The first study of adsorption of methylene blue by Black Titania (B-TiO_2) nanoparticle in aqueous solution

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Abstract

In this study, the elimination of methylene blue (MB) by adsorption on Black Titania (B-TiO_2) in an aqueous solution in the dark room is investigated. Preparation of B-TiO_2 was carried out via the reduction of white TiO_2 by NaBH_4 in a tube furnace under an inert gas atmosphere at 600°C. Characterization of the absorbent was carried out by XRD, N_2 adsorption-desorption, SEM mapping, photoluminescence, EDX analysis, Zeta potential, DLS, and FT-IR. The maximum adsorption capacity of B-TiO_2 was found to be 88.65 mg g⁻¹. The rate-limiting step was the intra-particle diffusion stage. The maximum adsorption was observed under the conditions: 26 mg of the B-TiO_2 at pH 6 and MB concentration of 10 mg L⁻¹. It was demonstrated that B-TiO_2 might be recycled six times with very good adsorption results while keeping its high removal efficiency.
Keywords: Black Titania, Nanoparticle, Methylene Blue, Adsorption isotherm, Kinetic studies.

1. Introduction

The use of coloring agents and dyestuff is indispensable in today's paper, plastic, food, and cosmetics industries. Their extensive use means they will have substantial effects on different aspects of the environment including an increase in the chemical oxygen demand (COD) of water bodies, adsorption of some of the sunlight entering water systems and have adverse effects on aquatic ecosystems, among others [1-3]. As the environmental issues get worse, they associate with the severe problems of the presence of dyestuff in sewage waters and subsequently, the method of treatments. One more efficient and advantageous option is using adsorbents. Adsorption is non-complicated and straightforward process to design and use. More importantly, it is insensitive to toxic chemicals [4]. For the investigation of the properties and the effect of several adsorbent materials, the most commonly used dyestuffs that attracted the most attention were methyl orange, methylene blue, and rhodamine B [5-8]. Methyl blue (MB) exists in many diverse materials including rubbers, pharmaceuticals, pesticides, varnishes, etc. as coloring agents and disinfectors. Graphene was proposed for MB’s adsorbent [9]. The magnetic composite bio sorbent could absorb MB with a capacity of 95 mg g\(^{-1}\) and recovering for four times [10]. A higher capability of absorbing MB was observed in organo-bentonite [11]. It was also observed that grafted cyclodextrin–chitosan with multiple functional groups can be a good candidate for MB adsorbent s [12]. The ability of activated carbon in absorbing MB, bromophenol blue, alizarine red-S, eriochrome black-T, malachite green, phenol red and methyl violet from aqueous media was examined [13]. The elimination of MB with sulfonate-functionalized Nano porous silica spheres [14] and the elimination of methylene blue with jute fiber carbon [15], carbon-doped graphitic carbon nitride [16], activated carbons [17], graphitic carbon nitride doped with the S-block metals [18], mesoporous carbon nitride [19], barium phosphate Nano-flake [20], Titania/gum tragacanth nanohydrogel [21], Binary TiO\(_2\)/reduced graphene oxide nanocomposite [22, 23], diphenylanthrazoline compounds [24], Soluble Graphene Nanosheets [25], Graphene Oxide/WO\(_3\) Nanorod Composites [26], Graphene Oxide Modified with Fe\(_3\)O\(_4\) Nanoparticles [27], CdS Nanostructures [28] and Porous Graphene Wrapped SrTiO\(_3\) Nanocomposite [29] have been introduced earlier.
Hydrogenation changes the important properties of nano TiO\textsubscript{2}. The synthesis of hydrogenated titanium dioxide (black titania, B-TiO\textsubscript{2}) was performed with extending optical adsorption to the infrared region [30]. An increase in the absorption is assigned to the introduction of the mid-gap energy level in B-TiO\textsubscript{2} above the valance band caused by the wide-spreading overlap of O and Ti orbitals associated with the hybridization of H orbitals with S orbitals of titanium in TiO\textsubscript{2} samples. (Scheme 1) These improved properties have led to an increase in research done on B-TiO\textsubscript{2} nanomaterials. Due to their properties, B-TiO\textsubscript{2} nanomaterials have been applied in various fields, e.g., photocatalysis, lithium-ion batteries (LIM), supercapacitor, fuel cell, field emission, and microwave adsorption and photo thermal therapy of cancer. The B-TiO\textsubscript{2} is a complex consisting of Ti\textsuperscript{4+} and Ti\textsuperscript{3+}, which is generally employed as a potential photocatalyst. During these photocatalytic reactions, we noticed its high adsorption properties. The adsorption property of black titania in addition to its photocatalytic property, is very attractive because it can expand the range of performances and applications as well as effectiveness of black titania. Therefore, in this work, we studied the adsorption properties of B-TiO\textsubscript{2}.

Our goal is to eliminate MB dye from water by studying and providing adsorption performance of B-TiO\textsubscript{2} in the dark room to avoid photocatalytic reactions (B-TiO\textsubscript{2}). First, B-TiO\textsubscript{2} was prepared and then the effects of crucial variables, including the concentration of MB dye and time were investigated (in optimized adsorbent dosage and pH). Independently, adsorption kinetics and isotherms were analyzed using various models, and the possible mechanisms for MB adsorption onto B-TiO\textsubscript{2} were discussed.

2. Experimental

The following models of instruments were sued for the characterization of the nanomaterials. A Philips Xpert X-ray diffractometer was applied to prepare the XRD patterns. FT-IR spectra were recorded on a WQF-510A FT-IR spectrophotometer. LEO 1430VP SEM-EDX instrument operation was applied in the Energy dispersive spectrometry (EDS) mode. An FEI NANOSEM 450 FESEM was used for the investigation of the morphologies of the adsorbent. JEOL JEM- 2100F provided TEM and HRTEM images, which were exploited to gather more information about microstructure. A UV–Vis spectrophotometer (Scinco 4100) was utilized to observe the UV-visible. Agilent G9800A Luminescence Spectrometer extracted the photoluminescence results.
2.1. Preparation of B-TiO₂

The used procedure was as follows: 1.50 g of anatase TiO₂ nanoparticles was mixed with 0.71 g of NaBH₄ powder (the molar ratio of TiO₂ and NaBH₄ is 1:1). The resulting powder was homogenized and calcinated at 600 °C in a tube furnace under argon gas for 30 minutes and then cooled slowly under the same atmosphere for 5 hours. In the last section, the black titania was washed with ethanol and distilled water.

3. Characterization of the adsorbent (B-TiO₂)

X-ray diffraction patterns were utilized to analyze the crystal phase and microstructure of B-TiO₂ that are presented in Figure 1. There are four typical crystal peaks at 26.8° (1 0 1), 37.5° (0 0 4), 42.6° (2 0 0), and 62.3° (2 0 4) with the anatase TiO₂ (JCPDS No. 21-1272) as a possible form [31]. The crystallite size was calculated using Scherrer’s formula:

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

(1)

Where \(D\) is the crystal size, \(K\) is Scherrer’s constant usually taken as (0.89), \(\lambda\) is the X-ray wavelength of Cu Kα radiation (\(\lambda=1.54056 \ \text{Å}\)), \(\beta\) is full width at half maximum (FWHM) of the (101) peak in radians and \(\theta\) is Bragg’s diffraction angle. \(D = \frac{(0.89 \times 1.54)}{(0.9 \times 2\pi/360)} \cos (26.7/2) = 9.02 \ \text{nm}\) which is in consist with the previously report [32]. On the other hand, the specific surface area of the prepared B-TiO₂ nanoparticles was also obtained using the formula below:

\[
S = 6 \times 10^3 / dD
\]  

(2)

Where \(d\) is the theoretical density particle (3.894 g/cm³) and \(S = 6 \times 10^3 / (3.894 \times 9.02) = 170 \ \text{m}^2\ \text{g}^{-1}\). This calculated specific surface area from XRD data is compatible with SEM-EdX mapping of prepared B-TiO₂ as shown in Figure 2. The SEM-EdX mapping method presented in Figures 2a-d was used to evaluate the morphological properties of the B-TiO₂. Spherical B-TiO₂ nanoparticles with dark colors are also shown in Figure 2a. In Figures 2b-d, bright lattice fringes with 0.350 nm of interplane distances are observed, which aptly conform to anatase B-TiO₂ (101) crystallographic planes [33]. The results of the EDX analysis verify that elemental compositions remain unchanged in comparison with starting materials. The unambiguous distributions of Ti and O elements are further demonstrated by EDX elemental mappings of the B-TiO₂ nanoparticles, which also show their homogenous distribution.
Charges on the surface of the B-TiO₂ sample were examined by Zeta potential analysis at pH=7. As Figure S1a presents, B-TiO₂ has a zeta potential of +23.7 mV. A dynamic light scattering (DLS) method was utilized to analyze the particle size distribution of the B-TiO₂. An ultrasonic field was used to disperse the samples in the form of powder and a suspension was made. The hydrodynamic diameter of the B-TiO₂ was measured to be around 38.2 nm (Fig. S1b). The small size of these particles is enough to create a balanced suspension in deionized water. FT-IR spectroscopy is an effective technique to identify the functional groups. The FT-IR spectra of TiO₂ and B-TiO₂ samples are shown in figure 3. For both samples, the broad peaks at 2805–3541 cm⁻¹ are related to the stretching vibration of the O-H surface absorbed water molecules. The adsorption bands located at about 562 cm⁻¹ is due to the Ti-O vibration. Furthermore, the broad peak at 420–830 cm⁻¹ is ascribed to the Ti-O-Ti [34].

Surface features, e.g., large surface area and high porosity of an adsorbent, can supposedly offer more active sites for efficient adsorption. On the basis of the classification of International Union of Pure and Applied Chemistry (IUPAC), the isotherm of the sample exhibits the typical type IV with H3 hysteresis loop in the relative pressure range of 0.4–1.0 (p/p₀) indicating that it has mesoporous structure characteristics. The pore size distribution in the peak at 5 nm also corresponds to the mesoporous structure. They are also likely to allow for the interconnected porous network at interiors. The formed network will allow it to interact with more reactants, which in turn will increase the adsorption ability. The N₂ adsorption-desorption isotherms of the B-TiO₂ are shown in Figure 4. The surface area of B-TiO₂ is 166 m²g⁻¹, the mean pore diameter is 5.1 nm and the total pore volume is 0.242 cm³ g⁻¹. This amount of porosity can be due to the sintering of nanoparticles at 600 °C during preparation of B-TiO₂. The value of the specific surface area that was obtained by the Porosimetry method (166 m²g⁻¹) is approximately according to the calculated value with XRD data (170 m²g⁻¹).

4. Adsorption isotherms study
Because of the large surface area, large pore volume and higher hydrothermal stability, the as-prepared B-TiO₂ has great potential for the MB adsorption. Adsorption consists of a series of mass transfer phenomena. Conventionally, it means the sample’s adhesion to a surface of a liquid or a solid material (i.e. adsorbent). Isotherms of adsorption are the identifying factors denoting the relations between adsorbent and adsorbates at a specific temperature at the equilibrium stage. It is possible to locate a proper model for the design process by properly
conforming experimental data to various isotherm models. These models will produce instrumental parameters in obtaining essential data regarding the mechanism, surface features, and the sorbent affinities [35]. The data collected from performed experiments have been fitted with some isotherm models to validate and examine their applicability. Table S1 shows the values of the coefficients obtained by these isotherm models. The $Q_m$ was approximated by investigating Langmuir's isotherm model [36]. A comprehensive monolayer exposure is thereby found on the sorbent's surface. The Langmuir's isotherm may be presented in linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} C_e$$

(3)

Where $Q_m$ is the maximum adsorption capacity (mg g$^{-1}$) and $K_a$ is the constant of adsorption equilibrium of Langmuir equation (L mg$^{-1}$). It could be stated that, as presented in Figure S2, unknown coefficients can be found with a plot of $C_e/q_e$ against $C_e$. The Freundlich's isotherm [37] is an experimental equation that can identify heterogeneous structures and can be presented in this way:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n_F} \ln(C_e)$$

(4)

Where $K_F$ is Freundlich constant (L g$^{-1}$), of sorption and is correlated with bonding energy. It also represents the amount of dye absorbed on the adsorbent. The $n_F$ value indicates the degree of nonlinearity between dye concentration and adsorption. In the case of $n_F = 1$, the adsorption is linear and $n_F < 1$ indicates that the adsorption process will be chemical. If it is greater than 1, physical adsorption is privileged [38].

As is shown in Table S1, $n_F$ is greater than one, which means the MB adsorption on B-TiO$_2$ is a physical process. It can be concluded through the above-presented results and $R^2$ values that Langmuir's isotherm (monolayer adsorption on a homogeneous surface of sorbents) shows a better mechanism for the equilibrium of the adsorption process ($R^2 = 0.989$) than Freundlich's ($R^2 = 0.957$). In Temkin's isotherm equation, there is a factor to consider adsorption interactions, that is, the heat of adsorption. The equation is written as the following:

$$q_e = B_T \ln(A_T) + B_T \ln(C_e)$$

(5)
Where \( B_T = \frac{R_T}{b_T} \) and \( b_T \) correlates with the adsorption heat. A plot of \( q_e \) versus \( \ln(C_e) \) was applied to estimate constants and coefficients of the linear isotherm (Fig. S2; Table S1). It is concluded through the examined data, because the correlation coefficient is not high enough (Figure S2), Temkin's isotherm cannot be the right mechanism to explain the MB adsorption onto B-TiO₂.

The most appropriate model that has fitted the experimental data might be Langmuir's isotherm (Fig. S3). Temkin's model promptly changes over to Langmuir's equation; however, if either \( C_e \) approaches zero, a Freundlich's isotherm will form, therefore, it may be justified that more adsorption is done physically.

### 5. Effect of contact time and initial dye concentration

Figure 5 displays the empirical results for MB adsorption on B-TiO₂ for different concentrations (60, 110 and 210 mg.g⁻¹) concerning contact time. Although the dye concentration is inversely proportional to the adsorption percentage, the real amount of the dye absorbed per unit mass of B-TiO₂ is enhanced at higher concentrations. After the increase of MB concentration from 60 to 210 mg. g⁻¹, the adsorption capacity also increased from 28.14 to 39.14 mg. g⁻¹. In all of the considered concentrations, the equilibrium was reached in 10 minutes that is decidedly smaller than some other conventional adsorbents of MB. The results are illustrated in Table (1). [38-51] It can be inferred from the single, continuous, and smooth curves led to saturation shown in Figure 5 that a monolayer of MB has possibly covered the surface of the B-TiO₂.

### 6. Adsorption kinetic study

It is necessary to have an understanding of how the adsorption kinetics works in order to evaluate the mechanism of the reaction. It will also help in identifying the best-operating conditions for adsorption. A few kinetic models were therefore employed for the MB adsorption kinetic study. The linear forms for pseudo-first-order and pseudo-second-order kinetic models are described as follows, respectively:
\[ \ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \tag{6} \]

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \tag{7} \]

Where \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the first and second-order kinetic rate constants.

The plots, according to eq (6) and eq (7) are shown in Figure (6). As seen in Table S2, the value of \( q_e \), determined by the pseudo-second-order reaction equation is close to the experimental one. This proves the pseudo-second-order is predominate. The \( R^2 \) value is close to one, as another statistical indicator value of significance has confirmed the pseudo-second-order kinetic rate model. As indicated in a normal pseudo-second-order reaction, the adsorption process may be influenced by the amount of both MB and the adsorbent [52]. The intra-particle diffusion kinetic model was investigated to examine the rate-determining stage of the MB adsorption on B-TiO\(_2\), as:

\[ q_t = k_{\text{dif}} t^{1/2} + C \tag{8} \]

Where \( K_{\text{dif}} \) is the rate constant of the intra-particle diffusion model (mg g\(^{-1}\) min\(^{-1/2}\)) and \( C \) designates the width of the boundary layer. This model entails three steps: 1) adsorbate molecules penetrate the solid surface from the aqueous solution, 2) intra-particle diffusion occurs and 3) the ultimate equilibrium is reached. Three linear regions, according to eq (8), are shown in Figure (6). This means that the adsorbent affected the dye adsorption by multiple procedures, not just one (Figure 7). As estimated from the second regression line (Table S2), \( R^2 \) value is close to 1, which indicates that the applied model has verified the rate-limiting step as the intra-particle diffusion step.

### 7. Reusability study

Economically and environmentally, being reusable is of crucial importance for the practicability of an adsorbent. Therefore, the reusability character was examined in the case of B-TiO\(_2\) by the adsorption process of MB. The method included six cycles of adsorption-desorption; the absorbed MB on B-TiO\(_2\) was desorbed by washing twice with ethanol. In this regard, after each cycle, the B-TiO\(_2\) was mixed with ethanol, centrifuged and dried to be ready for the next adsorption cycle. Each cycle was repeated several times to compensate for the adsorbent weight loss. The whole cycle was repeated six times. There was no considerable
decrease even after six cycles (Figure S4). With such a high reusability quality, B-TiO$_2$ is a very good candidate for the adsorption of MB from industrial sewer waters.

8. Conclusion
Experiments with B-TiO$_2$ for removing MB from aqueous solutions in the dark room have shown excellent results and the maximum adsorption capacity was 88.65 mg. g$^{-1}$. After examining experimental data, the equilibrium isotherms were found to fit significantly to the Langmuir isotherm. The adsorption process was completed in just 10 minutes. The rate-determining stage in MB adsorption by B-TiO$_2$ may be the intra-particle diffusion stage. Washing with EtOH can quickly regenerate B-TiO$_2$, which can be reused multiple times to adsorb MB while keeping its efficiency relatively the same.

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Supplementary data

Supplementary data is available at:

http://scientiairanica.sharif.edu/jufile?ar_sfile=171059

References:


Scheme 1. Energy levels and band gaps of B-TiO$_2$.

Figure 1. XRD pattern of B-TiO$_2$. 

Figure 2. SEM-EdX mapping (a-d) and EDX analysis of B-TiO$_2$ (e).

Figure 3. FT-IR spectra of TiO$_2$ (a) and B-TiO$_2$ (b).
Figure 4. N\textsubscript{2} adsorption-desorption isotherm (a) and pore diameter distributions (b) of B-TiO\textsubscript{2}.
Figure 5. Effect of contact time and initial dye concentration on the adsorption capacity and MB adsorption. [pH = 6, RT]

Figure 6. Plots of pseudo-first-order and pseudo-second order. [pH = 6, RT]
Figure 7. Intraparticle diffusion model for the MB adsorption on B-TiO$_2$. [pH = 6, RT ]

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**Table 1.** Comparison between maximum adsorption capacities for MB for different adsorbents.

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorbent</th>
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<th>Time (min)</th>
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<td>88.65</td>
<td>10</td>
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