Adsorption of Methylene Blue by Hydroxyl-Aluminum Pillared Montmorillonite

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Summary: A purified raw montmorillonite and hydroxy-aluminum pillared montmorillonite have been prepared from a natural bentonite from Magnhoa, Algeria. These materials have been analyzed by X-ray fluorescence spectroscopy, X-ray diffraction, Infrared spectroscopy and nitrogen adsorption-desorption measurement. The pillared montmorillonite provided a certain increase of interlayer basal spacing and BET surface area and consequently the improvement of its capacities adsorption and decolorization of Methylene Blue. The adsorption properties of these materials were studied as a function of contact time, solution pH, initial Methylene Blue concentration and temperature. The adsorption kinetics and isotherms were well fitted by pseudo-second order and Freundlich models, respectively. In addition to that, thermodynamic studies showed an exothermic and a spontaneous process.

Keywords: Methylene blue; Hydroxyl-aluminum pillared montmorillonite; Adsorption; Waste water; Pollution.

Introduction

Organic dyes play important role in various applications. Synthetic Organic dyes discharges pose a great problem for the environment and human health as these latter are generally non-biodegradable [1-3]. Among different types of dyes, Methylene blue (MB) is a basic dye having many uses such as dyeing industry [4]. MB discharges in water lead to disagreeable color and consequently decrease sunlight penetration [5]. MB can cause some harmful effects on the human health such as eye burns, convulsions, and skin irritation. Moreover, it has thermal and light stabilities, complex structure, and low biodegradability [6]. In that regards, it was necessary to treat the MB effluents before throwing in aquatic environment.

Various methods were used for wastewater treatment including chemical [7], biological [8], advanced oxidation process [9] and physical [10, 11]. Among these methods, adsorption remains a relatively used technique and easily to implement because its availability, low cost, and high efficiency [12, 13]. In recent years, there are many research focus on developing new adsorbents for efficient removal of MB from aqueous solution such as graphene oxide [14-18], nanotubes [19], nanocomposite [20-22], metal oxide [23-25], biosorbents [26-29], and activated carbon [4, 30-33]. Activated carbon has been the most widely used because of its high adsorption capacity of organic matter. Nevertheless, this absorbent has a higher cost and remains difficult to regenerate [34]. The search of another effective and less expensive adsorbent is therefore interesting. In this context, the use of clay materials is of great interest because of its low cost, abundance in nature and effectiveness [35].

Clays materials are classified in various types such as kaolinites, palygorskites, chlorites, and smectites [36]. Montmorillonite belongs to smectite and has been widely studied for its capacity to adsorb synthetic dyes [37-44]. However, raw bentonites usually exhibit small surface area due to the strong restack of layers, limiting their applications in dye removal [45]. The inorganic cations (e.g., Na⁺ and Ca²⁺) can be replaced with cationic surfactants or polycationic species, and the resulting materials are regarded as organobentonite or pillared bentonite, respectively [46].

Various hydroxymetal polycations have been employed to synthesize pillared bentonite, e.g., hydroxylaluminum, hydroxyzirconium, hydroxyiron, hydroxytitanium, and hydroxychromium [47-54]. Among these polycations, Al₃⁺ has the most popularity because of its keggin structure, high molecular weight, and high positive charge [55]. Pillared bentonite improves the removal efficiency of heavy metals [49, 56-63], Oxyanions [64-69], organic contaminants [64] and dyes [70-73]. So far, there are only two reports on the use of Al-pillared bentonite as absorbent for the removal of Methylene Blue from aqueous solutions [74, 75].

The main objective of this work was to prepare hydroxy-aluminium pillared montmorillonite using Algerian bentonite. This new material was characterized by X-ray fluorescence spectrometry (XRF), X-ray nanotubes [19], nanocomposite [20-22], metal oxide [23-25], biosorbents [26-29], and activated carbon [4, 30-33]. Activated carbon has been the most widely used because of its high adsorption capacity of organic matter. Nevertheless, this absorbent has a higher cost and remains difficult to regenerate [34]. The search of another effective and less expensive adsorbent is therefore interesting. In this context, the use of clay materials is of great interest because of its low cost, abundance in nature and effectiveness [35].

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The first and main step in the preparation of hydroxyl-aluminum pillared montmorillonite was the preparation of the pillaring solution. The pillaring solution of hydroxyl-aluminum oligomeric cations ([Al₃(OH)₈(H₂O)₄]³⁺) was prepared following the procedure previously reported by Wang et al. [77, 78]. It consists of addition drop by drop of Na₂CO₃ solution (0.4 mol/l) to AlCl₃·6H₂O solution (0.2 mol/l) under vigorous stirring at 80°C in order to obtain a OH⁻/Al³⁺ molar ratio of 2.4. The resulting solution was stirred at 80°C for 2 h, and then aged for 24 h at room temperature. The second step in the preparation of hydroxyl-aluminum pillared montmorillonite was the intercalation by adding the pillaring solution to the water suspension of Na-Mt (1 wt %) at 80°C under vigorous stirring up to reach an Al³⁺/Na-Mt ratio of 10 mmol/g. The mixture was stirred for an additional 2 h at 80°C and subsequently aging at 60°C for 24 h. The product was centrifuged, followed by washing with distilled water and the solid was dried at 80°C and ground into powder. This pillared sample was noted as OH-Al-Mt.

**Characterization methods**

The X-ray diffraction patterns were performed employing a Philips X Pert MP diffractometer with Ni-filtered CuKα radiation using a powder sample. Chemical composition of the samples was determined by X-ray fluorescence spectrometry using a model Philips Magix Pro spectrometer with X-ray tube and Kα radiation for Rh. Spectrometer contains two flows: Ar + Methane and scintillation flow. Fourier transform infrared spectroscopy of the samples were measured using a “Spectrum Two” (Perkin Elmer, Inc.) spectrometer.

The spectra range for KBr is 8300 – 350 cm⁻¹ for the optic system and between 6000 and 550 cm⁻¹ for ZnSe mesures with a resolution of 2 cm⁻¹. Surface area and pore size distribution were determined by using N₂ as the sorbate at 77 K in a static volumetric apparatus (Micrometrics ASAP 2010 sorptometer). Samples (ca 0.2 g) were outgassed prior to use at 453 K for 16 h under vacuum (6.6 × 10⁻⁹ bar). Surface areas were calculated employed the BET equation, while pore volumes were determined from N₂ uptake at a relative pressure (p/p₀) of N₂ equal to 0.99. The microporous surface and micropore volume were determined employing Horvath Kawazoe (HK) method [79]. Scanning electron microscopy (SEM) images of samples were obtained using a Quanta-650 scanning electron microscope (FEI).

**Adsorption experiments**

Batch experiments were carried out in water bath shaker (Heidolph Unimax 1010) using a glass flask by adding 1 g/l of Na-Mt and OH-Al-Mt in 25 ml of initial concentration 100 mg/l of MB solutions and thermostated at 299 ± 1 K. The adsorption properties of these materials were studied as a function of contact time (10 - 420 min), solution pH (2 - 10), adsorbents dose (5 - 200 mg) and temperature (20, 30, and 50°C) for optimizing the operating conditions. Samples of 4 ml were withdrawn and centrifuged to separate the adsorbent from the solution. The supernatant was analyzed by UV–Vis spectrophotometer (Genesys-10) at the maximum wavelength of absorption λₘₐₓ = 665 nm. The MB concentration of each experiment was carried out with calibration curves obtained by plotting the optical densities as a function of MB concentration.
The pH of MB solutions was adjusted using 0.1 mol/l H₂SO₄ and 0.1 mol/l NaOH aqueous solutions, and was measured using a pH meter (AD 1030). Adsorption isotherm experiments were carried out by adding 1 g/l of adsorbents in 25 ml of MB solutions at different concentrations (4 - 150 mg/l) for desired contact time and pH. The amounts of adsorbed MB in the equilibrium per mass unit of the sample, qₑ (mg/g), and the removal efficiency of the MB, E (%), were calculated according to Eqs. (1) and (2), respectively:

\[ qₑ = (C₀ - Cₑ) \times \frac{V}{m} \]  

(1)

\[ E (%) = \frac{C₀ - Cₑ}{C₀} \times 100 \]  

(2)

where C₀ is initial concentration of MB (mg/l), Cₑ is equilibrium concentration of MB (mg/l), V is the volume of MB solution (ml), and m is the mass of adsorbent (mg).

Results and Discussion
Characterization of the materials

The X-ray fluorescence data for the Na-Mt and OH-Al-Mt are reported in Table 1. As observed, the SiO₂ content in OH-Al-Mt was significantly lower than that in parent clay Na-Mt. This fact is principally due to the higher Al₂O₃ content which clearly indicates the insertion of Al₁₃³⁺ into the interlayer spacing as pillars, although it is possible that it can be also settled in minor amounts over the montmorillonite sheets. Table 1 also illustrates that the amount of Na₂O in the OH-Al-Mt was significantly decreased after pillaring processes. This result is in agreement with previous finding [55, 80-81], denoting that this decrease is mainly due to the cation exchange between Na⁺ and Al₁₃⁺.

X-ray diffraction patterns and relative basal spacing of Na-Mt and OH-Al-Mt are illustrated in Fig. 1 and Table 1. The angle reflections due to the basal d₀₀₁ reflection of silicate layers allowed us to obtain information about the effect of intercalation on the basal spacing of the clay. In particular, it can clearly be seen that the diffraction peak at 2θ = 7.04° of Na-Mt is shifted to lower angle around 4.78° in OH-Al-Mt. This shift clearly indicates an enlargement of the basal spacing of the clay as a consequence of the pillaring process (from 12.5 Å of the parent clay to about 18.5 Å of the OH-Al-Mt, see in Table 1). This value confirms values previously reported for the used Al₁₃ as a pillaring species [73, 82, 83]. The observed enlargement of the basal spacing is due to the intercalation of Al₁₃⁺ cations between montmorillonite layers. Fig. 1 also shows that the (001) peak of OH-Al-Mt was lower intensity than that of the starting Na-Mt in agreement with previous results obtained by Tepmatee and Siriphannon [80].

![XRD patterns of Na-Mt and OH-Al-Mt.](image)

The textural properties of the samples are shown in Table 1. It is clear that the BET surface area and pore volume of OH-Al-Mt were greater than those of Na-Mt, which are in agreement with results previously reported [55, 73, 75, 77, 78]. Micropores are known to contribute to most of the adsorption capacity [84, 85]. After modification with Al₁₃, the micropore surface area and micropore volume increased to 127.3 m²/g and 0.07 cm³/g, respectively. These results could be assigned to the insertion of Keggin-Al₁₃ into the interlayers of the montmorillonite.

The nitrogen adsorption desorption isotherms for the samples are presented in Fig. 2a. The isotherms shapes are composite type I and type IV isotherms. Similar shapes have been reported for other pillared materials [86, 87]. At low relative pressures (P/P₀ < 0.5), isotherms were characterized by type I isotherms according to the Brunauer, Deming, Deming and Teller classification (BDDT) [88], which is characteristic of microporous systems [89]. Note that, a significant higher amount of adsorbed nitrogen molecules were achieved for OH-Al-Mt compared to the Na-Mt, indicating the opening of the pore structure of the clay after the pillaring process and so, the improvement of its adsorption capacity. On the other hand, the plot of samples isotherms at higher P/P₀ values would correspond to the type IV, which is characteristic of materials having relatively large pores. Moreover, the presence of a hysteresis loop in the isotherms (type H₃ according the International Union of Pure and Applied Chemistry (IUPAC) classification [89], indicates some degree of mesoporosity (mesoporosity arises from stacking defects inherent in the clay itself, as evidenced by the hysteresis loop seen in the adsorption isotherm of the starting clay). The hysteresis loop, characteristic of materials with slit-like pores, is consistent with the structure expected for materials prepared by expanding a laminar structure.
Table 1: Chemical composition (wt%), basal spacing (d_{001}) and textural properties of Na-Mt and OH-Al-Mt.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Chemical composition (Wt%)</th>
<th>Basal spacing d_{001} (Å)</th>
<th>BET surface area (m²/g)</th>
<th>Micropore Surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>Al₂O₃: 17.75, SiO₂: 58.52, Na₂O: 2.72</td>
<td>12.5</td>
<td>59.3</td>
<td>13.0</td>
<td>0.009</td>
<td>0.11</td>
</tr>
<tr>
<td>OH-Al-Mt</td>
<td>Al₂O₃: 25.26, SiO₂: 49.68, Na₂O: 0.17</td>
<td>18.5</td>
<td>182.9</td>
<td>127.3</td>
<td>0.069</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Fig. 2: Nitrogen adsorption-desorption results: a) isotherms and b) micropore size distribution (HK method).

The micropore size distribution curves (Fig. 2b) were calculated from Horvath-Kawazoe (H-K) method. The primary peaks at about 5.2 - 5.4 Å in the curves of samples correspond to the main population of pores, but with a continuous distribution of pores in the range of 5.4 - 11 Å, which are in agreement with results previously reported [78].

The FTIR spectra of Na-Mt and OH-Al-Mt in the range of 4000–400 cm⁻¹ are shown in Fig. 3. The band at about 3617 cm⁻¹ is assigned to the stretching vibration of octahedral OH groups, which are attached to Al³⁺ or Mg²⁺ [90]. The absorption peak at 1634 cm⁻¹ is attributed to OH deformation of interlayer water. The intensity of this band changed, which could be explained due to some changes of the H₂O content with the replacement of the intercalated Al polycations [91]. The most intense band at 990 cm⁻¹ shifted to 1003 cm⁻¹ near the Si-O stretching vibration in the tetrahedral sheet, the intensity also decreased from Na-Mt to OH-Al-Mt. This finding is in agreement with other investigations obtained by Zhao et al [55] that demonstrated that Al_{13} species were intercalated into the interlayers of the montmorillonite. The band situated at 515 and 463 cm⁻¹ characterize the montmorillonite and correspond to the Si-O bending vibrations.

SEM was used to study the changes in morphology of Na-Mt and OH-Al-Mt (Fig. 4). It can be seen that the Na-Mt is constituted of fine particles and the morphologies of these particles indicated that the sample had the lamellar structure (Fig. 4a). After modification with Al_{13}, the OH-Al-Mt is composed of fine and large particles, explaining that some of lamellas were disposed to form a stacking structure (Fig. 4b), which was consistent with extended the interlayer space, increased the surface area and consequently increased adsorption capacity.
Adsorption experiments

Effect of contact time and adsorption kinetics

Several studies were established the effect of contact time on the amounts of adsorbed dye onto a fixed adsorbent mass [92-95]. The effect of contact time on the adsorption capacities of Na-Mt and OH-Al-Mt for MB was illustrated in Fig. 5. As observed, the rate of adsorption was fast at initial 30 min due to the adsorption of MB on the external surface of adsorbents. After that, slow adsorption occurred that referred to the MB diffused into the pores and was absorbed by the internal surface of the adsorbents. The last stage reflects the adsorption equilibrium of adsorbents within 120 min and the final adsorption capacities were calculated to be about 67 mg/g and 90 mg/g for Na-Mt and OH-Al-Mt, respectively. Subsequently, no further adsorption was observed. Hence, the optimum contact time was chosen as 120 min. However, the pillared clay has a higher adsorption capacity than the Na-Mt. It can be related to the pillaring process which results in materials with altered chemical composition, extended the interlayer space, increased the surface area and consequently increased adsorption capacity. Additionally, Al13 had a higher positive charge (+7) than Na (+1), leading to the enhancement of adsorption performance of the modified montmorillonite [55].

The adsorption kinetics is an essential feature on the investigation of the pollutants decolorization. In order to investigate the adsorption kinetics and mechanism of MB adsorption on adsorbents, pseudo-first order and pseudo-second order models were used to fit the kinetics process. The pseudo-first-order equation in linear form [96] is given by:

\[
\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t
\]

and the expression of the linear form of the pseudo-second-order model [97, 98] is given as:

\[
\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t
\]

where \(q_e\) and \(q_t\) are the amounts of MB (mg/g) adsorbed on the adsorbent at equilibrium and at a given time \(t\) (min), respectively. \(k_1\) (min\(^{-1}\)) and \(k_2\) (g/mg.min) are the pseudo-first-order and the pseudo-second-order rate constants, respectively.

Table 2 illustrates the kinetic parameters and correlation coefficients values. It was found that of the both adsorbents, the pseudo-second-order model fitted well the experimental results with \(R^2 = 0.99\). Similar reports are available in literature [4-6, 18, 29, 35, 73, 99-108].
Table 2: Adsorption kinetics parameters of MB on Na-Mt and OH-Al-Mt.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo-first order model</th>
<th>Pseudo-second order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_e (mg/g)</td>
<td>K_1 (min^-1)</td>
</tr>
<tr>
<td>Na-Mt</td>
<td>64.71</td>
<td>0.044</td>
</tr>
<tr>
<td>OH-Al-Mt</td>
<td>55.46</td>
<td>0.032</td>
</tr>
</tbody>
</table>

In order to determine a minimum adsorbent amount that is economically realizable in wastewater treatment process, we have investigated the efficiency of sorbent dosages on the elimination of MB. Fig. 7 showed that the % removal of MB increased from 53% to 67% and 78% to 90% for Na-Mt and OH-Al-Mt, respectively, as adsorbent amount increased from 0.2 to 1 g/l. This fact can be assigned to increase in the adsorptive surface area and adsorption sites that can take up MB cations become more available. Subsequently, the removal rate did not affected by further increase in adsorbent dose, indicating saturation state. When the adsorbent dosage is low, the dye ions can easily access the adsorption sites by contrast when the adsorbent dosage is high, the dye ions can hardly access the adsorption sites until the attainment of equilibrium. The percentage removal for Na-Mt was lower than that for modified clay, indicated that the adsorption ability of OH-Al-Mt was dramatically enhanced by Al_13 modification. According to this experiment, 1 g/l adsorbent dose (optimal adsorbent dosage) was chosen for the successive experiments.

Effect of adsorbent dose

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Adsorption isotherms

The adsorption isotherms were carried out at different initial concentrations (4 to 200 mg/l) during 120 minutes at room temperature and adsorbent dose 1g/l. The isotherms are formed by plot adsorbed amount of MB versus equilibrium concentration. The Fig. 8 depicts the adsorption of MB by Na-Mt and OH-Al-Mt. It can be seen that for both adsorbents, the amount of Methylene Blue adsorbed increases with an increase in initial adsorbate concentration, due to the increased driving force of the concentration gradient [120]. A similar effect has been observed with previously reported [18, 105]. The OH-Al-Mt exhibited higher adsorption capacity than the Na-Mt in same operating conditions, due to the altered chemical composition, enlarged the interlayer space and their higher BET specific surface area.

\[
\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \left( \frac{1}{q_m} \right) C_e \\
\log q_e = \log K_T + \left( \frac{1}{n} \right) \log C_e \\
q_e = B_T \cdot \ln K_T + B_T \cdot \ln C_e
\]

where \(q_m\) (mg/g) and \(K_L\) (l/mg) are Langmuir constants respectively related to the maximum adsorption capacity and the adsorption energy. \(K_F\) and \(n\) are Freundlich constants respectively related to the adsorption capacity ((mg/g)(l/mg)^n) and the adsorption intensity. \(B_T = RT/b\), \(T\) is the temperature (K), \(R\) is the universal gas constant (8.314 J/mol K), and \(b\) is the Temkin constant related to heat of adsorption (J/mol).

The fitted constants for Langmuir, Freundlich and Temkin isotherm models at room temperature are summarized in Table-3. The coefficient of determination (R^2) values in the Freundlich isotherm model were above 0.99, which were higher than that for the Langmuir and Temkin isotherms, indicating a very good mathematical fit by this model. Similar results have been reported for the adsorption of Basic Fuchsin, Basic Green and Acid Turquoise Blue A [73] by hydroxy-aluminum pillared bentonite, direct orange 34 [121] by halloysitic clay, methylene blue [113] by zeolite-activated carbon composite. Generally, the value of \(n\) in the range of 2–10 indicates good, 1–2 moderately difficult and below 1 poor adsorption characteristics [44]. The measured 1/n was below to the unit, which means the adsorption was favorable. In addition to that, adsorption of any contaminant is considered favorable (0 < K_L < 1); unfavorable (K_L > 1), linear (K_L = 1) and irreversible (K_L = 0) [44]. The measured K_L were below to the unit, indicated the favorable adsorption of MB onto both adsorbents.

For comparison, results obtained from the literature on Methylene Blue monolayer adsorption by various clays are summarized in Table 4. It is seen that the OH-Al-Mt shows a high affinity for MB molecules and the q_m of the Langmuir adsorption isotherm is much higher to that in previous results [74, 75, 103, 106, 114, 122-131].

Effects of temperature and thermodynamic studies

Temperature is an important parameter for the adsorption process. A plot of the MB uptake as a function of temperature (293, 313 and 333 K) is shown in Fig. 9. The adsorbed amounts of MB were decreased from 67.36 to 64.9 mg/g and 90.58 to 87.36 mg/g for Na-Mt and OH-Al-Mt, respectively, as temperature increased from 293 K to 333 K. This result shows that adsorption onto the adsorbents is favorable at low temperature and thus suggesting that the adsorption process is exothermic. According to [104], the dye molecules escape from the solid phase to the solution with increase the temperature.

![Graph showing adsorption isotherms of MB onto Na-Mt and OH-Al-Mt](image-url)
Table-3: Isotherm model parameters for adsorption of MB onto Na-Mt and OH-Al-Mt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>q_m (mg/g)</th>
<th>Langmuir K_L (l/mg)</th>
<th>R²</th>
<th>l/n</th>
<th>Freundlich K_F (mg/g)</th>
<th>R²</th>
<th>E_T (kJ/mg)</th>
<th>Temkin K_F (l/mg)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>111.11</td>
<td>0.024</td>
<td>0.95</td>
<td>0.89</td>
<td>2.96</td>
<td>0.998</td>
<td>22.4</td>
<td>0.56</td>
<td>0.87</td>
</tr>
<tr>
<td>OH-Al-Mt</td>
<td>142.86</td>
<td>0.30</td>
<td>0.91</td>
<td>0.44</td>
<td>28.97</td>
<td>0.99</td>
<td>14.69</td>
<td>29.75</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table-4: Comparison of monolayer adsorption of MB onto various clays.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbed amount (mg/g)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>52.76</td>
<td>[122]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>77</td>
<td>[123]</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>57.38</td>
<td>[124]</td>
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<td>Sepiolite</td>
<td>110</td>
<td>[125]</td>
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<tr>
<td>Clay</td>
<td>6.3</td>
<td>[126]</td>
</tr>
<tr>
<td>Raw ball clay</td>
<td>34.65</td>
<td>[114]</td>
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<tr>
<td>Modified Ball clay</td>
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<td>[114]</td>
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<tr>
<td>Spent activated clay</td>
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<td>[127]</td>
</tr>
<tr>
<td>Zn-PILC</td>
<td>27</td>
<td>[74]</td>
</tr>
<tr>
<td>Montmorillonite</td>
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<td>[128]</td>
</tr>
<tr>
<td>Tsu-Mont</td>
<td>73</td>
<td>[75]</td>
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<tr>
<td>Chitosan/bentonite</td>
<td>95.24</td>
<td>[129]</td>
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<tr>
<td>Carbon/montmorillonite composites</td>
<td>82.6</td>
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</tr>
<tr>
<td>Montmorillonite modified with iron oxide</td>
<td>69.11</td>
<td>[106]</td>
</tr>
<tr>
<td>Mt/CoFe_2O_3 composite</td>
<td>106.38</td>
<td>[103]</td>
</tr>
<tr>
<td>Al-PILC</td>
<td>21</td>
<td>[74]</td>
</tr>
<tr>
<td>Alumina pillared clays</td>
<td>40</td>
<td>[75]</td>
</tr>
<tr>
<td>Na-Mt</td>
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<tr>
<td>OH-Al-Mt</td>
<td>142.85</td>
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</tbody>
</table>

Fig. 9: Effects of temperature on the MB adsorption capacity of Na-Mt and OH-Al-Mt.

The thermodynamic behavior of the adsorption of MB onto the adsorbents were defined by Gibb’s free enthalpy ($\Delta G^\circ$: kJ/mol), enthalpy ($\Delta H^\circ$: kJ/mol) and entropy ($\Delta S^\circ$: J/mol.K) and were calculated using the following equations [104]:

$$\ln \left( \frac{q_{m}}{C_e} \right) = \frac{\Delta S^\circ}{R} - \frac{(\Delta H^\circ)^\circ}{RT}$$  \hspace{1cm} (8)

$$\Delta G^\circ = \Delta H^\circ - T \times \Delta S^\circ$$  \hspace{1cm} (9)

where $m$ is the adsorbent dose (1 g/l), $C_e$ is the equilibrium concentration (mg/l) of the MB in solution, $q_e$ is the amount of MB adsorbed at equilibrium (mg/g), R is the gas constant (8.314 J/mol K) and T is the temperature (K).

The values of $\Delta H^\circ$ and $\Delta S^\circ$ are calculated from the slope ($-\frac{\Delta H^\circ}{R}$) and the intercept ($\frac{\Delta S^\circ}{R}$) of the plots of $\ln \left( \frac{q_e}{C_e} \right)$ against $\frac{1}{T}$ (figure not shown). The $\Delta G^\circ$ values were calculated using Eq. (9). The determined values of the thermodynamic parameters are given in Table 5. The values of $\Delta G^\circ$ were found to be negative under various temperatures which indicated the favorable nature of MB adsorption onto adsorbents and spontaneous process under the experiment condition. The negative value of $\Delta H^\circ$ suggests that the adsorption of MB onto adsorbents was exothermic and the negative $\Delta S^\circ$ value can be attributed to the decline in the disorder at the solid/solution interface. Generally, when the $\Delta H^\circ < 25$ kJ/mol, the adsorption is physical and when $\Delta H^\circ$ is in the range 40–200 kJ/mol, the adsorption is chemical [99]. In this study, $\Delta H^\circ$ is less than 25 kJ/mol and thus adsorption is physical.

Table-5: Thermodynamics parameters of MB adsorption onto the Na-Mt and OH-Al-Mt.

<table>
<thead>
<tr>
<th>Adsorption system</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol.K)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Mt</td>
<td>-2.96</td>
<td>-4.07</td>
<td>-1.77</td>
</tr>
<tr>
<td>OH-Al-Mt</td>
<td>-8.76</td>
<td>-11.14</td>
<td>-5.50</td>
</tr>
</tbody>
</table>

Conclusions

In this work, the removal of MB from water solutions was investigated by employing as adsorbents a purified raw montmorillonite (Na-Mt) and hydroxy-aluminum pillared montmorillonite (OH-Al-Mt). OH-Al-Mt had a good ordered layers structure with insertion of Al$_{13}^{7+}$ cations, which caused an increase in the clay spacing. Its specific surface area is about three times larger than that of the parent Na-Mt due principally to the creation of a remarkable microporous network.

The optimized conditions for MB dye removal by adsorbents were confirmed at 1 g/l adsorbent dosage, equilibrium time 120 min, natural pH (6.1) and decreased with the increase of
temperature. The adsorption of Methylene Blue onto both clays obeyed pseudo-second-order kinetics. The pillared clay has a higher adsorption capacity than the Na-Mt. The best equilibrium adsorption isotherm fit was obtained with the Freundlich model. Thermodynamic studies showed that the adsorption is spontaneous and exothermic process.

Acknowledgments

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References


42. S. Hong, C. Wen, J. He, F. Gan and Y.S. Ho, Adsorption thermodynamics of methylene blue
65. V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud and J.C. Bollinger, Arsenic adsorption onto pillared clays and iron oxides, J. Colloid Interface Sci., 255, 52 (2002).
90. K. Bukka, J.D. Miller and J. Shabtai, FTIR study of deuterated montmorillonite: structural


