Removal of two cationic dyes by adsorption on F400 commercial activated carbon

Eliminación de dos colorantes catiónicos mediante adsorción sobre carbón activado comercial F400

Remoção de dois corantes catiônicos por adsorção em carvão ativado comercial F400

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ABSTRACT
In this investigation, we studied the removal of two cationic dyes, methyl green MG and malachite green MC G, by a commercial adsorbent. This adsorbent is a F400 activated carbon with a specific surface area of 1203 m². g⁻¹, which is expected to be high compared with ordinary adsorbents. Adsorption tests were carried out on
both dyes in batch mode. The results show that both kinetics are fast, with equilibrium reached after 20 minutes and 30 minutes respectively for Methyl Green and Malachite Green. The kinetics of both dyes are well adapted to pseudo-second order, and for the intraparticle diffusion model, two lines can be distinguished for each dye, proving the existence of two adsorption steps. The isotherm for this system reveals an L-type shape for both dyes, in line with the classification of Giles & al. so there is little competition for sorption sites between solvent and adsorbate. The adsorption isotherms for methyl green by PAC obeyed the Langmuir, Freundlich and Temkin models, while that for malachite green followed only the Langmuir isotherm, with a much higher maximum amount.


**RESUMO**
Nesta investigação, estudámos a remoção de dois corantes catiónicos, verde de metilo MG e verde de malaquite Mc G, por um adsorvente comercial. Este adsorvente é um carvão ativado F400 com uma área de superfície específica de 1203 m$^2$. g$^{-1}$, que se espera ser elevada em comparação com os adsorventes comuns. Foram efectuados testes de adsorção de ambos os corantes em modo descontínuo. Os resultados mostram que ambas as cinéticas são rápidas, com o equilíbrio atingido após 20 minutos e 30 minutos, respetivamente, para o verde de metilo e o verde de malaquite. A cinética de ambos os corantes está bem adaptada à pseudo-segunda ordem e, para o modelo de difusão intrapartícula, podem ser distinguidas duas linhas para cada corante, provando a existência de duas etapas de adsorção. A isotérmica para este sistema revela uma forma do tipo L para ambos os corantes, de acordo com a classificação de Giles & al. pelo que existe pouca competição pelos sítios de adsorção entre o solvente e o adsorbato. As isotérmicas de adsorção do verde de metilo pelo PAC obedeceram aos modelos de Langmuir, Freundlich e Temkin, enquanto a do verde de malaquite seguiu apenas a isotérmica de Langmuir, com uma quantidade máxima muito superior.


**RESUMEN**
En esta investigación estudiamos la eliminación de dos colorantes catiónicos, verde de metilo MG y verde de malaquite Mc G, mediante un adsorbente comercial. Este adsorbente es un carbón activado F400 con una superficie específica de 1203 m$^2$. g$^{-1}$, que se espera que sea alta en comparación con los adsorbentes ordinarios. Se realizaron ensayos de adsorción con ambos colorantes en modo discontinuo. Los resultados muestran que ambas cinéticas son rápidas, alcanzándose el equilibrio a los 20 y 30 minutos respectivamente para el Verde de Metilo y el Verde de Malaquita. Las cinéticas de ambos colorantes se adaptan bien al pseudo-segundo orden, y para el modelo de difusión intrapartícula se distinguen dos líneas para cada colorante, lo que demuestra la existencia de dos etapas de adsorción. La isoterma para este sistema revela una forma tipo L para ambos colorantes, en línea con la clasificación de Giles & al. por lo que hay poca competencia por los sitios de adsorción entre el disolvente y el adsorbato. Las isotermas de adsorción para el verde de metilo por PAC
obedieron a los modelos de Langmuir, Freundlich y Temkin, mientras que la del verde de malaquita sólo siguió la isoterma de Langmuir, con una cantidad máxima mucho mayor.


1 INTRODUCTION

Due to the release of waste contain hazardous metals by various industrial sectors, including fertilizer and pesticide production, metallurgy, steel and iron production, fuel and energy production, etc., water pollution is a problem for the environment that affects the entire world today (Hussein et al. 2018). The manufacturing procedures of the textile, printing, dyeing, and papermaking sectors have all used different dyes (Sahoo; Prelot 2020; Murugesan et al. 2022). These dyes have gotten into water courses in huge quantities, creating a risk to the water's environmental safety. Even at trace amounts, the dyes in the effluents can cause a number of hazardous byproducts to be created by oxidation, hydrolysis, and other chemical reactions, which may directly or indirectly affect human health by boosting the risk of cancer, tumors, and allergies (Katheresan et al. 2018; Pathania et al. 2017). Developing straightforward, extremely effective, and economic techniques to remediate dye wastewater is thus required (Khuluk; Rahmat, 2019; Batana; Bouars; Aouissi, 2022a). Several chemical and physical treatment technologies, which include chemical precipitation, photodegradation, electro-coagulation and flocculation, reverse osmosis, ion exchange and toxic sludge removal, have been established and developed to combat the pollution caused by hazardous metals and treat dye-laden effluents, but these have major downsides. Adsorption, on which the present research is based, is by far the best approach, as it is inexpensive, simple to use, widely available and generates practically no toxic by-products (Rajan et al., 2019).

The principle of adsorption treatment is to trap dyes in a solid material called adsorbent. There are several solid materials such as clays, zeolites, activated alumina, silica gel, sludge, biomasses, agricultural residues, industrial by-products
and activated carbon that can be used in decolorization processes (Bentahar et al. 2015; Rahmani et al. 2021)

Activated carbon has been chosen as an adsorbent for treating colored effluents due to its high porous structure, large specific surface area and high adsorption capacity.

Our objective is to study the removal of malachite green and methyl green which are two basic dyes by adsorption on F400 activated carbon, which requires a good knowledge of the characteristics of both pollutants as well as the adsorbent and the removal mechanism of these pollutants.

In this research, the specific surface area of the adsorbent selected was determined. The initial concentration of the pollutant and the contact time were studied for their influence on the adsorption phenomenon. Adsorption kinetic models (pseudo-first-order, pseudo-second-order and intra-particle diffusion) and equilibrium isotherm models (Langmuir, Freundlich and Temkin) were also evaluated.

The aim of this research is to eliminate two cationic dyes using a commercial activated carbon and its application in the purification of effluents contaminated by industrial dyes.

2 EXPERIMENTAL METHODS

2.1 ADSORBENT PREPARATION

The adsorbent is an activated carbon F400 purchased from Biochem-Chemopharma, it is of bituminous oil origin, activated at high temperature under oxygen. It must be dehydrated for 24 hours at 110°C in an oven before each usage in order to remove the moisture and increase its specific surface.

2.2 CHARACTERIZATION OF THE ADSORBENT

The CAP was characterized using the Brunauer-Emmett-Teller (BET) area and therefore the porous property were measured by determining the N₂ adsorption isotherm at -196°C with an adsorption analyser (Micromeritics ASAP 2020 Plus 2.00). Before adsorption, the sample was degassed under vacuum at 120°C for 12 hours.
2.3 PREPARATION OF DYE SOLUTION

Malachite green (C$_{23}$H$_{25}$Cl$_2$N$_2$) Mc G and methyl green (C$_{26}$H$_{33}$Cl$_2$N$_3$) MG were used without any prior purification. A measured quantity of each dye was dissolved in 50 mL of distilled water to create a stock solution of 1 g. L$^{-1}$. The test solution (10 mg. L$^{-1}$) was prepared by diluting the stock solution with distilled water (BATANA; REBIZI; GUIBADJ, 2022b; KARIM et al., 2010). At a wavelength of 620 nm and 635 nm respectively (Table 1), Mc G dye and MG dye analysis were carried out using a UV-vis spectrophotometer.

| Table 1 – Physico-chemical characterization of methyl green and malachite green |
|----------------------------------|----------------------------------|
| Name                             | Methyl green (MG)                | Malachite green (Mc G)          |
| Other names                      | Basic Green 5; Cl 52020          | Aniline green; Basic green 4;    |
|                                  |                                  | Diamond green B; Victoria green B|
| Structure                        | ![Structure MG]                  | ![Structure Mc G]               |
| molecular weight (g. mol$^{-1}$) | 458.47                           | 364.91                          |
| Wavelength (λ$_{max}$) nm         | 632                              | 620                             |

Source: Chemical Book

2.4 BATCH SORPTION KINETICS

To determine the impact of contact time (t, in min) on the adsorption process, experiments were carried out in batch mode at 298 K and an initial concentration $C_0 = 10$ mg. L$^{-1}$ of each dye with a mass of 15 mg of activated carbon stirred at a constant speed of 250 rpm. Different samples are subsequently taken at different times. To remove PAC particles suspended in the samples, centrifugation was performed (Sinal TD4 A), the supernatant liquid was analyzed by SP3000 U.V. Visible (nano OPTIMA) to measure the remaining dye concentration at a specific time ($C_t$, in mg. L$^{-1}$).

The adsorption capacity ($q_t$, in mg. g$^{-1}$) was calculated using (equation 1)

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

(1)
where:

\( (V, \text{ in } \text{L}) \) is the volume of dye solution and \((m \text{ in } \text{g})\) is the mass of adsorbent to be used.

In order to interpret the experimental data and give essential information for the use of activated carbon for the adsorption of the two dyes, we adopted three kinetic models known as Pseudo First Order (equation 2) (Lagergren, 1898), Pseudo Second Order (equation 3) (Blanchard, 1984) and Intra Particle Diffusion (equation 4) (Weber; Morris, 1963).

\[
\text{Pseudo First Order} \quad \ln \left( q_e - q_t \right) = \ln q_e - k_1 t 
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)
\]

\[
\text{Intra Particle Diffusion} \quad q_t = k_{id} t^{\frac{1}{2}} + C 
\]

where:

- \( q_t \) and \( q_e \) are the amounts of dye adsorbed (in mg. g\(^{-1}\)) at any time \( t \) and equilibrium respectively;
- \( k_1 \) is the pseudo-first order rate constant (min\(^{-1}\)),
- \( k_2 \) is the pseudo second order rate constant (g. mg\(^{-1}\). min\(^{-1}\)),
- \( k_{id} \) is the intraparticle diffusion rate constant (mg. g\(^{-1}\). min\(^{1/2}\)),
- \( C \) is the thickness of the boundary layer.

### 2.5 ADSORPTION ISOTHERM

The adsorption isotherm was carried out at ambient temperature and at the initial pH of the dye solutions for different concentrations of each individual dye ranging from 5 mg. L\(^{-1}\) to 40 mg. L\(^{-1}\). The adsorbent mass was kept at 15 mg for 30 minutes, with stirring at 250 rpm.

The equilibrium adsorption isotherm is the most crucial design parameter that explains the interaction between the adsorbate and the adsorbent. Therefore, to represent the equilibrium sorption data in the current investigation, the isotherm
models of Langmuir (Langmuir, 1916) is the most used in the fields of adsorption because it is applicable to low concentrations (equation 5). The Freundlich model (Freundlich, 1906) is used to describe heterogeneous systems, characterized by the heterogeneity factor 1/n, it describes the reversible adsorption and not limited to the formation of the monolayer. It can be described by the (equation 6) and Temkin’s model (Temkin, 1940) at suggests that the heat of adsorption of all molecules decreases linearly to the maximum binding energy. This isotherm can be modeled using the (equation 7)

Langmuir model
\[ \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \]  \hspace{1cm} (5)

Freundlich model
\[ \ln q_e = n \ln C_e + \ln k_F \]  \hspace{1cm} (6)

Temkin model
\[ q_e = \frac{R T}{b_T} \ln C_e + \frac{R T}{b_T} \ln k_T \]  \hspace{1cm} (7)

where:

- \( q_m \) (in mg. g\(^{-1}\)) and \( K_L \) (L. mg\(^{-1}\)) are Langmuir parameters representing the maximum uptake capacity per unit of PAC mass and the Langmuir constant respectively;
- \( K_F F \) ((mg. g\(^{-1}\)) (L. mg\(^{-1}\))\(^{1/n}\)) and \( n \) are the Freundlich constant associated with the capacity’s adsorption and parameter characterizes the heterogeneity of the system;
- \( K_T \) (L. g\(^{-1}\)) and \( b_T \) are the Temkin constants,
- \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and
- \( T \) is the absolute temperature (K).

3 RESULTS AND DISCUSSIONS

3.1 SURFACE AND POROSITY ANALYSIS

According to the BET classification, \( N_2 \) adsorption by PAC (Figure 1) follows type IV showing the presence of multilayer adsorption and mesopores (XUE-LEI et al., 2019). Type H3 describes the hysteresis loop. For particles with parallel-plate shaped pores, the latter is obtained (Naranjo et al., 2015)
Figure 1 – N₂ adsorption–desorption isotherms of PAC.

![Graph showing N₂ adsorption–desorption isotherms of PAC.](image)

Source: Authors

The BET transform estimates the specific surface area to be 1203.736 m².g⁻¹. This specific surface area is supposed to be exceptionally high when compared to ordinary adsorbents (Bessaha et al., 2019). The average pore size and pore volume are 45.247 Å and 0.392004 cm³.g⁻¹, respectively (Boujibar et al., 2019).

3.2 BATCH SORPTION KINETICS

The MG dye and Mc G dye removal kinetics were evaluated by using 15 mg of CAP. The effect of contact time on adsorption of both dyes and kinetic models are illustrated in Figure 2.

According to Figure 2, the adsorption process for both dyes is initially fast and during the first few minutes, before slowing down and reaching a plateau (saturation) after 20 minutes for the MG dye, where the adsorbed amount is equal to 63.27 mg. g⁻¹, and an equilibrium reached after 30 minutes for the Mc G dye with an adsorbed amount of approximately 68.91 mg. g⁻¹, which remains practically constant until the end of the experiment. We fitted the experimental results using the PFO, PSO and IPD kinetic models.
Table 2 lists the parameters from the kinetic models and the coefficients of linear regression ($R^2$).

The values of $q_{e, cal}$ for both dyes (MG and Mc G) in the pseudo first order for a concentration of 10 mg L$^{-1}$ are relatively low in comparison to those found experimentally. However, the pseudo second order's calculated adsorbed amounts, are nearly identical to the experimental one.

We may conclude that the pseudo-second order kinetic model well describes the adsorption kinetics of MG and Mc G by PAC since the correlation coefficients for the pseudo-second order model are higher and closer to unity than those for the pseudo-first order (Benjelloum et al., 2021; Batana; Rebizi; Guibadj, 2022b).
Table 2 – Kinetic sorption parameters of pseudo-first-order, pseudo-second-order and intra-particle diffusion models

<table>
<thead>
<tr>
<th>Kinetics models</th>
<th>qₑₑₓ𝑝 (mg. g⁻¹)</th>
<th>MG</th>
<th>Mc G</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO</td>
<td>k₁ (min⁻¹). 10⁻³</td>
<td>27.14</td>
<td>14.43</td>
</tr>
<tr>
<td></td>
<td>qₑₑ, cal (mg. g⁻¹)</td>
<td>4.25</td>
<td>20.05</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.264</td>
<td>0.604</td>
</tr>
<tr>
<td>PSO</td>
<td>K₂ (g. mg⁻¹. min⁻¹)</td>
<td>8.11. 10⁻²</td>
<td>9.62.10⁻³</td>
</tr>
<tr>
<td></td>
<td>qₑₑ, cal (mg. g⁻¹)</td>
<td>63.17</td>
<td>67.20</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>IPD</td>
<td>K₁₁ (mg. g⁻¹. min⁻¹/²)</td>
<td>21.04</td>
<td>3.063</td>
</tr>
<tr>
<td></td>
<td>C₁ (mg. g⁻¹)</td>
<td>21.85</td>
<td>48.085</td>
</tr>
<tr>
<td></td>
<td>R₁²</td>
<td>0.958</td>
<td>0.895</td>
</tr>
<tr>
<td></td>
<td>K₁₁₂ (mg. g⁻¹. min⁻¹/²)</td>
<td>0.44</td>
<td>1.545</td>
</tr>
<tr>
<td></td>
<td>C₂ (mg. g⁻¹)</td>
<td>60.86</td>
<td>49.982</td>
</tr>
<tr>
<td></td>
<td>R₂²</td>
<td>0.840</td>
<td>0.989</td>
</tr>
</tbody>
</table>

Source: Authors

For the IPD model, we can distinguish two lines for each dye, which prove the existence of two adsorption steps.

The first step represents the diffusion from the outer film and through the boundary layer of the outer surface of the activated carbon. This stage takes place during the first minutes of agitation, and with a high adsorption rate.

The second stage is the intra-particle diffusion which is characterized by a slowing down of the adsorbed quantity, it is thus like a stage of limitation of the adsorption rate. From the results of Table 1, we clearly notice that the kid diffusion velocities of the first stage are higher than those of the second stage for both dyes, this was confirmed by experiments, which concluded that the velocity of the second stage is slow compared to the first one (Batana; Taouti; Guibadj, 2019).

We can discern two lines for each dye in the DIP model for both dyes, demonstrating the existence of two adsorption stages.

The first stage is represented by the diffusion via the boundary layer and outer film of the activated carbon's outer surface. With a high adsorption rate, this stage occurs in the first few minutes of agitation.

The second stage, known as intra-particle diffusion, is characterized by a slowing down of the amount adsorbed; as a result, it is comparable to a stage of adsorption rate limitation (Murugesan et al., 2019; Batana; Rebizi; Guibadj, 2022b).
3.3 ADSORPTION ISOTHERM

The models of the adsorption isotherms of MG and Mc G by activated carbon are illustrated in Figure 3.

Figure 3 – (a) Adsorption isotherm of MG and Mc G on PAC (b) Langmuir model (c) Freundlich model (d) Temkin model.

The isotherm of this system reveals an L-type (commonly known as Langmuir) form for the two dyes, in conformity with the classification of Giles & al. (Batana; Bouras; Aouissi, 2022a). As a result of the nature of the sorption isotherms, there is not much competing for the sorption sites between the solvent and the adsorbate (Rajan et al., 2017). The constants and linear regression coefficients $R^2$ of the three different isotherms for the two dyes are provided in Table 3:
Table 3 – Langmuir, Freundlich and Temkin isotherm parameters of removal of MG and Mc G onto PAC

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>MG</th>
<th>Mc G</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_m$ (mg. g$^{-1}$)</td>
<td>174.825</td>
<td>248.139</td>
</tr>
<tr>
<td>$k_L$ (L. mg$^{-1}$)</td>
<td>2.79</td>
<td>0.748</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.035</td>
<td>0.118</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999</td>
<td>0.993</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.127</td>
<td>0.181</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.997</td>
<td>0.984</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_F$ (mg. g$^{-1}$)</td>
<td>132.57</td>
<td>142.52</td>
</tr>
<tr>
<td>$n$</td>
<td>7.874</td>
<td>5.524</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.979</td>
<td>0.84</td>
</tr>
<tr>
<td><strong>Temkin</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_T$ (L. mg$^{-1}$)</td>
<td>1030.52</td>
<td>40.62</td>
</tr>
<tr>
<td>$a_T$ (L. mg$^{-1}$)</td>
<td>0.128</td>
<td>68.18</td>
</tr>
<tr>
<td>$b_T$ (j. mol$^{-1}$)</td>
<td>0.975</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Source: Authors

With an $R^2$ value of 0.99 for the two dyes and maximum adsorption capacities of 174.825 mg g$^{-1}$ for MG and 248.139 mg g$^{-1}$ for Mc G, it is clear from the table above that the adsorption data and the Langmuir model exhibit a strong association. The computed value of $R_L$ for both dyes is between 0 and 1, showing that activated carbon is a good choice for adsorption (Sahoo; Prelot, 2020).

The value of $1/n$ less than 1 and between 0.1 and 0.5 for both dyes show typical adsorption that occurred on a heterogeneous surface of adsorbent, which makes this model remain credible in predicting adsorption data. This is a favorable adsorption process for the Freundlich model.

The values of $n$ that were determined in this study were greater than 1, suggesting the physical process of adsorption for each dye (Nandiyanto et al., 2020).

The $b_T$ constants for both dyes for this process were evaluated using Temkin model, and the calculated values for this constant were positive, implying that an exothermic reaction had actually occurred (Batana; Rebizi; Guibadj, 2022b).

4 CONCLUSIONS

Adsorption tests of both dyes (Methyl Green dye and Malachite Green dye) on commercial activated carbon showed that retention was rapid between 20 minutes and 30 minutes with quantities retained at equilibrium varying between 63 mg g$^{-1}$ and 68 mg g$^{-1}$. This retention follows a pseudo second-order kinetics and the intra-particle diffusion is not the only limiting step.
Equilibrium isotherms were performed at room temperature. The adsorption of MG and Mc G molecules using PAC obeyed Langmuir, Freundlich and Temkin for the first dye while the second only obeyed the Langmuir isotherm with a much higher maximum amount. The results of the present investigation suggest that powdered activated carbon can be used as an environmentally and economically affordable adsorbent for the removal of MG and Mc G from aqueous solutions.

This study showed that powdered activated carbon could prove a highly effective and widely used adsorbent for removing undesirable and toxic substances from aqueous media at both low and high concentrations.

The results obtained from this research demonstrated the effectiveness of adsorption of pollutants on activated carbon for both academia and society world, and its broad contribution to environmental protection through the treatment of colored water.

Further investigation and examinations could explore the removal of different toxic and undesirable pollutants generated by different industrial sectors, which has implications for water purification strategies in various applications.
REFERENCES


