Adsorption and Photocatalytic Properties of Surface-Modified TiO₂ Nanoparticles for Methyl Orange Removal from Aqueous Solutions

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ARTICLE INFO
Article history:
Received: 31 July 2016
Final Revised: 12 Sept 2016
Accepted: 14 Sept 2016
Available online: 16 Sept 2016
Keywords:
Methyl Orange
TiO₂ nanoparticles
Surface-modification
5-Sulfosalicylic acid.

ABSTRACT
Surface-modified titanium dioxide nanoparticles by 5-sulfosalicylic acid (5-SA-TiO₂) were prepared in ethanol by the chemisorption process. The effects of surface improvement on the photocatalytic degradation and adsorption of methyl orange (MO) were studied in a batch system by considering various parameters such as contact time, adsorbent dosage, pH, initial dye concentration and temperature. The adsorption and photocatalytic degradation kinetics of MO using the improved nanoparticles have also been investigated. The results show that the adsorption and photocatalytic degradation processes were well fitted with the pseudo-second-order kinetic model ($R^2 > 0.99$). In addition, the equilibrium data for the adsorption process have been evaluated using Langmuir, Freundlich and Temkin isotherms. The adsorption isotherm of MO onto modified TiO₂ nanoparticles fitted into the Temkin equation. Prog. Color Colorants Coat. 9 (2016), 249-260 © Institute for Color Science and Technology.

1. Introduction
Azo chromophores are a group of colorant materials characterized by the presence of an azo group (-N=N-) but can contain two, three, or more azo groups. Since their discovery in the 19th century, azo colorants have been widely used in various industries and accounting for over 50% of all commercial dyes [1, 2]. In addition to their use as colorants, azo dyes have been employed for many applications, such as in ink jet printing [3], thermal transfer printing [4], photography [5], color additives [6], biomedical area [7], molecular recognition [8], light controlled polymers [9], liquid crystal industry [10]. Moreover, most of these dyes such as anionic dye methyl orange (MO) are toxic, carcinogenic, and mutagenic [11, 12]. Thus, dye elimination from wastewaters before their discharge into the environment is very essential [13].

In recent years, many procedures such as adsorption, photocatalysis, chemical oxidation, coagulation/flocculation, biological treatment, ozonation, ion exchange, etc. have been developed for separating organic contaminants from water and wastewaters [14-19]. Among the various techniques for removal of organic pollutants, adsorption process has been proven as a highly effective removal method due to its efficiency, simplicity and applicability. In addition, any material that has pores can be used as adsorbent [14, 20]. Several natural and synthetic
adsorbents such as activated carbon, chitin, TiO₂, nano-TiO₂, etc. have been used to remove contaminants from wastewaters [21-28]. Among them, nano-TiO₂ have commercial interests for their low cost, photocatalytic activity, large specific surface area, nontoxicity, long service life, high efficiency and simple assembly technology [29, 30]. However, the use of TiO₂ was limited by its polarity, high surface free energy, and poor dispersing capability [31]. Therefore, in order to enhance the photocatalytic activity and adsorption ability, various colorless organic compounds have been used for the surface modification of TiO₂. This surface modification can be done by the interactions between organic coatings and -OH groups on the TiO₂ surface [32]. However, the design and efficient operation of adsorption processes require equilibrium adsorption data. The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems [33]. In the present study, surface-modified TiO₂ nanoparticles for the elimination of methyl orange (MO) were synthesized and characterized by means of XRD, SEM, FT-IR. The effects of several parameters such as contact time, photoadsorbent dose, pH, dye concentration and temperature were examined. The photocatalytic and adsorption kinetics, thermodynamics and adsorption isotherms were also studied.

2. Materials and methods

2.1. Chemicals

Methyl orange (MO) was supplied commercially, and used without further purification. The chemical structure of MO is shown in Scheme 1. Titanium isopropoxide (TIP) was obtained from Merck Chemical Company. 5-Sulfosalicylic acid was obtained Commercially 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 Milli-Q water ion-exchange system and was used in all experiments.

2.2. TiO₂ nanoparticles preparation and its surface modification with 5-sulfosalicylic acid

TiO₂ nanoparticles were synthesized using the titanium isopropoxide (TIP) according to a method described in the literature [34]. In situ surface modification was carried out through stirring TiO₂ nanoparticles for 60 min in the saturated solution of 5-sulfosalicylic acid. It was worth noting that the color of the TiO₂ changed into yellow, indicating that a chemical reaction takes place (i.e., chemisorption) between 5-sulfosalicylic acid (surface modifier) and TiO₂. After filtration, the modified TiO₂ was washed with water three times and then heat-treated for 30 min at 105 °C. The resulting powders were characterized by XRD, FT-IR and SEM.

2.3. Batch adsorption experiments

To achieve the equilibrium data, the photocatalytic degradation and adsorption of methyl orange from aqueous solutions onto nano 5-SA-TiO₂ was done using batch technique. Methyl orange concentration changes over time with respect to various parameters such as the amount of absorbent, pH, initial dye concentration and temperature were evaluated. The effect of pH on the adsorption of MO was examined by mixing 0.02 g 5-SA-TiO₂ with 25 mL MO solution (20 μM) with the pH values ranging from 3.0 to 10.0. The pH of the samples was adjusted by adding µL quantities of 0.5 M HCl or NaOH. After the photocatalytic degradation and adsorption process, the liquid and solid phases were separated by centrifuging. The UV-Vis spectro-photometer was employed for absorbance measurements of the samples. The maximum wavelength (λmax) used for determination of residual concentration of MO in solution was 460 nm. Moreover, the concentrations of MO in the liquor were determined using standard curve. The amount of MO removed was determined by using the following equation:

\[ Q_e = \frac{(C_0 - C_e)V}{m} \]  

where \( Q_e \) is the adsorption capacity of adsorbent, \( C_0 \) and \( C_e \) are concentration of MO at the initial and equilibrium states, respectively, \( V \) (L) is the volume of the solution and \( m \) is the weight of adsorbent (g).
3. Results and discussion

3.1. Characterization of samples

The XRD patterns of TiO$_2$ and 5-SA-TiO$_2$ nanoparticles are shown in Figure 1. As shown in Figure 1a, characteristic peaks of TiO$_2$ (2θ = 25°, 38°, 48°, 54°, 55° and 63°) are observed for both pure TiO$_2$ and surface-modified TiO$_2$ nanoparticles. These diffraction peaks are attributed to anatase phase. As shown in Figure 1b, the intensity of diffraction peaks in the surface-modified TiO$_2$ is decreased, which indicates that the surface modification of TiO$_2$ nanoparticles. This confirms the existence of 5-Sulfoisalicylic acid surface modifier in TiO$_2$ nanoparticles. The useful groups present in the improved TiO$_2$ nanoparticles can be evaluated using FT-IR spectroscopy. Figures 2a and 2b show the FT-IR spectra of the pure TiO$_2$ and 5-SA-TiO$_2$, respectively. The FT-IR spectra of the 5-SA-TiO$_2$ nanoparticles show the presence of new absorption peaks (cm$^{-1}$) such as OH (3406), C=O (1680), C-O (1470), SO$_3$H (1164 and 1224). These functional groups indicate that the 5-Sulfoisalicylic acid as modifier is chemically immobilized on the surface of nanoparticles. Thus, it can be recognized that the TiO$_2$ nanoparticles are modified with 5-Sulfoisalicylic acid. In addition, in order to investigate the morphology of the obtained adsorbents, the SEM images of TiO$_2$ and 5-SA-TiO$_2$ nanoparticles are illustrated in Figures 3a and 3b. It was found that the surface modifier could not only affect the dispersibility of the modified TiO$_2$ nanoparticles, but also change their morphology and size. Furthermore, SEM study of TiO$_2$ and 5-SA-TiO$_2$ indicate that the particle size of the prepared samples is less than 60 and 65 nm, respectively.

![Scheme 1: Molecular structure of Methyl Orang.](image1)

![Figure 1: XRD pattern of prepared samples: (a) TiO$_2$; (b) 5-SA-TiO$_2$.](image2)
3.2. Effect of pH value on the adsorption and photocatalytic degradation of MO

Figure 4 shows the effect of pH value at a range of 3.00-9.00 on the MO removal onto 5-SA-TiO₂. As shown in Figure 4, the removal capacity increased with increasing pH value from 3.0 to 5.0 and then decreased with the further increase of the pH from 5.0 to 9.0. So, the optimum pH value for the removal of MO was 5.0. The MO acid dye give negatively charged ions (SO₃⁻) when dissolved in water. On the other hand, the TiO₂ surface would remain positively charged in acidic medium and negatively charged in alkaline medium. Thus, in acidic medium, positively charged surface of sorbent tends to adsorb anionic species.
3.3. Effect of 5-SA-TiO$_2$ dosage on adsorption and photocatalytic degradation of MO

The effect of catalyst dosage on the adsorption and photocatalytic degradation of MO from aqueous solution is shown in Figure 5, in which the MO removal efficiency increased with the addition of 5-SA-TiO$_2$ from 0.02 to 0.08 g/L in the adsorption process, because the adsorption surface and accessibility of more adsorption sites increased. However, on the basis of the adsorption capacity in terms of mg adsorbed per gram of 5-SA-TiO$_2$, the capacity decreased with increasing the amount of material. This may be attributed to the association of adsorption sites, resulting in a decrease in total surface area presented to the dye molecules and an increase in dispersion path length [35]. Meanwhile, from the Figure 5, it is observed that the photocatalytic degradation of MO increased from 51 % to 82.6 % with increasing the dosage of 5-SA-TiO$_2$ photoadsorbent from 0.02 to 0.08 g/L. It is due to the increase of active sites for the production of OH free radicals. However, the amount of dyes adsorbed and free dyes remains constant even with further addition of the 5-SA-TiO$_2$. Therefore, the optimum dosage of 5-SA-TiO$_2$ for the adsorption and photodegradation of MO was selected as 0.02 g/L in the experiments.

3.4. Effect of initial dye concentration on the adsorption and photocatalytic degradation of MO

The effect of initial dye concentration on the adsorption and photodegradation of MO is shown in Figure 6. The adsorption of MO dye molecules decreased with an increase in the dye concentration. In other words, the amount of the MO adsorbed onto 5-SA-TiO$_2$ material 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. Furthermore, the effect of initial dye concentration on the degree of photocatalytic degradation using 5-SA-TiO$_2$ as catalyst was studied by varying initial dye concentrations from 5 to 20 mg/L. It is observed that the photocatalytic degradation of MO decreases with increasing 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$_2$. 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 MO increases, the photons get intercepted before they can reach the adsorbent surface. As a result, it has been found that the removal efficiency of MO is high for the photocatalytic degradation compared to that of adsorption process.
3.5. Effect of temperature on the adsorption and photocatalytic degradation of MO

The effect of the temperature on MO removal from aqueous solution by 5-SA-TiO$_2$ was studied at 298, 308 and 318 K, as shown in Figure 7. As the contact time was increased, similar increases in the MO removal efficiency were observed at different temperatures. The contact times required to removal efficiency of MO were approximately 50-60 min for the different temperatures. Moreover, the adsorption of MO decreased with increasing temperature as shown in Figure 7. Similar observations have been reported in the literature [36]. It can be explained by the fact that higher temperatures most certainly lead to an increase in the solubility of the MO organic dye. In addition, when temperature increased, the intermolecular forces between the organic compounds and the active sites of the adsorbent weakened. Therefore the MO dye was more difficult to adsorb.

3.6. Adsorption isotherm

It is important to evaluate the 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 adsorption equilibrium data collected from the MO dye concentrations (50-200 mg/L) and different temperatures were fitted 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 equivalent, whereas the Freundlich 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 [37].
The mathematical expression for the Langmuir isotherm is:

$$
\frac{C_e}{q_e} = \left( \frac{1}{q_m b} \right) + \left( \frac{1}{q_m} \right) C_e
$$

where $q_e$ (mg/g) is the amount of the dye adsorbed at the equilibrium, $C_e$ (mg L$^{-1}$) is the equilibrium concentration of dye in solution, $q_m$ (mg g$^{-1}$) is the Langmuir constant demonstrating maximum monolayer capacity, and $b$ is the Langmuir constant associated with the sorption energy.

Freundlich isotherm can be expressed as follows:

$$
q_e = K_f C_e^{1/n}
$$

where $K_f$ (mg/g)(L/mg)$^{1/n}$ and $n$ (dimensionless) are constants that account for all factors affecting the adsorption process, such as the adsorption capacity and intensity. The Freundlich constants $K_f$ and $1/n$ can be respectively determined from the intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$.

Temkin isotherm can be used in the following form:

$$
q_e = A \ln K_T + A \ln C_e
$$

$$
A = \frac{RT}{b}
$$

where $K_T$ (mg/g) is the equilibrium binding constant corresponding to the maximum binding energy, the constant $A$ and $b$ are related to the heat of sorption and the heat of adsorption, respectively. Values of $K_T$ and $b$ were calculated from the intercept and slope of the plots of $q_e$ versus $\ln C_e$. The Langmuir, Freundlich and Temkin isotherm parameters and the correlation coefficient ($R^2$) are summarized in Table 1.

As illustrated in Table 1, the correlation coefficient ($R^2$) for the Temkin isotherm model was 0.999. In other words, the $R^2$ of the Temkin isotherm was greater than that of the two other isotherms for the adsorption of MO. This indicates that the adsorption of MO onto the 5-SA-TiO$_2$ nanoparticles adsorbent is better described by the Temkin isotherm model than the Langmuir and Freundlich isotherms.

In addition, the $q_m$ value of MO on 5-SA-TiO$_2$ adsorbent have been compared with those of other adsorbents (Table 2). It was found that 5-sulfosalicylic acid-modified TiO$_2$ nanoparticles as adsorbent had a relatively high adsorption capacity ($q_m$) toward MO. Meanwhile, it has been found that the removal efficiency of MO is very high for the photocatalytic degradation compared to that of adsorption process.
Table 2: The $q_m$ values for the adsorption of MO on different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>34.83</td>
<td>[38]</td>
</tr>
<tr>
<td>Protonated cross-linked chitosan</td>
<td>89.30</td>
<td>[39]</td>
</tr>
<tr>
<td>Y-Fe$_2$O$_3$/SiO$_2$/chitosan composite</td>
<td>34.29</td>
<td>[40]</td>
</tr>
<tr>
<td>Acid modified carbon coated monolith</td>
<td>147.06</td>
<td>[41]</td>
</tr>
<tr>
<td>Nanoporous core–shell Cu@Cu$_2$O nanocomposite</td>
<td>344.84</td>
<td>[42]</td>
</tr>
<tr>
<td>5-sulfosalicylic acid modified TiO$_2$</td>
<td>42.91</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 3: Kinetic constants of pseudo-first-order and pseudo-second-order models with correlation coefficients.

<table>
<thead>
<tr>
<th>Removal process</th>
<th>Dye (mg/L)</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>5</td>
<td>0.016</td>
<td>167.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.015</td>
<td>181.2</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.013</td>
<td>221.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.014</td>
<td>69.3</td>
</tr>
<tr>
<td>Photocatalytic degradation</td>
<td>5</td>
<td>0.0162</td>
<td>30.63</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.0178</td>
<td>48.62</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.0165</td>
<td>62.07</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.0191</td>
<td>19.10</td>
</tr>
</tbody>
</table>

3.7. Decolorization kinetics

Several kinetic models were developed to understand both the photocatalytic degradation and adsorption kinetics. Kinetics study of photocatalytic decolorization of MO dye in the presence of 5-SA-TiO$_2$ particles was investigated 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 MO removal using the 5-SA-TiO$_2$ as photocatalyst was studied by the pseudo first-order and pseudo-second-order kinetic models. The liner plots 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 are shown in Figure 8 (photodegradation) and Figure 9 (adsorption). The constants of the two models with the correlation coefficients are shown in Table 3. As shown in Table 3, the value of the correlation coefficient $R^2$ for the pseudo-second-order model was greater than 0.99 for the photocatalytic degradation process. The correlation coefficients of all initial MO concentrations are 0.99, which are very close to 1. These results show that the photocatalytic degradation of MO dye in aqueous solutions using the 5-SA-TiO$_2$ particles can be described by pseudo-second-order kinetic model. A similar study was performed for MO adsorption onto 5-SA-TiO$_2$ as adsorbent (Table 3).

3.8. Thermodynamic studies

The temperature is usually an important factor which affects many adsorption processes, and it is an indicator of the adsorption nature. The thermodynamic parameters, such as ΔH°, ΔS° and ΔG° for 5-SA-TiO$_2$ can be related to the distribution coefficient of the solute between the solid and liquid phases. The effect of temperature on the adsorption and photocatalytic degradation of MO was evaluated at 298 K. The calculated thermodynamic parameters are given in Table 4. According to Table 4, the adsorption and photodegradation of MO using the 5-SA-TiO$_2$ are spontaneous.
### Table 4. Thermodynamic parameters of the MO removal using the 5-SA-TiO$_2$ particles at 298 K.

<table>
<thead>
<tr>
<th>Removal process</th>
<th>T (K)</th>
<th>$C_e$ (mg L$^{-1}$)</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$K_c$</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>298</td>
<td>0.091</td>
<td>20.87</td>
<td>229.34</td>
<td>-13.428</td>
<td>-10.74</td>
<td>7.67</td>
</tr>
<tr>
<td>Photocatalytic degradation</td>
<td>298</td>
<td>0.80</td>
<td>43.75</td>
<td>546.87</td>
<td>-1.56</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### Figure 8: Pseudo-first-order (a) and pseudo-second-order (b) kinetic plots for photocatalytic process.

#### Figure 9: Pseudo-first-order (a) and pseudo-second-order (b) kinetic plots for adsorption process.

### 3.9. Proposed reaction mechanism

After surface modification of TiO$_2$ nanoparticles (self-assembly), both the adsorption ability and photodegradation activity were improved 2.26 and 5.13 times, respectively. The role of 5-sulfosalicylic acid on the improvements TiO$_2$ photocatalyst might be due to the enhancement of the affinity between MO and the 5-SA-TiO$_2$, larger surface areas by the reduction in particle size, and the increased formation of mobile OH radicals [43]. However, the photocatalytic reaction process can be proposed as follows [44].

$$\text{MO} + \text{O}_2^- \text{ or } \cdot\text{OH} \rightarrow \text{peroxylated or hydroxylated intermediates } \rightarrow \text{degraded products}$$
3.10. Regeneration and reusability of 5-SA-TiO₂

The recovering and reusability of the 5-SA-TiO₂ photocatalyst was investigated for the removal of MO. In a typical experiment, 10 mL of an aqueous MO (20 mg/L) solution was mixed with 0.02 g of 5-SA-TiO₂ photocatalyst under UV light and stirred for 3 h in the optimum condition. The 5-SA-TiO₂ was subsequently collected from the solution by filtration and washed with ethanol. The washed 5-SA-TiO₂ photocatalyst was then used in the next experiment. This procedure was repeated for the eight absorption experiment cycle. The results show that the adsorption capacity of 5-SA-TiO₂ for MO was not significantly changed after four cycles which then slowly decreased. After six cycles, the MO removal efficiency was about 91.6%. Thus, results show the reusability of 5-SA-TiO₂ photocatalyst for MO removal.

4. Conclusion

Surface-modified titanium dioxide nanoparticles by 5-Sulfosalicylic acid (5-SA-TiO₂) were successfully synthesized and used for the adsorption and photodegradation of MO from aqueous solution. The structure analysis by SEM, XRD and FT-IR confirmed the surface modification of TiO₂ nanoparticles by 5-sulfosalicylic acid. The Temkin isotherm was found to be the best fitting isotherm model. Kinetic studies showed that both adsorption and photodegradation processes followed pseudo-second-order kinetics at a fixed adsorbent dosage. Thermodynamic studies showed that the adsorption process was spontaneous and exothermic. Comparison of photocatalytic activity and adsorption properties of 5-SA-TiO₂ clearly showed that the photocatalytic degradation process was more effective for decolorization of MO from the aqueous media.

5. References

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