



## SYNTHESIS, CHARACTERIZATION AND ADSORPTION BEHAVIORS OF MODIFIED BENTONITE TOWARDS METHYLENE BLUE

Abdeldjabbar BELBEL,<sup>a\*</sup> Chouaieb ZAOUCHE<sup>b</sup> and Noureddine DJEBBARI<sup>c</sup>

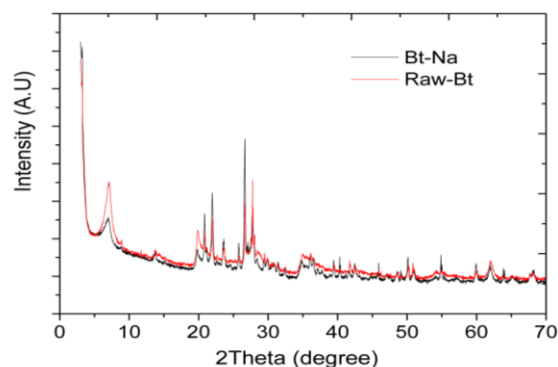
<sup>a</sup> Department of Chemistry, Ziane Achour University of Djelfa, BP 3117, Algeria

<sup>b</sup> Material Sciences Department, Faculty of Science, University of Biskra, 07000 Biskra, Algeria

<sup>c</sup> Laboratory of Separation and Purification Technologies Department of Chemistry, Tlemcen University, Box 119, Algeria

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This study aims to evaluate the effect of two surfactants hexadecyl(trimethyl)azanium;bromide (CTAB) and 1-butyl-3-methylimidazol-3-ium;chloride (BMIMCl) intercalation in bentonite (Bt) on methylene blue dye adsorption. The modified clays were characterized in detail using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA). The XRD analysis showed the increase of basal spacing ranged between 20.99 Å and 14.19 Å for Bt-CTAB and Bt-BMIM respectively. The FTIR is another tool to investigate the presence of organic matter on the clay surface. More specifically, the results showed that the formation of new bands of vibrations (1400–1500 cm<sup>-1</sup> and 2800–2900 cm<sup>-1</sup>). Then the organoclays were used to the adsorption of methylene blue. In presence of surfactant the maximum adsorption capacities of Bt-CTAB and Bt-BMIM according to the langmuir model were 47.186 mg·g<sup>-1</sup> and 42.28 mg·g<sup>-1</sup>, respectively. According to the results algerian bentonite sample tested in this paper can effectively remove methylene blue from aqueous solutions.



### INTRODUCTION

Modified clays have drawn much attention from the academe to the industrial communities for a long time.<sup>1,2</sup> They represent a new generation of adsorbents for both organic and inorganic pollutants; this is due to their small particle size, swelling capacity, anisotropic shape, reactive. They represent a new generation of adsorbents for both organic and inorganic pollutants; this is due to their small particle size, swelling capacity, anisotropic shape, reactive

surfaces, large specific surface area and high ion exchange capacity.<sup>3</sup> The advantage that the organoclays present is the possibility of changing their properties by varying the structure of the intercalated organic species<sup>4</sup> the combination of the hydrophobic nature of the organic species and the layered structure of the silicate layers leads to unique physicochemical properties. As a consequence, a number of previous studies have demonstrated that the interlayer spacing distance is a function of the lengths of intercalated molecules.<sup>5,6</sup>

\* Corresponding author: belbel.dj@gmail.com

Industries are the main source of water pollution due to release of toxic pollutants that are harmful to humans, animals and water bodies. One of such important pollutant is dyes that are widely used in many industries such as textiles. Some dyes can be carcinogenic and not biodegradable.<sup>7</sup> Among the most used dyes in the industry is methylene blue (MB), a cationic dye generally found in the chemical or biological fields: pharmaceutical, food, plastics, and dyeing.<sup>8</sup> Because of its special structure, MB is highly soluble in aqueous solutions and almost nonbiodegradable, it lasts for a long time in the environment.<sup>9</sup> For this cause, it is important to eliminate this type of pollutant from industrial discharges before they are evacuated into water streams. Various physicochemical and biological treatment methods have been reported to remove organic dyes from waste water. Adsorption is proven to be a practical way for the treatment of dye waste water due to its efficiency, selectivity and cost-effective nature.<sup>10-12</sup> Inspired by previous research, the current study focuses on the preparation and characterization of two types of organobentonite, with the aim of producing organoclays with higher thermal stability. This work underscores the importance of the use of Algerian-origin clays and the diverse nature of the modifiers for the efficient adsorption of Methylene blue dye. The intercalation of chemical reagents such as (CTAB<sup>+</sup>) and (BMIM<sup>+</sup>) inside the interlayer space was investigated by TGA, XRD and FTIR. Then, the organo-clays were used to the adsorption of MB dye from aqueous solutions.

## EXPERIMENTAL

### 1. Materials and methods

#### 1.1. Materials

The raw bentonite (Bt) from deposits of the Roussel site in Maghnia (western Algeria) were supplied by ENOF (an Algerian manufacture specialized in the production of non-ferric products and useful substances) company. The nature of bentonite is to absorb kinds of cationic from solution by exchange between the balance of cation charged negative layers and cations in solution is referred to as capacity cation exchange (CEC), and the values of CEC can be expressed in centimole of positive charge per kilogram of mineral clay to dry the same with miliequivalent per 100 g of clay (meq.100 g<sup>-1</sup>). The cation exchange capacity (CEC) of the bentonite has been given by the research of Makhoukhi et al and was found to be 67.5 meq.100 g<sup>-1</sup>.<sup>13</sup> The material was purified according to the method published in a previous study.<sup>14</sup> Homoionic clay (Bt-Na) was prepared by exchanging ions between Bt and

NaCl.<sup>15</sup> The chemical reagents used were hexadecyl(trimethyl)azanium; bromide (C<sub>19</sub>H<sub>42</sub>BrN) (CTAB, SIGMA-ALDRICH) and 1-butyl-3-methylimidazol-3-ium;chloride (C<sub>8</sub>H<sub>15</sub>ClN<sub>2</sub>) (BMIMCl), which were obtained from the Tokyo Chemical Industry (Japan). Methylene Blue (MB; CAS Number: 122965-43-9; Color Index Number CI-52015), supplied by PanReac AppliChem (Spain), is used as adsorbate without further purification.

#### 1.2. Characterization

Powder XRD analyses were performed on a Panalytical empyrean diffractometer (Netherlands) using Ni-filtered Cu K $\alpha$  as the source of radiation. The samples were all scanned from 3° to 80° with scanning speed of 6° min<sup>-1</sup>. Thermogravimetric analysis (TGA) for all samples was performed using the (LABSYS evo). Approximately, 40 mg of samples was heated from room temperature to 1000°C at a rate of 5°Cmin<sup>-1</sup> in a nitrogen atmosphere. The FTIR spectra of samples were obtained in the region 4000–400 cm<sup>-1</sup> from a BIO-RAD FTS-40 Spectrometer. The elemental analysis data of the clay sample were obtained through EXRF -S2 PUMA model of Bruker.

#### 1.3. Preparation of Modified Bentonite

The synthesis of organ clays was performed as follow: 1 g of homoionic clay (Bt-Na) was first dispersed in about 100 mL of deionised water, to which a desired amount of cetyltrimethylammonium bromide or Butylmethylimidazolium was slowly added. The concentrations of CTAB were 0.8 CEC, 1.2 CEC (or 2 CEC) of BMIMCl.<sup>16</sup> The organophilic activation was carried by ultrasound during 1 h (or 30 min) of BMIMCl<sup>16</sup>. The mixtures were stirred at room temperature using (vibra-cell Ultrasonic model VC-505). The processing conditions are set at the frequency of 20 kHz and the rated output power of 500W. The resulting suspension must then be filtered, washed several times with distilled water and finally dried in vacuum oven at 80 °C for 24 hours.

#### 1.4. Dye adsorption on Material

The Methylene Blue was adsorbed on the materials as follow: 10 mg (or 30 mg) of clays Bt-Na-CTAB-or Bt-Na-BMI was dispersed in 10 mL (or 30 mL) of Methylene Blue solution (MB) with concentrations from 60 to 300  $\mu$ M for the isotherm study (or 50  $\mu$ M for the kinetic study). The mixture was stirred for 15 min at 240 rpm at room temperature. For kinetic study, the contact time was from 5 to 30 min by 2 min step. After that, the mixture was separated via centrifugation at 2000 rpm for 5 min to separate the adsorbent. The dye concentrations in the solution were determined with (UviLine 9400-SECOMAM) UV-visible spectrophotometer.

## RESULTS

### 1. Structural Characterization

#### 1.1. X-ray Fluorescence Characterization

In the present study, we have examined an Algerian clay mineral exchanged with some

selective surfactants compounds, the elemental chemical analysis of the clay sample and physico-chemical characteristics of this bentonite clay are

gathered in Table 1. As shown in Table 1, these values are in the same range than the one previously reported by M. Boufatit *et al.*<sup>14</sup>

Table 1

Chemical analysis of material clays of Roussel from Maghnia, Algeria

Chemical analysis (%)										
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	MnO	Na <sub>2</sub> O	K <sub>2</sub> O
Our study	54.92	16.92	0.05	0.13	1.95	0.75	4.29	0.02	1.23	0.73
Others <sup>14</sup>	54.10– 54.98	18.04– 19.02	0.14– 0.16	< 0.05	1.98– 2.94	1.05– 2.95	1.05– 2.95	2.49	0.86– 2.40	1.14– 1.21

### 1.2. X-ray Diffraction Analyses

XRD analyse were performed on the homoionic clay are shown in Fig. 1. Examination of the diffractograms indicates that the remaining impurities consist of quartz (Q). The interlayer distance of the main peak  $d_{001}$  which characterizes sodium bentonite (Bt-Na) is 12.6 Å are in the same range than the one previously reported.<sup>16</sup>

Moreover, after the reaction of the Bt-Na with CTAB<sup>+</sup> increasing of  $d_{001}$  value to 20.8 Å (for CEC < 1) was observed, which corresponds to a bilayer intercalated with alkylammonium chains.<sup>17</sup> Beyond

this concentration (for CEC > 1) an interlayer distance of 21 Å was obtained (Fig. 2, Table 2).

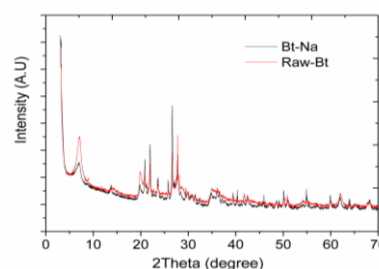


Fig. 1 – X-ray diffraction of raw and sodium bentonite.

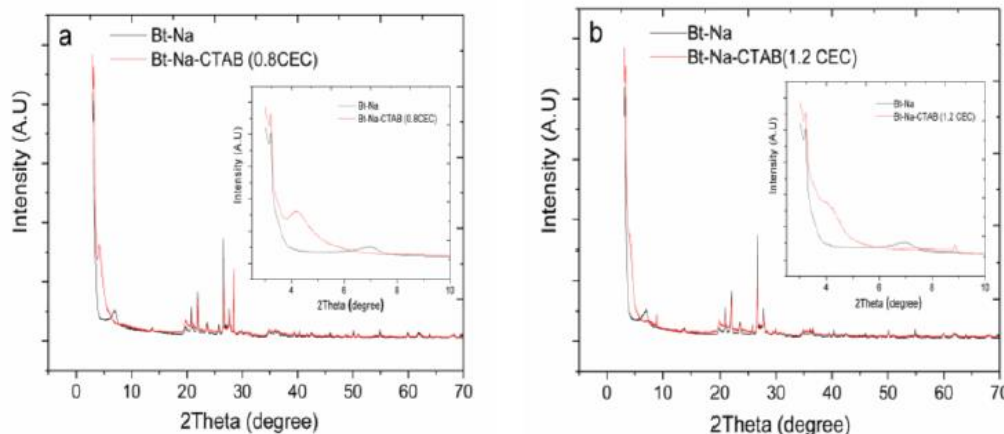


Fig. 2 – XRD spectrum of the CTAB modified bentonite.

Table 2

Interlayer spacing of sodium and modified bentonite

Sample	Bt-Na	Bt- CTAB		Bt-BMIM
CEC	/	0.8	1.20	2
$d_{001}$ (Å)	12.60	20.80	21	14.19

Which is higher than the value reported by Khenif *et al.*,<sup>18</sup> an interlayer spacing around 19 Å was obtained by stirring for 24 h for the preparation

of CTAB/Clay. In our case, the basal distance of interfoliar space of the obtained materials is 21 Å during 1 h of ultrasound treatment. The effect of cavitation also generates greater pressures and temperatures leading thereafter to a greater division and dispersion of clay sheets.<sup>16</sup> For the BMIM<sup>+</sup> (Fig. 3) in interlayer distance 14.19 Å was obtained, this confirms that the BMIM<sup>+</sup> is intercalated inside interlayer space. Thus, the BMIM<sup>+</sup> ions form a monolayer, which can be explained by the extremely short alkyl chains.<sup>19</sup>

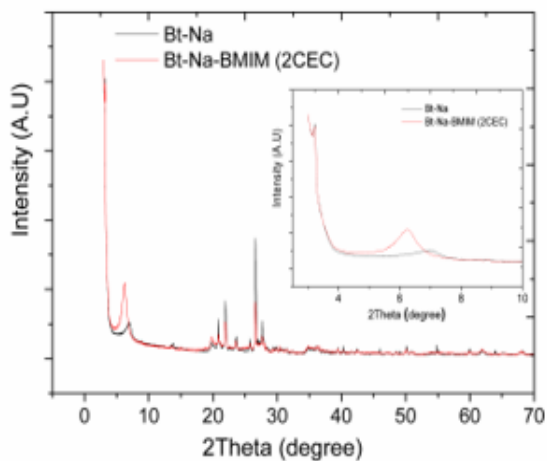


Fig. 3 – XRD spectrum of the BMIM modified bentonite following percentage of the clays CEC.

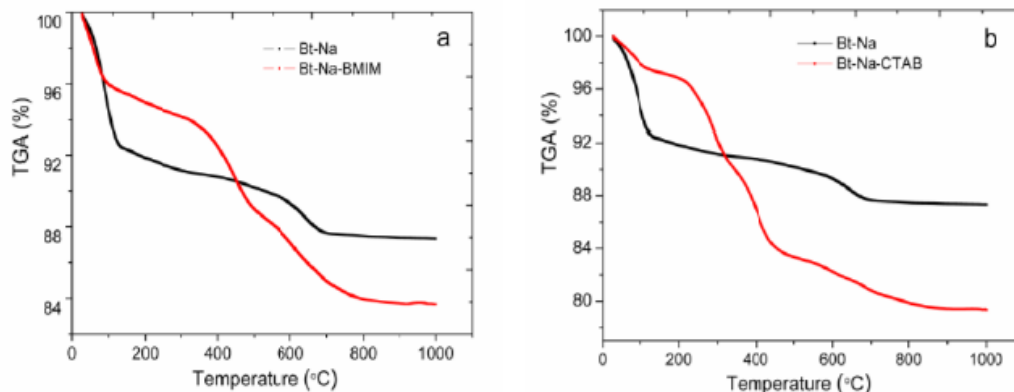


Fig. 4 – TGA curves of: a) Bt-Na-BMIM; b) Bt-Na-CTAB.

In addition, the weight loss observed in the range 300–1000°C could not be exclusively associated to the dehydroxylation phenomenon of the clay as it was higher for the intercalated montmorillonites (10.25%) than for the pure one (3.65%). This suggested that the dehydroxylation of Bt-Na was superimposed on the decomposition of organic matter<sup>21</sup>.

For the Bt-Na-CTAB, the first mass loss (2.64%) in the ATG curve (Fig. 4b), is related to the dehydration of the external surface adsorbed water, the other step is attributed to surfactant degradation (centered at 293°C). The decomposition temperatures of pure surfactant (CTAB) have been noted to be 194°C, which is lower than the decomposition temperatures of surfactants introduced in organoclays.<sup>22,23</sup> This result clearly demonstrates that the surfactant molecules are bonded to the Mt siloxane layer. This key result shows a higher temperature is needed to remove the surfactant molecules bonded on the clay surfaces.<sup>24</sup>

### 1.3. Thermo Gravimetric Analysis TGA

The TGA curve of Bt-Na shows a first weight loss (7.46%) from room temperature up to approximately 130°C (Fig. 4a) which was attributed to the elimination of adsorbed water. A small weight loss of up to 4.35% was observed for Bt-Na-BMIM intercalated bentonite in this temperature range, indicating that the surfactants intercalation provided hydrophobic montmorillonite. The weight loss of 2.2% occurred in the temperature range between 570°C and 800°C of Bt-Na sample was attributed to the dehydroxylation of structural hydroxyl groups.<sup>20</sup> The thermal decomposition of the Bt-Na-BMIM began at similar temperatures than this determined for pure ionic liquid (220°C) and continued then much more slowly (Fig. 4a).

The TGA analysis revealed the following findings: Bt-MIM began and completed decomposition before Bt-CTAB, this difference could be attributed to nature and the physico-chemical properties of cationic surfactant intercalated. In addition, Fig. 5 showed that the thermal stability could be arranged in the following order: Bt-BMIM < Bt-CTAB.

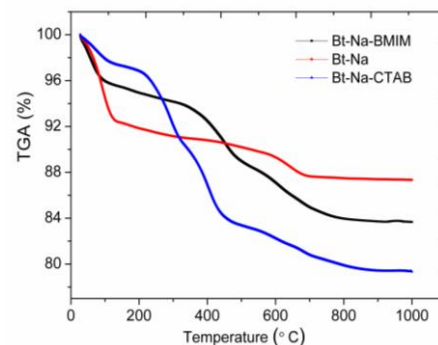


Fig. 5 – TGA curves of the purified and modified bentonites.

### 1.4. FTIR analyses

The FTIR spectra of the purified bentonite and its modified counterparts are shown in Figs. 6a and 6b. All products exhibit two moderately intense bands at  $3619\text{ cm}^{-1}$  and  $3432\text{ cm}^{-1}$ , which might be ascribed to the stretching mode of the OH functional groups of

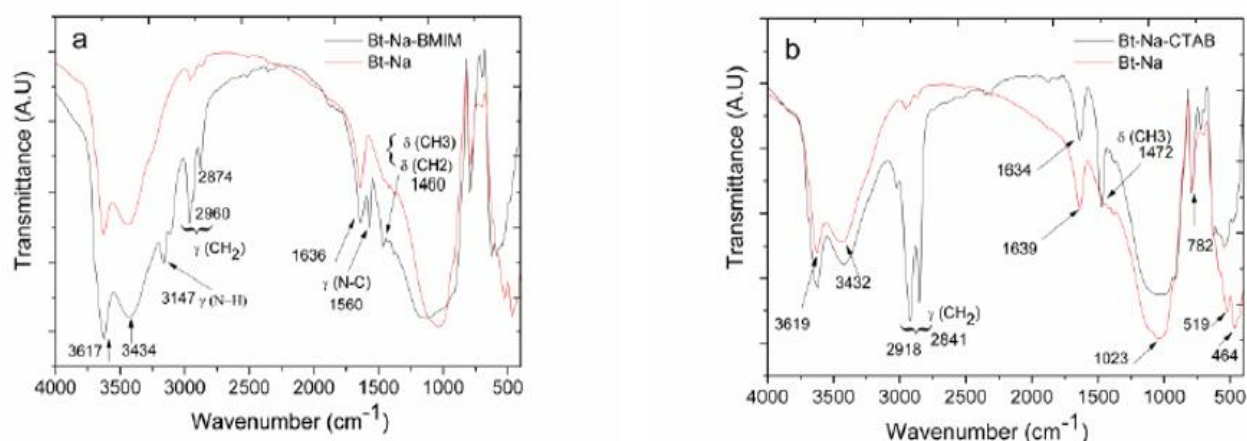


Fig. 6 – FTIR spectra of Bt and its organo modified counterparts: a) Bt-Na-BMIM: b) Bt-Na-CTAB.

Various bands were obtained after the modification of Bt-Na by CTAB<sup>+</sup> or BMIM<sup>+</sup>. The new bands were obtained at  $2874\text{ cm}^{-1}$  and  $2960\text{ cm}^{-1}$  which are assigned to the elongation vibrations of alkyl chains ( $-\text{CH}_2$  and  $-\text{CH}_3$ ), the intensity of these bands varies according to the concentration of the surfactant as well as the length of its alkyl chain.<sup>6</sup> The band at  $1590\text{ cm}^{-1}$  is the signature of the stretching of N-C bonds of the imidazole moieties.<sup>29</sup> The  $\nu(\text{N-H})$  band is responsible for a very weak band near  $3147\text{ cm}^{-1}$ .<sup>21</sup> Appear of these characteristic bands confirms the presence of CTAB<sup>+</sup> or BMIM<sup>+</sup> on Bt, and also confirms the results obtained by the XRD analysis.

## 2. Adsorption of Methylene Blue on Modified Bentonite

Kinetic studies (not shown) displayed that for the methylene blue molecules, the adsorption kinetic was very quick. The maximum adsorption equilibrium was reached at least after 20 minutes of contact with the adsorbents. To go further in our investigation, the sorption isotherm of MB on modified clays was studied (Figs. 7a and 7b). The experimental results were fitted using Langmuir<sup>30</sup>

molecule of water of crystallisation.<sup>25</sup> The band at  $1636\text{ cm}^{-1}$  is attributed to the deformational vibrations of H-O-H adsorbed water molecules.<sup>26</sup> The band due to asymmetric Si-O-Si stretching vibration is normally in the region  $1100\text{--}1000\text{ cm}^{-1}$ . The angular deformation bands at  $519$  and  $464\text{ cm}^{-1}$  are attributed to the Si-O-M type bonds (M = Mg, Al or Fe).<sup>27,28</sup>

equation (1) and Freundlich<sup>31</sup> equation (2) respectively

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = k_F C_e^{\frac{1}{n}} \quad (2)$$

where  $q_m$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the maximum adsorption capacity and  $K_L$  ( $\text{L}\cdot\text{mg}^{-1}$ ) is the Langmuir equilibrium constant,  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the adsorption capacity at equilibrium,  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the equilibrium concentration of dye in solution,  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity respectively.

The calculated parameters of Langmuir, Freundlich isotherms for the adsorption of MB dye modified clays listed were being in Table 3. However, from these data the adsorption of MB onto clay samples was fitted well to all of the isotherm models as indicated by the correlation coefficient ( $R^2$ ) values in Table 3. Based on the Langmuir isotherm, the maximum adsorption capacities ( $q_m$ ) of the used samples were  $47.186\text{ mg/g}$  for Bt-Na-BMIM and  $42.281\text{ mg/g}$  for Bt-Na-CTAB. These values of adsorption capacity are higher than the one reported for Methylene Blue on modified clay materials.<sup>32,33</sup>



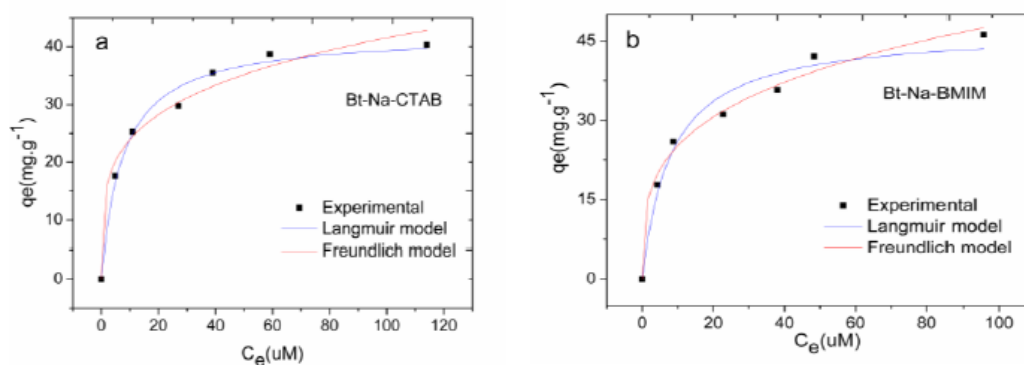


Fig. 7 – MB sorption isotherms on modified bentonites fitted with the Langmuir and Freundlich models: a) Bt-Na-CTAB; b) Bt-Na-BMIM.

Table 3

Fitting parameters obtained for Langmuir and Freundlich isotherms

Sample	Langmuir model			Freundlich model		
	$q_m(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	$R^2$	$K_F(\text{mg}\cdot\text{g}^{-1})$	$n$	$R^2$
Bt- CTAB	42.281	.0131	0.988	13.779	4.184	0.980
Bt- BMIM	47.186	0.123	0.974	13.217	3.571	0.987

## CONCLUSIONS

The BMIM and CTAB has been successfully exchanged with a homoionic bentonite Bt-Na. The intercalation processes was demonstrated by XRD and FTIR. The adsorption isotherms at room temperature towards methylene displayed that the maximum adsorption capacity of the organoclays followed the order Bt- BMIM > Bt- CTAB . The maximum adsorption capacity of the used homoionic bentonite blue is 47.186  $\text{mg}\cdot\text{g}^{-1}$  in the case of Bt- BMIM. Several parameters such as pH, temperature or contact time could be explored in further work to optimize the adsorption parameters.

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