The first study of adsorption of methylene blue by Black Titania (B-TiO$_2$) nanoparticle in aqueous solution

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Received 30 July 2021; received in revised form 9 November 2021; accepted 17 October 2022

Abstract. This study investigates the elimination of Methylene Blue (MB) by adsorption on Black Titania (B-TiO$_2$) in an aqueous solution in the dark room. B-TiO$_2$ was prepared 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 adsorbent was carried out by X-Ray Diffraction (XRD), $N_2$ adsorption-desorption, Scanning Electron Microscopy (SEM) mapping, photoluminescence, Energy Dispersive X-ray spectrometry (EDX) analysis, Zeta potential, Dynamic Light Scattering (DLS), and Fourier Transform Infrared Spectrometer (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. Maximum adsorption was observed under the following conditions: 26 mg of 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.

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1. Introduction

The use of coloring agents and dyestuff is indispensable in today’s paper, plastic, food, and cosmetics industries. The extensive use of these materials points to their substantial effect on different aspects of the environment, e.g., increase in Chemical Oxygen Demand (COD) of water bodies and adsorption of some of the sunlight entering water systems. They also exert adverse effects on aquatic ecosystems [1–3]. Following the aggravation of the environmental problems, severe problems ensue, e.g., presence of dyestuff in sewage waters and subsequently, lack of treatment methods. One efficient and advantageous option is use of adsorbents. Adsorption is a non-complicated and straightforward process for the purposes of design and use. More importantly, it is insensitive to toxic chemicals [4]. To investigate the properties and the effect of several adsorbent materials, the most commonly used dyestuffs that attract the most attention were methyl orange, Methylene Blue (MB), and Rhodamine B [5–8]. MB exists in many diverse materials including rubbers, pharmaceuticals, pesticides, varnishes, etc. as coloring agents and disinfectors. Graphene was proposed for MB adsorption [9]. The magnetic composite biosorbent could absorb MB with a capacity of 95 mg g$^{-1}$ and recover four times [10]. The stronger capability to absorb MB was observed in organo-bentonite [11]. It was also concluded that grafted cyclodextrin-chitosan with multiple functional groups could be a good candidate.
for MB adsorption [12]. The ability of activated carbon to absorb 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 removal of MB 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 nanoflake [20], titania/gum tragacanth nanohybrid [21], binary TiO$_2$/reduced graphene oxide nanocomposite [22,23], diphenylanthrozoline 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$_2$. The synthesis of hydrogenated titanium dioxide (Black Titania, B-TiO$_2$) was performed by extending optical adsorption to the infrared region [30]. Increase in the absorption results from the introduction of the mid-gap energy level in B-TiO$_2$ above the valance band caused by the wide-spraying overlap of O and Ti orbitals associated with the hybridization of H orbitals with S orbitals of titanium in TiO$_2$ samples (Scheme 1). These improved properties have led to an increase in the scope of research done on B-TiO$_2$ nanomaterials. Due to their properties, B-TiO$_2$ nanomaterials have been applied to various fields, e.g., photocatalysis, Lithium-Ion Batteries (LIM), supercapacitor, fuel cell, field emission, and microwave adsorption and photothermal therapy of cancer. B-TiO$_2$ is a complex composition of Ti$^{4+}$ and Ti$^{3+}$, which is generally employed as a potential photocatalyst. During these photocatalytic reactions, we noticed its high adsorption properties. The adsorption property of B-TiO$_2$ and its photocatalytic property are quite attractive and they can expand the range of performances and applications as well as effectiveness of B-TiO$_2$. Therefore, this study investigates the adsorption properties of B-TiO$_2$.

Our goal is to eliminate MB dye from water by studying and providing adsorption performance of B-TiO$_2$ in the dark room to avoid photocatalytic reactions (B-TiO$_2$). First, B-TiO$_2$ is prepared and then, the effects of crucial variables including the concentration of MB dye and time are investigated (at optimized adsorbent dosage and pH). Adsorption kinetics and isotherms are analyzed separately using various models and the possible mechanisms for MB adsorption on to B-TiO$_2$ are discussed.

2. Experimental

The following models of instruments were used for the characterization of the nanomaterials. A Philips Xpert X-ray diffractometer was applied to prepare the X-Ray Diffraction (XRD) patterns. Fourier Transform Infrared Spectrometer (FT-IR) spectra were recorded on a WQF-510A FT-IR spectrophotometer. LEO 1430VP SEM-EDX instrument operation was applied in the Energy Dispersive X-ray Spectrometry (EDS) mode. An FEI NANOSEM 450 FESEM was used for the investigation of the morphologies of the adsorbent. JEOL JEM- 2100F provided Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (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-TiO$_2$

The used procedure is as follows: 1.50 g of anatase TiO$_2$ nanoparticles were mixed with 0.71 g of NaBH$_4$ powder (the molar ratio between TiO$_2$ and NaBH$_4$ is 1:1). The resulting powder was homogenized and calcinated at 600°C in a tube furnace under argon gas.

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

![Scheme 1. Energy levels and band gaps of B-TiO$_2$.](image-url)
for 30 minutes and then, cooled slowly under the same atmosphere for 5 hours. In the last section, B-TiO₂ 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, as 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:

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

where \( D \) is the crystal size, \( K \) Scherrer’s constant usually taken as (0.89), \( \lambda \) the X-ray wavelength of Cu Kα radiation (\( \lambda = 1.54056 \) Å), \( \beta \) Full Width at Half Maximum (FWHM) of the (1 0 1) peak in radians, and \( \theta \) Bragg’s diffraction angle. \( D = (0.89 \times 1.54)/(0.9 \times 2\pi/360) \cos(26.7/2) \approx 9.02 \) nm, which is inconsistent with the previous report [32]. Moreover, the specific surface area of the prepared B-TiO₂ nanoparticles was obtained using the formula below:

\[ S = 6 \times 10^2/dD, \]

where \( d \) is the theoretical density particle (3.894 g/cm³) and \( S = 6 \times 10^2/(3.894 \times 9.02) = 170 \) m²/g⁻¹. This calculated specific surface area from XRD data is compatible with SEM-EDX mapping of the prepared B-TiO₂, as shown in Figure 2. The SEM-EDX mapping method presented in Figure 2(a)–(d) was employed to evaluate the morphological properties of B-TiO₂. Spherical B-TiO₂ nanoparticles with dark colors are also shown in Figure 2(a). In Figure 2(b)–(d), bright lattice fringes with 0.350 nm interplane distances are observed, which aptly conform to anatase B-TiO₂ (1 0 1) crystallographic planes [33]. The results of the Energy Dispersive X-ray spectrometry (EDX) analysis verify that elemental compositions remain unchanged in comparison with starting materials. The unambiguos distributions of Ti and O elements are further demonstrated by EDX elemental mappings of 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 presented by Figure S1a (Supplementary data), 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 B-TiO₂. An ultrasonic field was employed 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 (Figure S1b (Supplementary data)). 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 correspond to the stretching vibration of the O-H surface-absorbed water molecules. The adsorption bands located at about 562 cm⁻¹ are seen due to 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 specific 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 is 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 corresponds to the mesoporous structure. The interconnected porous network at interiors is also likely allowed. The formed network facilitates the interaction with more reactants which, in turn, will increase the adsorption ability. The N₂ adsorption-desorption isotherms of B-TiO₂ are shown in Figure 4. The surface area of B-TiO₂ is 166 m²/g⁻¹, the mean pore diameter 5.1 nm, and the total pore volume 0.242 cm³/g⁻¹. This amount of porosity results from the sintering of nanoparticles at 600°C during B-TiO₂ preparation. The value of the specific surface area is determined by a Porosimeter as 166 m²/g⁻¹, which is almost consistent with the value calculated based on XRD data (170 m²/g⁻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 MB adsorption. Adsorption comprises a series of mass transfer phenomena. Conventionally, it means the sample adhesion to the surface of a liquid or a solid material (i.e., adsorbent). Isotherms of adsorption are the identifying factors that denominate the relations between adsorbent and adsorbates at a specific temperature in equilibrium. It is possible to find 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 sorbent affinities [35]. The data collected from performed experiments have been fitted with some isotherm models to validate and examine their applicability. Table S1 (Supplementary data) shows the values of the coefficients obtained by these isotherm models. Qₘ 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 a linear form.

Figure 2. SEM-EDX mapping (a-d) and EDX analysis of B-TiO₂ (e).

Figure 3. FT-IR spectra of TiO₂ (a) and B-TiO₂ (b).
adsorption on B-TiO₂ is a physical process. Based on the above-presented results and R² values, it can be concluded that Langmuir’s isotherm (monolayer adsorption on the homogeneous surface of sorbents) shows a better mechanism for the equilibrium of the adsorption process (R² = 0.989) than Freundlich’s (R² = 0.957). In Temkin’s isotherm equation, the heat of adsorption is a factor that considers adsorption interactions. This equation is written as follows:

\[ q_e = B_T \ln(A_T) + B_T \ln(C_e). \]  

where \( B_T = R_T/b_T \) 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 (Figure S2 (Supplementary data); Table S1(Supplementary data)). It is concluded based on the examined data that since the correlation coefficient is not large enough (Figure S2 (Supplementary data)), Temkin’s isotherm cannot be the right mechanism to explain the MB adsorption on to B-TiO₂.

The most appropriate model that fits the experimental data is Langmuir’s isotherm, perhaps (Figure S3 (Supplementary data)). Temkin’s model promptly changes into Langmuir’s equation; however, if \( C_e \) approaches zero, Freundlich’s isotherm is formed. Therefore, it is justified that greater adsorption be done physically.

5. Effect of contact time and initial dye concentration

Figure 5 displays the empirical results for MB adsorption on B-TiO₂ at different concentrations (60, 110, and 210 mg g⁻¹) concerning contact time. Although the dye concentration is inversely proportional
Table 1. Comparison between maximum adsorption capacities for MB for different adsorbents.

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorbent</th>
<th>$Q_m$ (mg g$^{-1}$)</th>
<th>Time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B-TiO$_2$</td>
<td>88.65</td>
<td>10</td>
<td>This work</td>
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<tr>
<td>2</td>
<td>Fiber carbon</td>
<td>225.64</td>
<td>75</td>
<td>[38]</td>
</tr>
<tr>
<td>3</td>
<td>C-C$_3$N$_4$-20</td>
<td>57.87</td>
<td>20</td>
<td>[39]</td>
</tr>
<tr>
<td>4</td>
<td>Natural zeolite</td>
<td>20.18</td>
<td>100</td>
<td>[40]</td>
</tr>
<tr>
<td>5</td>
<td>Chitosan modified zeolite</td>
<td>37.04</td>
<td>-</td>
<td>[41]</td>
</tr>
<tr>
<td>6</td>
<td>Active carbon</td>
<td>9.81</td>
<td>40</td>
<td>[42]</td>
</tr>
<tr>
<td>7</td>
<td>Apricot stones</td>
<td>36.68</td>
<td>80</td>
<td>[43]</td>
</tr>
<tr>
<td>8</td>
<td>Cherry sawdust</td>
<td>39.84</td>
<td>150</td>
<td>[44]</td>
</tr>
<tr>
<td>9</td>
<td>NSS-SO$_3$</td>
<td>208</td>
<td>60</td>
<td>[45]</td>
</tr>
<tr>
<td>10</td>
<td>MCN</td>
<td>360.8</td>
<td>50</td>
<td>[46]</td>
</tr>
<tr>
<td>11</td>
<td>Peat</td>
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<td>[47]</td>
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<tr>
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<td>SBA-15</td>
<td>280</td>
<td>60</td>
<td>[48]</td>
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<td>60</td>
<td>[49]</td>
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<tr>
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<td>Mesoporous hybrid xerogel</td>
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<td>120</td>
<td>[50]</td>
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</table>

Figure 6. Plots of pseudo-first-order and pseudo-second-order, (pH = 6, RT).

to the adsorption percentage, the real amount of dye absorbed per unit mass of B-TiO$_2$ increases at higher concentrations. Following the rise of MB concentration from 60 to 210 mg g$^{-1}$, the adsorption capacity also increases from 28.14 to 39.14 mg g$^{-1}$. In all of the considered concentrations, the equilibrium was achieved in 10 minutes, being 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 leading to saturation shown in Figure 5 that a monolayer of MB may cover the surface of B-TiO$_2$.

6. Adsorption kinetic study

Having a deeper knowledge of how adsorption kinetics works in order to evaluate the mechanism of the reaction is quite necessary. It helps identify the best-operating conditions for adsorption. A few kinetic models were, therefore, employed for the MB adsorption kinetic study. The linear forms of pseudo-first-order and pseudo-second-order kinetic models are respectively described as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t,$$  \hspace{1cm} (6)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t,$$  \hspace{1cm} (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 are shown in Figure 6 according to Eqs. (6) and (7). As seen in Table S2 (Supplementary data), the value of $q_e$ determined by the pseudo-second-order reaction equation is close to the experimental one. This proves that the pseudo-second-order reaction equation
is predominant. $R^2$ value, as another statistical indicator, is close to one, thus confirming 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 examined to determine the rate-determining stage of the MB adsorption on B-TiO$_2$ as follows:

$$q_t = k_{diff} t^{1/2} + C,$$

where $K_{diff}$ 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 affects the dye adsorption through multiple procedures rather than only one procedure (Figure 7). As estimated from the second regression line (Table S2 (Supplementary data)), $R^2$ value is close to 1, which indicates that the applied model has verified the rate-limiting step as an intra-particle diffusion step.

7. Reusability study

Reusability is crucial, economically and environmentally, to the viability of an adsorbent. Therefore, the characteristic of ‘reusability’ was examined in the case of B-TiO$_2$ by the adsorption process of MB. The method included six adsorption-desorption cycles; the absorbed MB on B-TiO$_2$ was desorbed by washing with ethanol twice. 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 (Supplementary data)). With such high reusability quality, B-TiO$_2$ can be considered a very good candidate for the adsorption of MB from industrial sewer waters.

8. Conclusion

Experiments on Black-Titania (B-TiO$_2$) for removing Methylene Blue (MB) from aqueous solutions in the dark room produced excellent results and the maximum adsorption capacity was achieved as 88.65 mg g$^{-1}$. After examining experimental data, the equilibrium isotherms were found to be significantly consistent with 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.

Acknowledgment

The authors acknowledge the National Elites Foundation of Iran and the University of Tehran for assisting this research financially.

Supplementary data

Supplementary data is available at: http://scientiairanica.sharif.edu/jufile?ar_sfile=171059

References


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