Research Article

Photocatalytic Degradation of Methylene Blue from Aqueous Medium onto Perlite-Based Geopolymer

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In this work, geopolymer synthesized with perlite and an alkaline activator medium was evaluated as a new adsorbent and photocatalyst for degradation of methylene blue (MB) dye from an aqueous medium. The functional group, the structure, and the morphology of the raw and the synthesized materials were characterized using FT-IR, XRD, and SEM analysis. The degradation of MB in the contaminated solution was examined using the spectrophotometric technique. Several analysis methods revealed the formation of the aluminosilicate gel after the geopolymerization reaction. The kinetics data with UV and without UV irradiations were well fitted with the pseudo-second-order equation. The results indicated that the degradation efficiency of cationic dye by perlite-based geopolymer without and with UV was up to 88.94% and 97.87% in 4 hours, respectively. The degradation efficiencies of methylene blue are in the following order: perlite-based geopolymer under UV irradiations is greater than perlite-based geopolymer without UV irradiations that is larger than UV irradiations. The overall experimental results suggested that the new elaborated material with synergetic adsorption and photocatalytic activities has a great potential for the treatment of water contaminated by hazardous substances.

1. Introduction

One of the major water-consuming industries in the world is the textile one, with an average of 1.6 million liters of water per day [1]. The textile industry uses a variety of chemical compounds that pollute water, such as dyes, heavy metals, and surfactants. The previously cited compounds are hazardous and hard to deteriorate. This makes them even more dangerous to the environment, which is why it needs to be removed from wastewaters before discharge in the aqueous system. Several wastewater treatment techniques such as ultrafiltration [2], membrane separation [3], ion exchange [4], coagulation/flocculation [5], electrochemical processes [6], adsorption [7, 8], and photocatalytic degradation [9] have been used to remove and degrade the dyes from water and wastewater. The photocatalytic degradation method is based on the degradation of organic pollutants in the presence of UV and a material doped by a photocatalyst. TiO₂ and ZnO are the most efficient photocatalyst materials used for degradation of organic pollutants from water and wastewaters [10]. The photodegradation technique presents a problem to eliminate products formed in the aquatic environment after photocatalytic degradation process. In the last years, several research studies have been focused on the synthesis of materials generally obtained by dispersing photocatalysts in natural materials or synthetic origin and developed the matrices rich by photocatalytics. These matrices have good chemical and physical properties, high degradation and adsorption capacities of organic pollutants, and ease of use and respects the environmental system. During the last decade, many studies have been focused on the organic pollutant degradation onto formed materials such as organic-inorganic hybrid nanocomposites [11], chitosan-gelatin-based hydrogel [12], Gd-TiO₂- GO nanocomposites [13], graphene/geopolymer nanocomposites [14], and fly ash-based geopolymer [9]. Among them, the
materials synthesized in this technique are geopolymers which are the inorganic polymers synthesized by aluminosilicate precursors. They can be natural (perlite, clay, etc.) or synthetic (fly ash, metakaolin, etc.) materials activated by alkaline activator solutions at a temperature below 100°C [15]. These materials used as adsorbents can adsorb harmful organic substances from the aquatic environment. The organic pollutant molecules adsorbed on the surface of these synthesized materials were not degraded. In order to resolve this issue, UV irradiation can be used since it is able to degrade the molecules that remain in the solution and adsorbed on the surface of the matrices. This study aimed to elaborate a perlite-based geopolymer using expanded perlite and alkali solution. The obtained material was valued as the photocatalyst and an adsorbent for the degradation and the photocatalytic processes were conducted out in the photocatalytic reactor and were carried out under similar conditions (C<sub>i</sub> = 30 mg/L, pH = 5). In our work, 0.1 g of the perlite-based geopolymer photocatalyst was added into a reactor that was filled with 100 mL of aqueous media contaminated by methylene blue of 30 mg/L. The reaction suspension was stirred at a constant speed (250 rpm). The ultraviolet light source was supplied by a mercury lamp of the Osram HQL 125WE27 type emitting a wavelength between 254 and 380 nm. At given time intervals, the reaction mixture was centrifuged in a centrifuge (ROTOFIX 32A) to separate the supernatant (catalyst particles) and the polluted solution. The filtrates were characterized with a UV-Vis spectrophotometer at a maximum absorption wavelength of 665 nm. The degradation efficiency was determined from the following equation [19]:

\[
\text{degradation efficiency} (\%) = \frac{A_0 - A_t}{A_0} \times 100 = \frac{C_0 - C_t}{C_0} \times 100.
\]

(1)

A<sub>0</sub> and A<sub>t</sub> are the initial absorbance and absorbance of dye at time t and C<sub>0</sub> and C<sub>t</sub> are the initial concentration and concentration of dye at time t (mg/L).

2.4. Adsorption and Photodegradation Test. The adsorption and photodegradation phenomena were evaluated by monitoring the efficiency degradation of organic compound methylene blue in aqueous solution using the perlite-based geopolymer. The photocatalytic processes were conducted out in the photocatalytic reactor and were carried out under similar conditions (C<sub>i</sub> = 30 mg/L, pH = 5). In our work, 0.1 g of the perlite-based geopolymer photocatalyst was added into a reactor that was filled with 100 mL of aqueous media contaminated by methylene blue of 30 mg/L. The reaction suspension was stirred at a constant speed (250 rpm). The ultraviolet light source was supplied by a mercury lamp of the Osram HQL 125WE27 type emitting a wavelength between 254 and 380 nm. At given time intervals, the reaction mixture was centrifuged in a centrifuge (ROTOFIX 32A) to separate the supernatant (catalyst particles) and the polluted solution. The filtrates were characterized with a UV-Vis spectrophotometer at a maximum absorption wavelength of 665 nm. The degradation efficiency was determined from the following equation [19]:

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2.5. Data Analysis. In this work, the pseudo-first-order, pseudo-second-order kinetic, and intraparticle diffusion models [18] were investigated to study the nature of the adsorption of the methylene blue molecules using the perlite-based geopolymer. Table 2 displays the equations and mathematical parameters of kinetic models.

3. Results and Discussion

3.1. Morphology and Structure of Samples

3.1.1. XRD Analysis. The X-ray diffraction patterns (XRD) were used to reveal the structure existing in perlite before and after the geopolymerization process. The X-ray diffraction patterns (XRD) of the perlite and synthesized material are exhibited in Figure 1. As shown, perlite is essentially consisting of amorphous mineral phases observed between 10° and 40° (2θ). After the geopolymerization reaction, the amorphous dump or halo has shifted to higher angles from 20 to 42° (2θ). This shifting reveals the formation of the new amorphous alumino-silicate phase in the geopolymer structure [20].

3.1.2. FTIR Analysis. FTIR analysis was used to indicate the functional groups existing in the raw material before and after activation. The FT-IR spectra of the samples are given in Figure 2. For perlite, the band located at 1632 cm<sup>-1</sup> is assigned to the vibration of OH groups. The large band observed at 1005 cm<sup>-1</sup> is assigned to the stretching vibrations of Si-O-M (M = Al or Si) [21]. The band located at
The band located at 1431 cm\(^{-1}\) is attributed to antisymmetric vibrations of CO\(_2\)^{3−} ions, revealing that sodium carbonate is present in the structure of the geopolymer [21]. The absorption band at 878 cm\(^{-1}\) is related to Si-O-Al stretching vibration. The stretching vibration of Si-O-M (M = Al or Si) at 1005 cm\(^{-1}\) in perlite shifted approximately 65 cm\(^{-1}\) after the activation process to 940 cm\(^{-1}\). The shifting and reduction of the large band of the raw material after activation of perlite are due to the dissolution of the perlite particles by the alkaline solution and the formation of the geopolymer material. These results are confirmed by XRD analysis.

### 3.1.3. SEM Analysis

SEM micrographs of the perlite and perlite-based geopolymer are shown in Figure 3. The structure of the raw material (Figure 3(a)) can be described as irregular particles with broken or ragged edges and flake-like form [23]. SEM image of activated perlite is presented in Figure 3(b). This micrograph revealed the formation of aluminosilicate gel in the perlite structure. This change in the perlite morphology indicates the dissolution of the precursor particles by alkali solution and the formation of aluminosilicate gel in the structure of the raw material [24].

### 3.1.4. Optical Study

The absorbance spectrum of the as-prepared sample is depicted in Figure 4. The optical band gap energy (\(E_g\)) was estimated based on absorbance data, as proposed by Wood and Tauc [25, 26]. According to Tauc equation, the optical absorption coefficient (\(\alpha\)) is related to the energy band gap by

\[
(\alpha h\nu) = A(h\nu - E_g)^n,
\]

where \(A\) is a constant of proportionality depending on the material, \(h\nu\) is the photon energy, and \(n\) is a constant that depends on the nature of the transition (2 for an indirect allowed transition and 1/2 for a direct allowed transition). The sample is found to depict an indirect optical band gap, and the extrapolation of the \((\alpha h\nu)^{0.5}\) vs. \(h\nu\) slope (inset of Figure 4) to the zero value of \((\alpha h\nu)^{0.5}\) gives an indirect optical band gap energy of 3.82 eV, affirming the semiconductor behavior of the sample [27, 28].
3.2. Degradation of Methylene Blue with UV. The study of the degradation of methylene blue in the aqueous solution by UV irradiation is presented in Figure 5. The results obtained from the variation in the absorbance of the pollutant over time show that the degradation of methylene blue by UV irradiation passed through series of decomposition. The first reaction is the oxidation of water molecules by UV irradiation to form hydroxyl radicals (\(\cdot\)OH). These radicals then attacked the N-S heterocyclic chromophore group and form intermediate products after series of reactions \[9\]. These obtained products were degraded and conducted to simple products such as H\(_2\)O and CO\(_2\) \[29, 30\]. Similar result was reported by Lin et al. \[31\].

3.3. Degradation of MB Dye at Different Conditions. To evaluate the photodegradation and degradation of MB dye by the perlite-based geopolymer, three experimental processes are carried out as presented in Figure 6. The first part of the experiments is to follow the degradation of MB alone in the solution under UV excitation. The second part is focused on the study of the adsorption of this pollutant in the presence of the geopolymer without UV irritation. The last step is dedicated to the investigation of the adsorption of
methylene blue by the geopolymer in the presence of UV irradiation. When the aqueous solution contaminated by MB is exposed to UV irradiation without a perlite-based geopolymer photocatalyst, the degradation efficiency rate is as low as 14.02% for 4h. The second approach shows a high degradation efficiency (88.94%) of the dye removal by the synthesized product without UV for 4h. The last approach indicated the highest degradation efficiency (97.87%) of dye removal by the formed material catalytic under UV for 4h. This mechanism of the photocatalytic reaction process can be presented as follows. Firstly, the organic pollutant can ionize as a cationic product in the aqueous medium, and then the cations are adsorbed on the perlite-based geopolymer structure surface, as presented in equations (3) and (4). When the metal oxide semiconductor particles of Fe2O3 in the raw material (in Table 1) are irradiated by UV, the excited electron (e−) and hole (h+) pairs are formed, as presented in equation (5). Subsequently, the transition metal ions of Fe3+ in the material ensnare electron (e−) and hole (h+) combine with H2O molecule to produce hydroxyl radical (equations (6) and (7)). Finally, the cations of MB dye adsorbed on the framework of theperlite-based geopolymer are oxidized by hydroxyl radicals to form the degradation products in equation (8). By comparing the experimental results, it can be seen that the degradation efficiency of MB which is of the order of the geopolymer with UV irradiations is greater than the adsorption by the geopolymer without UV irradiations which is larger than UV irradiations without the geopolymer (direct photolysis).

The perlite-based geopolymer, associated with UV radiations, possesses better adsorption and photodegradation properties for methylene blue molecules than the perlite-based geopolymer without UV. This performance is due to the synergistic effect rather than simple linear combination of the perlite-based geopolymer powder and UV irradiation for removal of methylene blue from aqueous solution.

### 3.4. Adsorption Kinetics

Adsorption kinetic was used to characterize the nature of the adsorption process between adsorbent and adsorbate. The kinetic models of methylene blue onto the perlite-based geopolymer were evaluated by three kinetic equations (Table 2). The experimental results of MB adsorption by the perlite-based geopolymer with and without UV irradiation are presented in Figures 7–9. The kinetic parameters and the determined coefficients are depicted in Table 3. The correlation coefficients by the pseudo-second-order equation are closer and more accurate compared with pseudo-first-order and intraparticle diffusion equations. The calculated qe values (15.51 mg/g under UV and 15.28 mg/g without UV) were close to the observed experimental values (qexp = 15.18 mg/g under UV and 15.20 mg/g without UV), respectively. This result revealed that the adsorption of MB dye by the perlite-based geopolymer under UV and without UV is following by the pseudo-second-order model. This kinetic model confirms that the adsorption process is based on chemisorption. This phenomenon can be explained by the interaction between the negatively charged adsorbent and the positively charged adsorbate [18].
4. Conclusion

The geopolymer produced by the alkali activator and perlite is used as an adsorbent and photocatalyst for degradation of cationic dye in aqueous media. The analysis by several methods revealed the formation of a new photocatalyst product. The kinetic data of the removal of dyestuff on the surface of the synthesized material were fitted by the pseudo-second-order model. The results obtained in this study suggest that the perlite-based geopolymer could be used as an efficient adsorbent and photocatalytic for the treatment of methylene blue contaminants in aqueous media.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Figure 8: Plots of the pseudo-order kinetics of MB dye adsorption on the geopolymer (a) without UV and (b) with UV.

Figure 9: Plots of the intraparticle kinetics of MB dye adsorption on the geopolymer (a) without UV and (b) with UV.

Table 3: Parameters of kinetics models for the adsorption of MB on the geopolymer.

| Condition  | $q_{ex}$ (mg/g) | Pseudo-first-order | Pseudo-second-order | Intraparticle diffusion |
|------------|----------------|--------------------|---------------------|------------------------|
|            |                | $k_1$ (min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | $k_2$ (g/(mg min)) | $q_e$ (mg/g) | $R^2$ | $k_p$ (mg/(g min$^{1/2}$)) | $I$ | $R^2$ |
| Without UV | 15.18          | 0.008              | 5.94               | 0.78 | 0.004 | 15.51           | 0.99 | 0.118 | 12.60 | 0.88 |
| With UV    | 15.20          | 0.011              | 2.59               | 0.70 | 0.020 | 15.28           | 0.99 | 0.047 | 14.30 | 0.67 |
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