Removal of methylene blue with a highly effective hydroxyapatite-silica nanocomposite

Herradi S., Zerrouk M., Bouayad A., Bouhazma S., Ouarsal R., Khaldi M., El Bali B., Lachkar M.*

1Engineering Laboratory of Organometallic, Molecular Materials and Environment, Faculty of Sciences, Sidi Mohammed Ben Abdellah University, 30000 Fez, Morocco
2Materials Engineering Laboratory for the Environment and Natural Resources, Moulay Ismail University, Faculty of Science and Technology, 52000, Errachidia, Morocco
3Independent Scientist, Marrakech, Morocco, ORCID: 0000-0001-6926-6286
*Corresponding author, Email address: mohammed.lachkar@usmba.ac.ma

Abstract: Two Hydroxyapatite-silica nanocomposite adsorbent (HApS220 and HApS230) were successfully synthesized using sol-gel technique. The samples were characterized by powder X-ray diffraction (XRD), Infrared spectroscopy (IR), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), which confirmed the formation of a Hydroxyapatite-silica nanocomposite. The synthesized powders were then used for adsorption of methylene blue (MB). Both compounds possessed high absorption capacities, the adsorption equilibrium time is around 10 min. HApS230 sample shows higher adsorption capacity compared to HApS220. Furthermore, isotherm studies show that the adsorption used is an ion exchange process and that Temkin isotherm describes the adsorption better compared to the Langmuir and Freundlich and Dubinin-Radushkevich isotherms. Kinetics studies confirm that the adsorption follow the pseudo-second order model and chemisorption mechanism. Thermodynamics’ studies confirm that the adsorption of MB on HAPs samples is a spontaneous endothermic process. The average removal effectiveness of MB reached about 89.02% (6.389 mg/g adsorption capacity) and 91.36% (6.55 mg/g adsorption capacity) for HApS220 and HApS230 respectively.

Keywords: Hydroxyapatite, silica, nanocomposite, adsorption, methylene blue, water.

1. Introduction

The human need for an easy lifestyle led to the continuous development of various industries. However, industrialization has a negative impact on the environment due to the disposal of contaminants in water, soil and air (Bouknana et al., 2014; Ibrahim et al., 2016; Permatasari and Rilyanti, 2021). Particularly, pollution of water is a big challenge especially in developing countries (Oun et al., 2021). Pollution may occur for example by organic dyes and heavy metals which are toxic and hazardous for aquatic life (Swamiappan et al., 2021; Amenaghawon et al., 2022; El Hammari et al., 2022). The dye industry by itself contribute to the water pollution by up to 20% of the total industrial waste water (Sharma et al., 2021). Among many dyes, MB is a cationic dye used in textile industry for dying cotton, wool, and silk (Annan et al., 2021; Oladoye et al., 2022). This dye has been
shown to be carcinogenic, teratogenic, and mutagenic for human (Azeez et al., 2022). Moreover, MB in water prevent sunlight from penetrating and thus contribute in the deterioration of the aquatic ecosystem (Temel et al., 2020). Thus, its removing is very interesting, and many techniques have been investigated, such as ion exchange (Khan et al., 2015), photocatalysis (Balasurya et al., 2021), coagulation/flocculation (Ihaddaden et al., 2022), ozonation (Javed et al., 2023), membrane separation (Silva et al., 2020) and adsorption (Somsesta et al., 2020). Among these processes, adsorption is a good choice due to its cost-effectiveness, simplicity and high removal percentage (Bhat et al., 2022). Activated carbon, usually derived from natural materials, is widely used for wastewater treatment owing to its high adsorption capacity; however, the high cost associated with its fabrication and its activation are a limiting factor (Hoijang et al., 2020; Ijagwe et al., 2021; Akartasse et al., 2022). Thus, the research of efficient, cost-effective and reusable adsorbents is of great interest. In this context, many materials have been tested for the removal of MB such as hydroxyapatite (Swamiappan et al., 2021; Aaddouz et al., 2023), silica (Peres et al., 2018), Clays (Hmeid et al., 2021), hydrogels (Yang et al., 2022) and polymers (Jiang et al., 2019). Hydroxyapatite (HAp) is a biomaterial, with the chemical formula Ca₁₀(PO₄)₆(OH)₂, is known by its low water solubility, thermal stability, its ions exchange ability and its high surface affinity for dyes and heavy metals (Ibrahim et al., 2020; Amenaghawon et al., 2022). To increase the HAp’s adsorption ability, an increase on its porosity is of great interest (Ghita et al., 2014). In this regard, the use of tetraethyl orthosilicate could be the key to improve the HAp’s porosity, which will be created during the polymerization of the silicon alkoxide (Yamada et al., 2018). Moreover, microwave heating permits the obtention of materials without agglomeration at low temperature in shorter time Compared with conventional heating (Zhu and Chen, 2014). Thus, this method, would give an economically efficient material which is important when it comes to its use at wastewater treatment plants.

In the present work, HA-SiO₂ (HApS) composite has been synthesized by sol-gel technique. The calcination of the as-prepared powders was performed in microwave oven, characterized and used for the adsorption of MB from aqueous solutions. To our knowledge, this is the first study that deal with the use of a microwave-heated HApS composite, at low temperature and short time, for the adsorption of MB.

2. Materials and methods

2.1 Materials

The precursors used to prepare HApS composite are calcium nitrate tetrahydrate Ca(NO₃)₂.4H₂O (Sigma Aldrich, purity: 99%), ammonium dihydrogen phosphate NH₄H₂PO₄ (Fluka, purity > 99%), tetraethoxysilane Si-(OC₂H₅)₄ (TEOS, Aldrich), ethanol and ammonia (NH₄OH) to adjust pH and deionized water. MB was used for adsorption experiment.

2.2 Synthesis of HApS nanocomposite

The HApS nanocomposite was synthesized using sol-gel technique as described in our previous work (Herradi et al., 2022). In brief, the first step consists in preparing a 0.835 M solution of calcium nitrates in ethanol to which, after total dissolution (15 min of stirring), 10 mL of TEOS was added. The resulting mixture is stirred for 15 minutes to homogenize. After stirring, a pH=4.5 is measured and adjusted to 10 by means of the ammonia solution; the mixture becomes of a milky appearance. In parallel, a 0.5 M solution of NH₄H₂PO₄ is prepared in deionized water. After total dissolution a pH=4.51 was found which is adjusted to 10. The second step consists in adding drop wise the

NH₄H₂PO₄ solution to the solution of Ca(NO₃)₂·4H₂O. The resulting mixture is stirred for 30 minutes. Then, a pH=9.89 was measured. The gel obtained was matured at 25°C for 48 hours in an oven. Then, the gel is filtered and washed several times with deionized water and then with acetone. This gel was transferred to the oven to dry for 24 hours at 80°C. The block obtained is crushed using an agate mortar. Then the powders obtained are heated by microwaves at 220°C and 230°C for 20 min (samples named HApS220 and HApS230).

### 2.3 Characterization of the HApS composite

The synthesized powders were analyzed by X-ray diffraction using Discover model equipped with a monochromatized Cu-Kα radiation (λ = 1.5406 Å). The diffraction patterns were obtained in the 2θ-range 20-80°. Fourier transform infrared spectroscopy (FTIR: Bruker VERTEX 70 spectrometer) was used to determine the functional groups of the obtained powders. The spectra were recorded from 400 to 4000 cm⁻¹ at 4 cm⁻¹ resolution. The surfaces of samples were analyzed before and after adsorption using a scanning electron microscope (SEM) coupled with Energy-Dispersive Spectroscope (EDS): ESEM Quanta 200 (FEI Company).

### 2.4 Adsorption experiments

Without any purification, MB (Figure 1) is employed as a model pollutant. The solutions are made by dissolving the dye in distilled water in the appropriate amounts.

![Figure 1. Methylene Blue](image)

The samples are filtered and a spectrophotometer UV/Visible of type JASCO V-630 was used to measure absorbance of the filtered solutions. The MB's maximum wavelength of absorption is 665 nm. The adsorption capacity qₑ (mg/g) and adsorption percentage (R) were calculated based on Eqn. 1 and Eqn. 2:

\[
q_e = \frac{C_i - C_f}{m} \times V \quad \text{Eqn. 1}
\]
\[
R(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad \text{Eqn. 2}
\]

where Ci and Ce stand for the dye's initial and equilibrium concentrations, expressed in (mg/L), respectively. V is the volume of the used solution, and m is the material mass (mg).

The effect of contact time, pH, initial dye concentrations, and temperature were separately studied in order to assess the impact of various parameters on the removal of MB.

### 3. Results and Discussion

#### 3.1. Characterizations

Figure 2 shows the XRD patterns of the microwave-heated powder at 220 and at 230°C for 20 min. The two patterns show some peaks of HAp namely (002), (211) and (300) which are in a good agreement with those of HAp reference (JCPDS: 00-024-0033) (You et al. 2019). The absence of the characteristic peaks of the phases relating to crystalline SiO₂ indicates the formation of a composite material made of HAp and amorphous SiO₂ (Bareiro and Santos, 2014). Furthermore, the broadness of
diffraction peaks indicates the formation of nanohydroxyapatite particles (Londoño-Restrepo et al., 2019). Yamada et al synthesized hydroxyapatite silica composite via hydrothermal method using TEOS as silica precursor with various phosphorous precursor concentrations while fixing pH at 12 (Yamada et al., 2018). They have found that all samples are composed of hydroxyapatite along with amorphous silica after calcination at 550 °C. In a recent study, Noviyanti et al, 2023, reported the synthesis of hydroxyapatite silica composite by mixing Hap and silica powders with various HAp:SiO₂ ratios of 90:10 (HApS90), 85:15 (HApS85), and 80:20 (HApS80). The mixture was then hydrothermally treated in water. Then the powder was dried at 110 °C. For all studied compositions, HApS composite was successfully synthesized without any secondary phase. The IR spectra of the microwave-calcined samples are shown in Figure 3.

![Figure 2](image_url). XRD diagrams for microwave heated HApS composite at 220°C and at 230°C

![Figure 3](image_url). IR spectra for microwave heated HApS composite at 220°C and at 230°C
For both spectra, the band at 466 cm\(^{-1}\) is attributed to the doubly degenerate bending mode \(\nu_2\) of the phosphate group, while the bands at 568-614 cm\(^{-1}\) are due to the triply degenerate bending \(\nu_4\) mode of the O–P–O bonds. The band at 1025 cm\(^{-1}\) is assigned to the triply degenerate asymmetric stretching mode \((\nu_3)\) of PO\(_3^3\)- (P–O bond). The band at 1437 cm\(^{-1}\) is due to the stretching mode \(\nu_3\) of CO\(_3^{2-}\) in B-type HAp (Garskaite et al., 2014). The band at 808 cm\(^{-1}\) could be attributed to the stretching of Si–O bonds in the silica polymer (Hoijang et al., 2020). Finally, the bands due to the adsorbed water are located at 1644 and 3427 cm\(^{-1}\).

The surface morphologies of synthesized samples were evaluated by the SEM characterization method as shown in Figure 4. SEM images of HApS220 sample before and after adsorption indicates that this sample is composed of nano-spherical particles (<80 nm). Moreover, no change was observed after adsorption. However, for sample HApS230, the particles size before adsorption were found to be above 80 nm, and no change has been observed after adsorption. The particles size and XRD results show that the pics are broad indicating the nanometric size of particles (Ferrairo et al., 2023).

![Figure 4. SEM images of HApS220 before (a) and after (b); and HApS230 before (c) and after (d) adsorption](image-url)

To check the various elements within the samples, before and after adsorption, elemental analysis was achieved by using Energy-Dispersive Spectroscope (EDS). As shown in Figure 5, the EDS spectra of HApS220 and HApS230 samples before adsorption confirm the presence of all major elements. In addition, Mg exist as a trace element and it may rise from non-stoichiometric hydroxyapatite (Ofudje
et al., 2018). However, after adsorption, the spectra reveal the existence of sulfur which confirms the adsorption of MB onto the samples. It is worth mentioning that the trace element of Na may rise from water, while the Carbone always exists in the spectra because it was used as a coating for samples before SEM-EDS analysis.

**Figure 5.** EDS spectra of HApS220 before (a) and after (b); and HApS230 before (c) and after (d) adsorption.
3.2 Adsorption experiments

3.2.1 Effect of contact time

To determine the time required to reach MB’s adsorption equilibrium on HApS220 and HApS230, experiments were performed on a 8 ppm solution. At regular time intervals, samples are taken and analyzed by UV-Visible spectrophotometer at λ = 665 nm. Figure 6 shows the adsorption capacity of HApS220 and HApS230 during various contact times. The adsorption of MB on HApS220 and HApS230 occurs mainly in two distinct steps. The first step is fast and corresponds to the external mass transfer while the second is slow and linked to the diffusion phenomenon (internal mass transfer) (Prajapati and Mondal, 2020; Haydari et al., 2023). Azzaoui et al., 2019, have synthesized nature-based composite in film form and used it as an adsorbent for toxic dyes from wastewater. The composite film was prepared by a double decomposition and coprecipitation methods using hydroxyapatite (HAp), hydroxyethyl cellulose (HEC), and polyethylene glycol (PEG)-1000. They found that adsorption started rapidly; and it was almost complete in the first few minutes and then became much slower.

[Graph showing adsorption capacity over time for HApS220 and HApS230]

Table 1. Comparison of equilibrium time of various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Equilibrium time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAp</td>
<td>20 min</td>
<td>(Aaddouz et al., 2023)</td>
</tr>
<tr>
<td>Natural Phosphate</td>
<td>30 min</td>
<td>(Assimeddine et al., 2022)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1h30 min</td>
<td>(Unugul and Nigiz, 2020)</td>
</tr>
<tr>
<td>Ordered mesoporous silica</td>
<td>3h</td>
<td>(Subhan et al.,2022)</td>
</tr>
<tr>
<td>Fly ash</td>
<td>1 h</td>
<td>(Dinh et al., 2021)</td>
</tr>
<tr>
<td>Halloysite nanotubes</td>
<td>72 h</td>
<td>(Zhao and Liu, 2008)</td>
</tr>
<tr>
<td>HApS220 and HApS230</td>
<td>10 min</td>
<td>This study</td>
</tr>
</tbody>
</table>

In an interesting work, Lakrat et al., 2017, have prepared a nano-HAp with a calcination at 900 °C. The nano-HAp was used then for the removal of methyl orange from water. They have found the same aforementioned results at first and second step, however, they found that the adsorption reaches a plateau after 30 min at T=298 K and T=313K while at T = 323 K, the adsorption continues to increase with time. Moreover, HApS230 shows higher adsorption capacity compared to HApS220. The removal efficiency was 91.36% for HApS230 and 89.02% for HApS220. In general, the adsorption of MB on the HApS powders is a fast process compared to previously studied adsorbents (Table 1), since the equilibrium time is around 10 min. Beyond that, the adsorbed quantity remains almost constant until 45 min. In the rest of our study, we will work with a time of 45 min.

3.2.2 Effect of pH

At room conditions, with a starting concentration of 8 ppm of adsorbate and an adsorbent mass of 8 mg, the impact of pH on the adsorption rate of MB was investigated over a wide pH range of 2 to 12 (Figure 7). The pH of the solution was adjusted to the desired values by adding HCl or NaOH (0.1 M). After 45 min stirring, the solution is recovered and analyzed by UV-Visible spectrophotometer. It is well known that the retention of a cation on an adsorbent typically rises as the surface's negative charge increases (Swamiappan et al., 2021). This explains why retention is more striking when pH is higher. The reaction is, however, highly complex and far from being a straightforward electrostatic attraction between opposing charge species. As it is shown in Figure 7, for pH values below 5, it is clear that there is little dye adsorbing on the surface of the HApS samples. The adsorption capacity is then gradually increased until pH reaches 5, and after that, it remains nearly constant as the pH rises above 7. the removal effectiveness increases from 86% (6.17 mg/g adsorption capacity) at pH=2 to 93.64% (6.72 mg/g adsorption capacity) at pH=12. According to earlier studies, these results may be explained by changes in the adsorbent's surface charge and/or the composition of the coloring agent (Afroze and Sen, 2018). In fact, at lower pHs, the main surface species are positively charged ≡CaOH+ and neutrals ≡P-OH sites, which cause colorant molecules that are positively charged to repel one another (Wie et al., 2015), (Allam et al., 2016). As a result, there is a decrease in MB adsorption. The two most significant surface species at higher pH values, neutral ≡CaOH and negative ≡PO−, create an electrostatic attraction with the colorant's positive charge, which results in a greater adsorption (Agougui et al., 2017). Moreover, the porous nature of silica network coupled to the high negative charges at its surface at higher pH, enhance the attraction of electrostatic forces towards the positive charges of MB solution (Esa and Sapawe, 2020). The proposed scheme of MB’s interaction with HApS composite is illustrated in Figure 8.

Figure 7. Effect of the initial pH values on the removal of (MB) using HApS220 and HApS230

3.2.3 Effect of initial concentration

To overcome the resistance to the transfer of mass of MB between the liquid and solid phases, the initial concentration of MB provided the necessary mortice force (Jabir et al., 2022; Haydari et al., 2022). Figure 9 presents the variation of the adsorbed quantity with the dye's starting concentration for HApS220 (a) and HApS230 (b). The results show that for the initial MB concentrations of 2, 4, 6 and 8 mg/L, respectively, the adsorption equilibrium of MB was achieved within 15 min. The average removal effectiveness of MB reached about 73.29% (1.289 mg/g adsorption capacity), 84.22% (2.97 mg/g adsorption capacity), 87.75% (4.7 mg/g adsorption capacity), and 89.02% (6.389 mg/g adsorption capacity).
capacity) and 73.41 % (1.292 mg/g adsorption capacity), 85.64% (3.01 mg/g adsorption capacity), 89.62% (4.8 mg/g adsorption capacity), and 91.36% (6.55 mg/g adsorption capacity) for HApS220 and HApS230 respectively. Thereafter, no observable concentration changes happened after adsorption equilibrium (25 min). The weakly crystalline HAS's fast adsorptive reaction rate was shown by the short equilibrium period. Similar results were obtained by Akartasse et al. using Hydroxypropyl methylcellulose (HAp/HPLC) composite (Akartasse et al., 2022). In fact, it has been reported that nano-hydroxyapatite exhibits rapid elimination efficiency for all MB concentrations which is important for wastewater treatment application (Swamiappan et al., 2021). Moreover, the lack of internal diffusion resistance may be responsible for the high rate of adsorption (Jabir et al., 2022).

Figure 8. Proposed scheme of MB’s interactions with HApS composite

Various starting MB concentrations were tested for their effects on adsorption equilibrium time, and the results indicated that these initial MB concentrations had little to no impact on this time. Furthermore, Figure 9 shows that when MB concentration increased, the actual amount of adsorbed MB per unit mass of HAS increased. The MB absorption at a fixed adsorbent dose was limited by the number of adsorption sites that were available. Further increases in MB concentration led to an excess increase in dye molecules, which lengthens the contact time between the active site over adsorbent and adsorbate, causing saturation and keeping adsorption capacity stable (Wei et al., 2015), which was also reported by Agougui et al. (Agougui et al., 2017).

Figure 9. Variation of the adsorbed quantity with the dye's starting concentration for: a) HApS220 and b) HApS230
3.2.4 Isotherm studies

The relationship between a substance's adsorption rate and its concentration in the equilibrium solution, at a given temperature, is known as the adsorption isotherm. The application of adsorption isotherms is essential from both theoretical and practical point of view. In fact, it makes it easier to describe how the adsorbate and adsorbent of any system interact. The parameters derived from the various models offer crucial details on the adsorption mechanisms as well as the surface traits and affinities of the adsorbent (Sadki et al., 2023). For studying experimental adsorption equilibrium data, various models are available i.e., Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R).

The Langmuir isotherm is based on the assumption that the adsorbate is covered in a monolayer on the homogenous sites of the adsorbent, that the energy of adsorption is uniform, and that there is no interaction between molecules adsorbed on nearby sites. The Eqn. 3 (Table 2) represents the Langmuir formula where Ce (mg/L) is the equilibrium concentration, K_L (l/g) is the Langmuir constant, q_m is the monolayer adsorption capacity, and q_e (mg/g) is the quantity of dye adsorbed at equilibrium (Langmuir, 1918).

The Freundlich isotherm assumes that the stronger binding sites are occupied first and that the binding strength diminishes with increasing site occupancy. It is based on adsorption to a heterogeneous surface or surfaces supporting sites with various affinities. The Eqn. 4 (Table 2) describes the Freundlich isotherm where C_e is the equilibrium concentration, K_F is the Freundlich constant, (n) is the heterogeneity factor, and q_e is the quantity of solute adsorbed per unit weight of adsorbent (mg/g) (Freundlich, 1906). Adsorption capacity is related to the value of K_F, whereas adsorption intensity is related to the value (1/n). When (1/n) <1, adsorption is advantageous and the adsorption capacity rises as new adsorption sites arise. Adsorption is linear when n = 1, implying that sites are homogeneous and there is no interaction between the adsorbed species. Adsorption bonds deteriorate and the ability for adsorption reduces. When (1/n) > 1 adsorption is unfavorable (Al-Ghouti and Da'ana, 2020). For the Temkin model, the heat of adsorption in the surface decreases linearly with the amount of surface coverage because this model accounts for the interactions between the molecules of the adsorbent and adsorbate. This model determines how temperature will affect adsorption. The Temkin isotherm can be described by the Eqn. 5 (Table 2) (Temkin and Pyzhev, 1940).

The Dubinin-Radushkevich (D-R) model is based on the observations that the free enthalpy of adsorption is correlated with the recovery rate (q_e/q_m) and the adsorption potential (ε) is variable. This model uses the free energy of adsorption to provide information on the process type (Dubinin and Radushkevich, 1947). The adsorption process is a physical function when E is between 1 and 8 kJ/mol (Hassan et al., 2020), while ion exchange is used in the adsorption process when E is between 8 and 16 kJ/mol (Bekchanov et al., 2023). Chemical adsorption occurs when E is in the range of 16-40 kJ/mol (Khan et al., 2018). Where (q_e/q_m) is the fraction of surface coverage, (β) constant related to the adsorption energy (mol²/J²). The Dubinin-Radushkevich (D-R) model is described by the Eqn. 6 (Table 2). The results obtained from the four models (Figure 10), show that the Temkin isotherm describes the adsorption better compared to the Langmuir and Freundlich and Dubinin-Radushkevich isotherms. The data's Temkin plot (Figure 10) showed a strong linear fit, and Table 3 presents the estimated parameters from slope and intercept. From the latter, it can be seen that the correlation coefficient R² (R² = 0.999) is extremely close to 1. The Temkin isotherm model postulates that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy, and that the adsorption heat of all molecules reduces linearly with the increase in coverage of the adsorbent surface (Hassan et al., 2020).
Table 2. Expressions of isotherms and their linear forms

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Equation</th>
<th>Eqn. N°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$\frac{1}{q_e} = \frac{1}{K_l q_m C_e} + \frac{1}{q_m}$</td>
<td>Eqn. 3</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\ln (q_e) = \ln (K_F) + \frac{1}{n} \ln (C_e)$</td>
<td>Eqn. 4</td>
</tr>
<tr>
<td>Temkin</td>
<td>$q_e = B_T \ln (K_T) + B_T \ln (C_e)$</td>
<td>Eqn. 5</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>$\ln (q_e) = \ln (q_m) - \beta (\varepsilon)^2$</td>
<td>Eqn. 6</td>
</tr>
</tbody>
</table>

The D-R isotherm reasonably reflected the adsorption of MB onto HApS samples, according to the correlation coefficients ($R^2 > 0.90$, Table 3). E is between 8 and 16 kJ/mol so the adsorption process used is an ion exchange process.

The result for $(1/n)$ of MB adsorption onto HApS220 and HApS230 in the current investigation was less than 1, indicating that adsorption is advantageous and the adsorption capacity rises as new adsorption sites arise.
Table 3. Isotherm constants for dye adsorption on the Surface of HApS220 and HApS230

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Value HApS220</th>
<th>Value HApS230</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$(mg.g$^{-1}$)</td>
<td>13.444</td>
<td>13.44</td>
</tr>
<tr>
<td></td>
<td>$K_L$(L/mg)</td>
<td>0.7235</td>
<td>0.798</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9389</td>
<td>0.9526</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.0932</td>
<td>0.0852</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$(mg$^{-1}$),L$^{1/n}$,g$^{-1}$</td>
<td>6.5777</td>
<td>7.8279</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.872</td>
<td>0.9031</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.899</td>
<td>0.8786</td>
</tr>
<tr>
<td>Temkin</td>
<td>$B_T$</td>
<td>9.9271</td>
<td>18.642</td>
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<tr>
<td></td>
<td>$K_T$</td>
<td>2.427</td>
<td>2.308</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.999</td>
<td>0.993</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>$E$(KJ/mol)</td>
<td>11.04</td>
<td>8.64</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.97</td>
<td>0.94</td>
</tr>
</tbody>
</table>

3.2.5 Kinetics studies

The effectiveness of dye adsorption onto the adsorbent is assessed using the kinetic investigation. Initial dye concentration of 8 mg/L and a temperature of 25°C were met for kinetic investigations. To study the mechanism governing the adsorption process, a number of kinetic models, including the pseudo-first- and second-order equations, have been used (Figure 11). The Expressions of used kinetic models are shown in Table 4.

Table 4. Expressions of kinetic models

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Equation</th>
<th>Eqn. No.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>ln($q_t$ - $q_e$) = $lnq_e - K_1t$</td>
<td>Eqn. 7</td>
<td>(Kali et al., 2022)</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>$t/q_t = 1/K_2q_e^2 + t/q_e$</td>
<td>Eqn. 8</td>
<td>(Kali et al., 2022)</td>
</tr>
</tbody>
</table>

$q_t$ adsorption capacity at each time point (mg.g$^{-1}$); $K_1$ pseudo-first-order kinetic model rate constant (min$^{-1}$); $K_2$ pseudo-second-order kinetic model rate constant (g.mg$^{-1}$.min$^{-1}$).

![Figure 11. Application of the PS1 model (a) and the PS2 model (b), for the adsorption of MB on HApS220 and HApS230](image_url)
The PS2 model, which has a correlation coefficient more than 0.99 for HApS220 and 1 for HApS230, clearly represents the best outcomes of our experiments, according to the findings of the linear regression of the pseudo-second order listed in Table 5. The calculated \( q_e \) values and the experimental data are in good agreement. These findings point to a chemisorption mechanism that involves covalent forces through the sharing or exchange of electrons between the sorbent and the sorbate (Vareda, 2023). Similar results have been reported elsewhere (Agougui et al., 2017), (EL Alouani et al., 2018), (Ingrachen-Brahmi et al., 2020).

**Table 5.** Kinetic parameters

<table>
<thead>
<tr>
<th></th>
<th>( q_e ) (exp) (mg.g(^{-1}))</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) (cal) K(_1) R(^2)</td>
<td>( q_e ) (cal) K(_2) R(^2)</td>
<td></td>
</tr>
<tr>
<td>HApS220</td>
<td>6.389</td>
<td>2.542 0.127 0.869</td>
<td>6.510 0.153 0.999</td>
</tr>
<tr>
<td>HApS230</td>
<td>6.557</td>
<td>2.542 0.127 0869</td>
<td>6.624 0.331 1</td>
</tr>
</tbody>
</table>

### 3.2.6 Thermodynamics studies

The influence of temperature on adsorption is studied for the same operating conditions with a MB concentration of 8 ppm. The Figure 12 presents the influence of the temperature on the adsorption of MB.

**Figure 12.** The effect of temperature on the adsorption of MB on HApS220 and HApS230

As the solution's temperature rises, more MB is adsorbed onto the surface. The adsorbed amount \( (q_e) \) increases from 6.4027 to 6.7160 mg/g for HApS220 and from 6.5571 to 6.7160 mg/g for HApS230 as the temperature rises from 298 to 333 K, indicating that the adsorption of MB is an endothermic process. This result can be confirmed by calculating the free enthalpy \( (\Delta G^0) \). The following equation can be used to determine the standard Gibbs free energy change \( (\Delta G^0) \) for the adsorption process:

\[
\Delta G^0 = - R \cdot T \cdot \ln K_c \quad \text{Eqn. 9}
\]

\( R \) is the gas constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\) and \( K_c \) is the Langmuir equilibrium constant. \( \ln(K_c) \) was plotted against \( 1/T \) (Figure 13). The values of \( \Delta H^0 \) and \( \Delta S^0 \) were estimated using the following relationships and the values are presented in Table 6:
\[ \ln(Kc) = -\frac{(\Delta H^0/RT)}{1} + \frac{(\Delta S^0/R)}{1} \]  \hspace{1cm} \text{Eqn. 10}

A straight line was obtained when the values of \( \ln(K) \) were plotted as a function of the temperature's inverse (1/T).

![Graph showing \( \ln(Kc) \) versus (1/T)](image)

**Figure 13.** Plots of \( \ln(Kc) \) versus (1/T)

**Table 6.** Thermodynamic constants

<table>
<thead>
<tr>
<th></th>
<th>( \Delta G^0 ) (KJ mol (^{-1}))</th>
<th>( \Delta H^0 ) (kJ mol (^{-1}))</th>
<th>( \Delta S^0 ) (J.mol (^{-1}).K (^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
<td>313 K</td>
<td>333 K</td>
</tr>
<tr>
<td>HApS220</td>
<td>-5.2339</td>
<td>-6.2959</td>
<td>-7.4169</td>
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<tr>
<td>HApS230</td>
<td>-5.8440</td>
<td>-6.6104</td>
<td>-7.4169</td>
</tr>
</tbody>
</table>

These results imply the following conclusions:
- The negative values of \( \Delta G^0 \) demonstrate that the adsorption of MB on HApS220 and HApS230 is a spontaneous process. At higher temperatures, the adsorption is even more advantageous because as the temperature rises, the values of \( \Delta G^0 \) values become more negative.
- The endothermic nature of the adsorption of MB on HApS220 and HApS230 is confirmed by the positive value of \( \Delta H^0 \).
- Positive entropy values indicate a rise in the degree of freedom of the adsorbed species (HApS affinity to MB) and a rise in disorder at the HApS/MB interface (Agougui et al., 2017), (Swamiappan et al., 2021).

**Conclusion**

Economically efficient hydroxyapatite-silica nanocomposite adsorbent has been successfully synthesized by sol-gel technique. It was found that the adsorption equilibrium is around 10 min. Moreover, the adsorption capacity of HAS220 and HAS230 increases when the MB concentration rise. In addition, it was observed that HAS230 shows the higher adsorption capacity. Interestingly, the adsorption of MB on HAS samples is a spontaneous endothermic chemisorption process. These findings make from our material a suitable adsorbent which may find use in wastewater treatment plants.
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Disclosure statement: Conflict of Interest: The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References


from human, bovine, and porcine bones, *Scientific reports* 9, 5915.  [https://doi.org/10.1038/s41598-019-42269-9](https://doi.org/10.1038/s41598-019-42269-9)


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