Original Research Article

Adsorption of azo dye methyl orange from aqueous solutions using TiO$_2$-SiO$_2$/alginate nanocomposite

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ABSTRACT

In this research work, TiO$_2$-SiO$_2$/alginate nanocomposite with high surface area has been prepared and applied as adsorbent for the removal of azo dye methyl orange from aqueous solutions. Characteristics of phases and crystallite size of TiO$_2$-SiO$_2$/alginate nanocomposite were obtained from XRD and the surface area and pore size distribution were achieved from BET and BJH analysis methods. TiO$_2$-SiO$_2$/alginate nanocomposite with pure anatase phase, the average crystallite size of 8.3 nm, has specific surface area of 188.4 m$^2$/g. To find the nature of adsorption procedure, the equilibrium adsorption isotherms were investigated. The linear correlation coefficients of Langmuir, Freundlich and Temkin isotherms were obtained. Based on results, Langmuir isotherm model fitted the experimental data better than the other models. According to the Langmuir isotherm model, the maximum adsorption capacity of TiO$_2$-SiO$_2$/alginate nanocomposite for sequestering methyl orange was about 68.85 mg/g. Furthermore, negative $\Delta G^0$ and $\Delta H^0$ values obtained through thermodynamic investigation indicated that the adsorption of methyl orange onto TiO$_2$-SiO$_2$/alginate nanocomposite was simultaneous and exothermic in nature, respectively.

Graphical Abstract

Introduction

TiO$_2$ has attracted much consideration in last score years not only for its effectiveness as materials for photoelectric conversion and catalysis, but also for its inexpensiveness, nontoxicity, easy production, outstanding chemical stability, and excellent degradation of organic pollutants [1]. To date, different investigations have been conducted that the application of mixed oxide such as TiO$_2$/SiO$_2$ is more effective than that of titanium dioxide [2]. The activity of TiO$_2$ can be improved via the addition of SiO$_2$ which enhances the available surface area of the catalyst, allowing an increase in adsorption of pollutant molecules. The improved adsorption of pollutant molecules on the surface of SiO$_2$, in turn improves the catalytic activity of TiO$_2$/SiO$_2$ mixed oxides as compared to pure TiO$_2$ [3]. However, it is difficult to remove nanosized crystals from treated wastewater because of the ir fine size; one effective alternative to overcome this problem is to find a suitable support for the immobilization of nanomaterials [4]. The usage of immobilized nanomaterials has several advantages, including easy separation of the adsorbent, high adsorbent density and enhancing the retention of adsorbent in the reactor [5]. The entrapment of adsorbents such as unsupported nanomaterials within a polymeric matrix is one of the techniques applied for immobilization. The application of polymeric matrixes such as alginate, chitosan and different resins is one of the most widely applied techniques to immobilize. In recent years, chitosan has demonstrated multifunctional performance with TiO$_2$ in heterogeneous photo catalysis procedure, including its application as a stabilizer, a recovery agent for enhancing the adsorption capacity of TiO$_2$/chitosan adsorbent in the removal of metal ions, and for increasing the adsorption photocatalytic procedure of dye and organic
pollutant species [6–8]. In addition, adsorption capacity of the chitosan for sequestering anionic dyes because of the electrostatic attraction between the protonated amine groups on the chitosan and the sulfonic groups of the anionic dyes would be beneficial to increase the adsorption of anionic dyes together with the immobilized adsorbent [9].

Herein from the viewpoint of environmental friendliness, TiO$_2$-SiO$_2$/alginate nanocomposite as an adsorbent was prepared, and we would like to further describe the possibility over the effectiveness of removal of anionic dye methyl orange from aqueous solutions. Meanwhile, characterization of nanocomposite and relevant investigations over the adsorption procedure and thermodynamic were also discussed. To the best of our knowledge, there is no report on the application of TiO$_2$-SiO$_2$/alginate nanocomposite for the adsorption of textile dyes such as methyl orange in aqueous solutions.

**Experimental**

*Materials and methods*

Titanium $n$-butoxide (TBOT), tetraethyl orthosilicate (TEOS), ethanol of absolute grade, sodium hydroxide, acetic acid, nitric acid and methyl orange were purchased from Merck Co (Germany). Chitosan, which was of analytical grade, was purchased from Sigma Aldrich, USA.

*Preparation of SiO$_2$/TiO$_2$ mixed oxides by sol–gel method*

SiO$_2$-TiO$_2$ mixed oxides with 15 mol% SiO$_2$ contents was synthesized via sol–gel method [3]. Initially, titanium $n$-butoxide was slowly dissolved in absolute ethanol. Then, distilled water was added drop by drop into a flask containing TBOT/EtOH mixture under reflux and magnetic stirring. The molar ratio of TBOT/EtOH/H$_2$O was 1:1:65. The yellowish transparent titania sol was yielded after continuously stirring for 3 h. Tetraethyl orthosilicate was dissolved in ethanol, after which a few drops of nitric acid were added to TEOS as catalyst. The pH of mixed solution was adjusted to about 3. The molar ratio of TEOS/EtOH was 1:2. Afterward, the mixture was kept in a water bath maintained at 70 °C for 2 h. This mixture was added drop wise to the titania sol and stirred for 1 h at reflux temperature. This solution was placed in a teflon-lined stainless steel autoclave, in which it was heated at 150 °C for 24 h, and then calcined at 500 °C for 2 h with a heating rate of 10 °C/min in air atmosphere.

*Preparation of TiO$_2$-SiO$_2$/alginate nanocomposite*

To prepare TiO$_2$-SiO$_2$/alginate nanocomposite, first chitosan (8 g) was dissolved in 1000 mL of 1 M acetic acid and mixed using magnetic stirrer at 100 rpm for 2 h. Then, TiO$_2$-SiO$_2$ (4 g) was added to
the concentrated solution and magnetically stirred for 1 h to reach homogeneity. The resulted mixture was kept for 8 h in a stable place. The weight ratio of chitosan to TiO₂-SiO₂ was 2:1. The mixture was added dropwise via a syringe to a 500 mL solution containing 15% NaOH and 85% ethanol. Then, they were stored in the solution for 24 h to allow the nanocomposite to be produced. The resulted nanocomposite was withdrawn from the solution and washed with deionized H₂O several times to remove impurities. The obtained nanocomposite was dried in room temperature.

Characterization of prepared samples

The crystal phase composition and the crystallite size of synthesized catalysts were recorded using X-ray diffraction (XRD) (Siemens/D 5000) with Cu Kα radiation (0.15478 nm) in the 2θ scan range of 10°–70°. The average crystallite size (D in nm) was calculated using Scherrer’s formula [10]:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]  

(1)

where \( k \) is a constant equal to 0.89, \( \lambda \) the X-ray wavelength equal to 0.154056 nm, \( \beta \), the full width at half maximum intensity (FWHM) and \( \theta \), the half diffraction angle. Transmission electron microscopy (TEM) observation was carried out on Zeiss EM 900–80 keV electron microscopy instrument. The texture and morphology of the prepared nanocomposite was measured via scanning electron microscope (SEM) (Philips XL-30ESM). The nitrogen adsorption and desorption isotherms at 77 K were measured using BELSORP mini II. The specific surface area and the pore size distribution (Average pore diameter and mean pore volume) were measured from the adsorption isotherm using the brunauer-emmett-teller (BET) method and from the desorption isotherm using the barret-joyner-halender (BJH) method, respectively.

Experimental procedure

Adsorptive removal of methyl orange was used as a model reaction to investigate the catalytic activity of synthesized samples. The catalytic activity measurements carried out at atmospheric pressure in a batch quartz reactor. For the batch adsorptive removal of methyl orange via TiO₂-SiO₂/alginate nanocomposite without light illumination, the set-up was placed inside a fully covered box in order to prevent any exposure towards light irradiation. In each run, 40 mg of prepared sample and 20 mg/L of dye were fed into the quartz tube reactor. The residual of dye was determined via UV-vis Perkin-Elmer 550 SE spectrophotometer at wavelength of 465 nm. The amount of methyl orange adsorbed onto prepared samples was calculated via Eq. (2):
\[
q = \frac{(C_0 - C)V}{M}
\]

where \(q\), \(C_o\) and \(C\) are the amount of adsorbed methyl orange (mg/g\(^{-1}\)), the initial concentration and the final concentration of dye in the solution (mg/L\(^{-1}\)), respectively. In addition, \(V\) is the volume of the solution (L) and \(M\) is the weight of the catalyst (g) [11].

**Results and Discussion**

**Characterization of prepared samples**

**X-ray diffraction**

XRD patterns of TiO\(_2\)-SiO\(_2\) and TiO\(_2\)-SiO\(_2\)/alginate samples are shown in Figure 1. Pure anatase phase can be seen for the prepared samples. No SiO\(_2\) crystal phase was observed in the samples. This shows that SiO\(_2\) existed as an amorphous phase in the SiO\(_2\)-TiO\(_2\) mixed oxides [12]. The shape and the location of the peaks of TiO\(_2\)-SiO\(_2\) and TiO\(_2\)-SiO\(_2\)/alginate sample are the same, indicating that TiO\(_2\)-SiO\(_2\)/alginate synthesis have no influence on the characteristic structure of TiO\(_2\)-SiO\(_2\). The average size of crystallites for TiO\(_2\)-SiO\(_2\) and TiO\(_2\)-SiO\(_2\)/alginate determined from the XRD pattern based on the Scherrer’s formula were about 10 and 8.3 nm, respectively. Smaller crystal size obtained for TiO\(_2\)-SiO\(_2\)/alginate implies that chitosan biopolymer is able to hinder the crystal growth of TiO\(_2\)-SiO\(_2\).

**TEM analysis of TiO\(_2\)-SiO\(_2\)/alginate nanocomposite**

Figure 2 shows TEM image of TiO\(_2\)-SiO\(_2\)/alginate nanocomposite. It can be seen that the particles exhibit a relatively uniform particle size distribution. The average size of the primary particles estimated from the TEM image is about 8-10 nm, which is in good agreement with that calculated from the XRD pattern using Scherrer equation.

**SEM analysis of TiO\(_2\)-SiO\(_2\)/alginate nanocomposite**

SEM image of TiO\(_2\)-SiO\(_2\)/alginate nanocomposite is shown in Figure 3. A rough structure on surface for prepared nanocomposite can be seen from this Figure. The roughened surface is suitable for sequestering dye molecules in aqueous phase. Also, Figure 3 implies TiO\(_2\)-SiO\(_2\)/alginate nanocomposite has a highly porous structure proposes the appropriate of the nanocomposite as adsorbent for removal of methyl orange from aqueous solutions.

**BET analysis**
Figure 4 shows nitrogen adsorption-desorption isotherms of TiO$_2$-SiO$_2$/alginate nanocomposite, which provide information about the structural properties and pore geometries of the prepared composite. From this Figure, TiO$_2$-SiO$_2$/alginate nanocomposite shows the isotherm of type IV. At high relative pressure range from 0.4 to 1, the isotherm exhibits a hysteresis loop of type H2 associated with the ink bottle pores, implying that the powders contain mesopores because of the aggregation of crystallites [13].

**Figure 1.** XRD patterns of a) TiO$_2$-SiO$_2$, b) TiO$_2$
SiO$_2$/alginate

![XRD patterns](image1)

**Figure 2.** TEM image of TiO$_2$-SiO$_2$/alginate nanocomposite

![TEM image](image2)
Figure 3. SEM image of TiO$_2$-SiO$_2$/alginate nanocomposite

Figure 4. N$_2$ adsorption–desorption isotherms of TiO$_2$-SiO$_2$/alginate nanocomposite

The hysteresis loop in the lower relative pressure range (0.4<P/P$_0$) was attributed to the finer intra-aggregated pores generated between intra agglomerated primary particles, and that in the higher relative pressure range (0.8<P/P$_0$<1) was associated with larger interaggregated pores formed via interaggregated secondary particles. The porous structure is believed to facilitate the transporting of reactant molecules and products through the interior space because of the interconnected porous frameworks and favor the harvesting of exciting light due to enlarged surface area and multiple scattering within the porous network [14]. Figure 5 shows the pore size distribution of TiO$_2$-SiO$_2$/alginate nanocomposite as estimated according to the BJH method from the adsorption branch. With hybridization of TiO$_2$-SiO$_2$ with alginate, the average pore size decreases slightly from 9.4 to 8.13 nm. The aggregation of smaller crystallites forms smaller pores.

BET characterization implies that hybridization of TiO$_2$-SiO$_2$ with alginate enhances its pore volume. Particularly, it reaches 0.295 cm$^3$/g$^{-1}$ for TiO$_2$-SiO$_2$/alginate composite, which is higher than
Adsorption of azo dye methyl orange from aqueous solution using TiO$_2$-SiO$_2$/alginate nanocomposite. The specific surface areas of TiO$_2$-SiO$_2$/alginate nanocomposite and TiO$_2$-SiO$_2$ are 188.4 and 95.03 m$^2$/g, respectively. It can be concluded that the hybridization of TiO$_2$-SiO$_2$ with chitosan may significantly increase its surface area. Chitosan inhibits particle growth during drying step because of mixed bond Ti/O/C, which can prevent the interaction among Ti particles. It is known that large specific surface area can allow more pollutants to be absorbed onto the surface of catalyst. Therefore, TiO$_2$-SiO$_2$/alginate nanocomposite is a catalyst with better activity.

The effect of reaction time

Figure 6 shows the adsorptive removal of methyl orange from aqueous solution using prepared samples. From Figure 6, the efficiency of methyl orange removal in the presence of TiO$_2$-SiO$_2$/alginate nanocomposite is higher than that of TiO$_2$-SiO$_2$. Particle size is an important parameter influencing catalytic activity, since it directly impacts the specific surface area of a catalyst. When particle size is small, the number of active surface sites increases. Therefore, more pollutants can be absorbed onto the surface of catalyst [14]. Also, the superior removal efficiency of TiO$_2$-SiO$_2$/alginate nanocomposite may be related to a larger surface area compared to TiO$_2$-SiO$_2$. A large surface area can be an important parameter in certain catalytic decolorization reactions, as a large amount of adsorbed organic pollutants promotes the reaction rate [15]. Accumulation of a substance between the liquid–solid interface or gas–solid interface because of physical or chemical associations is termed an adsorption procedure. Adsorption process can be controlled via physical parameters on most of the adsorbents such as polarity, Van der Waals forces, hydrogen bonding, dipole–dipole interaction, π–π interaction, etc. [16]. So, the design of an adsorbent generally depends on the type of substance to be adsorbed or removed. Methyl orange as an anionic dye can be removed via an adsorbent showing strong affinity toward negatively-charged species. The incorporation of TiO$_2$ with Ti-OH groups into the chitosan with positively charged amino groups led to the grafting of these functional groups which is desirable for the adsorption of methyl orange containing negatively charged carboxylic groups. This electrostatic force of attraction could be the essential driving force leading to the increased adsorption of methyl orange. So, the presence of chitosan in synthesized nanocomposite plays a crucial role in the removal of anionic dye from aqueous solutions [17].

From Figure 5, the removal of methyl orange by adsorption onto catalysts was very fast during the initial contact time, and then slowed down. This behavior could be attributed to the availability of a large number of vacant surface sites during the initial stage of adsorption procedure. However,
with passage of time, the remaining vacant surface sites are difficult to be occupied because of repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase [18].

**The effect of temperature and thermodynamic study**

This part of experiments was performed via changing the temperature between 298 and 328 K. As a result, the amount of adsorbed methyl orange was declined with enhancing temperature (Figure 7). It can be described by the fact that the mobility of pollutant molecules enhances with enhancing temperature, resulting in escaping the adsorbed methyl orange from the surface of adsorbent to the solution [19]. The adsorption of methyl orange onto nanocomposite is temperature-dependent; thus, some suitable information about the enthalpy and entropy of adsorption can be achievable. The thermodynamic investigation was carried out to reach a better understanding of the adsorptive behavior of methyl orange toward nanocomposite. The free energy change or Gibbs free energy ($\Delta G^\circ$)
Adsorption of azo dye methyl orange from...

(kJ/mol), enthalpy change (ΔH⁰) (kJ/mol) and entropy change (ΔS⁰) (kJ/mol/K) for the adsorption of MB were calculated through Eqs. (3) and (4):

$$\Delta G^0 = -RT \ln K_D$$  \hspace{1cm} (3)

$$\ln K_D = \left(\frac{\Delta S^0}{R}\right) - \left(\frac{\Delta H^0}{RT}\right)$$  \hspace{1cm} (4)

where R, T (K) and K_D (q_e/C_e) are the universal gas constant, temperature and the distribution coefficient, respectively [20]. To investigate the thermodynamic of methyl orange adsorption onto TiO₂-SiO₂/alginate nanocomposite, thermodynamic constants such as ΔG⁰, ΔH⁰ and ΔS⁰ were calculated using Eqs. (3) and (4). The thermodynamic parameters were tabulated from the plot of ln KD versus 1/T (Figure 7). The values of these parameters are summarized in Table 1. As exhibited, the negative ΔH⁰ and ΔG⁰ values, demonstrated that the adsorption of methyl orange onto TiO₂-SiO₂/alginate nanocomposite was exothermic and spontaneous in nature, respectively [20]. The value of ΔG⁰ was declined with enhancing temperature from 298 to 328 K, suggesting favorable adsorption of methyl orange onto nanocomposite at low temperature. The negative value of ΔS⁰ reveals the decrease of degree of freedom of adsorbed dye on the binding sites of the nanocomposite at the solid–solution interface, indicating a strong binding of dye ions onto the active sites [21].

Adsorption isotherm analysis

The equilibrium adsorption isotherms can be used to investigate the nature of adsorption process and describe the interaction of solutes with adsorbent. Langmuir, Freundlich and Temkin models as the most widely used isotherm models were investigated. The linear form of the Langmuir model is shown via Eq. (5):

![Figure 7. Thermodynamic profile for methyl orange adsorption onto TiO₂-SiO₂/alginate nanocomposite](image-url)
Table 1. Obtained parameters from thermodynamic study of methyl orange adsorption onto TiO$_2$-SiO$_2$/alginate nanocomposite

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>($\Delta G^0$) (kJ/mol$^{-1}$)</th>
<th>($\Delta S^0$) (kJ/mol$^{-1}$ K$^{-1}$)</th>
<th>($\Delta H^0$) (kJ/mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-1.299</td>
<td>-0.064</td>
<td>-20.56</td>
</tr>
<tr>
<td>303</td>
<td>-1.046</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>308</td>
<td>-0.765</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>313</td>
<td>-0.415</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[
\frac{1}{q_e} = \left( \frac{1}{K_l q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}
\]  

(5)

where $q_m$ (mg/g$^{-1}$), $q_e$ (mg/g$^{-1}$), $C_e$ (mg/L$^{-1}$) and $K_l$ (L/mg$^{-1}$) are the maximum amount of adsorbed dye per unit weight of the adsorbent, the amount of methyl orange adsorbed at equilibrium, the equilibrium concentration of methyl orange and the affinity of the binding sites (Langmuir constant), respectively [22]. Essential features of Langmuir isotherm model can be expressed in term of separation factor, $R_L$, as below equation:

\[
R_L = \frac{1}{1 + K_l C_0}
\]

(6)

where $C_0$ (mg/L$^{-1}$) is the initial dye concentration [23]. The linear form of the Freundlich isotherm model is shown via Eq. (7):

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K_F
\]

(7)

where n and $K_F$ (mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$ are the constant related to the adsorption intensity and the constant related to adsorption capacity, respectively [24].

The linear form of the Temkin isotherm model is shown via Eq. (8):

\[
q_e = B_1 \ln C_e + B_1 \ln K_T
\]

(8)

where $K_T$ (L/g$^{-1}$) and $B_1$ are equilibrium binding constant and the heat of adsorption, respectively [25].

The values of Langmuir, Freundlich and Temkin parameters can be estimated from the slope and intercept of linear plots of $1/q_e$ versus $1/C_0$, $\ln q_e$ versus $\ln C_e$ and $q_e$ versus $\ln C_e$, respectively. From the slopes and intercepts, the values of $q_m$, $K_l$, n, $K_F$, $B_1$ and $K_T$ were calculated and exhibited in Table 2.
As can be seen in Table 2, the obtained correlation coefficient for Langmuir isotherm model ($R^2=0.993$) was higher than that of Freundlich model ($R^2=0.958$) and Temkin model ($R^2=0.979$), which implies the suitability of Langmuir isotherm model for describing adsorption of methyl orange onto TiO$_2$-SiO$_2$/alginate nanocomposite. Based on Langmuir model, the maximum adsorption capacity of TiO$_2$-SiO$_2$/alginate nanocomposite for the adsorption of methyl orange was found to be 68.85 mg/g$^{-1}$. The values of $R_L$ arranged as $R_L=0$, $0<R_L<1$ and $R_L>1$ propose that adsorption is irreversible, favorable and unfavorable, respectively. Table 2 shows that $R_L$ values are between 0.291 and 0.84, which indicates the adsorption of methyl orange onto TiO$_2$-SiO$_2$/alginate nanocomposite is favorable [26].

Table 2. Isotherm parameters for methyl orange adsorption onto TiO$_2$-SiO$_2$/alginate nanocomposite

<table>
<thead>
<tr>
<th>Type of isotherm model</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir isotherm</strong></td>
<td></td>
</tr>
<tr>
<td>$q_m$ (mg/g$^{-1}$)</td>
<td>68.85</td>
</tr>
<tr>
<td>$K_L$ (L/mg$^{-1}$)</td>
<td>0.108</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.291-0.84</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.993</td>
</tr>
<tr>
<td><strong>Freundlich isotherm</strong></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (mg/g$^{-1}$)</td>
<td>4.092</td>
</tr>
<tr>
<td>$n$</td>
<td>1.45</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.958</td>
</tr>
<tr>
<td><strong>Temkin model</strong></td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>17.23</td>
</tr>
<tr>
<td>$K_T$ (L/g$^{-1}$)</td>
<td>0.183</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.979</td>
</tr>
</tbody>
</table>

**Conclusion**

The present study was carried out to prepare and investigate the efficiency of TiO$_2$-SiO$_2$/alginate nanocomposite to adsorb and degrade methyl orange from aqueous solution. The XRD results showed that the crystallite size decreased but an increase in surface area, pore volume, and adsorption ability was observed. SEM analysis proved a highly porous structure for TiO$_2$-SiO$_2$/alginate nanocomposite, which is suitable for sequestering dye molecules in aqueous phase. The average size of the primary particles estimated from the TEM image was about 8–10 nm. Among various isotherm models, the Langmuir isotherm showed the best fit to experimental data. The
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separation factor, $R_L$ was obtained less than 1, implying the favorable nature of methyl orange adsorption on TiO$_2$-SiO$_2$/alginate nanocomposite. Besides, the results of thermodynamic investigation showed that the adsorption of methyl orange by TiO$_2$-SiO$_2$/alginate nanocomposite is spontaneous and exothermic.

Acknowledgments

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Disclosure Statement

No potential conflict of interest was reported by the authors.

References
