

Removal of Methylene Blue from Water Using Hydroxyapatite Submitted to Microwave Irradiation

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Abstract

This study investigated the power of hydroxyapatite adsorbent prepared by a combined precipitation-microwave method, for removing a cationic dye methylene blue in aqueous media. The used adsorbent was characterized by X-ray diffraction (XRD) and infrared spectroscopy (IR). The adsorption tests were conducted in batch mode. The effect of temperature, the pH of the solution and the mass of the adsorbent on the adsorption were determined. It is found that the adsorption was pH and temperature dependent. The kinetic study showed that the second-order model gives a better description of the kinetics of the adsorption reaction than the first-order model. Analysis of adsorption isotherms using different classical models showed that adsorption may be governed by the isotherms of Langmuir. The thermodynamic parameters were determined from the values of the maximum adsorption capacity and equilibrium constants.

Keywords

Microwave, Hydroxyapatite, Methylene Blue, Adsorption, Kinetic, Isotherms

1. Introduction

The majority of dyes from different industries such as textile, tannery, and food may generate toxic and carcinogenic substances that present a significant source of environmental contamination when discharged directly

into the environment without any specific treatment [1]. Therefore, the removal of these contaminants does not only depend on the biological degradation [2]. In this context, several methods have been used: coagulation-flocculation [3] precipitation, membrane filtration [4] and electrocoagulation [5]. The adsorption technique is proven as efficient, reliable, and low cost process for removal of pollutants, namely when the adsorbent is abundant and inexpensive [6]. The widely used adsorbent is the active coal despite its relatively high price. The active coal has long remained as the most requested solid because of its very high adsorption capacity, its large specific surface between 400 and 2000 m²/g, but it can be replaced by other materials able to adsorb organic and inorganic pollutants at lower cost [7]. This has led to a search for materials at low cost as alternative adsorbent materials. In the last decade, hydroxyapatite has known increasing interest for various applications in the bio-medical field as bone substitutes [8], bone tissue [9] dental implant [10] and soft tissue repairs [11]; indeed, hydroxyapatite became the basic material used for hard tissue replacement of bone or teeth because of its bio-compatibility and its moldable character. The hydroxyapatite is also widely used for chromatography [12]-[15] and as nanostructured heterogeneous catalyst for the oxidation reactions, by incorporation of cations such as Ru³⁺ and La³⁺ [16]. Moreover, hydroxyapatites have also shown their efficiency to remove different species from polluted water or soil [17]-[21]. Many reports have been focused on rapid, low-temperature, and low-cost heating available for elaboration of hydroxyapatite. Recently, new methods of rapid sintering assisted field have been developed. Microwave processing of materials is a technology that can provide a new, powerful, and significantly different tool to process materials or to improve the performance characteristics of existing materials [22]-[24]. Compared with conventional methods this heating offers many advantages including shorter synthesis time, rapid heating, fast reaction, easy reproducibility, narrow particle distribution, high yield, high purity, efficient energy transformation and throughout volume heating. Electricity consumption can be reduced by more than half by using microwave-assisted sintering [25]. It is obvious that the preparation method of the hydroxyapatite could affect its adsorption capacity. Up till now, the reported works on the hydroxyapatite as adsorbent concerned mainly that elaborated by solid state or soft chemistry methods. In the present work, we are interested in studying the adsorption of methylene blue (MB) on hydroxyapatite elaborated by a precipitation process followed by microwave irradiation. Throughout the manuscript this adsorbent is named microwave-HAP. The influence of different parameters on the adsorption such as: the contact time, the initial concentration of MB, the pH of the solvent is studied. The kinetics and isotherms of the adsorption process are also investigated.

2. Materials and Methods

2.1. Adsorbate

The removal of organic dyes, especially methylene blue (MB) has been studied by several authors [26]-[28] and showed that it has a very good adsorption affinity and high adsorption on solid supports. Methylene blue (MB) used as pollutant in this study (adsorbate) [8] is a cationic dye (chloride of 3,7-bis(dimethylamino-phenazathionium) index CI 52015; its formula is C₁₆H₁₈N₃SCl, its molecular weight is 319.85 g·mol⁻¹, and the maximum absorption occurs at wavelength of 664 nm. The chemical structure of MB dye is shown in (Figure 1).

2.2. Synthesis and Characterization of the Hydroxyapatite (Adsorbent)

HAP was synthesized by the co-precipitation according to the procedure described elsewhere [29]. The synthesis could be summarized in the following steps. The hydroxyapatite was first synthesized by precipitation from two reagents of calcium nitrate solution Ca(NO₃)₂·4H₂O (0.02 mol in 100 ml of distilled water) and ammonium dihydrogen orthophosphate NH₄H₂(PO₄) (0.01 mol in 100 ml of distilled water). The solution of calcium nitrate was stirred at room temperature with NH₄H₂(PO₄) solution added by drops. The pH of this solution was adjusted

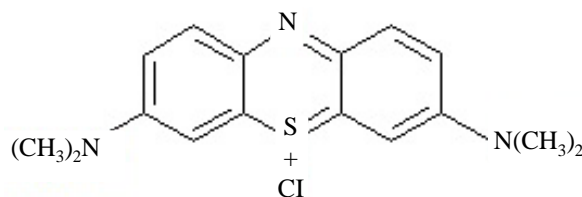


Figure 1. The chemical structure of methylene blue.

to 9 by adding ammonia solution. The solution is agitated during 24 hours. The resulting precipitate is filtered and washed with distilled water in order to eliminate nitrates. Finally, the obtained precipitate is subjected to a microwave radiation by using a microwave MaRS5 model (power output 1500 W, microwave frequency 245 MHz). The mixture was heated in the microwave oven for 3 min.

The identification of the obtained powder was performed by X-ray diffraction (XRD) technique, using a Bruker D8 Advance apparatus. Infrared spectroscopy (IR) was used to identify the vibrational groups of the sample by using a Bruker Tensor 25. Infrared spectra were recorded in the 4500 - 500 cm^{-1} region.

2.3. Adsorption Experiments

The experiments of adsorption were performed in batch method. The adsorption tests were carried out by introducing an amount of adsorbent precisely weighed into a 100 ml solution of pure methylene blue dye $20 \text{ mg}\cdot\text{l}^{-1}$. The samples were taken every 10 minutes after a predetermined contact time. The colored solution was separated from the adsorbent by centrifugation at 2600 rpm for 5 min and analyzed for MB measurements. The adsorbed quantity was determined by measuring the concentration of the solution before and after adsorption by using the Equation (1). The concentration of the solution was determined using UV-visible spectrophotometer (VWR, V 3100).

$$q_e = \frac{(c_0 - c_e) \cdot v}{m} \quad (1)$$

where, q_e (mg/g) is the quantity of the dye adsorbed per unit of adsorbent mass, C_0 (mg/l) is the initial dye concentration, C_e (mg/l) is the concentration of dye at the measured time, m the adsorbent mass (g) and V the volume (l) of the adsorption solution.

3. Results and Discussion

3.1. Characterization of the Microwave-HAP

Figure 2 shows the XRD pattern of the elaborated adsorbent under microwave irradiation. According to the XRD analysis, the pattern shows that the material corresponds to the hydroxyapatite which crystallizes in the hexagonal system with the parameters $a = b = 9.41 \text{ \AA}$ and $c = 6.931 \text{ \AA}$ (JCPDS 74-0566). One can note that no characteristic peaks of impurities such as calcium hydroxide and calcium phosphates were observed. This means that the obtained microwave-HAP phase is pure under the used experimental conditions. Furthermore, the XRD pattern **Figure 2** suggests that the synthesized microwave-HAP may be composed of small-sized and poorly crystalline apatite since the characteristic peaks are broad.

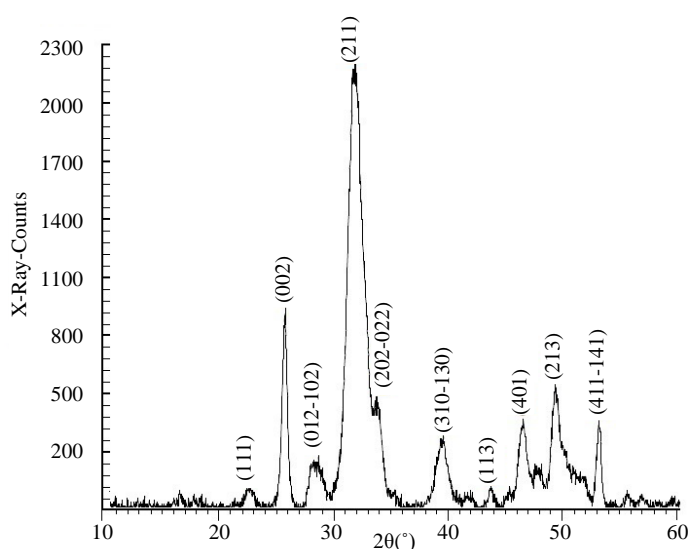


Figure 2. XRD pattern of the microwave-HAP powder.

The IR spectrum of the sample is presented in **Figure 3**. The main features of this spectrum reveal the presence of band associated to isolated PO_4^{3-} units, water and/or hydroxyl molecules. Indeed, the spectrum is characterized by two bands at 3250 cm^{-1} and 1654 cm^{-1} due to the presence of water in the crystal lattice. One can also observe the presence of two bands at 3450 and 631 cm^{-1} corresponding to stretching vibration of OH bonds. Furthermore, the spectrum contains the vibrational modes associated to the phosphate (PO_4^{3-}) group: $\nu_1 = 1352\text{ cm}^{-1}$, $\nu_2 = 1209\text{ cm}^{-1}$, $\nu_3 = 962\text{ cm}^{-1}$ and $\nu_4 = 564\text{ cm}^{-1}$. In agreement with the XRD analysis, the appearance of the phosphate mode vibration at 962 cm^{-1} does indicate the crystalline structure of the microwave-HAP phase formation [30]. There is also a low-intensity band at 875 cm^{-1} which could be ascribed to the structural HPO_4^{2-} entities. From the IR analysis, one can state that the obtained results are in agreement with the XRD analysis since all the structural units contained in the crystalline structure are identified by IR spectroscopy.

3.2. Influence of Different Parameters on MB Adsorption

3.2.1. Effect of Contact Time

The experiment is performed under the following conditions: mass of microwave-HAP $m = 20\text{ mg}$, ambient temperature $T = 25^\circ\text{C}$ and pH of the solution is equal to 6.5. The methylene blue adsorption onto microwave-HAP as a function of contact time is presented in **Figure 4**. The adsorption capacity increases rapidly to about 30 mg/g in 4 minutes. After this initial fast adsorption period, the uptake of MB is much slower and no detectable concentration changes occurred after adsorption equilibrium (4 min). The same experiment is done by using different initial MB contents but not shown here. The results show that the initial MB concentration has little or no effect on the equilibrium time. It is reported [31] that a fast absorption rate could be due to the absence of internal diffusion resistance which allows the rapidly adsorption of MB from the aqueous solution. The short equilibrium time reveals the efficiency and high adsorptive reaction rate of the synthesized microwave-HAP and suggests its possible uses in practical applications.

3.2.2. Effect of Solution pH

The pH of the dye solution plays an important role in the adsorption process, in particular on the capacity of adsorption. For instance, the value of the pH affects the efficiency of adsorption since both the order of ionization of the adsorbate and the surface properties of the adsorbent varied with pH of the solution [32]. The variation of the adsorption as a function of pH is presented in **Figure 5**. The pH of the solution varies from 2 to 12 by using NaOH solution (1N) and HCl (1N). The experiments were performed at ambient temperature by keeping constant the contents of methylene blue and microwave-HAP (20 mg). The percentage of dye removal was calculated by the following Equation (2):

$$\text{Removal\%} = 100 \times \frac{(c_0 - c_e)}{c_0} \quad (2)$$

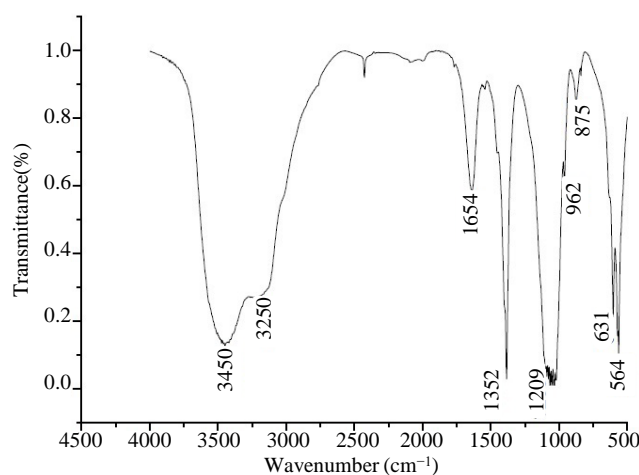


Figure 3. IR Spectrum of the microwave-HAP powder.

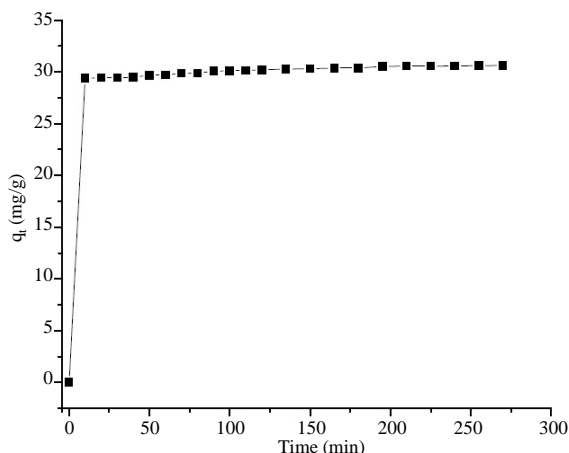


Figure 4. Effect of contact time on methylene blue adsorption.

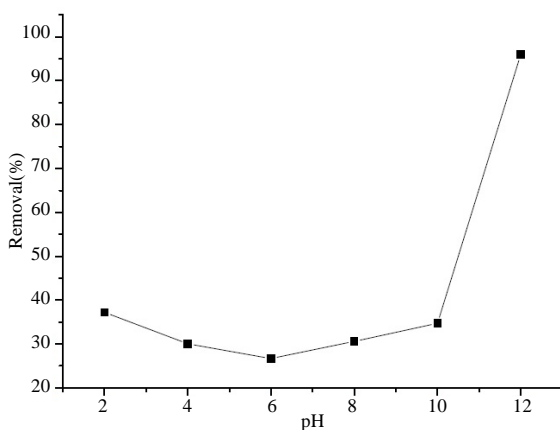
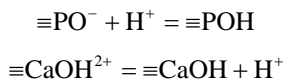


Figure 5. Effect of pH on the removal of methylene blue by microwave-HAP.

where, C_0 the initial dye concentration (mg/l), C_e the equilibrium concentration (mg/l).

From **Figure 5**, one can see that the percentage of dye adsorption presents a flat minimum in the pH range 6 - 8. The maximum adsorption is observed at pH = 12. When, the solution pH varies from 2 to 6, the percentage of adsorption decreases slowly. When the pH increases from 6 to 12 it induces a rapid increase of the adsorption of MB. These results can be explained by the change in surface charge of the adsorbent and/or the nature of the dye [33]. These authors proposed that while MB dye is a positively charged cation the reactions responsible for the surface properties of HAP in aqueous solutions are:



In the lower pH region the positively charged (CaOH^{2+}) and neutral $\equiv\text{P-OH}$ sites prevail on HAP surface, making surface charge of HAP positive. In the basic medium neutral (CaOH) and negatively charged (PO^-) species predominated, causing HAP surface to become negatively charged.

Therefore, the point of zero charge (pH pzc) of the adsorbent is the main parameter influencing the adsorption phenomenon. The pH pzc value of the hydroxyapatite is found to be in the range 6 - 7.2 [34]. When the solution pH is above the pH pzc the surface of the hydroxyapatite is negatively charged. At pH below the pH pzc, the surface of the hydroxyapatite is positively charged [34] [35]. According to the above, the adsorption of MB as a cationic dye on the adsorbent microwave-HAP could be explained as follow: the electrostatic attraction between the negatively charged surface of the microwave-HAP and the positively charged group of the dye is more sig-

nificant at pH above 7.2 hence the percentage of adsorption of the dye increases. On the contrary, in the acidic medium positively charged surface sites on microwave-HAP and MB cations are submitted to electrostatic repulsions which do not favor the adsorption of MB. Indeed, when the solution is acidic the competition of excess protons (H^+) with MB cations for active adsorption sites in microwave-HAP could also explain the lower adsorption. Similar behavior has been observed elsewhere [36]. However, despite the electrostatic repulsion and/or H^+ competition a considerable amount of MB was adsorbed by microwave-HAP at lower pH values (Figure 5), which suggested that other mechanisms might involve in the MB adsorption process. One possible mechanism is related to that reported in the literature [37] [38]. It was reported that a strong H-bonding interaction between (P-OH) group of HAP particles and (N) of the MB molecule could contribute toward adsorption of MB molecules [37]. Indeed, the nitrogen atom of MB might interact with Ca^{2+} groups of HAP via Lewis acid-base interaction [38]. A representative scheme of different possible interactions of MB with the HAP surface is given in Figure 6. In general, we can consider that at an acidic media, adsorption mechanisms involves (2) and (3) modes while in a basic one, adsorption mechanisms involves (1) and (2) interactions.

3.2.3. Effect of Temperature and Thermodynamic Parameters of the Process

To investigate the influence of temperature on the adsorption of MB onto the microwave-HAP we have carried out isotherm studies at four temperatures 25°C, 45°C, 65°C and 75°C. During the measurements, the mass (20 mg) of the adsorbent, the concentration of MB ($20 \text{ mg}\cdot\text{l}^{-1}$), the contact time and the pH (6.5) were kept constant. The variation of the adsorbed capacity of MB as a function of the temperature is plotted in Figure 7. It is observed that the adsorption depends strongly on the temperature. For instance, the increase in the temperature from 25°C to 75°C induces an increase in the capacity of the adsorption from 28.371 mg/g to 33.504 mg/g. This could be due to the increase of the diffusion rate MB molecules on the outer layer of the adsorbent surface; this increase has a positive effect on adsorption [39]. To get more insight the adsorption process, the thermodynamic parameters such as standard enthalpy change (ΔH°), the Gibbs free energy change (ΔG°) and standard entropy change (ΔS°) have been determined using the following equations:

$$\Delta G^\circ = -RT \ln(K_D) \quad (3)$$

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$

where R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}$) and T is solution temperature in K.

The equilibrium constant (K_D) can be calculated using the below equation:

$$K_D = \frac{q_e}{C_e} \quad (5)$$

Equilibrium constant (K_D) for the adsorption process was determined by plotting $\ln q_e/C_e$ vs q_e and extrapolating to zero q_e [40]. By plotting $\ln K_D$ versus $1/T$ as shown in Figure 8 one can calculate values of ΔH° and ΔS° .

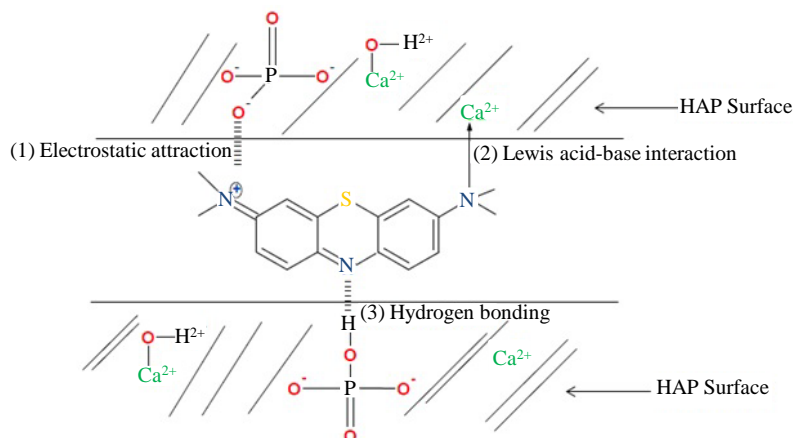


Figure 6. Schematic representation of the possible interactions between microwave-HAP and MB at various pH values.

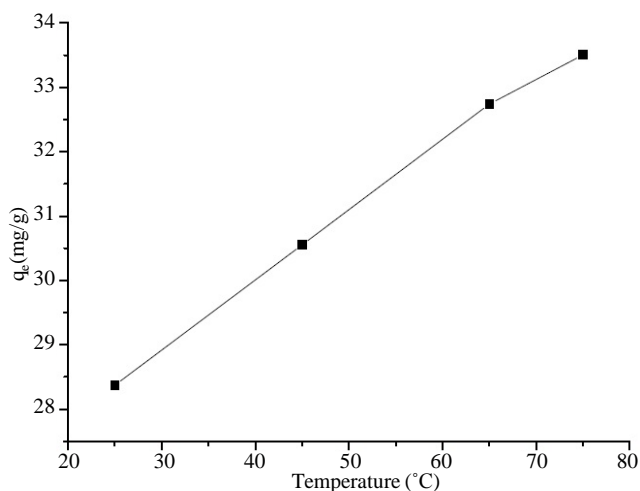


Figure 7. Effect of temperature on the adsorption of MB on microwave-HAP.

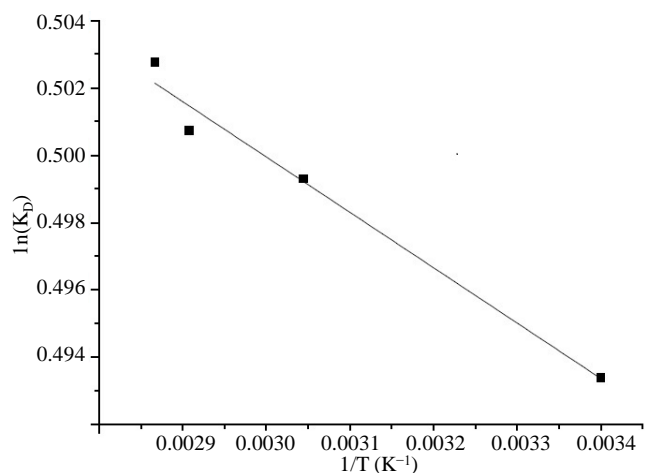


Figure 8. Plots of $\ln(K_d)$ versus $1/T$ for the adsorption of MB on microwave-HAP.

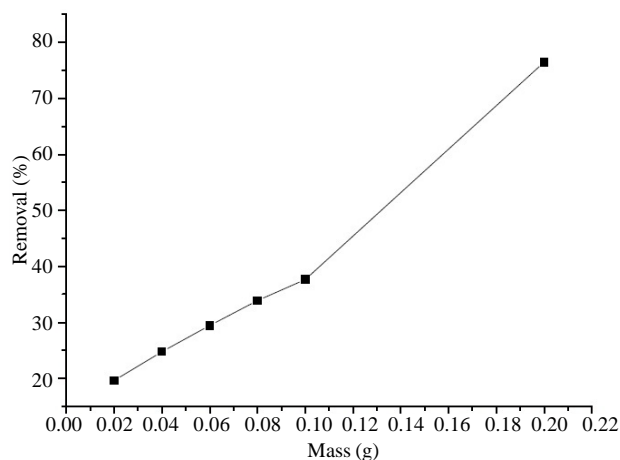
The above thermodynamic parameters are determined and are gathered in **Table 1**. ΔH° and ΔS° determined for the different temperatures have the same values to that obtained for the temperature 298 K. The positive value of ΔH° suggests the endothermic nature of the adsorption, which is supported by the increase of the adsorption capacity of MB onto the microwave-HAP with the temperature (**Figure 7**). Based on ΔH° value which it is a small positive value compared to 40 kJ/mol [41] one can state that the adsorption of MB onto microwave-HAP could be a physisorption process. The positive value of ΔS° depicts the increasing degree of disorder at the solid-liquid interface during the adsorption of methylene blue [26] [42]. Besides, it is clear to see that the values of free energy ΔG° at all of the tested temperatures were negative, this confirms that the adsorption is spontaneous and thermodynamically favorable [43]. Generally, the change in free energy ΔG° in the case of physical adsorption ranges from -20 to 0 kJ/mol and in the case of chemical adsorption it ranges from -80 to -400 kJ/mol [44]. This further indicated that the physisorption might dominate the adsorption of MB onto microwave-HAP.

3.2.4. Effect of the Adsorbent Mass

The effect of the adsorbent mass was studied at constant temperature while keeping pH at 6.5 and the dye concentration at $20 \text{ mg}\cdot\text{l}^{-1}$. The used adsorbent masses are 20, 40, 60, 80, 100 and 200 mg. The removal percentage of the dye was calculated by the Equation (2). **Figure 9** depicts the mass dependence of the dye removal. It is

Table 1. Thermodynamic parameters for MB adsorption at equilibrium on microwave-HAP.

| T (K) | ΔG° (kJ·mol ⁻¹) | ΔH° (kJ·mol ⁻¹) | ΔS° (J·mol ⁻¹ ·K ⁻¹) |
|---------|--|--|--|
| 298 | -0.44 | 0.81 | 4.21 |
| 318 | -0.53 | | |
| 338 | -0.61 | | |
| 348 | -0.65 | | |

**Figure 9.** Effect of the adsorbent mass on the adsorption of BM.

observed that the adsorption of MB increases when the mass of adsorbent increases. This improvement can be justified by the increase of the adsorption sites with increasing mass. This favors therefore the discoloration phenomenon [45].

4. Isotherm Studies

The adsorption isotherms describe the distribution of the MB dye between the solution and the microwave-HAP adsorbent when the adsorption process reaches an equilibrium state. There are several applicable isotherm models, but the most widely used are the Langmuir and the Freundlich models [46] [47] the adsorption isotherms data were analyzed according to these two models as described below.

The Langmuir equation is adapted to describe the adsorption behavior of homogeneous surfaces. The adsorption Langmuir model is applied on the following assumptions: 1) strong uniform adsorption sites, 2) the monolayer coverage, and 3) no lateral interaction between adsorbed molecules. The linear form of this isotherm is represented as follows [48]:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_L \cdot q_m} \times \frac{1}{C_e} \quad (6)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/l) is the equilibrium concentration, K_L (l/g) is the Langmuir constant and q_m is the monolayer adsorption capacity.

In addition, the essential feature of the Langmuir isotherm can be expressed by a dimensionless term called the R_L separation factor. This factor is used to predict whether an adsorption system is “favorable” or “unfavorable”. It is defined [19] as:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (7)$$

On the other hand Freundlich isotherm approves the heterogeneity of the surface and assumes that the adsorption occurs on sites with different adsorption energy. The adsorption energy varies depending on the coverage area [49]. Equation (8) represents the Freundlich isotherm.

$$q_e = K_F C_e^{1/n} \quad (8)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent ($\text{mg}\cdot\text{g}^{-1}$), C_e is the equilibrium concentration, K_F is the Freundlich constant and (n) is the heterogeneity factor. The value K_F is related to the adsorption capacity, while the value of ($1/n$) is related to the adsorption intensity. When $n = 1$, the adsorption is linear, meaning that sites are homogeneous and there is no interaction between the adsorbed species; when $1/n < 1$, adsorption is favorable and the adsorption capacity increases while new adsorption sites appear. When $1/n > 1$ adsorption is not favorable, adsorption bonds become weak and the adsorption capacity decreases [50].

Let us now to consider the above models. The Langmuir isotherm equation (Equation (6)) was applied to the adsorption data to quantify the adsorption capacity of the microwave-HAP powders. The Langmuir plot (Figure 10) of the data displayed a good linear fit and the derived q_m and K_L parameters from slope and intercept are presented in Table 2. From this latter, one can note that the correlation coefficient R^2 ($R^2 = 0.9968$) is very close to 1 and the maximum adsorption capacity is 33.3 mg/g.

The calculated value of R_L is 0.1 which indicates that the adsorption is favorable. This good correlation between the data and the Langmuir adsorption model assumes monolayer coverage of MB on homogeneous sites of microwave-HAP, uniform energy of adsorption, and no interaction between MB species adsorbed on neighboring sites.

In parallel, the adsorption data was also plotted using the Freundlich model under the same experimental conditions (Figure 11). The numerical values of K_f and ($1/n$) calculated are gathered in Table 2. The numerical value of $1/n = 0.2$ indicates that the adsorption using heterogeneous sites is favorable. Nevertheless, based on the correlation coefficient (R^2) values in the present study, the Langmuir isotherm provides the best fit for the experimental data.

According to the obtained results, it seems that the microwave irradiation of the hydroxyapatite is very benefit for the adsorption of the MB since the adsorption parameters are improved compared to that obtained for non-irradiated hydroxyapatites [51] [52].

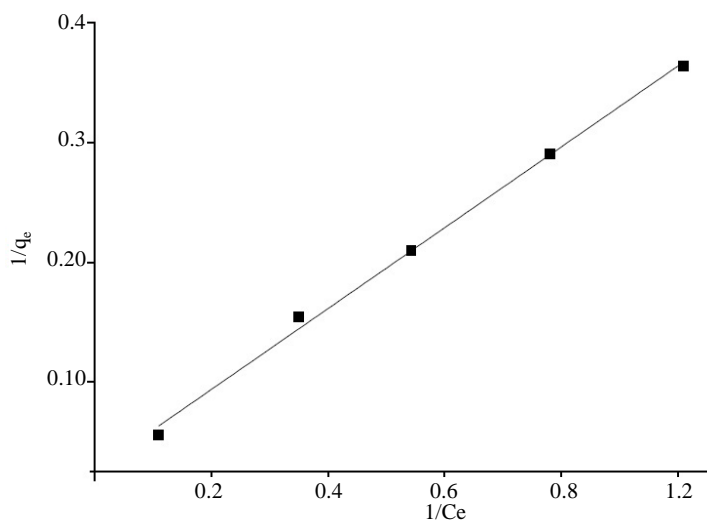


Figure 10. Langmuir plot for BM adsorption on microwave-HAP.

Table 2. The adsorption parameters for Freundlich and Langmuir models.

| Isotherme of Langmuir | Isotherme of Freundlich |
|-----------------------|-------------------------|
| K_L (l/mg) 0.5 | K_f (l/Kg) 0.01 |
| q_m (mg/g) 33.3 | n 0.2 |
| R^2 0.9968 | R^2 0.9817 |
| R_L 0.1 | |

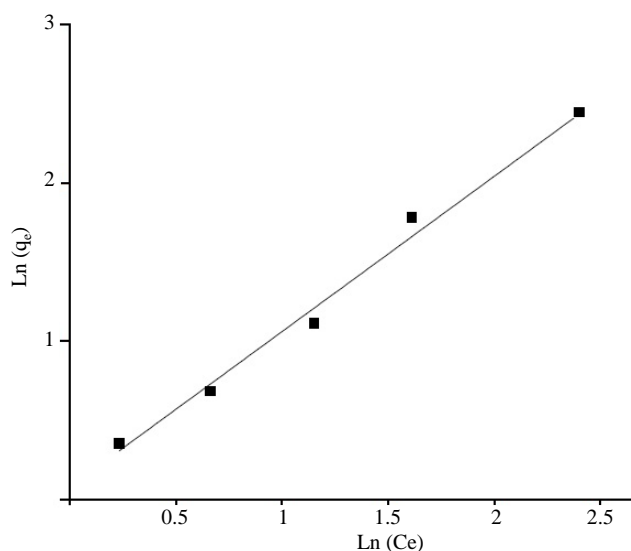


Figure 11. Freundlich plot for BM adsorption on microwave-HAP.

In order to assess the performance of microwave-HAP as an adsorbent for MB, the adsorption capacity of microwave-HAP were compared with those of other adsorbents examined for the removal of MB in the literature **Table 3**. The maximum adsorption of MB is $33.3 \text{ mg}\cdot\text{g}^{-1}$, which is significantly higher than the other adsorbents listed in **Table 3**.

5. Kinetics Studies

Several formalisms are given in the literature to describe the adsorption kinetics. All these formalisms bring some information on the adsorption rate and mechanism of the adsorption. In this study, two models were applied to describe the adsorption kinetic mechanism: the pseudo-first-order and the pseudo-second-order model [53].

The kinetic model of the pseudo-first-order is expressed as follows:

$$\frac{d q_t}{d t} = k_1 (q_e - q_t) \quad (9)$$

where q_e and q_t are adsorption capacity (mg/g) at equilibrium and at time t , respectively. k_1 is the adsorption rate constant (min^{-1}).

After integration and application of boundary conditions this model can be expressed in a linear form as Equation (10):

$$\log(q_e - q_t) = \log(q_e) - k_1 \cdot \frac{t}{2.303} \quad (10)$$

The plot of $\log(q_e - q_t)$ versus (t) is given in **Figure 12**. From this figure one can extract the values of k_1 and q_e parameters and they are given in **Table 4**.

It is clear from the analysis of $\log(q_e - q_t)$ according to time that it is not linear, and consequently the adsorption of methylene blue on microwave-HAP cannot be described by the pseudo-first order.

After this conclusion, we have applied the second model to fit the experimental data obtained from the kinetic experiments. The linear form of the equation of pseudonym second-order is expressed as follows:

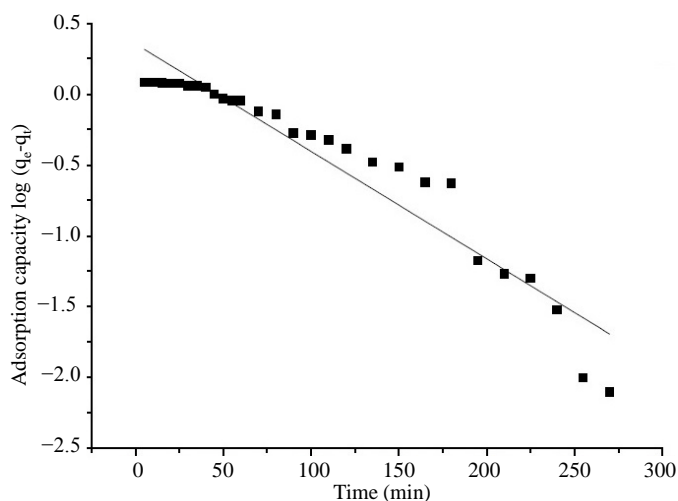
$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \quad (11)$$

where q_e and q_t designate the absorption capacity (mg/g) at equilibrium and time t , respectively. A constant k_2 represents the constant rate of adsorption (g/mg·min).

The parameters q_e and k_2 are obtained by representing t/q_t versus t (**Figure 13**). The obtained values for these parameters are gathered in **Table 4**.

Table 3. Maximum adsorption capacity of MB onto various types of adsorbent relative to Langmuir model.

| Adsorbents | Maximum adsorption ($\text{mg}\cdot\text{g}^{-1}$) | References |
|------------------------|--|------------|
| HAP | 0.7 | This study |
| Microwave-HAP | 33.3 | This study |
| Poorly crystalline HAP | 14.27 | [52] |
| HAP | 0 | [51] |

**Figure 12.** $\log(q_e - q_t)$ versus time according to the first-order kinetic model (■: experiment ; ___ fit linear).**Table 4.** Adsorption capacity, rate constant and correlation coefficient obtained from the studied kinetic models.

| $q_{e,\text{exp}}$ (mg/g) | Pseudo-first order | | | Pseudo-second order | | |
|---------------------------|----------------------------|-------------|--------|----------------------------|------------------|-------|
| | $q_{e,\text{calc}}$ (mg/g) | K_1 (min) | R^2 | $q_{e,\text{calc}}$ (mg/g) | K_1 (g/min·mg) | R^2 |
| 30.61 | 2.11 | 0.016 | 0.9196 | 30.67 | 0.022 | 1 |

The linear variation (**Figure 13**) of t/q_t with the time suggests that the pseudo-second order model describes well the kinetic behavior of the methylene blue adsorption on microwave-HAP. The experimental data can be fitted with the equation:

$$t/q_t = 0.0326t + 0.0476, \text{ with a correlation coefficient } R^2 = 1.$$

The analysis of the data given in **Table 4** showed perfectly that the experimental adsorption capacity q_e is very close to that obtained by the pseudo second order model. Therefore, according to this latter model, we can state that the adsorption of methylene blue on the microwave-HAP involves the chemisorption process in addition to the physisorption.

6. Conclusion

In the present work we have tested the adsorption of the cationic dye MB on the hydroxyapatite elaborated using a combined precipitation and microwave irradiation technique. The results show that the adsorption kinetic of the dye on microwave-HAP is well described by the second-order model. The adsorption isotherms are described satisfactorily by the Langmuir model. The temperature has a positive effect on the adsorption of MB suggesting that its adsorption is an endothermic process. The dye adsorption was also influenced by the pH of the solution. The percentage of adsorption of the dye decreases as the medium pH increases up to 6. With further increase of pH the percentage of adsorption of the dye increases rapidly. This behavior is correlated with the change of the electrostatic charges on the surface of the hydroxyapatite. It is also shown that the microwave irradiation has a positive effect on the adsorption.

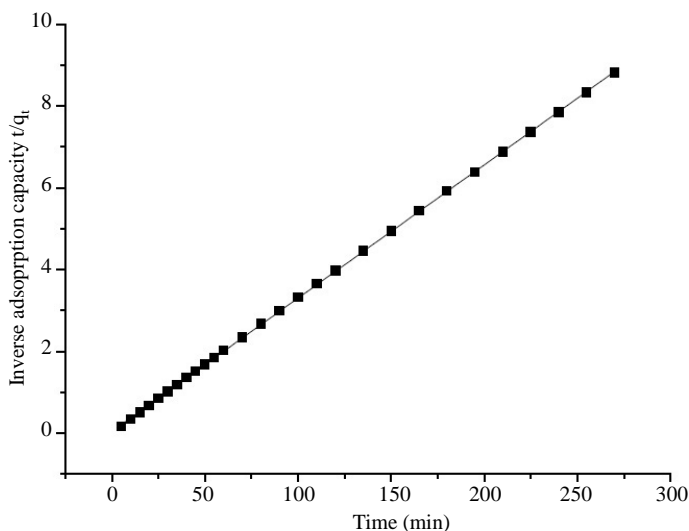


Figure 13. Second order kinetic model applied to the adsorption of MB on the microwave-HAP (■: experiment ; — fit linear).

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