Use of rice husk ash as a potent adsorbent of malachite green: kinetic and equilibrium studies

Alexis SIDJOU SIDJOU 1, Armand TCHAKOUNTE 1*, Silvain TOME 1, Charles Mélea KEDE 1,2, Joseph DIKA MANGA 1

1Département de Chimie, Faculté des Sciences, Université de Douala, P.O. Box 24175, Douala, Cameroun.
2Département de génie des procédés, Ecole Nationale Supérieure Polytechnique de Douala, Université de Douala, P.O. Box 2701, Douala, Cameroun.

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ABSTRACT
In this work, an adsorbent was prepared by calcination of rice husks and used as a membrane to remove malachite green contained in an aqueous solution. The synthesized adsorbent was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. The kinetics and equilibrium of malachite green adsorption on rice husk ash was studied in batch. The effects of contact time and initial concentration were examined. The results show that the maximum adsorption capacity of malachite green by calcined rice husks is 8.58 mg/g for an initial concentration of 60 mg/L after an equilibrium time of 90 min. Langmuir, Freundlich, and D-R models were used to describe the adsorption isotherms. It was found that the Langmuir model perfectly describes the adsorption equilibrium with its correlation coefficient close to unity. This implies a monolayer adsorption of malachite green. The adsorption kinetics was modeled using the pseudo first order, pseudo second order and Elovich models. The pseudo-second order model better describes the adsorption kinetics of malachite green by rice husk ash. These results show that rice husk ash is a suitable adsorbent for the removal of malachite green in aqueous solution.

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1. Introduction:
The growth of industrial activities is currently one of the cause of the proliferation of toxic pollutants in the environment. These pollutants include heavy metals, phenolic derivatives, pesticides and dyes [1].

As industrialization continuous to grow, one of the main problems faced by the textile industry is the removal of dyes from their wastewaters before depositing it in the environment. Dyes are visible pollutants although they are not generally toxic; they can affect the aquatic diversity by blocking the passage of light through water [2-3].

The phenomenon of water pollution becoming one of the major concerns in research, relentless work is continually undertaken to alleviate it, while focusing on the most difficult pollutants to eliminate [4]. This is the case of malachite green, which is a N-methylated diaminotriphenyl-methane dye generally used for the dyeing of cotton, wool, silk, leather, paper and also widely used in distilleries for coloring purposes. It is also used as a therapeutic agent and as antiseptic but only for external applications on wounds and ulcers. Despite its numerous uses, its oral consumption is toxic, hazardous and carcinogenic due to the presence of nitrogen. When it’s discharged into streams, it will affect the aquatic life and causes detrimental effects in liver, gills, kidney, intestine, gonads and pituitary gonadotrophic cells [5]. In humans, it may cause...
irritation with redness and pain. Upon contact with eye will lead to permanent injury of human eyes. It is known to be highly toxic to mammalian cells and act as a tumor-enhancing agent. Despite the large amount of data on its toxic effects, malachite green is still used in aquaculture and other industries [6]. As a result, it becomes essential to eliminate it, and various depollution processes are used with this in mind.

The depollution processes already developed are, among others, membrane processes [7], photocatalytic processes [8], filtration [9], electrolysis [10], electrocoagulation [11], chemical oxidation [12], ion-exchange [13], ozonation [14], membrane separation [15], and aerobic and anaerobic microbial degradation [16]. However, all such methods suffer from one or other limitations, and none of them were successful in completely removing the color from wastewater. Liquid-phase adsorption processes are efficient for removal of colors, odor, organic and inorganic pollutants from the industrial wastewater. Currently, the most commonly used adsorption agent in industry is activated carbon, which was successfully tested also for the removal of dye from wastewater. Although commercial activated carbon is a preferred adsorbent for color removal, its widespread use is restricted due to high cost, and its regeneration and reuse makes it more costly [17].

However, due to the high production rate of commercial activated carbons, they are difficult to access and their precursors are not renewable. This is how developing low-cost activated carbon from agricultural waste turns out to be a more attractive and profitable way, because the biomass used is available, renewable in abundance and inexpensive. Rice husk ash are a reflection of this method of preparation since they are part of the waste available in abundance and cheaply, and are therefore good precursors for the preparation of activated carbons intended to eliminate the MG.

The objective of this work is to valorize rice husk ashes by using them as adsorbents for the adsorption of malachite green.

2. Materials and methods:
2.1. Materials and chemicals:
Rice husk ash is a solid obtained from rice processing mill after burning of rice husk. Rice husk ash was collected from local rice mill, North West, Cameroon. Rice husk ash, after collection it was homogenized and dried at 105 °C for 3 h and cooled to ambient temperature in a desiccator. Malachite green (MG) was obtained from BDH. X-ray diffraction (XRD) analysis is carried out to identify the properties of RHA. X-ray fluorescence (XRF) analysis is carried out to determine chemical compositions of RHA.

2.2. Batch adsorption procedure:
The batch adsorption studies were carried out to optimize parameters such as initial MG concentration, adsorbent dose, solution pH and contact time on the effective removal of the MG from the aqueous solution using RHA samples. 30 mL of the MG solution with varying concentrations (10–100 mg/L), adsorbent dosages (0.1–0.6g), solution pH (2.0–8.0) and contact times (5–120 min) was taken in 100 mL Erlenmeyer flasks and then the mixture was kept in a rotary shaker. The concentration of the residual MG in the solutions was measured using by ICP/OES. The percentage removal of the MG was calculated by using the equation (1):

\[
\text{% Removal} = \frac{(C_0 - C_e)}{C_0} \times 100
\]  

Where Co (mg/L) and Ce (mg/L) are the initial and equilibrium concentrations of MG solution, respectively. The amount of adsorbed MG was also calculated using the following equation:

\[
Q = \frac{(C_0 - C_e) \times V}{m}
\]

Where Co and Ce are the concentrations of MG in the solution initially and at equilibrium (mg/g), respectively, V is the volume of the MG solution (L), and m is the mass of the adsorbent (g).

2.3. Adsorption kinetic study:
To fit experimental adsorption kinetic data and to further understand the adsorption process mechanism, as well as the rate limiting step during adsorption process, pseudo-first, pseudo-second order kinetic and Elovich models were developed. The pseudo-first order model assumes a physical adsorption as the dominant mechanism [18]. The model can be expressed by the following equation:

\[
Q_t = q_e (1 - \exp(-k_1 t))
\]

Where Q, is the adsorption capacity at any time (mg/g), q, is the equilibrium adsorption capacity (mg/g), k, is the pseudo first-order kinetic rate constant (min⁻¹), and t is the time (min).

The pseudo-second order model supposes that chemical adsorption is the dominant mechanism. The model is expressed as follows [19]:

\[
Q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}
\]
Where, $Q$, and $q_e$ ($\text{mg/g}$) are the amount of MG adsorbed at time $t$ and at equilibrium, respectively and $k_2$ ($\text{g.mg}^{-1}.\text{min}^{-1}$) is the second-order rate constant.

Ellovich kinetic model is given as follows [20]:

$$Q_t = (1 + \beta)\ln(1 + \alpha \beta t) \quad (5)$$

Where $\beta$ is the desorption constant related to the activation energy of chemisorption (g/mg) and $\alpha$ is the initial adsorption rate (mg/(g.min)).

2.4. Equilibrium study:
Generally, the effectiveness of adsorption depends largely on the equilibrium between solid and liquid phase. Three parameters isotherm models were used to explain the MG adsorption towards the selected adsorbent such as Langmuir, Freundlich and Dubinin-Radushkevich (D-R).

The Langmuir isotherm is valid for monolayer adsorption on an energetically homogeneous surface with a limited number of identical sites [21]. The equation below give the expression of Langmuir isotherm model:

$$Q_e = \frac{q_m b C_e}{1 + b C_e} \quad (6)$$

Where $Q_e$ is the equilibrium adsorption capacity (mg/g), $C_e$ is the equilibrium MG concentration in solution (mg/L), and the Langmuir constants $q_m$ and $b$ represent the maximum adsorption capacity (mg/g) and the energy of adsorption (L/mg), respectively.

Freundlich isotherm model has the following form [22]:

$$Q_e = K_F C_e^n \quad (7)$$

where $C_e$ is the concentration of MG at equilibrium (mg/L), $K_F$ is the Freundlich constant [((mg/g)/(L/mg))(1/n)] related to the bonding energy, and $n$ is a measure of deviation from the linearity of adsorption (g/L).

Unlike Langmuir and Freundlich, Dubinin-Radushkevich (D-R) isotherm model is not based on ideal assumptions. It is a more general model, applied to estimate the nature of adsorption process; whether it is physical or chemical with its mean free energy. The general form of D-R isotherm equation is expressed following this equation:

$$q = q_{D-R} \exp(-\beta \varepsilon^2) \quad (8)$$

Where $q$ is the amount of solute adsorbed per unit weight of adsorbent (mg/g), $q_{D-R}$ is the maximum adsorption capacity (mg/g), $\beta$ the activity coefficient related to adsorption free energy (mg$^2$/J), $\varepsilon$ the polanyi potential which is defined as [23]:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

3. Results and discussion:
3.1. Physicochemical characterization of rice husk:

The chemical composition of rice rusk ash is summarized in Table 1. It is observed that after the carbonization, RHA principally contains SiO$_2$ (84.12 wt%) with a significant amount of K$_2$O (4.95 wt%), MgO (3.22 wt%) and P$_2$O$_5$ (3.82 wt%).

The noteworthy value of loss of ignition (LOI) 0.28 wt% confirms the partial carbonation of organic species in RHA after thermal treatment. Then the RHA use here is an active coal with high inorganic species.

<table>
<thead>
<tr>
<th>Oxide (wt%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
<th>MnO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA</td>
<td>80.2</td>
<td>1.54</td>
<td>0.48</td>
<td>0.57</td>
<td>3.22</td>
<td>4.95</td>
<td>0.15</td>
<td>0.09</td>
<td>3.03</td>
<td>0.14</td>
<td>5.63</td>
</tr>
</tbody>
</table>

The figure 1 represents the diffractogram of calcined rice husk. It is observed on this figure the dump located between 20 and 35°, indication the presence of amorphous phases. The indice of crystallinity of this diffractogram is about 37.6 %. These crystalline phases are essentially constituted of cristobalite alpha (71.6%) and tridymite (28.4%). These two phases are crystallized forms of SiO$_2$. These observations indicate that only a part of SiO$_2$ contained in the RHA is crystallized and the other constituent are in the amorphous phase.

Figure 2 depicts the FTIR spectrum of RHA. The main band at 1066 cm$^{-1}$ is attributed to asymmetric stretching SiO$_2$ unit and the band at 792 cm$^{-1}$ is assigned to Si–OH and/or Al–OH, Si–O or Al–O and Al–O symmetric stretching vibration and bending vibration of Si–O–Si, respectively [24-25]. The band at 2118 cm$^{-1}$ is attributable to aliphatic C-H stretching [26], confirming the presence of organic species.
The micrographs and spectrum of the elemental chemical analysis of RHA are presented in Figure 3. The micrograph (a) reveals that the RHA consists mainly of two phases. The agglomerated particle phase is dispersed in small amounts in the RHA. According to the micrograph (b) this phase consists of the silicon oxide crystals, corroborating with the results of the mineralogical analysis. These chemical analyses of micrographs (a) and (b) confirm once again that the RHA is mainly composed of SiO$_2$.

3.2. Equilibrium studies:

3.2.1. Effect of pH:
The figure 4 shows us that in strongly acidic medium (pH = 2) we observe a weak adsorption of the MG which is due to the electrostatic repulsion between the positively charged malachite green and the excess of protons. Beyond pH=2 we observe an increase of the adsorption capacity of the MG until reaching its maximum of 7. 7 mg/g at pH = 6 due to a considerable decrease of protons limiting this repulsion. At pH=7, a slight decrease of adsorption is observed due to the repulsion between the surface of the adsorbent and the presence of a partial negative charge on the MG due to the oxalate ion.

3.2.2. Effect of adsorbent dosage:
The effect of adsorbent dose on the percentage removal of MG from solution is shown in Fig.5. We observe that the percentage of adsorption of MG increases with the increase of the mass of RHA. This is mainly due to an increase in the
sorptive surface area and the availability of more active binding sites on the surface of the adsorbent with increase in adsorbent dose. The optimal dose of RHA needed for a maximum MG elimination rate (96%) is 0.5g.

3.2.3. Influence of initial MG concentration on the adsorption of MG and adsorption isotherms:
Adsorption experiments of MG concentration from 10 to 100 mgL\(^{-1}\) with a fixed adsorbent dose at pH 6 for RHA were performed (fig.6). It is observed that increasing the initial concentration of MG has a positive impact on the adsorption capacity. This phenomenon may be attributed to the rise in the concentration gradient and this augmentation of the adsorption capacity is also due to the higher adsorption rate and the exploitation of all available binding sites for adsorption at higher MG concentration.

**Figure 4.** Effect of initial pH on the adsorption of MG onto RHA.

**Figure 5.** The effect of adsorbent dose on the percentage removal of MG unto RHA.

**Figure 6.** Effect of initial concentration on the adsorption of MG.
Equilibrium data from the effect of initial MG concentration were compared with three non-linear isotherm models Langmuir (Langmuir 1918), Freundlich (Freundlich 1906) and Dubinin-Radushkevich (D-R). In order to understand the mechanisms of MG fixation on RHA, as it can be seen in Table 2 and figure 7, Langmuir adsorption isotherm models have high correlation coefficient value ($R^2 = 0.925$). Indicates that an adsorption of the MG on the RHA in monolayer on homogeneous active sites. The separation factor $R_L$ shows us that the adsorption is favorable because $R_L$ is between 0 and 1 [27]. Based on the correlation coefficient values, the experimental data gave estimable fits within the following isotherm order: Langmuir > DRK > Freundlich.

![Graph showing adsorption isotherm studies for the removal of MG by RHA.](image)

**Figure 7.** Adsorption isotherm studies for the removal of MG by RHA.

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>RHA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir model</strong></td>
<td></td>
</tr>
<tr>
<td>$q_m$ (mgg$^{-1}$)</td>
<td>19.937</td>
</tr>
<tr>
<td>$K_L$ (Lmg$^{-1}$)</td>
<td>0.061</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.141</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.925</td>
</tr>
<tr>
<td><strong>Freundlich model</strong></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (mgg$^{-1}$) (mg/L)$^{1/n}$</td>
<td>1.752</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.604</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.681</td>
</tr>
<tr>
<td><strong>Dubinin–Radushkevich model</strong></td>
<td></td>
</tr>
<tr>
<td>$q_m$ (mgg$^{-1}$)</td>
<td>11.436</td>
</tr>
<tr>
<td>$E_a$(kJ/mol)</td>
<td>0.205</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.684</td>
</tr>
</tbody>
</table>

### 3.3. Influence of contact time on the adsorption of MG and kinetic studies:

Fig.8 illustrates the effect of contact time on the MG adsorption at optimal pH (pH = 6) and the contact time of (5-120 min). As indicated in Fig.8, the MG adsorption efficiency was increased sharply up to 90 min and then it reached the equilibrium state right after 90 min. The sharp increase in the adsorption efficiency may be due to the existence of enormous vacant active sites in the adsorbent surface. However, by raising the contact time the availability of MG to the active sites on the adsorbent surface is limited, which makes the adsorption efficiency reduce [28].
The adsorption mechanism and the rate at which the MG was removed from the aqueous solution were estimated by using adsorption kinetic models. In this study, three kinetic models such as pseudo first-order, pseudo second-order, and Elovich kinetic model were used to examine the adsorption kinetics for the removal of MG onto the RHA, and the results were shown in Fig. 8. The estimated parameters such as pseudo first-order kinetics constant ($k_1$) and $q_e$, the pseudo second-order kinetic constant ($k_2$) and $q_e$, and the Elovich kinetic model constant $\alpha$ and $\beta$ are listed in Table 3. 

The analysis of data from the pseudo second-order equation suggests that the adsorption of MG onto RHA is controlled by chemisorptions [29]. In addition, Table 3 and figure 8 also indicates that the adsorption capacity ($q_{e,cal}$) calculated from the pseudo second-order model is well suited to the experimental data ($q_{e,exp}$). Therefore, it can be concluded that the kinetics of MG adsorption on RHA fits best to the pseudo second-order model.

Table 3. Adsorption kinetic data for the removal of MG by RHA.

<table>
<thead>
<tr>
<th>Model</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Elovich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>$Q_e$ (mg/g)</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Value</td>
<td>8.086</td>
<td>0.096</td>
<td>0.901</td>
</tr>
</tbody>
</table>

Figure 8. Effect of contact time for the removal of MG by RHA.

Figure 9. Adsorption kinetic fit for the removal of MG by RHA.
4. Conclusion:
The aim of the recent work was to evaluate the adsorption capacity of the RHA towards the MG dye. The physicochemical characterizations reveal that the rice husk ashes are mainly composed of amorphous silicas. The MG adsorption kinetics is best described by the pseudo-second order model while the equilibrium data are in agreement with the Langmuir isotherm. These results show that RHA are a potential candidate for dye removal.

References:


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