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A B S T R A C T

The sonocatalytic performance of the synthesized TiO2/Montmorillonite K10 (TiO2/MMT) nanocomposite was studied in removal of Basic Blue 3 (BB3) from water. The TiO2/MMT nanocomposite was prepared by hydrothermal method. Scanning electron microscope, X-ray diffraction and Fourier transform infrared were used to characterize the synthesized nanocomposite. The average size of TiO2 nanoparticles decreased from 60–80 nm to 40–60 nm through the immobilization of this semiconductor on the surface of MMT. The obtained results indicated that the sonocatalytic activity of TiO2/MMT nanocomposite was higher than that of pure TiO2 nanoparticles and MMT particles. Furthermore, the main influence factors on the sonocatalytic activity such as the BB3 concentration, pH of solution, TiO2/MMT dose, power of ultrasonic generator, and inorganic salts were studied. The intermediates of BB3 degradation during the sonocatalytic process in the presence of the TiO2/MMT nanocomposite have been monitored by gas chromatography−mass spectrometry.

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1. Introduction

Textile industries are substantial sources of environmental pollution, as they consume large amounts of water and produce enormous volume of wastewater in the dyeing and finishing operations [1]. The dyes used in textile industry can be easily identified in the environment by the human eye and cause aesthetic problems. They are not easily biodegradable and cause microtoxicity to aquatic life [2]. In addition, due to the reduction of light penetration, self-purification of streams slows down [3]. Therefore, stringent arrangements should be considered for the removal of dyes before the effluent is discharged into rivers and lakes.

Over the past few years, ultrasound (US) has been extensively used to degrade molecular structures of organic pollutants. Considerable destruction ability of this process is mostly attributed to direct pyrolysis of pollutants and/or production of reactive radicals such as hydroxyl radicals (OH) that are able to induce the degradation of a number of organic pollutants [4]. Volatile organic compounds may evaporate into the bubble and be pyrolysed under the generated harsh conditions, while non-volatile compounds be degraded by the produced OH and other reactive radicals [5]. The organic dyes are nonvolatile compounds and can hardly be entered the bubbles for pyrolysis. Therefore, dyes are mainly degraded by sonoochemically produced reactive radicals [6]. These reactive radicals and paralytic media are produced through the phenomenon of cavitation. In this phenomenon, directing high frequency ultrasonic waves into liquids leads to cyclic formation, growth and implosive collapse of microbubbles which subsequently leads to production of spots with high local pressure and temperature [7].

Despite the different advantages of the sonochemical degradation process, its degradation rate for many organic pollutants is very low. This is attributed to low efficiency of reactive radical formation [8,9]. Therefore degradation of the organic pollutants using this method needs several hours and consequently, the required energy and cost is high [9].

Application of semiconductive catalysts in the sonocatalytic process is one of the promising approaches to enhance performance of the ultrasonic in degradation of pollutants [9]. Applying the catalysts enhances the performance of sonochemical degradation process by providing additional nucleation sites for development of cavity microbubble and subsequently increases the pyrolytic degradation and reactive radical generation. As a result sonocatalytic degradation as highly efficient process has a potential to use in decolorization of textile dyeing wastewater [10].
Sonocatalytic performance of variety of semiconductors i.e. TiO$_2$ [7], ZnO [11] and CdS [12] has been reported. TiO$_2$ is most commonly used semiconductor with superb sonocatalytic activity [13]. Different methods have been reported to improve the catalytic performance of TiO$_2$ i.e. the doping with transition metal or non-metal atom and immobilization on the surface of materials with a large surface area [13].

In this study, TiO$_2$ nanoparticles have been synthesized and immobilized on the surface of Montmorillonite K10 (MMT) for sonocatalytic degradation of an organic dye. The influencing factors on the performance of sonocatalytic degradation process, such as BB3 concentration, pH of solution, TiO$_2$/MMT dose, and power of ultrasonic generator have been studied. The effect of organic salts on the decolorization of BB3 has been also investigated.

2. Materials and methods

Montmorillonite K10 (MMT) was purchased from Sigma-Aldrich Co. (USA) with a surface area of 220–270 m$^2$/g. Table 1 lists the chemical and mineralogical compositions of the MMT which indicates that SiO$_2$ and Al$_2$O$_3$ are basic constituents of this clay. C.I. Basic blue 3 (BB3) was purchased from Boyakhsaz Co., Iran. Chemical structure and characteristics of BB3 are listed in Table 2. All other chemical reagents and dispersants were in analytical grade.

2.1. Synthesis and characterization of TiO$_2$/MMT nanocomposite

TiO$_2$/MMT nanocomposite was prepared through synthesis of TiO$_2$ nanoparticles and their immobilization on the surface of MMT. A flow chart for the preparation of the TiO$_2$/MMT nanocomposite particles is shown in Fig. 1.

X-ray powder diffraction (XRD) measurements of synthesized TiO$_2$ particles, MMT and TiO$_2$/MMT composite were carried out on a PANanalytical XPert PRO diffractometer (Germany) with Cu-K$\alpha$ radiation (45 kV, 40 mA, 0.15406 nm) to identify crystal structures of these materials. Scanning electron microscope (SEM) model MIRA3 FEG-SEM Tescan (Czech) was used to detect morphology and particle sizes of these compounds. The TiO$_2$, MMT and TiO$_2$/MMT samples were analyzed with a Fourier transform infrared spectroscopy (FTIR) model Tensor 27, Bruker (Germany) in a wavenumber range of 4000–400 cm$^{-1}$ using the KBr pellet technique.

2.2. Sonocatalytic decolorization process

A controllable ultrasonic apparatus with frequency of 40 kHz was used to sonocatalytic decolorization of the BB3 solution. Batch studies were performed to evaluate the effect of BB3 concentration, pH of solution, TiO$_2$/MMT dose, power of ultrasonic generator, and different inorganic salts on decolorization efficiency. For each sonocatalytic degradation experiment, 100 mL of the dye solution of containing 5–20 mg/L of BB3 and 0.25–1.5 g/L of the TiO$_2$/MMT composite were added in a 250-mL erlenmeyer. pH of solution was adjusted using 1, 0.1, and 0.01 M HCl or NaOH solutions. The concentration of the BB3 solution, pH of solution, TiO$_2$/MMT dose and power of ultrasonic generator was selected according to the values proposed in experimental design to evaluate their effect on decolorization efficiency. At a defined time interval, the BB3 concentration in the ultrasonic reaction was determined by using the UV–vis spectrophotometer (WPA Lightwave S2000, England) at $\lambda_{max} = 654$ nm. Decolorization efficiency (%) = [(C$_0$ – C$_t$)/C$_0$] x 100, was used to determine the percent of degradation of BB3, where C$_0$ is the initial concentration of BB3 solution and C$_t$ is its concentration after certain time (t) ultrasonic irradiation.

Organic intermediates were analyzed by using a gas chromatography–mass spectrometry (GC/Mass) equipped with an Agilent 6890 gas chromatograph with a 30 m–0.25 mm HP-5MS capillary column and an Agilent 5973 mass spectrometer (Agilent Technologies, Palo Alto, Canada).

3. Results and discussion

3.1. XRD analysis

XRD patterns of the MMT, TiO$_2$ and TiO$_2$/MMT shown in Fig. 2. For the MMT, peak was observed at 2 Theta of 26.5$^\circ$ corresponds to the interlayer spacing of this clay [14]. Interlayer spacing of MMT was quantitatively evaluated using Debye–Schererr equation d = ($\lambda$/4sin$\theta$) where d is the Debye–Schererr constant (0.89), $\lambda$ is the X-ray wavelength (0.15406 nm), $\beta$ is width of the peak with the maximum intensity in half height and $\theta$ is the diffraction angle [15]. The result obtained from analyses of XRD pattern by using the Debye–Schererr equation indicated that the interlayer spacing of MMT was about 29 nm. The XRD patterns of the synthesized TiO$_2$ (Fig. 2b) exhibited diffraction peaks around 2 Theta of 25.3$^\circ$, 37.9$^\circ$, 47.8$^\circ$, 54.3$^\circ$, 55$^\circ$, and 62.7$^\circ$, which were attributed to the characteristic (111), (004), (200), (105), (211), and (204) planes of anatase TiO$_2$ (JCPDS 21-1272), respectively [16]. The average crystallite size calculated using the Debye–Schererr equation is approximately 25 nm. The XRD pattern of Fig. 2c shows diffraction peaks attributed to both TiO$_2$ and MMT confirming the synthesized TiO$_2$/MMT nanocomposite indicating the immobilization of TiO$_2$ nanoparticles on the surface of MMT.

3.2. FTIR analysis

FTIR analysis was performed to investigate the variations on functional groups of TiO$_2$, MMT during preparation of TiO$_2$/MMT nanocomposite. The FTIR spectra of TiO$_2$, MMT and TiO$_2$/MMT are shown in Fig. 3. The differences of FTIR spectrum between MMT, TiO$_2$, and TiO$_2$/MMT are obvious. The pure MMT has

<table>
<thead>
<tr>
<th>Composition</th>
<th>CAS number</th>
<th>EC number</th>
<th>Main chemical composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>SiO$_2$ Al$_2$O$_3$ Fe$_2$O$_3$ MgO Other</td>
</tr>
<tr>
<td>Montmorillonite K 10</td>
<td>1318-93-0</td>
<td>215-288-5</td>
<td>67.6 14.6 2.9 1.8 13.1</td>
</tr>
</tbody>
</table>

Table 2 Characteristics of C.I. Basic Blue 3.

![Chemical structure of C.I. Basic Blue 3 (BB3)](image)
absorbance peaks at 472, 530, 785, 1050, 2845, 2924 and 3420 cm\(^{-1}\) in the spectrum (Fig.3 a) corresponding to Si–O–Si deformation, Al–O–Si deformation, Al–O stretching vibration, Si–O stretching vibration, interlayer H–O–H molecules, symmetric stretching vibration of C–H, asymmetric stretching vibration of C–H, and stretching vibration of –OH, respectively [17–21]. Fig. 3b shows the spectra corresponding to the TiO\(_2\). Absorption band at 480 cm\(^{-1}\) is assigned to the stretching vibration of Ti–O band [22]. The bands at 1630, 2845, 2924 and 3420 cm\(^{-1}\) were

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**Fig. 1.** A flow chart for the preparation of the TiO\(_2\)/MMT nanocomposite.

**Fig. 2.** XRD patterns of samples (a) MMT, (b) TiO\(_2\) and (c) TiO\(_2\)/MMT.

**Fig. 3.** FTIR spectra of (a) MMT, (b) TiO\(_2\) and (c) TiO\(_2\)/MMT.
associated with interlayer H–O–H molecules, symmetric stretching vibration of C–H, asymmetric stretching vibration of C–H, and stretching vibration of –OH, respectively.

Comparing the IR spectra of TiO$_2$/MMT nanocomposite (Fig. 3c) with that of the pure TiO$_2$ and MMT indicate the development of new adsorption peak at wavenumber 935 cm$^{-1}$ attributed to Ti–O–Si stretching vibration [23]. This result indicates the development of new Ti–O–Si band between TiO$_2$ and MMT during the preparation of TiO$_2$/MMT nanocomposite.

3.3. **SEM analysis**

The morphology of the MMT, TiO$_2$ and TiO$_2$/MMT revealed by SEM are illustrated in Fig. 4. Fig. 4b shows the SEM micrograph of synthesized TiO$_2$ particles. Size distribution of TiO$_2$ particles in this figure was determined using Manual Microstructure Distance Measurement software (Nahamin Pardazan Asia Co., Iran). As it shown in Fig. 4f the TiO$_2$ particles was synthesized in nanosized dimension with average width of 60–80 nm. SEM micrograph of TiO$_2$/MMT composite (Fig. 4c) confirmed the presence of TiO$_2$ particles on the surface of MMT comparing with that of non-coated MMT (Fig. 4a). Close observation (Fig. 4d) indicates the size of immobilized TiO$_2$ particles were mainly in nanometer range. Size distribution of TiO$_2$ nanoparticles is shown in Fig. 4g that indicates that most of the TiO$_2$ particles in TiO$_2$/MMT nanocomposite are in the range of 40–60 nm. This result indicates that the average size of TiO$_2$ nanoparticles immobilized on the surface of MMT was smaller than that of pure TiO$_2$ nanoparticles.

The EDX microanalyses (wt.%) of the prepared TiO$_2$/MMT nanocomposites are illustrated in Fig. 4e. It can be clearly seen that the TiO$_2$/MMT nanocomposite contained main elements, viz. C, O, Si, Ti, Mg, Al, Na and K. Comparing this result which chemical composition of MMT illustrated in Table 1 approved the immobilization of TiO$_2$ nanoparticles on the surface of MMT in TiO$_2$/MMT nanocomposite sample.

3.4. **Effect of operational parameters on sonocatalytic process**

3.4.1. **Effect of pH**

pH plays an important role on the surface charge of TiO$_2$/MMT and the generation of reactive radicals. Therefore initial pH of BB3 solution was adjusted to different value covering the acidic, neutral/near neutral, the basic regime to investigate the effect of solution pH on the decolorization of this solution. In this series of experiments the initial dye concentration was fixed at 10 mg/L, power of ultrasonic generator was 300 W, and TiO$_2$/MMT dosage was 1 g/L. The obtained results presented in Fig. 5 show the slightly increase of the decolorization efficiency with the increase in solution pH up to 7 and significant decreased afterward. pH of solution influences on approaching the cationic BB3 molecules to the surface of TiO$_2$/MMT as an important step for the dye oxidation to take place. The pH of zero point charge (pHzpc) for the TiO$_2$ is 6.8 [24]. At solution with pH < 6.8, the surface charge of the TiO$_2$ is positive and the electrostatic repulsion between the positive surface charge and the cationic BB3 molecules prevent approach of these molecules to the surface of the TiO$_2$ where reactive radicals produced throw sonocatalytic process. Therefore decolorization efficiency was low. As the pH of the system increases, the positive charge of TiO$_2$ decreased. At the pH values higher than 6.8, the surface charge changed to negative. A negatively charged TiO$_2$ surface...
favors the approach of dye cations to the surface of TiO2 were reactive radicals produced through sonocatalytic approaches. Consequently decolorization efficiency was increased.

More increase in pH of solution led to increase coulombic repulsion between the negative charged TiO2/MMT surface and the OH⁻ [25]. This fact could hinder the production of reactive radicals and thus decrease the decolorization efficiency.

3.4.2. Effect of TiO2/MMT dosage

A series of sonocatalytic decolorization experiments were conducted with different TiO2/MMT dosage from 0.25 to 1.5 g/L to investigate the effect of catalyst in BB3 decolorization process. As expected, the obtained results (Fig. 6) indicate that decolorization efficiency was increased with catalyst dose. This can be attributed to increase in sonocatalyst active sites and consequently development of more cavitation microbubbles which led to produce more reactive radicals with the increase of TiO2/MMT catalyst dose [26].
3.4.3. Effect of initial concentration of BB3

To investigate the effect of initial BB3 concentration, the sono-catalytic decolorization experiments were done with different BB3 concentration for 90 min, while keeping other parameters as catalyst dosage, initial pH and power of ultrasonic generator were 1 g/L, 7 and 300 W, respectively. It can be seen from Fig. 7 that the decolorization efficiency of BB3 solution generally decreases with an increase in the initial BB3 concentration. The increase in the BB3 concentration while the $/C_5OH$ concentration was constant led to inefficient oxidation of dye molecules and consequently low decolorization efficiency. Moreover, high concentrated BB3 solution polar as a non-volatile organic compounds affects on cavities [27].

3.4.4. Effect of inorganic ions on sonocatalytic degradation of BB3

Sonocatalytic decolorization of BB3 in the industrial wastewater was simulated by adding sodium sulfate, sodium carbonate and sodium chloride to dye solution. As can be seen in Fig. 8 the chloride ion has highest decreasing effects on decolorization efficiency. This ion may catch the sonocatalyically developed -OH through the Eq. (1) and consequently decrease the efficiency of sonochemical degradation process [28]:

\[ \cdot\text{OH} + 2\text{Cl}^- + H^+ \rightarrow \cdot\text{Cl}_2^- + H_2O \]  

As can be seen decreasing effect of carbonate and sulfate anions on decolorization efficiency of BB3 solution was lower than that of chloride ion. Presence of these ions in dye solution inhibited the sonocatalytic degradation because of their scavenging effect on reaction of positive holes and reactive radicals [29].

3.4.5. Effect of ultrasonic power

The effect of the power of ultrasonic generator on the decolorization of BB3 was investigated at the experimental condition in Fig. 9.
which catalyst dosage was 1 g/L, initial pH was 7 and the BB3 concentration was 10 mg/L. Obtained results (Fig. 9) indicate that when the power of ultrasonic generator ranged from 150 W to 540 W, the decolorization efficiency increased with power. An increase in the power of ultrasonic generator would increase degradation efficiency in two essential ways. Firstly, turbulence of solution increases with power which led to increase in mass transfer rate of BB3, reactive radicals and degradation byproducts between surface of composite and solution bulk [30]. Secondly, cleaning action of the ultrasonic irradiation increased with power and consequently available active sites on the catalyst surface were enhanced [31]. Generally, combination of these two basic led to increase in production of reactive radical and decolorization efficiency.

3.5. Comparison of the activity of MMT, TiO2 and TiO2/MMT

Fig. 10(a and b) shows the decolorization profiles of BB3 with initial concentration of 10 mg/L at pH of 7 in different adsorption and sonocatalytic processes. The obtained results indicated that the decolorization of BB3 in the presence of US/MMT, US/TiO2, and US/TiO2/MMT is higher than that of MMT, TiO2, and TiO2/MMT. Presence of the catalyst provides additional nuclei for formation of microbubble and hot spots in the solution through heterogeneous acoustic cavitation [13]. Comparing of BB3 decolorization in the presence of MMT and TiO2/MMT shows that sonocatalytic activity of TiO2/MMT is higher than that of the bare TiO2. It can be attributed to decreasing the size of TiO2 particles in TiO2/MMT nanocomposite. This leads to increase in available surface area and consequently enhance in nucleation, collapse and rebound of cavitation bubbles near the solid boundary due to existing of more nucleation sites on the surface of this catalyst. This increases the sonocatalytic activity of TiO2/MMT in comparison with bare TiO2.

3.6. The intermediates during BB3 degradation

The intermediates during BB3 degradation in the sonocatalytic decolorization process were identified by GC/Mass by the peaks formed, and the molecular structure of BB3 is reported in Table 3. Twelve intermediate compounds with high match factor of mass

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Structure</th>
<th>Retention time (min)</th>
<th>Main fragments</th>
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</thead>
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<tr>
<td>1</td>
<td>2-Methyl-5-(1-methylethyl) phenol</td>
<td><img src="123" alt="Structure" /></td>
<td>11.717</td>
<td>150, 135, 91</td>
</tr>
<tr>
<td>2</td>
<td>2,5-Diethylphenol</td>
<td><img src="123" alt="Structure" /></td>
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<td>135</td>
</tr>
<tr>
<td>3</td>
<td>2-Methyl-4-(1-methylethyl)-2-cyclohexenone</td>
<td><img src="123" alt="Structure" /></td>
<td>8.543</td>
<td>152, 110, 81, 55</td>
</tr>
<tr>
<td>4</td>
<td>(1S,4S,5R)-1-Isopropyl-4-methylbicyclo[3.1.0]hexan-3-one</td>
<td><img src="123" alt="Structure" /></td>
<td>3.982</td>
<td>221, 110, 81, 55</td>
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<tr>
<td>5</td>
<td>1,2-Dimethylcyclohexene</td>
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<td>95, 67</td>
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<tr>
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<td>4,4-Dimethyl-2-cyclopenten-1-one</td>
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<td>177, 116, 75&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
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<td>2-(1,1-Dimethyl) Phenol</td>
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<td>135, 77</td>
</tr>
<tr>
<td>9</td>
<td>1,5-Dimethylcyclohexene-5-carboxaldehyde</td>
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<td>N,N-Dimethyl-1-dodecanamine</td>
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<td>Cyclopropane,1,1-dimethyl-2-(3-methyl-1,3-butadienyl)</td>
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<td>136, 93</td>
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<td>2.95</td>
<td>146, 124, 100&lt;sup&gt;a&lt;/sup&gt;</td>
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</table>

<sup>a</sup> Value corresponding to the trimethylsilyl derivative.
spectrum were identified as shown in this table. Generation of these intermediates during the decolorization of BB3 confirmed active degradation of this pollutant throw the sonocatalytic degradation process.

4. Conclusions

The results of the present study showed that immobilizing the TiO2 nanoparticles on the surface of MMT led to decrease in size of nanoparticles and increase its sonocatalytic performance. The decolorization efficiency of BB3 solution increased with the increasing TiO2/MMT nanocomposite dose and power of ultrasonic generator and decrease in initial BB3 concentration. The optimal pH value of the solutions was observed at 7.0. The effect of investigated inorganic anions on the decolorization of BB3 is in the following decreasing order: Cl− > CO3−2 > SO4−2.

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