Original Article

Evaluation of methylene blue removal by plasma activated palygorskites

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ABSTRACT

Clay minerals with fibrous morphology, such as palygorskite, have been applied as adsorbents to remove pollutants from the environment and reduce toxic compounds, such as dye, in aquatic media. Although natural palygorskite has good dye removal performance, chemical modification can improve its adsorption sites and desired properties. In this study, palygorskite was activated in H2/N2 plasma flow for 2, 4, and 6 h to produce new adsorbents for the removal of methylene blue (MB). The solids were characterized using X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetry, scanning electron microscopy (SEM) coupled to dispersive energy X-ray spectrometry and nitrogen adsorption/desorption measurements. The plasma technique induced structural defects in the palygorskite by the removal of coordinated and zeolithic water molecules, which altered the palygorskite’s specific surface area and pore volume. The adsorption capacity of the activated plasma samples for the removal of MB increased from 35.66 in the natural palygorskite to 54.17 mg g−1 in the activated samples.

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1. Introduction

In the last decade, studies were conducted to minimize the environmental pollution caused by effluents released by the textile industry and other organic compounds [1–10]. Dyes are resistant to chemical, photochemical or biological degradation [5,7,11–13]. Additionally, the toxic nature of dyestuff has teratogenic, mutagenic, and carcinogenic effects on aquatic and human organisms [14].

Methylene blue (MB) is a potential pollutant that has been accumulating in water bodies, owing to its use in various areas [14–16]. Amongst the various processes for removing organic or inorganic pollutants from water [17–20], adsorption is a promising technique because it offers flexibility, efficiency, and reversibility [21–23]. In this context, several materials have been investigated for the removal of pollutants from water. Amongst these materials, biochar (BC) and graphene have
been widely investigated [24,25]. These types of carbon materials have some desirable properties, including large specific surface area, excellent ion exchange capacity, high porosity, and abundant oxygen functional groups [24,26]. However, the development of new materials with properties similar to those of BC materials has been attracting attention, and mineral-based adsorbents have been reported to have great application potential in wastewater treatment [21,27,28].

Palygorskite is a clay mineral with a 2:1 layered structure and fibrous morphology. This mineral has unique properties, such as high chemical stability, large surface area, porous structure, and Lewis and Bronsted acids on its surface [29–32]. Moreover, palygorskite has low cost, high availability, and easy handing. In the industry, clay minerals, including palygorskite, are used as general adsorbents for the treatment of contaminated water and sewage, and also naturally eliminate cationic and anionic pollutants by ion exchange, adsorption, or a combination of both [33–35].

Natural clay minerals can also be modified to improve their physical and chemical characteristics and adsorption properties. Different methods of modifying clay minerals include acid activation [36], thermal [37], solvothermal [38] and magnetic approaches, intercalation [39], organophilization [40], and others. However, some processes occasionally require expensive chemicals that also generate byproducts that are harmful to the environment [29,41].

The chemical modification of clay minerals using plasma is an emerging method. Plasma is generated under low pressure and contains chemical species, free radicals, heat species, and ultraviolet (UV) radiation in different concentrations [42]. In the plasma treatment process, gases such as argon (Ar), oxygen (O2), nitrogen (N2), and carbon dioxide (CO2), are applied to the materials’ surface to obtain or improve the desired surface properties [43]. Plasma treatment is an innovative, efficient, and non-polluting material modification method that can be used to improve the performance of adsorbents by the formation or activation of surface functional groups for pollutant adsorption in aqueous solutions [43–47].

Various studies have attempted to improve the surface of clay mineral samples such as bentonite [45] and kaolinite [48]. Montmorillonite has been treated in an aqueous suspension with gliding arc plasma to modify its surface properties, including the formation of more hydroxyl groups on the edges of the silicate [49]. Montmorillonite powder has also been plasma-treated with argon [50], and it was observed that gradual dehydrozation was accompanied by increasing disorder in the interlayer structure during the early stages of dehydrazion. However, to the best of our knowledge, this approach has not been implemented in palygorskite modification using the plasma technique.

The objective of this study was to develop new adsorbents based on clay minerals for MB removal by activating palygorskite using the plasma technique as a viable alternative. Considering that the success of adsorption depends on selecting an appropriate adsorbent [51], this paper describes, for the first time, the activation of a palygorskite clay mineral through plasma treatment (H2/N2) for 2, 4, and 6 h. Natural and activated palygorskite was used to remove the MB dye, and the influence of various experimental parameters on adsorption, including the adsorbent dosage, pH, time, concentration, and temperature, was systematically investigated. Finally, the experimental data were fitted to different kinetic and isothermal equilibrium models, and a possible mechanism for adsorbent-adsorbate interaction is proposed.

2. Methods

2.1. Materials and chemicals

The palygorskite used in this study was collected at Guadalupe (latitude: 6.79166 south; longitude: 43.57059 west) in the state of Piauí, Brazil. The chemicals used in this study were hydrogen peroxide (Impex), hydrochloric acid (Dynamic), sodium hydroxide (Dynamic), and MB dye (Contemporary Chemical Dynamics). All reagents were analytical grade and deionized water was used in all preparations.

2.2. Palygorskite purification

The clay mineral was deagglomerated by maceration, then sieved to a particle size below 125 μm, and suspended in deionized water. To remove the organic material, the sample was treated with hydrogen peroxide according to a previously reported procedure [52]. The process consisted of treating a 100.0-g palygorskite sample with 150 mL of 30% (w/w) hydrogen peroxide solution, and keeping the mixture under constant mechanical agitation for 24 h [52]. Subsequently, the solid (PAL-N) was separated by centrifugation, washed to remove excess hydrogen peroxide, dried in an oven at 100 °C for 24 h, and sieved again [53].

2.3. Modification of palygorskite using plasma technique

To perform the plasma modification, samples of purified palygorskite (PAL-N) with an approximate mass of 1.5 g were shaped into pellets with a diameter of 2 cm and thickness of 0.5 mm. By using pellets, drag is avoided when the sample is plasma-treated. The system (Fig. SM1) used in the plasma technique was manufactured by SDS Plasma, and operated with a current of 2 A and maximum voltage of 1200 V. In the vacuum chamber, the samples were exposed to gases controlled by flowmeters, which regulated the internal atmospheric pressure and temperature. The plasma technique consists of pre-sputtering the pellets with a flow rate of 160 mL·min−1 Ar and 40 mL·min−1 H2 at 1.5 Torr and 150 °C for 1 h. Then, the pellets were plasma-treated with a flow rate of 80 mL·min−1 H2 and 20 mL·min−1 N2 under 2.5 Torr at 200 °C for 2, 4 and 6 h. The tablet surfaces were later scraped and stored in a desiccator under a controlled atmosphere before characterization [42,45]. The samples were named PAL-xH, where x refers to the treatment time (2, 4, and 6 h).

2.4. Characterization

The materials were characterized using structural, textural, thermal, and morphological techniques. X-ray diffraction (XRD) patterns were carried out using a Shimadzu model D600-XRA with CuKα radiation (λ = 0.15406 nm), operating at 40 kV
and 30 mA. The angle 2θ was measured in the range of 2 to 40° with a scan speed of 2° min⁻¹. Fourier transform infrared spectra (FTIR) were obtained using a Bruker Vertex 70 FTIR spectrophotometer. The measurements were made using the 1% sample KBr pellet method in the 4000-400 cm⁻¹ region, in transmission mode, and 64 scans with a resolution of 4 cm⁻¹. Thermal analysis (TG/DTG) was performed using the Q600 SDT instrument (TA Instruments) in the temperature range of 10 to 1000 °C with a heating rate of 10 °C min⁻¹ and an argon flow of 100.0 mL min⁻¹. The morphology of the samples was verified using a scanning electron microscope coupled with a field electron emission (EGF) dispersive energy X-ray spectrometer (EDS; Quanta FEI 250). The nitrogen adsorption/desorption measurements were made using the 2200 E instrument (NOVA). Before measuring, all samples were outgassed at 150 °C for 2 h. The specific surface area and pore volume were determined using the BET method [54].

2.5. Adsorption tests

Adsorption assays were systematically conducted to evaluate the influence of various parameters, such as the adsorbent dosage, pH, contact time, concentration, and temperature. The adsorption tests were carried out in triplicate, and the mean values were recorded.

2.5.1. Adsorbent dosage

Batch experiments were conducted for the adsorption isotherm by suspending a fixed mass of adsorbent with a dye volume in a series of flasks containing MB solutions with specific concentrations. In the adsorbent dosage investigation, 40.0 mL of the 100.0 mg L⁻¹ solution were used, and the mass of each solid ranged from 20.0 to 50.0 mg. The suspension was stirred at room temperature for 24 h. Then, centrifugation was performed, the aliquots were removed from the supernatant solution, and the amount of dye was determined by UV-Vis spectrometry with a Cary 60 UV-VIS ultraviolet-visible spectrophotometer at 555 nm [3,55].

The amount of adsorbate retained in each of adsorbent, \( q_e (\text{mg g}^{-1}) \), was calculated using Eq. (1) [56,57], as follows:

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

where \( C_i \) (mg L⁻¹) is the initial adsorbate concentration, \( C_f \) (mg L⁻¹) is the final adsorbate concentration, \( m \) (g) is the adsorbent mass, and \( V \) (L) is the volume of the adsorbent-adsorbate solution.

2.5.2. Influence of pH

The pH investigations were conducted with 40-mL solutions at a dye concentration of 100 mg L⁻¹ and pH 3-12, in contact with the 10-mg mass of the adsorbent samples (PAL-N, PAL-2H, PAL-4H, and PAL-6H) under stirring at room temperature for 24 h. The initial pH was adjusted with 0.1 mol L⁻¹ NaOH or HCl solutions. The investigation did not consider pH values lower than 3 or higher than 12, because the dye exhibited spectral changes related to the displacement of the maximum absorption wavelength. The procedure described in Section 2.5.1 was adopted to quantify the MB in the solution and determine the pollutant removal.

2.5.3. Influence of contact time

The contact time was investigated with the optimal adsorbent dosage and pH. Therefore, the dye/solid samples were constantly agitated at room temperature at different times for 5–180 min. Subsequently, the suspensions were centrifuged and the dye in the supernatant was quantified.

2.5.4. Influence of initial dye concentration and temperature

The effect of the initial concentration on adsorption was investigated between 10.0 and 100.0 mg L⁻¹ of dye concentration using the solid mass and pH determined by a previous study. The samples with 40.0 mL of dye solution and adsorbent were agitated for a duration equal to the adsorption equilibrium time at different temperatures (25, 35 and 45 °C). Then, the solid was separated to determine the dye concentration in the supernatant [58–60].

2.5.5. Kinetic models

The linear forms of the pseudo-first order [61], pseudo-second order [62], and intraparticle diffusion [63] equations expressed by Eqs. (2–4), respectively, were applied to the experimental adsorption data.

\[
\ln(q_e,\text{exp} - q_t) = \ln(q_e,\text{cal}) - k_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e,\text{cal}^2} + \frac{1}{q_e,\text{cal}} t
\]

\[
q_t = K_{id} t^{1/2} + C
\]

where \( q_{e,\text{exp}} \) (mg g⁻¹) is the amount adsorbed per gram of adsorbent, \( q_t \) (mg g⁻¹) is the amount adsorbed per gram of adsorbent at time \( t \) (min), \( k_1 \) (min⁻¹) is the pseudo first order adsorption rate constant, \( k_2 \) (g (mg min⁻¹) is the pseudo-second order velocity constant, \( K_{id} \) (mg g⁻¹ min⁻¹/2) is the intraparticle diffusion constant, and \( C \) (mg g⁻¹) is the constant related to the diffusion resistance.

2.5.6. Equilibrium models

The experimental data for the concentration isotherms were fitted to the Langmuir [64] and Freundlich models [65] using the linear forms of Eqs. (5) and (6), as follows:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]

\[
\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e
\]

where \( q_e \) (mg g⁻¹) is the equilibrium adsorption capacity, \( C_e \) (mg L⁻¹) is the equilibrium concentration of the pollutant, \( q_{\text{max}} \) (mg g⁻¹) is the theoretical maximum amount of the equilibrium pollutant, \( K_L \) (L mg⁻¹) is the Langmuir constant, \( K_f \) (L g⁻¹) is a constant related to the adsorption capacity, and \( n_f \) is a constant related to the adsorption intensity and adsorption spontaneity.
3. Results and discussion

3.1. Characterization

The XRD patterns of the palygorskite before and after plasma modification are shown in Fig. 1a. The reflections were indexed based on the JCPDS-ICDD crystallographic cards 31-0783 (palygorskite) and 85-0794 (quartz). The XRD of pure palygorskite exhibited the typical indexed planes of (8.46°, 110), (19.88°, 040), (20.88°, 121), and (35.50°, 161), and quartz impurity (2θ = 26.66°, d = 0.34 nm; 2θ = 32°, d = 0.276 nm). These results are in agreement with the results obtained by previous studies [31,53,66].

The characteristic reflections of palygorskite were maintained by all samples after plasma treatment; however, some alterations in the reflection positions were observed. For PAL-2H, the 2θ values changed to 8.38°, 19.80°, 20.72°, and 35.26°; for PAL-4H, they changed to 8.46°, 19.88°, 20.9°, and 35.42°; for PAL-6H, they changed to 8.54°, 19.86°, 20.86°, and 35.44°. The alterations in the 2θ values occurred in the following order PAL-2H < PAL-4H < PAL-6H. Therefore, the higher exposition of the sample to plasma treatment resulted in higher modifications in the long range order. Notably, these changes were associated with small distortions in the clay mineral structure [31,67].

Fig. 1b shows the infrared spectra for PAL-N, PAL-2H, PAL-4H, and PAL-6H. The PAL-N spectrum exhibited several characteristic palygorskite bands, which agrees with the results obtained by previous studies [30,35,64]. The band at 3545 cm⁻¹ is attributed to the characteristic OH stretching in the Al-Fe³⁺-OH or Al-Mg-OH groups; the 3616 and 3269 cm⁻¹ bands correspond to OH stretching in the octahedral Me-OH sites (Me: Mg, Al, Fe); the 3552, 3404, and 1658 cm⁻¹ bands are related to the OH vibrations of the coordinated and zeolitic water molecules; the 1196 cm⁻¹ band is attributed to the Si-O stretching; the 1436 cm⁻¹ band is associated with carbonate impurities; the 1093 and 512 cm⁻¹ bands are associated with the Si-O-Si vibrations; the 910 cm⁻¹ band corresponds to the deformation of the Al-OH bond [26,52,66,68]. By comparing all spectra shown in Fig. 1b, alterations in the short range order were observed when the same absorptions occurred in the samples after plasma treatment under the conditions considered in this study. Therefore, the infrared investigation did not indicate the introduction of new functionalities on the clay surface after the plasma treatment modified the active surface.

The thermogravimetric curves (TG/DTG) are shown in Fig. 1c and d. Three thermal decomposition events were observed in the pristine and plasma-activated samples. The first thermal event corresponded to the loss of physisorbed water and others gases or impurities present in PAL-N. The second event corresponded to the loss of zeolite water and coordinated water. The third event was related to the structural dehydroxylation of palygorskite [38]. The DTG results (Fig. 1d) indicate that the plasma-activated samples exhibited lower mass losses at lower degradation temperatures compared with those observed for pristine palygorskite. For PAL-N, the first thermal event occurred at a maximum temperature of 79 °C with a mass loss of 5.84%. This event also occurred for PAL-2H (73 °C, mass loss of 4.43%), PAL-4H (69 °C, mass loss of 4.14%), and PAL-6H (73 °C, mass loss of 4.35%).
Fig. 2 – SEM images and particle size distribution for (a) PAL-N, (b) PAL-2H, (c) PAL-4H and (d) PAL-6H.
The second thermal event for natural palygorskite occurred at a maximum temperature of 201 °C with a mass loss of 2.85%. This event was also observed for PAL-2H (189 °C and 3.12%), PAL-4H (185 °C and 2.90%), and PAL-6H (192 °C and 2.92%).

The decrease in maximum temperature for the first two events in the modified samples may be related to the defects of the crystal lattice caused by the destabilization of water molecule coordination in the palygorskite structure after plasma treatment. This result is in agreement with the XRD and FTIR results, and indicates that the long and short range orders of the clay mineral were maintained [50].

In the third thermal event, none of the activated samples underwent significant changes with regard to the maximum event temperature and mass loss, compared with the PAL-N results.

Micrographs were obtained by scanning electron microscopy (SEM), and the average particle size was obtained from the histograms of the 50 microstructures present in the micrographs of Fig. 2. The pristine clay mineral (Fig. 2a) has fibrous shape, and forms agglomerates of tapes or needles with varying lengths. In the histogram, the average length of fibers between 0.3 and 3.0 μm is in agreement with that reported by previous studies [31,69].

The average microfiber size for PAL-2H, PAL-4H, and PAL-6H (Fig. 2b–d) exhibited significant variations compared with PAL-N. The PAL-2H sample underwent a major change in the morphology of natural palygorskite microstructures (mean size of 1.7 μm), whereby the tapes and needles decreased to a size of 0.7 μm. The PAL-4H and PAL-6H microstructures had a mean size of 1.3 and 1.5 μm, respectively. These size changes indicate that, during the activation period in the plasma, the palygorskite microstructures ruptured as a result of mechanical shocks between the particles of the plasma atmosphere and the palygorskite microstructures, which reduced the average microstructure size [31]. These results are in agreement with the thermal analysis results, which indicates destabilization in the connections between the inverted strips that were possibly broken.

The EDS data (Fig. S2) reveal that PAL-N, PAL-2H, PAL-4H, and PAL-6H had the same chemical constituents regardless of exposure time. This indicates that the chemical composition of the clay surface was maintained without the incorporation of elements from the plasma atmosphere. Therefore, it was confirmed that the plasma treatment only activated the sites in the precursor material.

The results for the specific surface area and the pore volume values for PAL-N, PAL-2H, PAL-4H, and PAL-6H were obtained using the adsorption and desorption nitrogen technique and are presented in Table 1. Both the surface area and pore volume values decreased after the exposure of palygorskite to plasma. However, with 6 h of treatment, the pores tended to return to their original size and volume (prior to

<table>
<thead>
<tr>
<th>Specific surface area (m² g⁻¹)</th>
<th>95</th>
<th>76</th>
<th>85</th>
<th>93</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume (cm³ g⁻¹)</td>
<td>0.047</td>
<td>0.029</td>
<td>0.035</td>
<td>0.040</td>
</tr>
</tbody>
</table>

**Table 1 – Specific surface area and pore volume obtained by adsorption/desorption nitrogen measurements for the pristine and plasma activated palygorskites.**

The effect of contact time (t) on MB adsorption for the pristine and plasma activated palygorskites. Inserted is MB.

**Table 2 – Kinetic parameters for the MB adsorption on PAL-N, PAL-2H, PAL-4H and PAL-6H.**
the plasma exposure). These results are in agreement with the results obtained by SEM. Moreover, similar results were obtained for bentonite activated using the cold plasma technique [45].

According to the activation time in the plasma (4 and 6 h), it was possible to observe a tendency whereby the microstructures fused and returned to the size of natural palygorskite. In fact, after exposure to plasma, the monocrystalline surface may contain traces of impurities or defects on the surface, which alters the morphology. For a polycrystalline surface, sputtering also changes the original topography of the surface, owing to the new components and crystallographic grain orientations.

### 3.2. Adsorption tests

The influence of the adsorbent dosage on MB dye removal (Fig. S3) consisted of a decrease in the amount of dye removal in the adsorbents (PAL-N, PAL-2H, PAL-4H, and PAL-6H), according to Eq. 1. When \( q_e \) decreases with the reduction of the adsorbate/adsorbent ratio, the system with the smaller amount of adsorbent mass will have the best capacity for adsorbing the dye. Hence, an increase in the adsorbent mass can favor the formation of agglomerates that hinder adsorption [22,56].

The influence of pH on the adsorption of MB dye (Fig. S4) in the adsorbents (PAL-N, PAL-2H, PAL-4H, and PAL-6H) consisted of the adsorption capacity of the MB dye being pH-dependent and increasing with a higher pH. In fact, considering that the pKa of MB is 3.8, for values above this pH value, the cationic species were the preponderant MB species in the solutions. The performance of the plasma-activated samples was better for dye removal. In acidic media, the Si-OH functional groups within the PAL-N, PAL-2H, PAL-4H, and PAL-6H materials are the primary sites for interaction with MB through hydrogen bonds. In basic media with pH 10, species 1 (Fig. S5a) are predominant and Si-O\(^-\) is the preponderant group owing to the deprotonation of Si-OH, which improves the electrostatic interaction between the cationic dye and the anionic charged surface, as illustrated by the schematic representation shown in Fig. S5(b). Similar results were obtained for MB removal using clay mineral samples [45,70] and activated coal [71]. Therefore, pH 10.0 was used in the subsequent tests.

The effect of contact time on MB dye adsorption (Fig. 3) in the adsorbent (PAL-N, PAL-2H, PAL-4H, and PAL-6H) indicates that the equilibrium time was reached at 30, 90, 60 and 60 min for dye removal by PAL-N, PAL-2H, PAL-4H, and PAL-6H, respectively. The equilibrium time variation between natural clay and clay activated using the plasma technique (2, 4, and 6 h) is related to the activation of adsorption sites after the proposed treatment. Consequently, the processes involving PAL-2H, PAL-4H, and PAL-6H took longer to reach a higher MB adsorption capacity in these materials. The adsorption results obtained during the contact time were adjusted to different kinetic models to investigate the mechanism of the adsorption process.

Figs. S7 and S8 present the results obtained by fitting the data to kinetic models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion) for the adsorption of dye in active solids. The obtained parameters are listed in Table 2. The coefficient of linear correlation values were close to 1 for the proposed pseudo-second-order model, which determines the chemisorption as a limiting step of the abovementioned adsorption processes [72,73].
The results obtained for the methylene blue adsorption dye on the palygorskite were compared with those obtained by previous palygorskite studies [75–79] (Table 4). The comparison results revealed that the activated samples behaved as an effective adsorbent for MB removal.

Notably, adsorption studies using the plasma activation of clay minerals are emerging in the literature. The reported results suggest that plasma treatment has a broad spectrum of applications for solid/liquid interface to pollutant removal, particularly with regard to heavy cations, gases, and emerging pollutants (drugs, cleaning materials, and personal hygiene materials).

Palygorskite is considered as an excellent adsorbent material owing to its large surface area and ion exchange capacity [29,30]. The plasma technique is fast and non-polluting [44,45]; however, the plasma generator equipment cannot process a large amount of clay, which does not facilitate the activation of material by plasma at industrial scale. Nevertheless, in the future, new devices may allow the exposure of large sample amounts to plasma activation [46].

4. Conclusion

The activation of plasma palygorskite (H₂/N₂) for 2, 4, and 6 h altered the surface of clay and improved the adsorbing properties of the resulting materials. Structural changes were observed in microstructures implicated in the removal of coordinated and zeolitic water molecules, and for a specific surface area and pore volume. Long plasma exposition increased the specific surface area without long-range alterations. The plasma activation of clay minerals resulted in a new adsorbent with better MB removal capacity, regardless of the sample. The proposed activation method is a useful approach for processing palygorskite to develop new materials for pollutant removal.

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### Table 3 – Parameters resulted of the fitting to Langmuir and Freundlich models for the MB adsorption of on PAL-N, PAL-2H, PAL-4H and PAL-6H.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature</th>
<th>R²</th>
<th>q_max (mg g⁻¹)</th>
<th>K_L (L mg⁻¹)</th>
<th>n</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL-N</td>
<td>25 °C</td>
<td>0.993</td>
<td>53.48</td>
<td>0.1252</td>
<td>9.37</td>
<td>This work</td>
</tr>
<tr>
<td>PAL-2H</td>
<td>25 °C</td>
<td>0.975</td>
<td>51.68</td>
<td>0.3855</td>
<td>16.65</td>
<td></td>
</tr>
<tr>
<td>PAL-4H</td>
<td>25 °C</td>
<td>0.981</td>
<td>54.17</td>
<td>0.0243</td>
<td>10.62</td>
<td></td>
</tr>
<tr>
<td>PAL-6H</td>
<td>25 °C</td>
<td>0.981</td>
<td>54.17</td>
<td>0.0243</td>
<td>10.62</td>
<td></td>
</tr>
</tbody>
</table>

The influence of the initial pollutant concentration on the adsorption of MB dye (Fig. 4) in the adsorbents (PAL-N, PAL-2H, PAL-4H, and PAL-6H) consisted of the MB adsorption capacity of the adsorbent being lower at higher temperatures, which indicates an exothermic process [74]. For sample PAL-2H, the MB removal was very close to 35 and 45 °C, considering the deviation in the data. The data for the equilibrium isotherms were adjusted to the Langmuir and Freundlich dye models shown in Figs. S9 and S10, and the results are presented in Table 3. Although the empirical models do not reflect the adsorption mechanism, they still provide sufficient information to interpret the adsorption process [22].

For all investigated systems, higher linear correlation coefficients (R² > 0.97) were observed in the data fitted to the Langmuir model, which indicates the formation of a monolayer on the solid surfaces. The maximum MB adsorption values were 35.66, 53.48, 51.68, and 54.17 mg per gram of PAL-N, PAL-2H, PAL-4H, and PAL-6H, respectively.

### Table 4 – Maximum adsorption capacities (q_max) and comparison with other palygorskites.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum adsorption capacity (q_max – mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAL-N</td>
<td>38.79</td>
<td>This work</td>
</tr>
<tr>
<td>PAL-2H</td>
<td>50.93</td>
<td></td>
</tr>
<tr>
<td>PAL-4H</td>
<td>42.26</td>
<td></td>
</tr>
<tr>
<td>PAL-6H</td>
<td>46.87</td>
<td></td>
</tr>
<tr>
<td>Palygorskite</td>
<td>48.39</td>
<td>[75]</td>
</tr>
<tr>
<td>700 °C-treated-palygorskite</td>
<td>78.11</td>
<td></td>
</tr>
<tr>
<td>Graphene/Palygorskite/TiO₂</td>
<td>6.71</td>
<td>[76]</td>
</tr>
<tr>
<td>Palygorskite-APTES</td>
<td>49.48</td>
<td>[77]</td>
</tr>
<tr>
<td>Chinese Palygorskite</td>
<td>48.39</td>
<td>[78]</td>
</tr>
<tr>
<td>Modified Palygorskite</td>
<td>26.00</td>
<td>[79]</td>
</tr>
</tbody>
</table>
Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.jmrt.2019.09.011.

REFERENCES


