Hydrothermal tuning of the morphology and crystallite size of zeolite nanostructures for simultaneous adsorption and photocatalytic degradation of methylene blue dye

Mostafa Y. Nassar *, Ehab A. Abdelrahman *

Chemistry Department, Faculty of Science, Benha University, Benha 13518, Egypt

Abstract

We herein have reported on tuning of the morphology and crystallite size of the hydrothermally prepared zeolite nanostructures by using different aluminum sources. The investigation revealed that aluminum sulfate and aluminum chloride precursors produced non-crystalline forms, while aluminum isopropoxide, alumina, and aluminum metal precursors generated analcime nanoparticles with crystallite size of ca. 94.79, 112.57, and 105.87 nm, respectively. However, sodium aluminate precursor gave a mixture of analcime and nacrite phases with a crystallite size of ca. 77.95 nm. The as-prepared nanostructures were identified using XRD, FT-IR, FE-SEM, EDS, UV-Vis spectroscopy and BET surface area. The results exhibited that the direct optical energy gaps (Eg) and BET surface area were found to be (3.29 eV and 20.18 m²/g), (3.15 eV and 16.28 m²/g), (3.21 eV and 18.67 m²/g), and (2.69 eV and 17.82 m²/g) for the zeolite products prepared using aluminum isopropoxide, sodium aluminate, alumina, and aluminum metal precursors, respectively. The results also showed that the as-prepared zeolite nanostructures could be simultaneously used as adsorbents and photocatalysts for the removal of methylene blue (MB) dye from aqueous solutions. The adsorption of methylene blue dye over the zeolite adsorbents obeys pseudo-second-order model and intra-particle diffusion model. Interestingly, zeolite photocatalyst prepared using aluminum isopropoxide degraded the MB dye with percentage of 85% and 100% within 180 and 110 min in the presence of UV and (UV + H₂O₂), respectively. The degradation processes followed the pseudo-first-order model. The prepared zeolites are proposed as promising candidates for the removal of MB from aqueous media.

1. Introduction

Zeolites are a crystalline material consist of silicon and aluminum metals which were arranged in tetrahedral shape TO₄ (T = Si, Al), where oxygen atoms connect neighboring tetrahedral [1]. In the zeolite framework, Al³⁺ replaces some of Si⁴⁺ in SiO₂ network, creating a negative charge on zeolite which is neutralized by positive ions such as NH₄⁺, Na⁺ and K⁺. These ions can be easily replaced by other ions; hence, this gives zeolites the characteristics and features which make them unique materials. The term zeolite was launched in the eighteenth century by Axel Fredrick (Swedish scientist) who was interested in metals. Zeolites have multiple applications in various fields. In the agricultural field: zeolites are used as fertilizer owing to their ability in ammonia exchange and absorption of excess water from the soil, then zeolites deliver this to the plant slowly, preventing root rot and reducing drought. Zeolites are also used in poultry farms to improve the efficiency of feeds and get rid of unwanted smells and strengthen immunity birds due to their high ability to remove ammonia which can cause blindness to poultry [2–10]. In the industrial field: zeolites are used in various applications such as fluid catalytic cracking, cement industry (because zeolites can reduce required heat during the manufacturing process; consequently, can reduce both fuel consumption and rising gas such as CO₂ and SO₂), natural gas purification in wells and oil refineries (due to their ability of removing CO₂ and SO₂ gases), chemical detergents industry, ceramics and porcelain industry, as well as electronics and sustainable production of hydrogen via water splitting [9–18]. In the environmental field: due to the toxicity of organic and inorganic pollutants, researchers have devoted much of their work to removing pollutants [19–30]. Owing to the ability of zeolites to adsorb organic and inorganic pollutants in addition to its semiconducting properties, those materials are used in water treatment. Zeolites can be used as adsorbents and photocatalysts to degrade different organic pollutants [30–33]. Natural zeolite found in nature in basaltic rocks and sediments that formed through the ages by the hot mineral water. Due to the scarcity of natural zeolites, scientists have devoted their effort to preparing

* Corresponding authors. Tel.: +20106872555; Tel.: +201010636875.
E-mail addresses: m.y.nassar@yahoo.com, m.y.nassar@fsc.bu.edu.eg (M.Y. Nassar), dr.ehab.saleh@yahoo.com, ehab.abdelrahman@fsc.bu.edu.eg (E.A. Abdelrahman).

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those materials industrially. Analcime is considered to be one of the most important types of industrial zeolites attributing to its vast applications such as membrane for fuel cells [34], separation of surfactant [35], removal of inorganic pollutants (such as SO$_4^{2-}$, Cu$^{2+}$, Cs$^+$, Sr$^{2+}$, and arsenic) and organic pollutants (such as methylene blue dye and tetracycline) [36–41]. It can be also used in oxidation of organic compounds such as formaldehyde, benzyl alcohol and cyclohexane [42–44]. Hydrothermal route proved its efficiency in synthesis of various metal oxides [20,45–47]. Therefore, this route has been adopted to prepare analcime either in presence of template (such as tetraethyl ammonium bromide, tetrapropyl ammonium hydroxide and ethylene diamine derivatives) [48–50] or in absence of organic template [51–55]. It is well-known that aluminum sources play a crucial role in the zeolite properties such as crystal size, surface area, morphology, Si/Al ratio and have no effect on the type of zeolite phase under the same preparation conditions [56]. Therefore, this discussion stimulated us to prepare zeolite nanostructures with smaller crystallite size and different phases using more facile route.

Herein, we have developed a new strategy to synthesize zeolite nanostructures with different phases and crystallite sizes using a hydrothermal route. Therefore, we have investigated the effect of aluminum sources such as aluminum sulfate, aluminum chloride, aluminum isopropoxide, sodium aluminate, alumina, and aluminum metal precursors on the type of zeolite phases, as well as on their crystal size, surface area, morphology. The as-prepared zeolite products were identified using several techniques. Moreover, the as-prepared zeolite compounds were applied to remove methylene blue dye from aqueous solutions. The as-fabricated zeolites were used as adsorbents and photocatalysts, simultaneously, for the first time, to the best of our knowledge. The photocatalytic properties of the as-prepared zeolites were investigated in the absence and presence of H$_2$O$_2$ under UV illuminations.

2. Experimental

2.1. Materials and reagents

All chemical used in the current investigation were of analytical grade and employed as received without further purification: The chemicals: sodium hydroxide pellets (NaOH), aluminum sulfate (Al$_2$(SO$_4$)$_3$·18H$_2$O), aluminum chloride (AlCl$_3$·6H$_2$O), aluminum isopropoxide (Al(OCH(CH$_3$)$_2$)$_3$), sodium aluminate (NaAlO$_2$), alumina (Al$_2$O$_3$), aluminum metal, Ludox AS30 colloidal silica (SiO$_2$, 30% suspension in H$_2$O), and methylene blue dye (MB; C$_{16}$H$_{18}$ClN$_3$S), were supplied by Sigma-Aldrich Chemical Company.

2.2. Preparation of zeolites using different aluminum sources

The zeolite products were prepared hydrothermally as follows: 7.72 g sodium hydroxide (0.193 mol) and an appropriate weight of an aluminum source [10.66, 7.73, 6.54, 2.62, 1.63, or 0.86 g of aluminum sulfate, aluminum chloride, aluminum isopropoxide, sodium aluminate, alumina or aluminum metal, respectively], so as to give 0.032 mol of aluminum cations, were dissolved in 69.5 mL deionized water in a Pyrex beaker. Afterward, 50 g of Ludox AS30 colloidal silica was dropwise added to the previously prepared aluminum solution under vigorous stirring. The reaction blend was stirred until it turned into gel. Then, the reaction blend was left for aging at room temperature (~25 °C) for 20 h. Therefore, the molar composition of the produced synthesis gel was 125SiO$_2$:8Al$_2$O$_3$. After that the reaction mixture was transferred into a Teflon-lined stainless steel autoclave set up at 180 °C for 5 days, in an electric oven. After completion of the hydrothermal reaction, the autoclave was then allowed to naturally cooled, and the precipitated product was collected by centrifugation. The zeolite samples were washed with water then with ethanol several times, and dried at 120 °C overnight in an oven.

2.3. Simultaneous adsorption and photocatalytic degradation of methylene blue dye

In a typical adsorption experiment, in Erlenmeyer flasks, 0.1 g of adsorbent (prepared using aluminum isopropoxide or sodium aluminate) was stirred with 50 mL of methylene blue dye solution (with an initial concentration of 10 mg/L) at 500 rpm for different interval times in dark place and at room temperature (~25 °C). At pre-defined time intervals, aliquots were withdrawn out of the flasks and centrifuged to separate the suspension zeolites. The remaining dye concentration in the
supernatant was determined employing an UV–Vis spectrophotometer at 663 nm wavelength. Afterward, when adsorption reached its maximum (i.e. equilibrium adsorption time), the degradation process of MB dye was investigated in the absence and presence of 2 mL of 0.5 M hydrogen peroxide solution under UV illumination using UV lamps (Philips at 365 nm 4 × 20 watt). After separating the catalyst by centrifugation, the absorption of the supernatant was measured at 663 nm at different time intervals using an UV–Vis spectrophotometer. % removal or degradation of methylene blue dye can be calculated using Eq.(1).

\[
\text{% Removal or degradation} = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]  

where, \(C_i\) (mg/L) is the initial concentration of MB dye (in case of adsorption process) or concentration of methylene blue dye after attaining equilibrium adsorption time in the dark (in case of photocatalytic degradation), \(C_f\) (mg/L) is the final concentration of MB dye solution after adsorption or photocatalytic degradation. The adsorption capacity of the adsorbents \(Q\) (mg/g) can be calculated using Eq.(2).

\[
Q = \frac{(C_i - C_f)V}{m}
\]

where, \(V\) (L) is the volume of the dye solution, and \(m\) (g) is the mass of the adsorbents.

2.4. Physico-chemical measurements

The XRD patterns of the prepared samples were collected on a 18 kW diffractometer (Bruker; model D8 Advance) with monochromated Cu Kα radiation (λ) 1.54178 Å. FT-IR spectra were recorded on a Nicolet iS10 FT-IR spectrophotometer in the 4000–4000 cm \(^{-1}\) region using the KBr disk technique. The FE-SEM images of the as-fabricated products were collected using a field emission scanning electron microscope (FE-SEM; JEOL, model JSM-6390). Elemental analysis was carried out using link, ISIS-300, Oxford EDS (energy dispersion spectroscopy) detector. The BET (Brunauer-Emmet-Teller) surface area and pore size of the as-produced products were estimated employing nitrogen gas adsorption isotherms on Quantachrome analyzer (Nova 2000 series, USA) at 77 K. The adsorption and/or degradation investigation were performed using an UV–Vis spectrophotometer (Jasco; model V530).

3. Results and discussion

3.1. XRD and surface texture studies

XRD patterns of the as-synthesized samples produced using aluminum sulfate, aluminum chloride, aluminum isopropoxide, sodium aluminate, alumina and aluminum metal are depicted in Fig. 1(A–F), respectively. It was found that the products prepared using aluminum sulfate and aluminum chloride were amorphous owing to the broad band appeared at 20 = 20–40°. Whereas, the samples synthesized using aluminum isopropoxide, alumina, and aluminum metal were analcime phase because of the appearance of peaks at 20 = 16, 18, 26 and 31–50° which can be perfectly indexed into the monoclinic type phase with cell constants: \(a = 13.689\) Å, \(b = 13.676\) Å and \(c = 13.665\) Å (space group Cmcm, JCPDS card 86-2455) [57]. The intense peaks

![Fig. 2. FT-IR spectra of the as-prepared zeolite products fabricated using: (A) aluminum isopropoxide, (B) sodium aluminate, (C) alumina, and (D) aluminum metal precursors.](image-url)
appeared at $2\theta = 12, 22$ and $28$ in along with the peaks of analcime for the sample obtained using sodium aluminate confirmed the presence of nacrite zeolite phase. This phase can be perfectly indexed into the monoclinic type phase with cell constants: $a = 13.689$ Å, $b = 13.676$ Å and $c = 13.665$ Å (space group Cmcm, JCPDS card 76-1781) [58]. Thus, we can conclude that aluminum sources can influence on zeolite phase products. Moreover, the acidic counter ion of aluminum source exhibited a significant effect on the type and crystallization of zeolite phase. It is well-known that aluminum sources play a significant role in the zeolite properties such as crystal size, surface area, morphology, Si/Al ratio. And, they have no effect on the type of zeolite phase under the same experimental conditions [56]. However, this study exhibited that aluminum sources played a crucial role in production of zeolites. This is based on that various phases of zeolites could be produced by changing aluminum sources.

The average crystallite size was estimated using the Debye–Scherrer formula (Eq. (3)):

$$D = \frac{0.9\lambda}{\beta \cos \theta_B}$$

(3)

where, $\lambda$, $\beta$, $\theta_B$ are the X-ray wavelength, full width at half maximum (FWHM) of the diffraction peak, and Bragg diffraction angle.
respectively. The XRD data revealed that the average crystallite sizes of zeolite nanostructures were found to be 94.79, 77.95, 112.57 and 105.87 nm for products prepared using aluminum isopropoxide, sodium aluminate, alumina and aluminum metal, respectively, as presented in Table 1.

The textural characteristics such as surface area and pore volume were evaluated from the low temperature nitrogen adsorption and summarized in Table 1. The BET surface area was found to be 20.18, 16.28, 18.67 and 17.82 m²/g, respectively; whereas, total pore volume was found to be 0.012, 0.015, 0.017 and 0.014 cc/g, respectively.

3.2. FT-IR studies

The FT-IR transmission spectra for samples prepared using aluminum isopropoxide, sodium aluminate, alumina and aluminum metal are shown in Fig. 2(A–D), respectively. Notably, all products revealed similar vibrational absorption bands. The bands appeared at about 1032 cm⁻¹ may be attributed to the asymmetric stretching vibration of T─O (T = Si, Al). Those appeared at about 630 cm⁻¹ may be assigned to M─O bond [59,60] and in the current case they can be attributed to T─O─T (T = Si, Al) symmetric stretching vibration. The bands appeared near 452 cm⁻¹ may be due to T─O─T (T = Si, Al) bending vibration [61]. The bands appeared at about 3617 and 1637 cm⁻¹ can be attributed to stretching and bending vibration of surface adsorbed zeolite water, respectively [62–66].

3.3. SEM and EDS studies

Fig. 3(A–D) shows FE-SEM images of the samples prepared using aluminum isopropoxide, sodium aluminate, alumina and aluminum metal, respectively. The results showed that the zeolites, prepared using aluminum isopropoxide and aluminum metal, are composed of spherical shapes with an average particle size of 17 and 3 μm, respectively, as outlined in Table 1. However, the zeolite products synthesized

<table>
<thead>
<tr>
<th>Aluminum precursor used for zeolite preparation</th>
<th>$E_g$ (eV)</th>
<th>Tripathy $n_\infty$</th>
<th>$\varepsilon_\infty$</th>
<th>$\lambda$</th>
<th>Moss $n_\infty$</th>
<th>$\varepsilon_\infty$</th>
<th>$\lambda$</th>
<th>Ravindra $n_\infty$</th>
<th>$\varepsilon_\infty$</th>
<th>$\lambda$</th>
<th>Herve-Vandamme $n_\infty$</th>
<th>$\varepsilon_\infty$</th>
<th>$\lambda$</th>
</tr>
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<tbody>
<tr>
<td>Aluminum isopropoxide</td>
<td>3.29</td>
<td>2.31</td>
<td>5.32</td>
<td>4.32</td>
<td>0.16</td>
<td>2.32</td>
<td>5.37</td>
<td>4.37</td>
<td>0.16</td>
<td>2.01</td>
<td>4.18</td>
<td>3.18</td>
<td>0.11</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>3.15</td>
<td>2.36</td>
<td>5.57</td>
<td>4.47</td>
<td>0.16</td>
<td>2.35</td>
<td>5.52</td>
<td>4.52</td>
<td>0.16</td>
<td>2.15</td>
<td>4.63</td>
<td>3.63</td>
<td>0.13</td>
</tr>
<tr>
<td>Alumina</td>
<td>3.21</td>
<td>2.63</td>
<td>6.90</td>
<td>5.90</td>
<td>0.20</td>
<td>2.49</td>
<td>6.23</td>
<td>5.23</td>
<td>0.18</td>
<td>2.56</td>
<td>6.58</td>
<td>5.58</td>
<td>0.19</td>
</tr>
<tr>
<td>Aluminum metal</td>
<td>2.69</td>
<td>3.03</td>
<td>9.16</td>
<td>8.16</td>
<td>0.25</td>
<td>2.72</td>
<td>7.35</td>
<td>6.35</td>
<td>0.21</td>
<td>2.99</td>
<td>8.97</td>
<td>7.97</td>
<td>0.25</td>
</tr>
</tbody>
</table>
using sodium aluminate and alumina are composed of spherical and irregular shapes with an average particle size of 4 and 3.5 μm, respectively, as presented in Table 1. Fig. 4(A–D) depicts EDS spectra of the as-prepared zeolites. The results indicated that all the as-synthesized samples are composed of Si, Al, Na and O as summarized in Table 1. The Si/Al molar ratio of the samples prepared using aluminum isopropoxide, sodium aluminate, alumina and aluminum metal were found to be 2.99, 0.29, 3.03 and 2.99, respectively.

### 3.4. Optical properties of the as-prepared zeolite products

The optical properties of the as-prepared zeolite nanostructures have been investigated by calculating the values of \( E_g, n, \epsilon_\infty, \chi \) and \( R \): where, \( E_g \) (eV) is an optical energy gap, \( n \) is a refractive index of substance (a measure of its transparency to the incident photons), \( \epsilon_\infty \) is a limiting dielectric constant (the ratio of the permittivity of a substance to that of free space or vacuum) describing the response of the

**Fig. 6.** Adsorption of methylene blue dye onto zeolite sample prepared using aluminum isopropoxide (A, B), and sodium aluminate (C, D) precursors.

**Fig. 7.** Pseudo-first-order (A, D), pseudo-second-order (B, E), and intra particle diffusion model (C, F) for the adsorption of MB dye on the zeolite product prepared using aluminum isopropoxide and sodium aluminate precursors, respectively.
substance to the electromagnetic radiation mediated through the interaction of photons and electrons, $\chi$ is linear optical susceptibility, and $R$ is reflectivity (defined through the ratio of the reflected power to incident power) and it describes the optical response of the surface of a substance.

UV–Vis absorption spectra of the as-prepared zeolite nanostructures were performed in nujol mull in order to estimate their optical energy gap. The optical energy gaps ($E_g$) can be determined using Eq. (4).

$$\alpha(h\nu)^y = K(h\nu - E_g)$$  \hspace{1cm} (4)

where, $\alpha$, $K$, $y$ are the absorption coefficient, a constant, and an integer equals either 2 for a direct allowed transitions or 1/2 for an indirect allowed transitions, respectively. We have plotted $(\alpha h\nu)^y$ versus $h\nu$ as shown in Fig. 5. It seems that direct allowed transitions are the predominant for the as-prepared zeolite products. The optical energy gap values of the as-prepared zeolite products were determined by extrapolating each graph so as $(\alpha h\nu)^y = 0$. The optical energy gap values indicate the semiconducting properties of the as-prepared zeolite products [68].

The estimated optical properties have been presented in Table 2. It is noteworthy that this is considered to be the first time to study the semiconductor properties of zeolites. Therefore, this opens up the possibility to use those materials as photocatalyst in photocatalytic degradation of organic dyes in aqueous solutions.

### 4. Simultaneous adsorption-photocatalytic degradation of methylene blue dye

The dual adsorption and photocatalytic degradation of methylene blue dye from aqueous solution have been investigated. In this light, based on the small crystallite size and high surface area, the as-prepared analcime phase (generated using aluminum isopropoxide) and the mixed phase of analcime and nacrite (prepared using sodium aluminate) have been used for this investigation. The effect of the contact time on the adsorption efficiency of the aforementioned zeolite

Table 3

<table>
<thead>
<tr>
<th>Aluminum precursor used for zeolite preparation</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Intra particle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$Q_e$ (mg/g)</td>
<td>$K_1$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Aluminum isopropoxide</td>
<td>0.89</td>
<td>0.49</td>
<td>0.0063</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>0.75</td>
<td>1.07</td>
<td>0.0387</td>
</tr>
</tbody>
</table>

\[ n^2 = 1 + \left( \frac{A}{E_g + B} \right)^2 \]  \hspace{1cm} (8)

where, $n_0 = 1.73$, $\alpha = 1.9017$ eV$^{-1}$, $\beta = 0.539$ eV$^{-1}$, A is hydrogen ionization energy (= 13.6 eV), and B is a constant (the difference between UV resonance energy and band energy gap (= 3.47)). In addition, limiting dielectric constant ($\varepsilon_\infty$), linear optical susceptibility ($\chi$) and reflectivity ($R$) have been determined by utilizing Eqs. (9), (10), and (11), respectively.

$$\varepsilon_\infty = n^2$$  \hspace{1cm} (9)

$$\chi = \varepsilon_\infty - 1$$  \hspace{1cm} (10)

$$R = [(n-1)/(n+1)]^2$$  \hspace{1cm} (11)

![Fig. 8. Photocatalytic degradation of methylene blue dye over zeolite sample prepared using aluminum isopropoxide precursor under UV irradiation in the absence of H$_2$O$_2$ (A–C) and in the presence of H$_2$O$_2$ (D–F).](image-url)
adsorbents for the removal of methylene blue dye was examined under the experimental conditions: 0.1 g of adsorbents, 50 mL of MB dye with an initial concentration of 10 mg/L at 25 °C. The results are displayed in Fig. 6(A) and (C), respectively. The data exhibited that the dye % removal using the as-prepared analcime zeolite enhanced rapidly until it reached ca. 24.85% in 150 min and the equilibrium state was attained, as shown in Fig. 6(B). The zeolite products, prepared using sodium aluminate precursor (i.e. a mixed phase of analcime and nacrite), % removal increased with increasing the contact time and reached 83.28% in only 60 min where the adsorption process attained the equilibrium state as depicted in Fig. 6(D). Notably, the equilibrium state was attained owing to saturation of active sites of the adsorbents at the equilibration time of adsorption. In addition, adsorption kinetics has a crucial role in the explanation of the adsorption mechanisms. Therefore, we have investigated adsorption of MB dye on the as-prepared zeolites using the following kinetic models: pseudo-first-order (Eq. (12)), pseudo-second-order (Eq. (13)) and intra-particle diffusion (Eq. (14)) [26].

\[
\log \left( \frac{Q_e}{Q_t} \right) = \log \left( \frac{Q_e}{K_1 t / 2.303} \right)
\]

\[
t / Q_t = \left( \frac{1}{K_2 Q_e^2} \right) + \left( \frac{1}{Q_e} \right) t
\]

\[
Q_t = K_{int} t^{0.5} + C
\]

where, \( Q_e \) (mg/g) is the adsorbed dye at equilibrium, \( Q_t \) (mg/g) is the adsorbed dye at time \( t \) (min), \( K_1 \) (1/min) is the pseudo-first-order rate constant of the adsorption process, \( K_2 \) (g/mg·min) is the pseudo-first-order rate constant of the adsorption process, \( K_2 \) (g/mg·min) is the pseudo-second-order rate constant of the adsorption process, \( K_3 \) (g/mg·min) is the intra-particle diffusion rate constant of the adsorption process.

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**Fig. 9.** Photocatalytic degradation of methylene blue dye over zeolite sample prepared using sodium aluminate precursor under UV irradiation in the absence of \( \text{H}_2\text{O}_2 \) (A–C) and in the presence of \( \text{H}_2\text{O}_2 \) (D–F).

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**Fig. 10.** Photocatalytic degradation of methylene blue dye without presence of any photocatalyst under UV irradiation in the absence of \( \text{H}_2\text{O}_2 \) (A, B) and in the presence of \( \text{H}_2\text{O}_2 \) (C, D).
second-order rate constant of the adsorption process, $C$ (mg/g) is the thickness of boundary layer, and $K_{int}$ (mg/(g·min$^{0.5}$)) is internal diffusion constant. $K_1$ and $Q_{e\text{cal}}$ values in (Eq. (12)) were determined by plotting log($Q_e - Q_t$) versus $t$, as shown in Fig. 7(A, D). Besides, $K_2$ and $Q_{e\text{cal}}$ values were calculated utilizing the plot of $t/Q_t$ against $t$ (Fig. 7(B, E)), and $K_{int}$ and $C$ values were estimated from the plot of $Q_t$ versus $t^{0.5}$ (Fig. 7(C, F)). The estimated kinetic parameters of the adsorption of MB dye on the as-prepared zeolites are listed in Table 3. The obtained results revealed that the adsorption of methylene blue dye over the zeolite adsorbents followed pseudo-second-order model because the value of the correlation coefficients ($R^2 = 0.99$) was close to unity compared to those obtained from the pseudo-first-order model ($R^2 = 0.89$ and 0.75) (Fig. 7(B, E)). Moreover, the fitness of pseudo-second-order model for describing the adsorption data was supported from the closeness of the calculated and experimental adsorption capacity as listed in Table 3. The intra-particle diffusion model supposes that the rate-controlling mechanism of methylene blue dye adsorption. However, the adsorption mechanism of methylene blue dye on the zeolite adsorbent was also controlled by some other mechanisms such as film diffusion and bulk diffusion [25,26].

Furthermore, the photocatalytic activity of the as-synthesized zeolites for the degradation of MB dye has been examined after attaining the adsorption-desorption equilibrium, as mentioned before. The photocatalytic degradation of MB dye over the as-synthesized zeolite photocatalysts was performed under UV irradiation. The results are displayed in Fig. 8(A, B, C) and (D, E, F), for the zeolite photocatalysts prepared using aluminum isopropoxide and sodium aluminate precursors, respectively. The results revealed that zeolite photocatalyst prepared using aluminum isopropoxide precursor degraded MB dye under UV illumination. The photocatalytic degradation percentage, under UV illumination, reached about 85% within 180 min and 100% within 110 min in the absence and presence of H$_2$O$_2$, respectively, as shown in Fig. 8. It was noted that the percentage of 85% remained constant with increasing irradiation time because the degraded compounds might block the effect of UV light.

On the other hand, the photocatalytic degradation efficiency of the zeolite product, prepared using sodium aluminate, reached about 100% within 180 and 120 min in the absence and presence of H$_2$O$_2$, respectively, as displayed in Fig. 9(A–F). Notably, degradation of MB dye was also investigated in the absence of the as-prepared photocatalysts under UV illumination in the presence of H$_2$O$_2$, and the results were depicted in Fig. 10(A–D). It was noticed that the degradation efficiency was higher and faster in the presence of the as-prepared zeolite materials.

Moreover, the photocatalytic degradation of MB dye over the as-prepared zeolite photocatalysts was quantitatively examined using the pseudo-first-order kinetic model (Eq. (15)), and the observed first-order rate constant ($K_{obs, 1}$) was calculated [21].

$$\ln \left( \frac{C_t}{C_0} \right) = -K_{obs, 1} t$$

where, $C_t$ (mg/L) is the remaining dye concentration at irradiation time $t$ and $C_0$ (mg/L) is the dye concentration after the adsorption equilibrium. Plotting $\ln(C_t/C_0)$ against $t$ of the photocatalytic degradation data are displayed in Fig. 8(C, F) and Fig. 9(C, F), for the zeolite photocatalysts prepared using aluminum isopropoxide and sodium aluminate precursors, respectively. The calculated $K_{obs}$ constants for both aforementioned photocatalysts are presented in Table 4. The results exhibited that the as-prepared zeolite photocatalyst generated from aluminum isopropoxide has the highest catalytic activity with $K_{obs}$ of 0.037 min$^{-1}$ under UV illumination in the presence of H$_2$O$_2$.

Table 4

<table>
<thead>
<tr>
<th>Aluminum precursor used for zeolite preparation</th>
<th>UV irradiation</th>
<th>UV irradiation + H$_2$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum isopropoxide</td>
<td>0.998</td>
<td>0.99</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>0.95</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Scheme 1. Proposed reactions of the photodegradation of MB dye in the presence of (UV only), (Zeolite + UV), and (Zeolite + H2O2 + UV).
In addition, the mechanism of photo-degradation process using UV only, (Zeolite + UV), and (UV + eolate + H2O2) has been depicted in Scheme 1. The excited methylene blue dye molecules will convert O₂ to O₂• when the dye molecules absorb UV-light. Then, the produced O₂• radicals may react with protons (generated from the autoprotolysis of water) to generate superoxide radicals, OOH•. Afterward, those produced radicals may eventually degrade MB dye molecules completely to carbon dioxide, water, and mineral acids [21]. Photocatalytic degradation of methylene blue dye molecules in the presence of zeolite, under UV illumination, usually includes the separation of electron-hole pairs, generated on the surface of zeolite, and the subsequent reduction–oxidation reactions. The electrons can be scavenged by the adsorbed molecular oxygen species, and the holes can be trapped by water or adsorbed methylene blue molecules. Then, methylene blue dye molecules may be degraded directly by the influence of photo-generated oxidants. Furthermore, adding hydrogen peroxide in the presence of zeolite and UV light may enhance the photo-degradation rate of methylene blue dye because the direct decomposition of hydrogen peroxide under UV light generating OH• radicals which directly may oxidize methylene blue dye molecules to carbon dioxide, water, and mineral acids, as shown in Scheme 1.

5. Conclusion

Different zeolite nanostructures have been prepared using a hydrothermal treatment of different aluminum precursors and Ludox AS30 colloidal silica. In this light, we have tuned the morphology, produced phase, and crystallite size of the zeolite products using different aluminum sources such as aluminum sulfate, aluminum chloride, aluminum isopropoxide, alumina, aluminum metal, and sodium aluminate. Interestingly, aluminum isopropoxide, alumina and aluminum metal precursors produced anatase phase while sodium aluminate generated a mixture of analcime and nacrite phases under the hydrothermal treatment of interest. The produced products have different morphologies and particle sizes based on the used aluminum precursor. The calculated optical energy gaps (Eg) revealed the semiconducting properties of the produced zeolites. The zeolite products prepared using aluminum isopropoxide and sodium aluminate showed simultaneous adsorption and photocatalytic properties; therefore, those samples were proposed as good candidates for the removal of MB dye from aqueous media.

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