and the amount of free dyes remains constant even with further addition of the 5-SA-TiO$_2$ nanoparticle as photoadsorbent. Therefore, 0.02 g as an optimal dosage of 5-SA-TiO$_2$ photoadsorbent for the degradation of MB was used in all the studies.

Effect of Initial Dye Concentration on MB Removal

The influence of initial dye concentration on the adsorption and photodegradiation efficiency of MB is shown in Fig. 6. In the adsorption process by 5-SA-TiO$_2$ nanoparticles, the removal efficiency of MB dye molecules decreased with an increase in the dye concentration. In other words, the amount of the MB adsorbed onto 5-SA-TiO$_2$ nanoparticle increased with an increase in the initial dye concentration of solution if the amount of adsorbent was kept unchanged. This is due to the increase in the driving force of the concentration gradient with the higher initial dye concentration. Therefore, the remaining amounts of dye molecules will be higher for high initial concentrations of dye.
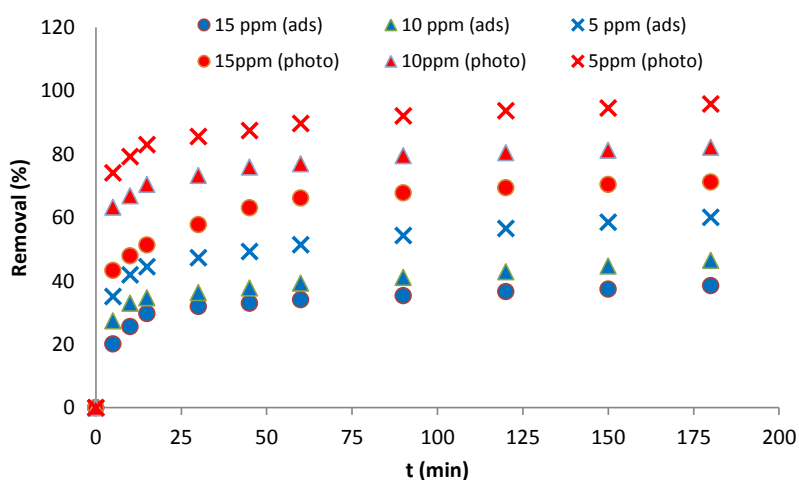
Fig. 6. The effect of initial dye concentration on the the adsorption and photodegradiation of MB on 5-SA-TiO2 (pH = 6, T=298 K and contact time 180 min).
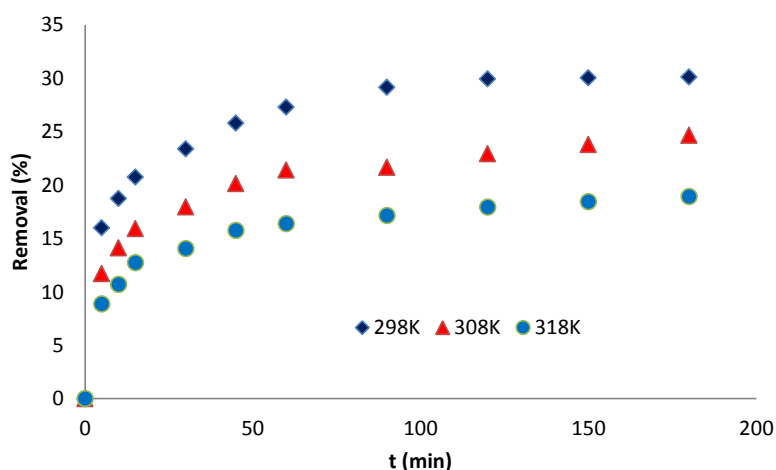

Fig. 7. The effect of temperature on the adsorption of MB on 5-SA-TiO2 nanoparticles (initial concentration 200 mg/L, pH = 6, and contact time 180 min.)

Furthermore, the effect of initial dye concentration on the degree of photodecolorization using 5-SA-TiO$_2$ nanoparticle as catalyst was studied by varying initial dye concentration from 5 to 15 mg/L. It is observed that the photodecolorization of MB decreases with increasing of the initial dye concentration. The presumed reason is that, when the initial dye concentration is increased, more and more dye molecules are adsorbed on the surface of 5-SA-TiO$_2$ nanoparticle. Therefore, the generation of OH free radicals will be reduced since the active sites for adsorption were covered by dye molecules. In addition, as the initial concentration of the MB increases, the photons get intercepted before they can reach the adsorbent surface. Consequently, it has been found that the removal efficiency of MB is high for photodecolorization compared to that of adsorption process.

Effect of Temperature on MB Removal

The effect of the temperature on MB removal from aqueose solution by 5-SA-TiO$_2$ nanoparticles was investigated at 298, 308 and 318 K. It is observed that contact times required to removal efficiency of MB were approximately 50-60 min for the different temperatures. In addition, the adsorption of MB decreased with increasing temperature as shown in Fig. 7. It can be explained by the fact that higher temperatures most certainly lead to an increase in the solubility of the dye. Moreover, when temperature increased, the intermolecular forces between the organic dye and the active sites of the

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Table 1. Kinetic constants of pseudo-first-order and pseudo-second-order models with correlation coefficients.

Removal process	Dye (mgL^{-1})	Pseudo-first-order			Pseudo-second-order		
		k$_1$ (min^{-1})	q$_e$ (mgg^{-1})	R^2	k$_2$ (g mg^{-1}min^{-1})	q$_e$ (mgg^{-1})	R^2
Adsorption	5	0.036	286.4	0.98	0.0020	58.83	0.99
	10	0.015	138.4	0.96	0.0023	84.75	0.99
	15	0.062	152.9	0.98	0.0029	30.96	0.98
	20	0.016	75.75	0.95	0.0050	25.64	0.99
Photodegradation	5	0.023	54.04	0.99	0.0027	51.83	0.98
	10	0.022	76.05	0.99	0.0015	98.03	0.98
	15	0.022	105.72	0.98	0.0017	17.33	0.97
	20	0.023	187.06	0.98	0.006	12.87	0.99

Table 2. Thermodynamic parameters of the MB removal using the 5-SA-TiO$_2$ nanoparticles at 298 K.

Process	T (K)	C$_e$ (mg L^{-1})	q$_e$ (mg g^{-1})	K$_c$	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
Adsorption	298	0.807	202.5	53.90	-9.878	-25.35	50.52
Photodegradation	298	0.768	751.25	650.43	-1.605	-74.93	2.52

adsorbent weakened. Therefore the MB dye was more difficult to remove.

Decolorization Kinetics:

Several kinetic models were developed to understand for both photocatalytic decolorization and adsorption kinetics. Kinetics study of photocatalytic decolorization of MB dye in the presence of 5-SA-TiO$_2$ nanoparticles was studied at 5, 10, 15 and 20 mg/L, and the decolorization rate was monitored by studying the contact time up to 150 min. The mechanism of MB removal using the 5-SA-TiO$_2$ nanoparticle as photocatalyst was studied by the pseudo first-order and pseudo-second-order kinetic models. The liner plot of ln(q$_e$-q$_t$) vs. t for the pseudo-first-order kinetic model and t/q$_t$ vs. t for the pseudo-second-order kinetic model is shown in Fig. 8. The constants of the two models with the correlation coefficients are shown in Table 1. As shown in Table 1, the value of the correlation coefficient R^2 for the pseudo-first-order model was greater than 0.99 for the photocatalytic degradeation process. The correlation coefficients of the two initial MB concentrations are equal to 0.99, which are very close to 1.0. These results show that the photocatalytic degradeation of MB dye in aqueous solutions using the 5-SA-TiO$_2$ nanoparticles can be described by pseudo-first-order kinetic model. A similar study was performed for adsorption of MB onto the 5-SA-TiO$_2$ as adsorbent (Fig. 9 and Table 1). However, the adsorption process of MB tends to follow pseudo-second-order kinetics in the presence of

5-SA-TiO$_2$ as adsorbent. It is also observed that the 5-SA-TiO$_2$ nanoparticle as photocatalyst exhibits better MB removal efficiency than that of the 5-SA-TiO$_2$ nanoparticle as adsorbent.

Thermodynamic Studies

The temperature is usually an important factor which affects many adsorption processes, and it is an indicator of the adsorption nature. The termodynamic parameters, such as ΔH°, ΔS° and ΔG° for 5-SA-TiO$_2$ nanoparticle can be related to the distribution coefficient of the solute between the solid and liquid phases. The effect of the temperature on the MB removal efficiency was evaluated at 298 K. The calculated thermodynamic parameters are given in Table 2. Acoording to the Table 2, the adsorption and photodegradation processes of MB using the 5-SA-TiO$_2$ nanoparticle are spontaneous.

Adsorption Isotherm

It is important to evaluate adsorption properties of 5-SA-TiO$_2$ adsorbent through analysis of the equilibrium data obtained from the experiments and the equilibrium relationship between adsorbed dye molecules and adsorbent. The isotherm results of MB on 5-SA-TiO$_2$ adsorbent at a constant temperature of 25°C were analyzed by the Langmuir, the Freundlich and the Temkin isotherm models. The Langmuir isotherm theory assumes the monolayer coverage of adsorbate over a homogeneous adsorbent surface where all sorption sites are found to be identical and energetically
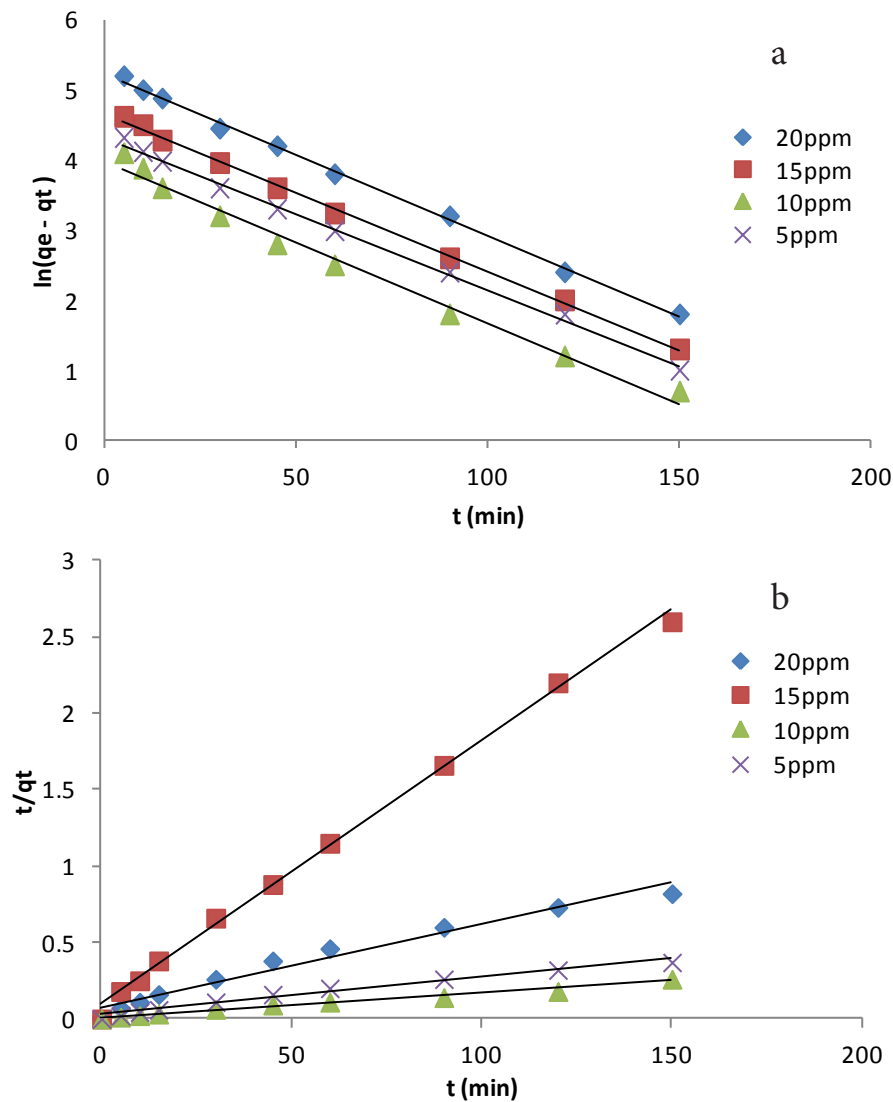
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Fig. 8. Pseudo-first-order (a) and pseudo-second-order (b) kinetic plots for the photocatalytic degradeation process.

equivalent, whereas the Frendlich isotherm model is valid for the multilayer adsorption on a heterogeneous adsorbent surface and predicts that the dye concentration on the adsorbent will increase with the increasing of the adsorbate concentration in the solution and lastly, the Temkin isotherm model assumes that the decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies [32]. The Temkin isotherm can be used in the following form:

$$q_e = \left(\frac{RT}{b}\right)\ln(AC_e) \qquad (3)$$

and can be linearized as:

$$q_e = B\ln A + B\ln C_e \qquad (4)$$

Where $B = RT/b$, b is the Temkin constant related to heat of adsorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The Langmuir, Freundlich and Temkin isotherm parameters and the correlation coefficient (R^2) are summarized in Table 3. As illustrated in Table 3, the correlation coefficient (R^2), for the Temkin isotherm model was 0.99. In other words, the R^2 of the Temkin isotherm was greater than that of the two other isotherms for the adsorption of MB. This indicates that the adsorption of MB onto the 5-SA-TiO₂ adsorbent is better described by the Temkin

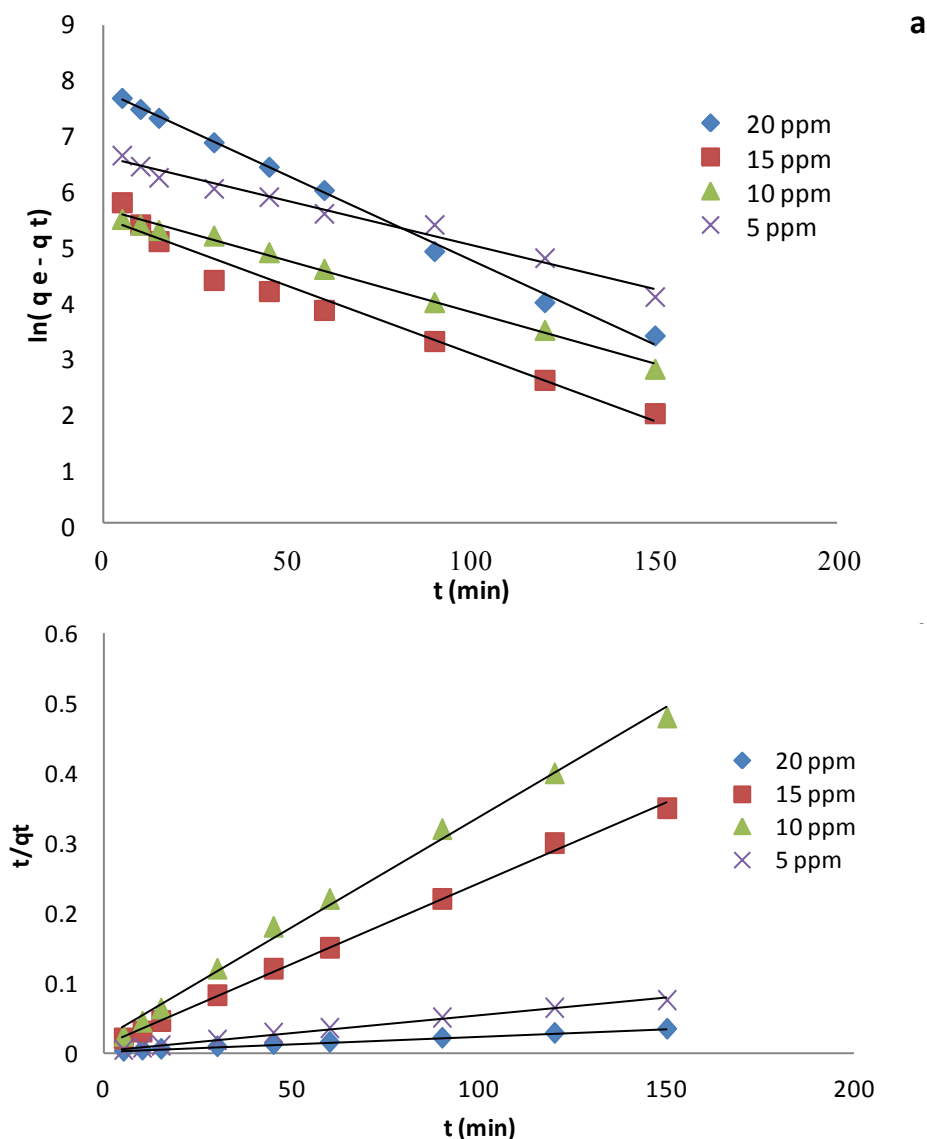*J. Water Environ. Nanotechnol., 2(2): 118-128, Spring 2017*

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Fig. 9. Pseudo-first-order (a) and pseudo-second-order (b) kinetic plots for the adsorption process.

Table 3. Langmuir, Freundlich and Temkin constants for adsorption of MB on 5-SA-TiO2 at 25 °C.

Langmuir			Freundlich			Temkin		
q_m (mg/g)	b (L/mg)	R^2	K_f ((mg/g))(Lmg^{-1})$^{1/n}$	n	R^2	A	B	R^2
9.8	6.71	0.90	1.93	1.30	0.88	5.74	0.212	0.99

isotherm model than the Langmuir and Freundlich isotherms.

CONCLUSION

In summary, the surface of TiO₂ nanoparticles was successfully modified by 5-sulfosalicylic acid (5-SA) through chemisorption process and used for removal of MB from aqueous solution. The structure analysis by XRD, FTIR and SEM confirmed the surface modification of TiO₂ nanoparticles by 5-sulfosalicylic acid. Comparison of photocatalytic activity and adsorption properties of 5-SA-TiO₂ nanoparticle has clearly showed that the photocatalytic degradation process was more effective for decolorization of MB from the aqueous media. The results indicated that the photocatalytic

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degradeation and adsorption of MB dye using the 5-SA-TiO$_2$ nanoparticles can be described by pseudo-first-order and pseudo-second-order kinetic models, respectively. Thermodynamic studies showed that the these both processes were spontaneous. In addition, the Temkin isotherm was found to be the best fitting isotherm model for the adsorption process.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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