

## Thermal and chemical modification of a halloysite and application to the adsorption of a cationic dye

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### ABSTRACT/RESUME

**Abstract:** Algerian halloysite was treated at 600 °C and with hydrochloric acid solutions of various concentrations. The resulting materials were characterised by elemental analysis, TG, TDA, TEM, XRD and nitrogen adsorption at 77 K. The modified halloysites were employed as malachite green (MG<sup>+</sup>) adsorbents from aqueous solutions. Thermal treatment at 600 °C results in the formation of dehydroxylated halloysite, due to –OH release from the structure. Acid treatment involves a relative increase in SiO<sub>2</sub> content. The ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> increased from 1.92 to 27.75, consequence of the leaching of Al ions from the octahedral layer. This phenomenon is accompanied by the progressive amorphisation of the structure with increasing HCl concentration. Thermo-chemical treatments preserve the tubular morphology, though the obtained tubes are somewhat damaged. Specific surface area increased significantly from 60.5 to a maximum of 503 m<sup>2</sup>/g. Total volume is mainly represented by mesopores. Microporosity grows progressively with HCl treatment, reaching a maximum of 21 %. The MG<sup>+</sup> adsorption onto the modified halloysites is rapid in the first 10 min. The adsorbed quantity decreased with increasing temperature. The affinity follows the sequence: H600-0.5N > H600-3N > H600-5N > H600.

### I. Introduction

Dyes are widely used in textile, paper, rubber, plastic, leather, cosmetic, and pharmaceutical and food industries. Their presence in wastewaters generates huge problems for the environment and living organisms because those are recalcitrant organic molecules, resistant to aerobic digestion, stable to light, heat and oxidizing agents [1]. A variety of techniques are nowadays available to test these contaminants. Among these may be mentioned biodegradation, reverse osmosis, advanced oxidation processes and adsorption. Biodegradation suffers from optimization problems, in addition to character relatively biorefractory of these compounds. Reverse osmosis, although very effective, is a high-cost process because membranes require a frequent replacement. Advanced oxidation processes are also considered to be high-cost methods [2]. Adsorption was found to be an effective, economical, and easy technique to implement. Its other advantages are applicability at

very low concentrations, suitability for using batch and continuous processes, little sludge generation, and possibility of regeneration and reuse. The application of minerals of kaolin group, low cost and easily available materials, received a special attention for the removal of cationic dyes and some other pollutants from wastewaters [3–7], because, after modification, their characteristics are remarkably improved. Modification can be achieved, inter alia, by thermal and/or acid activation [8]. The objectives of this study were to investigate the modifications undergone by Algerian halloysite owing to thermal treatment, at 600 °C, and acid activation with HCl solutions of concentrations 0.5, 3, 5, 7 N. The obtained solids were applied to remove malachite green (MG<sup>+</sup>) from aqueous solutions.

#### II.1. Preparation

Raw halloysite from Djebel Debbagh, Guelma (eastern region of Algeria) was used in this work. Its characteristics were reported in a previous work

[9]. Three hundred grams of halloysite were heated at 600 °C for 2 h [10], in air atmosphere, to make sure that this clay dehydroxylates. On the other hand, it is well-known that 2 h is a time sufficient so that heat penetrates until the interior of the particles and induces some transformations, for a certain number of materials [11,12]. Acid treatment was carried out by contacting 45 g of the preheated clay with 1125 ml of hydrochloric acid solution (solid/solution ratio: 1/25) of different concentrations (0.5, 3, 5, and 7 N) at 70 °C for 4 h. After chemical activation, the solid was filtered and repeatedly washed with distilled water to remove any unspent acid. The activated clays were then dried at 110 °C for 2 h and stored for further use. The samples were named H600, H600-0.5N, H600-3N, H600-5N and H600-7N.

## II.2. Characterisation

The modified halloysitic materials were characterised by elemental analysis, thermal analysis, transmission electron microscope (TEM), X-ray diffraction (XRD), and sorptometric studies. Chemical analysis of the solids was determined by ICP-AES on a Perkin-Elmer instrument. Thermal analysis (TG-DTA) was performed on a Netzsch Sta 409 C instruments (Germany). Approximately 190 mg of halloysite was heated in an alumina crucible with a heating rate of 17 °C/min, under an atmosphere of high purity N<sub>2</sub>. TEM images were determined with a JEOL 2100 electron microscope. An EDX detector for X-ray energy dispersive analysis is attached to this microscope. The clay sample was previously ultrasonically dispersed in ethanol for 5 min. X-ray powder diffraction patterns were obtained using a Philips PW 1830 diffractometer with CoK<sub>α</sub> radiation ( $\lambda=0.1789$  nm) operating at 40 kV and 25 mA. The XRD data were collected over a  $2\theta$  range of 5–90° with a step width of 0.03° ( $2\theta$ ).

The assessment of samples porosity and the crystallites surface were carried out by nitrogen adsorption-desorption. These measurements were performed at 77 K via an ASAP 2010 instrument (Micromeritics), using helium and nitrogen of 99.99% purity as supplied by Air Liquide. The samples were first out-gassed under secondary vacuum at 623 K for 12 h. Specific surface areas were calculated by BET method. External surface areas and micropore volumes were determined by t-plot method. Mesopore volumes and size distributions were calculated from the desorption branch of the corresponding nitrogen isotherm, using the Kelvin equation and the BJH method with the parameters for the thickness of the adsorbed layers from Harkins-Jura equation

## II.3. Adsorption procedure

A stock solution of malachite green (C.I.: 42555, chemical formula C<sub>52</sub>H<sub>54</sub>N<sub>4</sub>O<sub>12</sub>, F.W.: 927,00 g/

mol, supplied by Biochem, chemopharma) of concentration 80 mg/L was prepared by dissolving the corresponding amount of MG<sup>+</sup> in distilled water. Adsorption experiments were performed via batch method. 0.02 g of modified halloysite was mixed with 20 ml of aqueous MG<sup>+</sup> solution at different concentration. pH of the dispersions was adjusted to 5. After each experiment, the solution was separated by filtration. The filtrate was analysed by visible spectrophotometry at 617 nm using a Shimadzu 1240 UV-vis spectrophotometer. The adsorbed amount was determined from the difference between the initial and final concentrations.

## III. Results and discussion

### III.1. Modification and characterisation

#### III.1.1. Chemical analysis

Chemical analyse and mass loss of the modified samples are listed in Table 1. After acid activation, fine powders were obtained comparatively to the calcined sample (H600). The whiteness of this powder increases with solution acidity. The mass loss also significantly increases until concentration 3 N, beyond it remains more or less constant, around 41%. Acid treatment involves an increase in the content of SiO<sub>2</sub> at the expense of that of Al<sub>2</sub>O<sub>3</sub>. The ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> increased from 1.92 to 27.75. The decrease in the alumina content in the acid treated samples can be ascribed to the leaching of Al ions from the octahedral layer, due to hydrolysis under acidic conditions. For the latter, it decreases from 2.01 to 0.03. This ICP study clearly indicates that chemical composition substantially changes up to 3 N. In the range 3–7 N, the composition remains almost unchanged, which is consistent with the results obtained from the mass loss.

The textural parameters are presented in Table 2. The micropore volume of H600 is negligible. Total volume is mainly represented by mesopores. Microporosity grows progressively with HCl treatment, reaching a maximum of about 21%. This microporosity falls to 15% for H600-7N. This shows that the structure of the thermally treated, acid-activated halloysites is sensitive as for the very strong HCl concentrations.

This damage is also strengthened by the reduction in total volume of H600-7N, namely 0.637 cm<sup>3</sup>/g. This deterioration would be explained by a collapse of the framework, probably due to the intensive extraction of Al<sup>3+</sup> cations from the octahedral layers. For the later experiments, the sample H600-7N was ignored.

The nitrogen adsorption-desorption isotherms (data not shown) of our samples belong to type IV, according to the IUPAC classification [28].

**Table 1.** Chemical analysis and loss mass of the solids halloysitic

| Samples  | SiO <sub>2</sub><br>(%) | Al <sub>2</sub> O <sub>3</sub><br>(%) | CaO<br>(%) | Fe <sub>2</sub> O <sub>3</sub><br>(%) | K <sub>2</sub> O<br>(%) | MgO<br>(%) | MnO<br>(%) | Na <sub>2</sub><br>(%) | Molar ratio<br>SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> |
|----------|-------------------------|---------------------------------------|------------|---------------------------------------|-------------------------|------------|------------|------------------------|---|
| H600-0N  | 44.71                   | 39.69                                 | 0.65       | 0.45                                  | 0.32                    | 0.05       | 2.01       | 0.34                   | 1.92  |
| H600-.5N | 57.31                   | 26.46                                 | 0.26       | 0.43                                  | 0.17                    | 0.02       | 1.09       | 0.11                   | 3.68  |
| H600-3N  | 72.2                    | 5.15                                  | 0.12       | 0.16                                  | 0.12                    | 0.01       | 0.82       | 0.25                   | 23.83   |
| H600-5N  | 73.03                   | 4.59                                  | 0.03       | 0.09                                  | 0.30                    | 0.003      | 0.05       | 0.16                   | 27.11   |
| H600-7N  | 73.28                   | 4.49                                  | 0.02       | 0.08                                  | 0.26                    | 0.002      | 0.03       | 0.14                   | 27.75   |

**Table 2.** Texturals parameters of the solids halloysitic

| Samples   | Specific surface<br>S <sub>BET</sub> (m <sup>2</sup> /g) | External surface<br>S <sub>ext</sub> (m <sup>2</sup> /g) | Internal surface<br>S <sub>int</sub> (m <sup>2</sup> /g) | Micropores volume<br>(cm <sup>3</sup> /g) | Mesopores volume<br>(cm <sup>3</sup> /g) | Micropore volume<br>Total Volume<br>(%) |
|-----------|--|--|--|---|--|---|
| H600-0N   | 60.5   | 48.9   | 11.6   | 0.005                                     | 0.268                                    | 1.8                                     |
| H600-0.5N | 115.4  | 62.1   | 53.3   | 0.023                                     | 0.279                                    | 7.6                                     |
| H600-3N   | 434.0  | 116.7  | 317.3  | 0.134                                     | 0.491                                    | 21.4                                    |
| H600-5N   | 503.3  | 146.3  | 357.0  | 0.152                                     | 0.597                                    | 20.3                                    |
| H600-7N   | 364.0  | 134.2  | 229.8  | 0.097                                     | 0.540                                    | 15.2                                    |

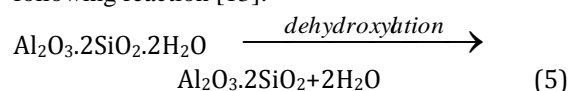
This isotherm type is typical of mesoporous structures. The specific, external and internal surface areas of the modified samples are summarised in Table 2. S<sub>BET</sub> increased significantly from 60.5 to a maximum of 503 m<sup>2</sup>/g (H600-5N), namely a ratio of 8.3. This increase is accompanied by that of internal and external surfaces, in a ratio of 30.8 and 3, respectively. This shows that leaching phenomenon increases primarily the internal surface of the materials. Chemical activation extracts Al<sup>3+</sup> cations from the octahedral sheet, destroys fragments of layers, causes the formation of “holes” in the halloysitic matrix and thereby ensures the accessibility of the internal surface. The reduction of S<sub>BET</sub> of H600-7N from 503 to 364 m<sup>2</sup>/g, associated with that of ratio of internal surface/S<sub>BET</sub>, from 30.8 to 19.8, might be explained by a collapse of the structure accompanied by that of the internal surface.

### III.1.2. Thermal analysis

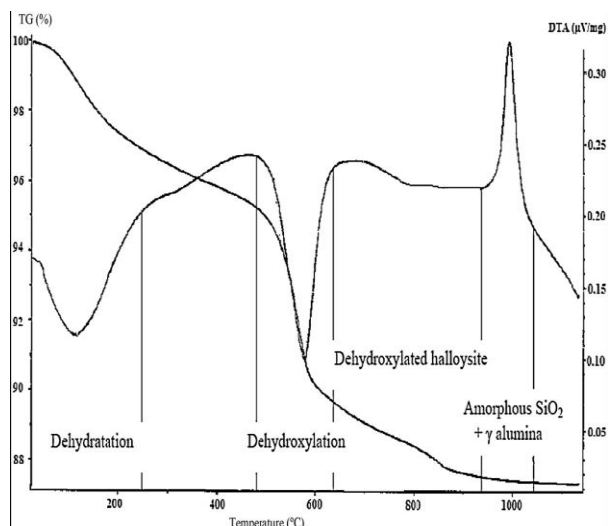
The TG and TDA curves of the starting material are depicted in Fig.1. Decomposition process takes place in three main steps: (i) an endothermic peak

in the range 50–240 °C, corresponding to the release of adsorbed water (surface and interlayer); (ii) a second endothermic peak, between 480 and 640 °C, due to structural decomposition. The peak centred at about 580 °C is assigned to the dehydroxylation of structural aluminol groups present in halloysite; (iii) a third exothermic peak at 993 °C attributed to the formation of amorphous SiO<sub>2</sub> and γ alumina [10, 13].

The thermogravimetric curve, TG, highlights a continual mass loss between 25 and 1100 °C. Total loss is 12.5%. In the dehydroxylation range, a steep slope was obtained. It corresponds to a major weight loss of 6.7%, between 400 and 700 °C. The dehydroxylation of halloysite consists in the following reaction [13]:



The choice of 600 °C as treatment temperature, before acid activation, has been fixed on the basis of this thermal analysis.



**Figure 1.** DTA and TG curves of halloysite

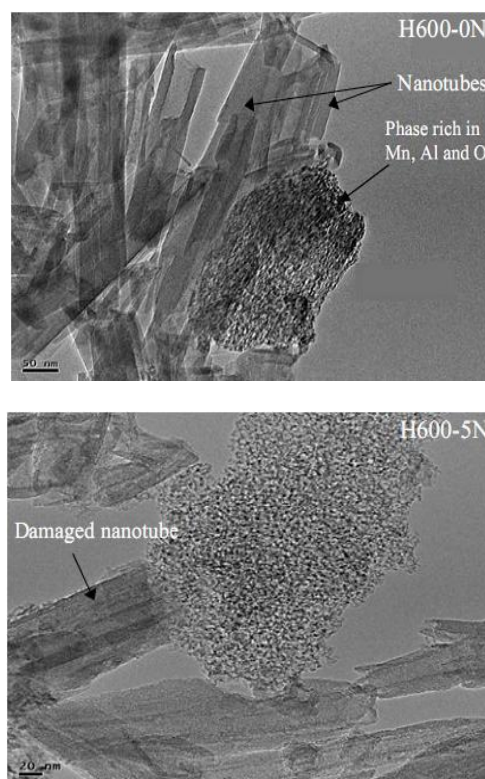
### III.1.3. Transmission electronic microscopy

TEM images of H600 and H600-5N are presented in Fig.2. H600 evidences particles having a cylindrical shape and contain a transparent central area that runs longitudinally along the cylinder, indicating that nanotubular particles are hollow and open-ended. The particles are of rather different sizes both in diameter and length. Their external and internal diameters vary from 30 to 180 nm and from 10 to 30 nm, respectively. These rolled tubes consist in a number of aluminosilicate sheets, curved, and closely packed. This morphology was also obtained for the unmodified halloysite [14] proving that thermal treatment at 600 °C conserves the tubular nature of the Algerian halloysite. A phase rich in Mn, Al and O was evidenced by EDX in microscope. The sample H600-5N (Fig.2) also leads to a tubular morphology, although the obtained tubes are damaged. Dehydroxylation phenomenon associated with the leaching of  $\text{Al}^{3+}$  somewhat alters the tubular morphology of halloysitic clays. The observation of these morphological details is of a great relevance. The defects on surface such as surface breakage or crystallographic defects could prove as potential reaction sites for the surface chemistry of halloysite nanotubes.

### III.1.4. X-rays Diffraction

The X-ray patterns of unmodified and activated halloysites are shown in Fig.3. The XRD diagram of the starting material showed a basal reflection at 7.6 Å ( $2\theta = 13.5^\circ$ ) with a shoulder at 10 Å (hh) ( $2\theta = 10.3^\circ$ ), corresponding to the (001) plane of the hydrated halloysite form (hh), also termed as halloysite-(10 Å). A feature of the X-ray pattern of halloysite having common tubular morphology is the very intense reflection at ~ 4.4 Å. Important structural changes were obtained after thermal

modification. The majority of the peaks characteristic of halloysite disappeared in the case of H600, indicating that H600 is almost amorphous in nature, and evidencing a large degree of structural disorder. This behaviour is due to the halloysite dehydroxylation at 600 °C, result of the –OH release from the structure, as discussed from thermal analysis. The X-ray patterns of the thermally treated and acid activated samples resemble to that of H600. A weak diffraction peak at a  $2\theta$  value of  $23.5^\circ$ , corresponding to the  $d$  value of 4.4 Å, is present for all samples. This means that the various structures maintain their tubular morphology [15], which is in accordance with the results obtained by TEM. In a first approximation, it can be observed that the intensity of the peak at  $29^\circ$  ( $d = 3.58$  Å) increased with acid concentration. It might correspond to the reticular plan occupied by silicons. It is well-known that acid treatment mainly attacks the octahedral sheet of which the centres are occupied by  $\text{Al}^{3+}$ . A hump is observed in the  $2\theta$  range  $23.5\text{--}29^\circ$  which grows with the concentration of HCl. This feature is probably due to the progressive amorphisation of the structure. The presence of sharp peak at 3.58 Å with a small FWHM might be due to the fact that heat-treated and acid-leached halloysites do not behave as clay mineral: the structure is dehydroxylated and becomes increasingly disordered.



**Figure 2.** TEM images of H600-0N and H600-5N.

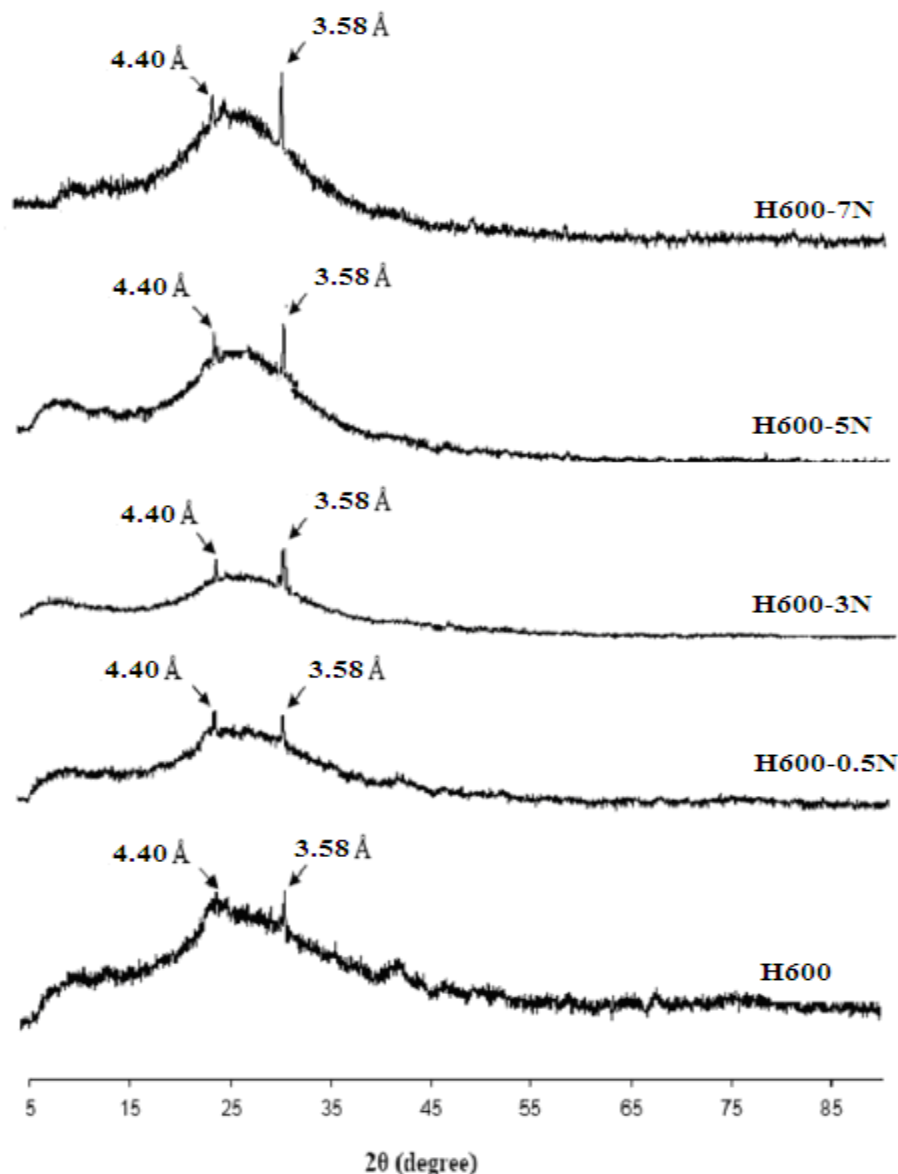


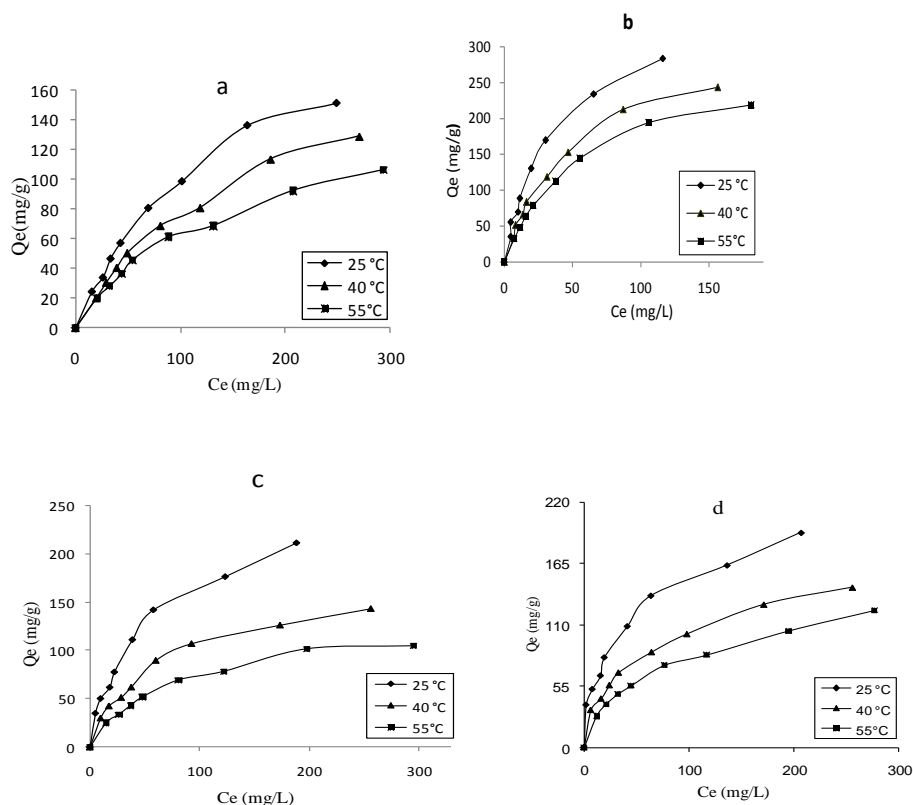
Figure 3. XRD spectra of halloysitic solids.

### III.2. Adsorption of malachite green

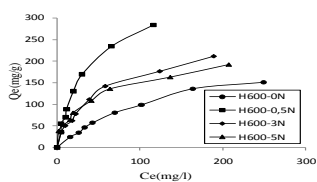
Adsorption isotherms of halloysitic solids are presented in Figure 4 and are of type L, according to the classification of Giles et al. [16]. These isotherms indicate that there does not exist a competition between solvent and adsorption sites of the adsorbent. Adsorbed quantity decreased with increasing temperature. As example, H600-0.5N adsorb 283.9 and 218.8 mg/g at 25 and 55 °C, respectively. High temperature reduced considerably the effectiveness of our adsorbents.

The affinity relating to modified halloysites, measured at 25 °C, is represented in figure 5. The

followed sequence is: H600-0.5N > H600-3N > H600-5N > H600-0N. This evolution cannot be explained by physicochemical properties such as specific surface. Other reasons must be invoked such as the surface acidity of the materials. The measurement of acidity can be realised by pyridine adsorption-desorption, followed by *in situ* FTIR spectroscopy [17]. H600-0.5N presents a maximum adsorption of 283.9 mg g<sup>-1</sup> at 25 °C. By comparing with other adsorbents such as bentonite (178.6 mg/g) [18], biomass (117.6 mg/g) [19], and activated slags (74.2 mg/g) [20], this material appears very effective for the elimination of cationic dyes.



**Figure 4.** Adsorption isotherms of malachite green by the solids halloysitic H600-0N; (b) H600-0.5N; (c) H600-3N; (d) H600-5N.



**Figure 5.** Adsorption Affinity of malachite green on halloysitic solids at 25 °C.



#### IV. Conclusion

Acid treatment involves an increase in SiO<sub>2</sub> content, at the expense of that of Al<sub>2</sub>O<sub>3</sub>. This dealumination, ascribed to the leaching of Al ions from the octahedral layer, is accompanied by the reduction of impurities CaO, Fe<sub>2</sub>O<sub>3</sub>, and MnO. TEM images evidenced nanotubular particles, hollow and open-ended. For higher acid concentrations, the dehydroxylation phenomenon associated with Al<sup>3+</sup> leaching somewhat alter the tubular morphology of halloysitic clays. The X-ray diffractograms showed that the thermal and acid treatments preserve tetrahedral SiO<sub>4</sub> sheets. This feature is accompanied by the progressive amorphisation of the structure with increasing HCl concentration. Specific surface area increased significantly from 60.5 m<sup>2</sup>/g (H600) to a maximum of 503 m<sup>2</sup>/g (H600-5N), namely a ratio of 8.3. This increase is primarily accompanied by that of internal surface. Total volume is mainly represented by mesopores. Microporosity grows progressively with HCl treatment, reaching a maximum of 21%. Up to a certain concentration, chemical activation extracts Al<sup>3+</sup> cations, destroys fragments of layers, causes the formation of "holes" in the halloysitic matrix and ensures the accessibility of internal surface. Adsorption isotherms of malachite green are of type L. Affinity followed the sequence: H600-0.5N > H600-3N > H600-5N > H600-0N. H600-0.5N has the best adsorption capacity, i.e., 283.9 mg g<sup>-1</sup>.

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