Removal of methylene blue by African hazelnut shell modified by zero valent iron and silver bimetallic nanoparticles

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ABSTRACT
This work focuses on MB sorption by hazelnut shell (HN) modified by zero valent iron and silver bimetallic nanoparticles. The purpose of this study is to understand the mechanisms that govern the elimination of MB and to find a suitable kinetics model of removal. Spectroscopic studies including FTIR, (TG-DSC), Methylene blue, Iodine number and effec of pH were used for its characterization. Equilibrium data was examined using a comparison of linear Langmuir, Freundlich and Temkin isotherm models. The Freundlich and Langmuir isotherm provided the best fit to the experimental data for MB as indicated by the values of the regression coefficient. The kinetic rates were modeled by using the Lagergren-first-order, pseudo-second-order, Elovich and Intraparticle diffusion model. The pseudo-second-order model was found to explain the adsorption kinetics most effectively. The presence of intra-particle diffusion mechanism was prominent, although it was not the sole rate-determining step. The results showed that HN, HN-Fe⁰ and HN-Fe⁰/Ag⁰, can be effective for removing MB from solution.

1. Introduction:
Nowadays, environmental pollution is the perilous problem all over the world. Especially contamination of water originates from different paths and causes great damage to the biosphere [1,2]. Textile industries have shown a significant increase in the use of synthetic complex organic dyes as colouring materials [3]. Dye is carcinogenic, affects reproductive organs and develops toxicity and neurotoxicity [4]. Moreover, an anaerobic degradation of methylene blue (MB) prevails in the production of carcinogenic and highly toxic amines. So there is a conclusive need of destruction of this hazardous waste from industrial effluents before disposal to the environment. Many kinds of biological, physical, and chemical processes have been developed for the remediation of water pollution, including membrane separation, coagulation, filtration, microbial degradation, and others. But all these methods involve some disadvantages and limitations like high cost and poor removal efficiency [5]. Earlier reports showed that a lot of research has been done on the photocatalytic degradation of synthetic dyes. But in the dislodgement process of organic waste, adsorption is supposed to be preferable over photocatalytic degradation, which sometimes leads toxic intermediates.

Nanotechnology is an immortally patulous area with enormous applications in various fields including food, agriculture, medical, pharmaceutical, catalysis, optical, and pollution control in a broad way [6]. In recent times, nanoscale zero-valent iron has received much attention from research areas like remediation of contaminated water and soil due to its high specific surface area, small particle size, and majestic reactivity of surface sites [7,8]. Apart from that, zero-valent iron nanoparticles...
(ZVIN) follows the maximal tenets of green chemistry as a non-toxic, inexpensive, and environmentally compatible material [9,10]. Novel metal crystallites such as silver and gold provide a more interesting research field due to their close lying conduction and valence bands in which electrons move freely [11]. The free electrons give rise to a surface plasmon absorption band which depends on both the particle size and chemical surrounding [11]. The stabilizers such as surfactants and ionic polymers cannot be easily removed from the surfaces of the formed silver colloids, which unavoidably affect the physiochemical properties of the resulting nanoparticles [11,12]. The most widely used substances for the stabilization of metal nanoparticles are ligands and polymers, specially natural or synthetic polymers with a certain affinity towards metals, which are soluble in suitable solvents [12-15]. The activated carbon is an efficient adsorbent for removal of many chemical species [16-19], however, its reusability is poor due to the loss during desorption.

So far, the removal of MB using (HN, HN-Fen, and HN-Feno/Agno) as an adsorbent has not been reported in the literature. Hence, the main objective of this investigation was to examine adsorption characteristic for MB on modified HN by iron and silver nanoparticles (HN-Fen and HN-Feno/Agno) coating on it. The effects of such factors as contact time, pH, isotherm and adsorption kinetics were also studied.

2. Materials and methods:

2.1. Sampling area and adsorbent:

The hazelnut shell used in this study comes from a small village on the national road number 7 called Bivouba (3°20.750’N and 10°5.890’E), located in South Region of Cameroon, Ocean division. Then the sample was grinded in a mortar and sieved as to pass through 125 μm mesh size. The Biomaterial sample stored in sterile, closed plastic containers and used as an adsorbent.

2.2. Preparation of HN-Fen and HN-Feno/Agno:

All chemicals used in this work were of analytical grade and provided by Aldrich Chemical Co. FeSO4.7H2O, NaBH4, HCl, NaOH and AgNO3 were used for the synthesis of HN-Fen and HN-Feno/Agno. Herein, we employed co-precipitation and reduction methods for the synthesis of HN-Fen [20,21]. Initially, 5 g FeSO4.7H2O was dissolved in 200 mL of ethanol: water (30:70, % v/v). Then, 5 g HN was added into the resulting mixture. HN-Fen were synthesized using the bottom-up method of dropwise addition of 0.125 M NaBH4. After addition of NaBH4 solution, the mixture was stirred for 45 min. The synthesized HN-Fen particles were then separated from the liquid phase and washed three times with acetone to prevent oxidation. Iron (Fe3+) was reduced to zerovalent iron (Fe0) by borohydride according to the reaction:

\[ \text{Fe}^{3+} + \text{BH}_4^- + 3\text{H}_2\text{O} + \text{support} \rightarrow \text{Fe}^0/\text{support} + 4\text{H}_2\text{O} + 4\text{H}^+ \]  \hspace{1cm} (1)

In the second step, 5 g HN-Fen powder was added to a diluted solution of AgNO3 (0.01 M) and the mixture was mixed on a shaker for 40 min at room temperature [21, 23]. Finally, NaBH4 3 M was added to complete the following reaction:

\[ \text{Ag}^+ + \text{BH}_4^- + 3\text{H}_2\text{O} + \text{HN-Fen} \rightarrow \text{HN-Feno/Agno} + 4\text{H}_2\text{O} + 4\text{H}^+ + 2\text{H}_2 \]  \hspace{1cm} (2)

The HN-Feno/Agno were separated and immediately washed many times with water and dried.

2.3. Adsorbate preparation:

All the chemicals used in the present work were of analytical reagent grade obtained from Aldrich Chemical Co. A methylene blue stock solution of 1000 mg L−1 was prepared by mixing 1 g of methylene blue in 1 L of de-ionized water. This stock solution was serially diluted to get the appropriate concentrations for conducting adsorption experiments [22-23].

2.4. Solid-Phase Characterization of HN, HN-Fen and HN-Feno/Agno:

The pH at the potential of zero charge of the HN, HN-Fen, and HN-Feno/Agno was measured using the pH drift method. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 250 °C to remove the dissolved carbon dioxide 100 mg was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graphs of final pH versus initial pH used to determine the zero point charge of the HN, HN-Fen, and HN-Feno/Agno [24].

The HN, HN-Fen and HN-Feno/Agno, activation temperature was fixed using thermogravimetry and differential thermal analysis (TG–DSC). A Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Nicolet, USA) was used to evaluate the distribution of functional groups on the surface between different materials at a resolution of 2 cm−1.

2.5. Aqueous Adsorption Characteristics:

2.5.1. Iodine number:

The iodine number was determined by using the sodium thiosulfate volumetric method. Standard iodine solution was added over adsorbents (100 mg) and after an equilibrium time of 5 min, the residual iodine concentration was
determined by titration with standard sodium thiosulfate using starch as an indicator. The iodine number was defined as the adsorbed quantities of iodine (mol g\(^{-1}\)) of adsorbents obtained by subtracting the residual concentration at equilibrium C\(_e\), from the initial concentration C\(_0\)

\[ Q_0 = \frac{C_0 - C_e}{m} V \]  

(3)

Where m and V are the mass of adsorbents sample and the volume of adsorbing solution respectively.

2.5.2. Methylene blue adsorption test:

The samples of HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\) were investigated for their aqueous adsorption of dyes using methylene blue. Adsorbents samples (100 mg) were mixed with MB in 50 mL stoppered erlenmeyer flasks. Batch experiments were carried out in the shaker at room temperature for 2h. The solutions were filtered and the concentrations of solutions were then determined by spectrophotometer at 659 nm. Then the quantity adsorbed was also calculated (mol.g\(^{-1}\)) of HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\) using equation (3).

2.6. Batch adsorption studies:

The adsorbate stock solution of 1000 mg.L\(^{-1}\) of methylene blue was diluted as required to obtain standard solutions containing 10–100 mg.L\(^{-1}\). Batch mode adsorption studies were carried out with 100 mg of adsorbent and 50 mL of MB solution of a desired concentration in 200 mL conical flasks and were stirred for predetermined time intervals at room temperature in a mechanical shaker. The removal kinetics of methylene blue was investigated by taking samples of the solution after the desired contact time (0–120 min). The residual concentration of methylene blue was determined using Spectroquant Pharo 300 spectrophotometer at 659 nm.

3. Results and discussions:

3.1. Characterization of HN, HN-Fe0 and HN-Fe0/Ag0:

FTIR spectroscopy was used to detect the vibrational characteristics of chemical functional groups attached with the sample fig 1. Three peaks observe at 3350.43, 3266.32 and 3282.45 cm\(^{-1}\) for HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\) respectively, this indicate the presence of O-H and N-H bond stretching [24]. The band at 2930.43 cm\(^{-1}\) observed on the HN curve can be assigned to the C-H stretching vibration of methylene [25]. The peaks observed at 1700 and 1600 cm\(^{-1}\) could be attributed to the carbonyl (C=O) stretching vibration of the amide linkage and stretching vibration of C-N of the aromatic amine [26]. The three curves show a weak absorption band between 1508 – 1507cm\(^{-1}\) can be assigned to the OH bending vibrational mode due to the absorption of moisture when FTIR sample disks were prepared in an open-air atmosphere [27]. A week band at about 1261 and 1226 where observed on the HN and HN/Fe\(^0\) curve It may be assigned to C-O stretching [28]. On the HN/Fe\(^0\)/Ag\(^0\) curve, an intense band is observed at about 1135.08cm\(^{-1}\). It can be apportioned to the C=O stretching of ether groups [29]. Mutual absorption peaks are observed at 1030.96, 1034.28 and 1029.08 cm\(^{-1}\) for HN, HN/Fe\(^0\) and HN/Fe\(^0\)/Ag\(^0\) and HN/Fe\(^0\)/Ag\(^0\) respectively with the HN and HN/Fe\(^0\)/Ag\(^0\) curve having a great intensity. These peaks can be assigned to C-OH bond stretching [29]. The peak at around 619.24cm\(^{-1}\) in the HN/Fe\(^0\) spectrum, is attributed to the Fe-O stretching vibration implying that the nZVI were successfully prepared and introduced into the HN [30].

![Figure 1. FTIR spectra of HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\).](image-url)
The result of thermogravimetric analysis of $\text{HN}$, $\text{HN-F}_0$ and $\text{HN-F}_0/\text{Ag}^0$ coupled with differential scanning calorimetry are shown in the fig 2, 3 and 4. The evolution of the mass loss of $\text{HN}$, $\text{HN-F}_0$ and $\text{HN-F}_0/\text{Ag}^0$ during the heat treatment can be divided into three steps. In the first step, we observe a slight decrease in weight which corresponds to a loss of 11.14%, 12.77% and 14.83% for $\text{HN}$, $\text{HN-F}_0$ and $\text{HN-F}_0/\text{Ag}^0$. This corresponds to the elimination of water absorbed by the biosorbents in the form of humidity. At these temperatures (78°C and 81°C), the HDSC curve shows a peak oriented toward the negative heat value, which shows that the loss water by evaporation or dehydration is accompanied by an exothermic reaction classified this loss mass in the range 50 - 200°C [28]. In the second step, we observe a rapid weight loss of 53.16% at 316°C, 64.55% at 311°C for $\text{HN}$ and $\text{HN-F}_0$ respectively. On the TGA curve for $\text{HN-F}_0/\text{Ag}^0$ in the range 200 - 311°C, we observe two weight loss; a rapid one of 25.48% at 273°C and a slow one of 12.29% at 306°C. These different weight losses according to literature correspond to structural water loss followed by the decomposition of cellulose and hemicellulose. The peaks corresponding to this weight losses are all oriented toward positive heat values, it correspond to an endothermic reaction during which an alveolar structure start to be form. Finally, a loss mass of 36.75% at 443°C and 36.22% at 359°C is observed respectively for $\text{HN}$ and $\text{HN-F}_0/\text{Ag}^0$. This loss mass correspond to the zone of thermal decomposition of $\text{HN}$, $\text{HN-F}_0$ and $\text{HN-F}_0/\text{Ag}^0$ was completed by 443, 471°C and 359°C respectively this permit us to fixe the calcination temperature at 480°C for $\text{HN}$, 500°C for $\text{HN-F}_0$ and 420°C for $\text{HN-F}_0/\text{Ag}^0$.

**Figure 2.** Curve of thermo-gravimetric analysis (TG and DSC) of $\text{HN}$.  

**Figure 3.** Curve of thermo-gravimetric analysis (TG and DTG) of $\text{HN-F}_0$.  


Iodine and methylene blue adsorption are considered a simple and quick test for evaluating the porous structure of micro and mesoporous adsorbents. Iodine has a small molecular size and can readily penetrate deep micropores of the HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\). So iodine number gives approximate measure of the micropore content of the HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\). Likewise, methylene blue number indicates the mesopore distribution in the adsorbents and indicates the ability of HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\) to adsorb medium size molecules. I\(_N\) and MB\(_N\) of HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\) is shown in (Fig.5 and table 1). In view of the above, our adsorbents are essentially microporous with a more pronounced microporosity for HN.

![Figure 4](image-url)  
**Figure 4.** Curve of thermo-gravimetric analysis (TG and DTG) of HN-Fe\(^0\)/Ag\(^0\).

![Figure 5](image-url)  
**Figure 5.** Adsorption of iodine and methylene blue onto HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\).

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>Methylene blue number (mg/g)</th>
<th>S(_{MB})(m(^2)g(^{-1}))</th>
<th>Iodine number (mg/g)</th>
<th>S(_{IN})(m(^2)g(^{-1}))</th>
<th>P(_{ZPC})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN</td>
<td>10.689</td>
<td>26.153</td>
<td>177.667</td>
<td>1912.80</td>
<td>7.8</td>
</tr>
<tr>
<td>HN/Fe(^0)</td>
<td>12.288</td>
<td>30.065</td>
<td>126.905</td>
<td>1366.29</td>
<td>8.15</td>
</tr>
<tr>
<td>HN/Fe(^0)/Ag(^0)</td>
<td>12.034</td>
<td>29.444</td>
<td>76.143</td>
<td>819.56</td>
<td>8.25</td>
</tr>
</tbody>
</table>

Observation of the values of pH\(_{ZPC}\) (table 1) indicates that all the biosorbents prepared and even the raw material are of a basic nature. These pH\(_{ZPC}\) values also make it possible to predict the suitable domain for the adsorption of our pollutant. For each adsorbent, when the pH of the solution is lower than the pH\(_{ZPC}\) the surface functional groups of the adsorbents will be protonated by an excess of proton H\(^+\) solution. the support is attractor of negatively charged adsorbate. On the contrary, if the pH of the solution is higher than the pH\(_{ZPC}\) surface functional groups will be deprotonated by the presence of OH\(^-\) ions of the solution so the support is attractor of positively charged adsorbate (promotes the adsorption of cationic dyes, increases electrostatic forces between the negative charge of the adsorbent and the positive dye charge) [30].

50
3.2. Effect of contact time of methylene blue:
Figure 6 illustrates the effect of contact time necessary to reach the equilibrium of adsorption of MB onto HN, HN-F\textsubscript{e}\textsuperscript{0} and HN-F\textsubscript{e}\textsuperscript{0}/Ag\textsuperscript{0} at the following conditions: 100 mg/l of the adsorbent and the contact time of 180 min. The amount of adsorption increases rapidly in the beginning and thereafter slowed gradually until the adsorption reaches the equilibrium in about 15 min. The variation in the extent of adsorption may also be due to the fact that initially all sites on the surface of adsorbent were vacant and the solute concentration gradient was relatively high [31]. After a period of time, the vacant surface sites are difficult to be available because of the repulsive forces between the MB adsorbed on the HN, HN-F\textsubscript{e}\textsuperscript{0} and HN-F\textsubscript{e}\textsuperscript{0}/Ag\textsuperscript{0} surface and the ions in solution [23,31]. Therefore, the mesopores of the surface of HN, HN-F\textsubscript{e}\textsuperscript{0} and HN-F\textsubscript{e}\textsuperscript{0}/Ag\textsuperscript{0} were saturated with MB in the initial stage of adsorption. Thereafter, the MB have to traverse farther and deeper into the pores encountering much larger resistance [32,33]. As result was the slowing down of the adsorption during the later period of adsorption [23].

![Figure 6: Kinetic curves of contact time on MB adsorption onto HN, HN-F\textsubscript{e}\textsuperscript{0} and HN-F\textsubscript{e}\textsuperscript{0}/Ag\textsuperscript{0}.](image)

3.3. Kinetic Studies:

3.3.1 First-order and Pseudo second-order kinetic models:
The mechanism of the adsorption process depends on the physical and chemical characteristic of the adsorbent and adsorbate. In order to investigate the kinetics adsorption of MB, the Lagergren-first-order. Ho’s pseudo-second-order and Elovich kinetic models were used. The pseudo-first order rate equation was proposed by Lagergren and is widely used for the adsorption of liquid/solid system [23]. The linear form of Lagergren equation is generally expressed as:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]  

(9)

Where \( k_1 \) (min\textsuperscript{-1}) is pseudo-first order rate constant at equilibrium, \( q_e \) and \( q_t \) are adsorption uptake of adsorbate at equilibrium and at time t(min), respectively. The pseudo-first order plots for MB are shown in figure 7.

Pseudo-second order model [33] suggests that both number of adsorption sites on the material surface and concentration of adsorbate ions in the liquid phase determine the rate. The linearized form of model is:

\[ \frac{t}{q_t} = \frac{t}{q_e} + \left( \frac{1}{k_2 q_e^2} \right) \]  

(10)

where \( h = k_2 q_e^2 \) and \( k_2 \) are initial and overall rate constants for adsorption which can be calculated from slope and intercept of plot \( t/q_t \) vs \( t \). The linear form of the pseudo-second order model was given by fig. 8.

In table 2, the values of the parameters and the correlation coefficients obtained at room temperatures are listed. It is clear from obtained data that pseudo second order kinetic model is more able to provide a successful description of MB adsorption onto HN, HN-F\textsubscript{e}\textsuperscript{0} and HN-F\textsubscript{e}\textsuperscript{0}/Ag\textsuperscript{0}. Moreover, the correlation coefficient values are quite well > 0.993. and much higher than those find by the pseudo-first order and elovich kinetic models.

3.3.2. Elovich kinetic model:
Elovich kinetic relationship, developed by is suitable to describe second order kinetics assuming that the actual solid surfaces are energetically heterogeneous [26]. The mathematical relationship in linearized form is:

\[ q_t = \frac{1}{\beta \ln(\alpha \beta)} + \frac{1}{\beta \ln t} \]  

(11)

Where \( \alpha \) (mgg\textsuperscript{-1}min\textsuperscript{-1}) is the initial adsorption rate and \( \beta \) (gmg\textsuperscript{-1}) is related to the extent of surface coverage and activation energy for chemisorption. In the present study, sorption data tested was fitted to the Elovich kinetic model (fig. 9), and values are given in Table 2. These values shown that initial adsorption rate was very high. and much of the MB was adsorbed rapidly on HN, HN-F\textsubscript{e}\textsuperscript{0} and HN-F\textsubscript{e}\textsuperscript{0}/Ag\textsuperscript{0} and then rate of adsorption slowed down. The results have further shown that the MB desorption rate was very high for HN and the Elovich kinetic model described the sorption process not better for the adsorbents.
Figure 7. Pseudo-first order kinetic plots for MB adsorption onto HN, HN-Fe° and HN-Fe°/Ag°.

Figure 8. Pseudo-second order kinetic plots for MB adsorption onto HN, HN-Fe° and HN-Fe°/Ag°.

Table 2. Kinetics parameters for MB adsorption onto HN, HN-Fe° and HN-Fe°/Ag°.

<table>
<thead>
<tr>
<th>adsorbents</th>
<th>Lagergren</th>
<th>Pseudo second-order</th>
<th>Elovich</th>
<th>Diffusion intraparticulaire</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_1/min^{-1}</td>
<td>R^2</td>
<td>K_2/g.min^{-1}</td>
<td>R^2</td>
</tr>
<tr>
<td>HN</td>
<td>0.030</td>
<td>0.647</td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>HN-Fe°</td>
<td>0.052</td>
<td>0.918</td>
<td>0.083</td>
<td>0.083</td>
</tr>
<tr>
<td>HN-Fe°/Ag°</td>
<td>0.047</td>
<td>0.554</td>
<td>0.007</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Figure 9. Elovich kinetic plots for MB adsorption onto HN, HN-Fe° and HN-Fe°/Ag°.
3.4. Intraparticle diffusion:
Once adsorbed on the surface, solute particles diffuse into the pores on the surface of adsorbent and form bonding, which may be the rate determining step [28,31]. Weber and Morris intraparticle diffusion model is given:

\[ q = f \left( \frac{D_s}{r_p^2} \right)^{1/2} = k_w t^{1/2} \]  

(12)

where \( k_w \) (m\(g^{-1}\)min\(^{-1/2}\)) is the rate constant for intraparticle diffusion \( k_w \) can be found from slope of plot \( \ln q_t \) vs \( \ln t \). For an adsorbing system the straight line should pass through the origin and the intercept value provides an idea about the deviation from intraparticle diffusion model or contribution of the film diffusion mechanism [31]. In case of Morris–Weber equation (Fig 10), the straight lines of methylene blue did not pass through the origin which demonstrated that intra-particle diffusion was not only the rate controlling step but other mechanisms were also involved in the rate determining step.

![Figure 10. Intraparticle diffusion plots for MB adsorption onto HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\).](image)

3.5 Influence of pH on the adsorption capacity of the biosorbents:
The study of the influence of pH on the adsorption capacity of the differents biosorbents was performed by varying the pH of MB solution from 2 to 12. Measuring the amount of MB adsorbed after stirring a mass of 0.1g of the different biosorbent in 50ml pollutant solutions allowed us to plot the variation curves of the quantities adsorbed as a function of pH as shown in fig 11.

![Figure 11. influence of pH variation on biosorbents adsorption capacity.](image)

It is observed that the adsorption is maximum in basic medium more particularly in the range 6 to 10. This could be explained by the fact that in strongly acidic medium, the surface functional groups of the adsorbents are protonated by an excess of proton solution and as a result the support is attractor of negatively charged adsorbate thus, causing repulsion between the adsorbent surface and MB since it is cationic. However, in basic medium the surface functional groups of adsorbent are deprotonated by the presence of hydroxide ions rendering the support attractor to positively charged adsorbate. This result was predictable from the zero point charge pH results.

3.6. Equilibrium isotherms:
The capacity of a HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\) can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the HN, HN-Fe\(^0\) and HN-Fe\(^0\)/Ag\(^0\). The biosorption isotherms were investigated using four equilibrium models, which are namely the Freundlich, Langmuir, and Temkin and isotherm models were analyzed.
The Langmuir sorption isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used isotherm for the biosorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in linear form [31].

\[
\frac{C_e}{Q_e} = \frac{1}{K_lQ_{\text{max}}} + \frac{1}{Q_{\text{max}}}C_e
\]  

(13)

where \(Q_e\) is the equilibrium MB concentration on the adsorbent (mgg\(^{-1}\)). \(C_e\) is the equilibrium (MB) concentration in the solution (mgL\(^{-1}\)). \(Q_{\text{max}}\) adsorbent (mgg\(^{-1}\)) and \(K_l\) is the monolayer adsorption capacity of the Langmuir adsorption constant (Lmg\(^{-1}\)) related with the free energy of adsorption. (Fig. 12 and table 3) indicate the linear relationship between the amount (mg) of MB sorbed per unit mass (g) of HN. HN-F\(_e\) and HN-F\(_e\)/Ag\(^0\)against the concentration of MB remaining in solution (mg/L). The coefficients of correlation \(R^2\) grouped in table 3 indicate that the adsorption of the MB onto HN. HN-F\(_e\) and HN-F\(_e\)/Ag\(^0\) fitted well the Langmuir model. In other hands. the sorption of MB onto HN. HN-F\(_e\) and HN-F\(_e\)/Ag\(^0\) was taken place at the functional groups/binding sites on the surface of the adsorbents which is regarded as monolayer biosorption [28].

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_f)</td>
<td>(n)</td>
<td>(R^2)</td>
</tr>
<tr>
<td>HN</td>
<td>1.015</td>
<td>3.256</td>
<td>0.960</td>
</tr>
<tr>
<td>HN-F(_e)</td>
<td>1.039</td>
<td>2.617</td>
<td>0.994</td>
</tr>
<tr>
<td>HN-F(_e)/Ag(^0)</td>
<td>1.013</td>
<td>2.922</td>
<td>0.960</td>
</tr>
</tbody>
</table>

**Figure 12.** Langmuir adsorption isotherm for removal of methylene blue onto HN. HN-F\(_e\) and HN-F\(_e\)/Ag\(^0\).

The Freundlich model assumes active sites of different energies and a heterogeneous adsorption surface. The Freundlich model [31] is:

\[
\log \left( \frac{x}{m} \right) = \log K_F + \frac{1}{n} \log C_e
\]  

(14)

where \(K_F\) is a constant relating the adsorption capacity and \(1/n\) is a parameter relating the adsorption intensity, which varies with the heterogeneity of the material (Fig. 13 and table 3). The values of \(n\) indicate that the type of adsorption is favorable in the range of 2–10. moderate in the range of 1–2 and poor if \(n < 1\). The \(n\) values (table 3) were between 0 and 10 indicating that the adsorption of MB onto adsorbents was favorable. However, the \(R^2\) values were found to be 0.960 for HN. 0.994 for HN-F\(_e\) and 0.960 for HN-F\(_e\)/Ag\(^0\). These results show that the equilibrium adsorption data were well described by Freundlich isotherm compared to the Temkin and Langmuir isotherms based on \(R^2\).

The Temkin isotherm contains a factor that explicitly takes into account of the adsorbent-adsorbate interactions. In this equation. it is assumed that. because of these interactions and ignoring very low and very large concentration values. the heat of adsorption of all molecules in the layer would decrease linearly with the coverage \([18,32]\). The linear form of the Temkin model is written as:

\[
Q_e = B\ln A_T + B\ln C_e
\]  

(15)
where $A_T$ is the equilibrium binding constant corresponding to the maximum binding energy. $B = RT/b$, $b$ (J/mol) is the Temkin constant related to the heat of adsorption. $R$ (8.314 J/mol K) is the universal gas constant and $T$ (K) is solution temperature.

The values obtained from the Temkin isotherm (Fig.14 and table 3) indicate that the adsorption of (MB) onto HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$ occurred via chemisorption. The values for $A_T$ were higher than 8 kJ mol$^{-1}$ and thus the mechanism involved is chemical adsorption. In the chemisorption process, the adsorbates adhere to the adsorbent through a weak chemical bond and thus this process is associated with relatively higher adsorption energies [33].

![Figure 13. Freundlich adsorption isotherm for removal of MB onto HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$.](image)

![Figure 14. Temkin adsorption isotherm for removal of MB onto HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$.](image)

4. Conclusion:

HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$ can be used as an effective adsorbent for removing (MB) from contaminated water sources. $I_S$ and MB$S$ are showed that HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$ are essentially micropores. The adsorption process is dominated by chemisorption and it was also found that the pore diffusion played an important role in the adsorption. The Freundlich isotherm showed a better fit than the Langmuir and Temkin isotherms, thus indicating the applicability of heterogeneity of (MB) on HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$. Results from this study suggest that HN, HN-Fe$^0$ and HN-Fe$^0$/Ag$^0$ are a very effective adsorbent for (MB).

References:


