Effect of Brønsted acidity of HY zeolites in adsorption of methylene blue and comparative study with bentonite

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Abstract
In the present study, HY zeolite with various Si/Al ratios have been used as adsorbents for the removal of a cationic dye; methylene blue, from aqueous solution using a batch process, and a comparative study with bentonite was conducted. Characterizations of the adsorbents were carried out by nitrogen adsorption–desorption, pyridine chemisorption followed by infrared spectroscopy and X-ray fluorescence. The effects of various parameters such as contact time, initial MB concentration, adsorbent concentration and solution pH were investigated. The adsorption of methylene blue on the zeolites is directly related to the Brønsted acidity where each molecule of MB corresponds to one Brønsted acid site. This means that the adsorption mechanism occurs via a cation exchange. So, adsorption of MB can be used to determine the Brønsted acidity of HY zeolites. The highest removal efficiency (181 mg g\(^{-1}\)) corresponding to 86% of the abatement rate has been obtained with the bentonite. At lower dye concentrations (\(\leq 50\) mg L\(^{-1}\)), HY (16.6) and bentonite have a close adsorption capacities, 93 mg g\(^{-1}\) (97%) and 96 mg g\(^{-1}\) (99%) respectively. For both material types, the pseudo-second-order kinetic model fits very well with the experimental data. Equilibrium data fitted well the Langmuir isotherm model in the studied concentrations range of MB.

Keywords Adsorption · Bentonite · Brønsted acidity · Methylene blue · Zeolite

Introduction
The industry has always been considered as a major source of pollution. Among the various pollutants released into the environment, dyes are found in large quantities because of the textile industry that consumes a large amount of water and thus releases a considerable fraction of these dyes in its aqueous effluents [1]. Dyes are not only visually detected and aesthetically displeasing, they affect aquatic life and photosynthesis reactions by preventing sunlight from penetrating water, their degradation is so dangerous to the aquatic environment and human life even at low concentrations. Different types of dyes exist and methylene blue is widely used in medicine, dyeing cotton, wood and silk. Its overuse can cause serious problems for human life, thus, it must be eliminated from our environment [2, 3]. Several techniques are used for the removal of organic and inorganic pollutants, such as: chemical oxidation processes [4], photocatalysis [5], decolorization [6], enzymatic elimination [7, 8] and adsorption [9, 10]. The simplest technique and most effective is adsorption, and the most widely used adsorbent is activated carbon because of its large surface area leading to a large adsorption capacity, but in recent decades much research has been conducted with the aim of replacing activated carbon because of its low selectivity and the difficulty of its regeneration [11, 12]. For this reason, other effective synthetic and natural adsorbents have been tested as silico-aluminates [13]. Bentonite is one of the most extensively used adsorbents of dyes removal and it has already been shown to have a high adsorption capacity [14]. The bentonite is not the only silico-aluminate used for the adsorption of organic molecules; other materials such as zeolites are very attractive because they offer several possibilities in terms of specific surface, pore size, Si/Al ratio, acidity and high thermal stability. However, a number of research studies have been conducted on dye removal using natural zeolite [15], and other investigations have been conducted on methylene blue removal using synthetic zeolite...
where the effect of experimental parameters has been examined such as pH, time, adsorbent concentration and initial dye concentration [16]. The effectiveness of the zeolites is related to their specific surfaces and the diameter of their pores [17]. So, in order to avoid the problems of diffusion, HY zeolite is suitable for removing organic molecules [18, 19]. HY zeolite has a tri-dimensional porous structure (porous volume accounts for 50% of total volume) in which pores form large interconnected cavities accessible by large openings (7.4 Å). Thus, HY zeolite structure provides a good accessibility for organic molecules to the internal adsorption sites.

In our study, in addition to these structural properties (specific surfaces and pores diameter), we want to examine the effects of the functional property of the HY zeolites on the adsorption of methylene blue. This study was not done before. For this purpose, we used zeolite in their protonic form (HY) at different Si/Al ratios to determine the effects of their acidity on their adsorption capacities to remove methylene blue (MB). The effect of pyridine adsorbed on the Brunsted and Lewis sites is determined by integrating the band areas at respectively 1545 cm\(^{-1}\) and 1454 cm\(^{-1}\) and using the following extinction coefficients: \(\varepsilon_{1545} = 1.13\) and \(\varepsilon_{1454} = 1.28\) cm\(^{-1}\) mol\(^{-1}\) [20].

The MB absorbance measurements were done at 666 nm with a UV–vis spectrometer (UV-SCAN, Shimadzu spectroscan 50).

### Materials and methods

#### Adsorbate and adsorbent

The three commercial zeolites HY (Si/Al = 2.9, Si/Al = 16.6, Si/Al = 30.0) were purchased from Zeolyst International, the acid-activated bentonite (Si/Al = 3.3) was donated to us by the Algerian industry Cevital; these samples were directly used as adsorbents without further post-treatment. Faujasite samples were denoted as HY (2.9), HY (16.6) and HY (30.0), where the numbers 2.9, 16.6 and 30.0 indicate the global Si/Al ratios determined by X-ray fluorescence. The adsorbate Methylene blue (3,7 bis (Dimethylamino)- phenazathionium chloride), (chemical formula, \(C_{16}H_{18}N_{3}SCl;\) M, 319.85 g mol\(^{-1}\)) was purchased from MERCK Eurolab S.A.

#### Physico-chemical characterizations

The Si/Al ratio of the materials was determined by X-ray fluorescence. The textural characteristics of the adsorbents were determined by nitrogen adsorption at 77 K using Micromeritics ASAP-2000. The specific surface area (\(S_{BET}\)) was calculated by the BET equation. The total pore volume (\(V_{\text{total}}\)) was estimated from nitrogen adsorption at a relative pressure of 0.97, the microporous volume (\(V_{\text{micro}}\)) was determined by the t-plot method and the mesoporous volume (\(V_{\text{meso}}\)) was the difference between \(V_{\text{total}}\) and \(V_{\text{micro}}\). The acidity of the different zeolites and the bentonite was determined by pyridine chemisorption followed by infrared spectroscopy using FT-IR NEXUS Thermo–Nicollet under secondary vacuum. The adsorbents were pretreated from room temperature to 450 °C (heating rate of 2 °C/min for 12 h) under secondary vacuum. After collecting the reference spectra, pyridine adsorption takes place at 150 °C. The amount of pyridine adsorbed on the Brunsted and Lewis sites is determined by integrating the band areas at respectively 1545 cm\(^{-1}\) and 1454 cm\(^{-1}\) and using the following extinction coefficients: \(\varepsilon_{1545} = 1.13\) and \(\varepsilon_{1454} = 1.28\) cm\(^{-1}\) mol\(^{-1}\) [20].

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#### Batch adsorption procedure and statistics

All the adsorption experiments, whatever the studied parameter, were carried out in batch conditions at 25 °C and under atmospheric pressure. Each adsorption experiment consisted in preparing 20 mL of dye solution by diluting the stock solution with distilled water to a given concentration and transferring them into an Erlenmeyer flask on a mechanic agitator. A weighted amount of adsorbent was then added to the solution and agitated mechanically for a given period. Thereafter the samples were centrifuged to separate the adsorbent from the liquid phase, and the dye concentration was determined by UV-visible spectrophotometry.

The amount of dye adsorbed was calculated using:

\[
q_t = \frac{V}{m} (C_0 - C_t)
\]

(1)

and abatement rate (%) was calculated using Eq. (2)

\[
\text{abatement rate} (%) = \frac{C_0 - C_t}{C_0} \times 100
\]

(2)

Where: \(q_t\) is adsorption capacity in (mg g\(^{-1}\)), \(C_0\) is the initial dye concentration (mg L\(^{-1}\)), \(C_t\) is the dye residual concentration (mg L\(^{-1}\)), \(V\) is the volume of dye solution in (L) and \(m\) is the total amount of adsorbent (g).

Each experiment was repeated three times and the mean results with the error bar (± standard deviation) were presented using MS Excel 2010. All the figures were drawn using MS Excel 2010.

### Results and discussion

#### Adsorbent characterization

The physicochemical properties of HY zeolites and bentonite are quoted in Table 1. The nitrogen adsorption-desorption isotherms of zeolites (not shown here) display an isotherm...
of type I according to the classification of IUPAC indicating that these materials are microporous and have a small external surfaces. The isotherms display a small hysteresis loop at high relative pressure formed by the agglomeration of zeolite crystals. For bentonite, the isotherm is type IV (not shown here) characterized by its hysteresis loop on the desorption branch. The significant enhancement of the N₂ adsorbed volume for high relative pressures is associated with the N₂ capillary condensation inside the mesopores. The specific surfaces were relatively important for all the zeolites and HY samples had higher BET surface areas than bentonite sample. The comparison of the microporous and the mesoporous volume indicates that the majority of the adsorption space of zeolites is in the micropore region. In contrast, the majority of the adsorption space of bentonite is in the mesopore region. Table 1 show that, the global Si/Al (zeolites) ratios obtained by bulk chemical analysis are very low compared to the Si/Al ratios of the tetrahedral framework (Si/Al_{framework}) drawn from TOT bands. These results indicate a presence of a fraction of extraframework aluminum species (EFAL) which is in agreement with the presence of Lewis acidities.

![Image of Table 1](attachment:table1.png)

The infrared spectra of HY samples after outgassing treatment (before pyridine adsorption) and after adsorption of pyridine is given in Fig. 1. Zeolites exhibits two well defined absorption bands at 3739 and 3629 cm⁻¹, assigned to the stretching vibrations of silanol groups, SiOH, and to the bridged hydroxyl, Al (OH) Si, responsible for Bronsted acidity, respectively [21]. Another band appears at 3564 cm⁻¹, suggesting the presence of at least two different acid sites, those corresponds to the bridged OH of the hexagonal prisms (3564 cm⁻¹) and the others to the supercages of the Faujasite structure at 3629 cm⁻¹ [22]. Furthermore, Bronsted and Lewis acidities have been quantified by pyridine adsorption at 150 °C integrating the absorption bands respectively at 1545 and 1454 cm⁻¹. The obtained values are summarized in Table 1. For the different Si/Al ratios of zeolites, the real number of the protonic sites is smaller than the theoretical concentrations of Bronsted acid sites. As a consequence of an incomplete protonic exchange of the alkali cations when the zeolite is transformed to the protonic form and dehydroxylation phenomena or even dealumination during the activation of the zeolite at high temperatures (500–550 °C). According to the Table 1, HY(2.9) zeolite has the highest number of Bronsted acid sites calculated theoretically (883 μmol g⁻¹) compared to HY (16.6) and HY (30.0) which have the theoretical Bronsted acidities of 651 and 518 μmol g⁻¹, respectively. These theoretical results are coherent because the number of Bronsted acid sites decreases as the Si/Al ratio increases. The number of Bronsted acid sites of HY(2.9) zeolite (192 μmol g⁻¹) able to retain pyridine at 150 °C is lower than HY (16.6) (443 μmol g⁻¹) and HY (30.0) (312 μmol g⁻¹). These results suggest that, the exchange rate of the alkaline cations of HY(2.9) is very low. In fact, in order to have a complete exchange of the alkaline cations by protons (exchange rate close to 100%), the operation must be repeated several times. In the case of HY(2.9) (highly alumined zeolite), the structure risks collapsing during the calcination step. The simple method which is the direct exchange (treatment with an acid solution) of the alkaline cations of the zeolites by protons is limited to zeolites with a high Si/Al ratio. When the Si/Al ratio of the zeolites is less than 10 (highly alumined zeolite HY (2.9)), the exchange of the alkaline cations often causes the collapse of their structure [22].

To avoid the collapse of the zeolites structures, no exchange of the alkaline cations was made. The zeolites are used with the acidity values determined by pyridine chemisorption
followed by infrared spectroscopy and mentioned in the Table 1. The effect of Brønsted acidity of zeolites on the adsorption of MB has been demonstrated.

**MB batch adsorption experiments**

**Effect of adsorbent concentration**

The effect of adsorbent concentration on the removal of MB dye at initial dye concentrations of 50.0 mg L\(^{-1}\) was evaluated by varying the adsorbent dosage from 0.05 to 2 g L\(^{-1}\). The abatement rate was increased until reaching a plateau (Fig. 2), varying from 37.5 to 100% for bentonite and from 24 to 100% for zeolite. This increase in the adsorption rate can be explained by an increase in the adsorbent surface, which implies a greater number of active sites [23, 24]. At adsorbent doses greater than 0.5 g L\(^{-1}\), the removal percentage of MB is not changing for the two studied materials. So for further experiments we will work with this solid concentration.

**Effect of pH**

Many studies suggest that pH of a solution is an important factor in the adsorption process because it affects both aqueous species speciation and the surface net charge of the adsorbent [25–27]. In this study, the effect of the initial solution pH on zeolites and bentonite was investigated in the range of (2–11) with initial dye concentration of 50 mg L\(^{-1}\), adsorbent dose of 0.5 g L\(^{-1}\) and temperature of 25 °C (Fig. 3). For bentonite, the pH had no significant effect over a wide pH range 2–11 and the removal efficiency of MB remained above 99% while for HY, at low pH value, the removal efficiency of MB decreases down to 70%. Rida et al. [28] have obtained results that are similar to
ours. At low pH, the decrease of the MB removal is attributed to a competition between the protons and the dye molecule on the adsorption sites as it has already been observed with MOR by Sohrabnezhad and Pourahmad [29]. As the pH increases, the acid sites become increasingly deprotonated, and the adsorbent become negatively charged resulting in an enhancement of the adsorption of the cationic MB.

### Effect of contact time and initial dye concentration

The effect of contact time on adsorption was studied for dye concentrations between 5 and 100 mg L\(^{-1}\) and adsorbent dosage of 0.5 g L\(^{-1}\). The adsorption efficiency of dye increases gradually with increasing contact time and reaches a plateau afterwards (Fig. 4). So, kinetics of removal efficiency of dye occurred in two steps: an initial rapid phase and a second slower phase. The fast MB removal rate at the initial stage was due to the fact that, initially, all adsorbent sites were free, on the other hand the OH groups on the adsorbents surface are deprotonated at pH = 7 which makes the surface charged negatively and led to fast adsorption of the cationic MB from the solution [26]. The increase of adsorption capacity with the increase of MB concentration is due to an increase in the driving force of the concentration gradient [25, 30]. The slower MB removal phase is due to the accumulation of dye particles in the vacant sites [2].

The contact time necessary to reach equilibrium depends on the initial dye concentration and on the nature of the materials. For the bentonite, the equilibrium is reached more quickly compared to zeolites. For an initial dye concentration of 5 mg L\(^{-1}\) and 10 mg L\(^{-1}\), equilibrium is reached after only 1 h for bentonite while it takes 2 h for HY. For initial dye concentration of 50 mg L\(^{-1}\) and 100 mg L\(^{-1}\) equilibrium is reached after 5 h for bentonite and 10 h for the zeolites. In the case of bentonite, the interlayer cations neutralize the randomly distributed negative charges on the octahedral sheet. And in this case the cations do not act as locks between two neighbouring sheets. Consequently, the crystal sheets are weakly bonded together and, thus, more water molecules can penetrate into the interlayer space which becomes larger and facilitates the diffusion of methylene blue molecules [31].

### Adsorption kinetics modeling and mechanism

In order to investigate the removal of MB using different adsorbents, pseudo-first-order, pseudo-second-order and
intra-particle diffusion kinetic models were used. The linear form of the pseudo-first order model is given by:

\[ \ln (q_e - q_t) = \ln (q_e) - k_1 t \]  

(3)

where \( q_t \) is the amount of adsorbate adsorbed at time \( t \) (mg g\(^{-1}\)), \( q_e \) is the amount of adsorbate adsorbed at equilibrium (mg g\(^{-1}\)), \( k_1 \) is the pseudo-first-order rate constant (h\(^{-1}\)) and \( t \) is the contact time (h).

The values of the adsorption rate constant, \( k_1 \), equilibrium adsorption capacity, \( q_e \) (theo), and the correlation coefficient, \( R^2 \), were determined from the plot of \( \ln (q_e - q_t) \) against \( t \) at different initial concentrations.

The linearized form of the second-order kinetic model is:

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

(4)

where \( k_2 \) is the pseudo second-order rate constant (g mg\(^{-1}\) h\(^{-1}\)).

To model the intra-particle diffusion the Eq. (5) is used:

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

(5)

where \( K_t \) is the rate constant of the intra-particle diffusion (mg g\(^{-1}\) h\(^{-1/2}\)) and \( C \) is the intercept. The thickness of the boundary layer is directly related to the value of \( C \).

The initial adsorption rates are also calculated by Eq. (6):

\[ h = K_2 q_e^2 \]  

(6)

where \( h \) is the initial adsorption rate constant (mg g\(^{-1}\) h\(^{-1}\)).

The experimental results of all the studied materials are not well described by the first-order model (not shown here). The pseudo-second-order model is close to the experimental data (Table 2), suggesting that this model is very well adapted for all adsorbents at different concentrations. The increase in initial dye concentration caused a decrease in the adsorption rate, \( K_2 \) (Table 2). Similar results have been observed by Wang et al. [32]. The initial adsorption rates increase according to the initial concentration and the highest values are obtained by the bentonite followed by HY (16.6).

For the intra-particle diffusion, the adsorption process occurs in two phases for all the different adsorbents except for bentonite at low initial concentrations. The two phases suggest that the adsorption process proceeds by surface adsorption followed by the intra-particle diffusion [33]. The first straight section is characterized by a fast uptake. This behavior can be explained by the availability of free sites on the external surface of the solid and strong adsorbate-adsorbent interactions.

At the second phase, adsorption becomes very slow because of the low diffusion of adsorbed molecules MB from the film surface through the micropores which are hardly accessible. For the bentonite at low concentration (5 and 10 mg L\(^{-1}\)), adsorption occurs in one step, and at high concentrations (50 and 100 mg L\(^{-1}\)), the adsorption is controlled by two steps, the first is attributed to the surface adsorption and the second is expressed as the intra-particle diffusion.

It has been reported by various researchers that the plots that do not pass through the origin, indicate that the intra-particle diffusion is not the only rate controlling step, then some other processes may control the rate of adsorption.

### Table 2 MB adsorption kinetics constants

| Adsorbent  | \( C_0 \) (mg L\(^{-1}\)) | \( q_e \) (exp) (mg g\(^{-1}\)) | \( q_e \) (theo) (mg g\(^{-1}\)) | \( K_2 \) (g mg\(^{-1}\) h\(^{-1}\)) | \( R^2 \) | \( H \) (mg g\(^{-1}\) h\(^{0.5}\)) | \( K_t \) (mg g\(^{-1}\) h\(^{-1}\)) | \( D_{50} \) (10\(^{-6}\) cm\(^2\) s\(^{-1}\)) | \( D_t \) (10\(^{-6}\) cm\(^2\) s\(^{-1}\)) |
|------------|--------------------------|-------------------------------|-------------------------------|-------------------------------|--------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| HY(2.9)    | 5                        | 9.9                           | 10.1                          | 0.136                         | 0.999  | 13.8                        | 0.47                        | 4.62                        | 4.59                        |
|            | 10                       | 17.6                          | 18.6                          | 0.043                         | 0.997  | 14.9                        | 2.27                        | 2.31                        | 2.05                        |
|            | 50                       | 52.4                          | 57.1                          | 0.009                         | 0.998  | 29.4                        | 11.49                       | 1.38                        | 0.73                        |
|            | 100                      | 58.2                          | 60.9                          | 0.015                         | 0.999  | 55.7                        | 14.41                       | 1.38                        | 0.41                        |
| HY(16.6)   | 5                        | 10.3                          | 10.3                          | 0.607                         | 1.000  | 65.3                        | 0.08                        | 4.86                        | 4.92                        |
|            | 10                       | 20.3                          | 20.6                          | 0.149                         | 0.999  | 63.6                        | 9.85                        | 4.86                        | 4.86                        |
|            | 50                       | 92.8                          | 96.2                          | 0.007                         | 0.999  | 67.3                        | 19.96                       | 1.46                        | 1.33                        |
|            | 100                      | 135.8                         | 142.9                         | 0.004                         | 0.996  | 84.0                        | 13.41                       | 1.46                        | 0.97                        |
|            | 5                        | 10.1                          | 10.2                          | 0.311                         | 0.999  | 32.4                        | 0.37                        | 4.38                        | 4.58                        |
| HY(30.0)   | 10                       | 19.9                          | 20.2                          | 0.131                         | 0.999  | 53.8                        | 0.99                        | 4.38                        | 4.51                        |
|            | 50                       | 74.4                          | 76.9                          | 0.009                         | 0.999  | 55.8                        | 11.98                       | 1.31                        | 1.01                        |
|            | 100                      | 81.4                          | 85.5                          | 0.008                         | 0.998  | 60.5                        | 14.20                       | 1.31                        | 0.55                        |
| Bentonite  | 5                        | 10.3                          | 10.1                          | 1.495                         | 1.000  | 153.7                       | 2.19                        | 7.35                        | 7.39                        |
|            | 10                       | 20.3                          | 20.5                          | 0.486                         | 1.000  | 204.0                       | 1.67                        | 7.35                        | 7.31                        |
|            | 50                       | 96.2                          | 100.0                         | 0.018                         | 0.999  | 180.0                       | 2.70                        | 2.94                        | 2.76                        |
|            | 100                      | 177.5                         | 188.6                         | 0.006                         | 0.999  | 213.6                       | 9.98                        | 2.94                        | 2.55                        |

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\( ^a \) Initial dye concentration

\( ^b \) Deduced from the kinetics curves at equilibrium (\( T = 25 ^\circ \text{C}, \) adsorbent dose = 0.5 g L\(^{-1}\), pH = 7)

\( ^c \) Calculated from the pseudo-second-order model

\( ^d \) Calculated from the intra-particular model
To determine the limiting step, calculating the coefficient of pore diffusion ($D_{pp}$) and coefficient of film diffusion ($D_f$) by the Eqs. 7 and 8 respectively tells us if pore diffusion is the only rate-controlling step [35].

$$D_{pp} = \frac{0.03 \, r^2}{t_{1/2}}$$  \hspace{1cm} (7)

$$D_f = \frac{0.23 \, r \, \varepsilon \, q_{e}}{t_{1/2} \, C_0}$$  \hspace{1cm} (8)

Where $r$ is the radius of the adsorbent, $\varepsilon$ the film thickness ($10^{-3}$ cm), $q_e$ the amount of adsorbed dye (mg g$^{-1}$), $C_0$ the initial concentration and $t_{1/2}$ is the time for half adsorption ($h^{0.5}$) of MB. If the value of the film diffusion coefficient $(D_f)$ is in the range of $10^{-6}$ to $10^{-8}$ cm$^2$ s$^{-1}$; film diffusion was the rate-determining step in the adsorption of MB. If pore diffusion was to be the rate determining step, the pore diffusion coefficient $(D_{pp})$ should be in the range of $10^{-11}$ to $10^{-13}$ cm$^2$ s$^{-1}$ [33]. The obtained values of $D_f$ and $D_{pp}$ (Table 2) are in the order of $10^{-6}$ cm$^2$ s$^{-1}$ indicating that the MB removal on zeolites and bentonite was controlled by film diffusion only.

### Isotherms of adsorption

Adsorption isotherms were carried out by varying the MB initial concentrations from 2 to 100 mg L$^{-1}$. Isotherms of adsorption for all zeolites and bentonite, are of type L (Fig. 5) according to the Giles classification [36]. The same type of isotherms has been obtained by Vadivelan & Vasanth-Kumar [2], indicating a good affinity of methylene blue with the adsorbents.

The equilibrium of adsorption was evaluated using Langmuir isotherm model, which is used to describe an adsorption onto a homogenous surface:

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} c_e + \frac{1}{q_{\text{max}} K_L}$$  \hspace{1cm} (9)

Where $C_e$ is the equilibrium concentration (mg L$^{-1}$), $q_e$ the amount of adsorbed dye molecule (mg g$^{-1}$), $q_{\text{max}}$ for a complete monolayer (mg g$^{-1}$) and $K_L$ is the constant related to the affinity of the binding sites (L mg$^{-1}$).

The regression coefficients $R^2$ obtained from the Langmuir model were very close to 1 (Table 3) suggesting that the Langmuir model describes very well the adsorption isotherm (Fig. 5). It is well-known that the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule on the surface had equal adsorption activation energy. The highest adsorption capacity is obtained for bentonite. However, the $K_L$ coefficient is very much higher for bentonite indicating its high affinity for MB dye. For zeolites, the slope between $q_{\text{max}}$ and the number of the Brønsted acid sites is 1 (Fig. 6), which means that one molecule of MB is adsorbed by one acid site of Brønsted. We can conclude that adsorption from the MB occurs only by a cation exchange and to determine the Brønsted acidity of HY zeolites we can use adsorption of methylene blue.

Table 4 summarizes the reported adsorption capacities of various MB adsorbents in the literature [37–42]. The data show that the adsorption capacity of zeolites approaches that of clays when their acidity increases. HY(16.6) has higher

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**Table 3** Parameter values of adsorption models

| Sample  | $q_{\text{max}}$ (μmol g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ |
|---------|-------------------------------|-------------------|-------|
| HY(2.9) | 186                           | 0.541             | 0.999 |
| HY(16.6)| 441                           | 0.980             | 0.998 |
| HY(30.0)| 252                           | 0.770             | 0.999 |
| Bentonite | 566                           | 3.660             | 0.999 |

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**Fig. 5** Langmuir modelization (continuous line) of MB adsorption isotherms over HY zeolites and bentonite ($T=25$ °C, adsorbent dose = 0.5 g L$^{-1}$, pH = 7)

**Fig. 6** $q_{\text{max}}$ versus number of Bronsted acid sites for HY zeolites
adsorption capacities than many of the other reported adsorbents for MB. Therefore, it can be concluded that zeolite HY is an efficient adsorbent for removal of MB from aqueous solution.

Conclusions

The adsorption of MB does not depend on solution pH from 5 to 11 while it depends on contact time, initial dye concentration and adsorbent amount. The equilibrium data fit perfectly the Langmuir model of adsorption, showing homogeneous distribution of active sites on all adsorbents surface. Zeolites can be used as adsorbent for the removal of MB from wastewater. The results show that adsorption of MB is highly dependent on the acid properties of zeolites. One molecule of MB is adsorbed by one Brønsted acid site. So, to determine the Brønsted acidity of HY zeolites we can use adsorption of methylene blue which is much cheaper than adsorption of pyridine. The maximum adsorption uptake is obtained with bentonite. At lower dye concentrations (< 50 mg L⁻¹), HY (16.6) and bentonite have the same adsorption efficiency (98%). The pseudo-second-order kinetic model agrees very well with the experimental results. The kinetics of MB adsorption in all adsorbents follows the intraparticle diffusion model, and the data related by two straight lines indicate that the intraparticle diffusion is not the only rate controlling step.

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Table 4 Comparison of MB adsorption capacities of various adsorbents

| adsorbents               | Adsorption capacity (mg g⁻¹) | Reference      |
|--------------------------|-------------------------------|----------------|
| bentonite                | 181                           | This study     |
| HY (16.6)                | 141                           | This study     |
| HY (2.9)                 | 59                            | This study     |
| HY (30.0)                | 81                            | This study     |
| activated carbon from    |                               |                |
| tobacco stalks           | 123.45                        | [37]           |
| gold nanoparticles loaded| 104–185                       | [38]           |
| Fly Ash-based Geopolymer | 37.04                         | [39]           |
| Pine cone                | 109.89                        | [40]           |
| Cold plasma treated bentonite | 303                        | [41]           |
| Kaolite                  | 58.8                          | [42]           |
| Montmorillonite          | 188.8                         | [42]           |

Compliance with ethical standards

Conflicts of interest The authors declare no conflict of interest.

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