REMOVAL OF METHYLENE BLUE IN AQUEOUS SOLUTION USING CHARCOAL PRODUCED FROM HOUSEHOLD SLUDGE.

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ABSTRACT: The contamination of bodies of water by effluents containing dyes has been an object of attention to several scholars. Several methods for treating colored effluents have been developed in the last decades. Among them, adsorption is certainly one of the most efficient, especially when performed with activated charcoal, which undergoes physical-chemical treatments to ensure a high internal porosity. Therefore, the present work proposes the use of charcoal produced from household sludge as a less expensive alternative for the removal of dyes. From a synthetic effluent, it was observed that methylene blue is adsorbed according to the pseudo-second order kinetic model and is best described by the Langmuir isotherm. Using 0.04 g of charcoal, a 99.51% removal (absence of apparent color) was obtained for solutions with concentration of 10 mg.L⁻¹ after 210 min.

KEYWORDS: methylene blue; dye removal; adsorption; household sludge-based charcoal

1. INTRODUCTION

Water quality is a function of both natural processes and anthropic action. However, the industrial sector has contributed to the alarming increase in water contamination. It is important to emphasize the role of the textile industries as polluting agents, since their effluents, besides being highly colored, have a very heterogeneous chemical composition, which affects the biochemical cycles of the aquatic biota and makes it difficult for photosynthesis to happen (KAO et al., 2001; BASTOS, 2002; KUNZ et al., 2002).

Considering the environmental risks involved in the disposal of textile effluents, several methods have been developed in order to promote their treatment. Adsorption is one of the most effective procedures in the removal of color from effluents and presents the possibility of reusing the adsorbent after a regeneration process (LAS CASAS, 2004; NIGAM et al., 1996; QIN, MA & LIU, 2009).

Thus, the present work seeks to study the feasibility of the use of coal produced from sludge from a Sewage Treatment Plant (STP) as the adsorbent to be used in the removal of methylene blue, evaluating its kinetic and equilibrium properties, as well as the sorption efficiency.

1.1. Kinetics of adsorption

Adsorption efficiency is controlled by the kinetics of the system. The main adjustment models for adsorption data in relation to time are pseudo-first order, pseudo-second order and intraparticle diffusion.

In 1898, Largergren developed a first order kinetic model applied to adsorption in solid-liquid systems (BERTOLINI, 2011), concluding that:

\[ \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \] (01)

where:
- \( q_e \) – species uptake at equilibrium (mg of adsorbate/g of adsorbent);
- \( q_t \) – species uptake at time \( t \) (mg of adsorbate/g of adsorbent);
- \( k_1 \) – pseudo-first order adsorption rate constant (1/min).
The constant \( k_3 \) can be calculated from the slope of the line \( \log(q_e - q_t) \) versus \( t \). The kinetic model of pseudo-second order can be represented as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]

where:
- \( k_2 \) – pseudo-second order adsorption rate constant \([\text{g/(mg.min)}]\).

From the graph line of \( t/q_t \) versus \( t \), the values of the constants \( k_2 \) and \( q_e \) can be calculated.

If the kinetic models above do not describe well the adsorption process, the intraparticle diffusion model can be used. As discussed by Weber and Morris (1963), if intraparticle diffusion is the velocity determinant, the adsorption removal varies with the square root of time. So:

\[
q_t = k_{\text{diff}} t^{1/2} + C
\]

where:
- \( k_{\text{diff}} \) – intraparticle diffusion coefficient \([\text{mg/(g.min}^{0.5}]\);
- \( C \) – constant related to diffusion resistance \([\text{mg/g}]\).

The value of \( k_{\text{diff}} \) can be obtained from the slope and the value of \( C \) of the intersection of the curve of the graph \( q_t \) versus \( t^{0.5} \).

1.2. Adsorption equilibrium

Adsorption equilibrium is reached when the number of molecules arriving at the surface of the adsorbent is equal to the number of molecules leaving that surface towards the fluid. The adsorbed molecules constantly exchange energy with the surface of the solid; however, they only depart from the atomic structure of the adsorbent if they absorb sufficient thermal energy so that the energy of their vibrations is greater than the binding energy of the adsorbent surface (RODRIGUES FILHO, 2012).

By means of adsorption equilibrium it is possible to know the amount of substance that can accumulate on the surface of an adsorbent. In order to express this accumulation, adsorption isotherms are commonly used, in which the amount of adsorbed substance per quantity of adsorbent as a function of the concentration of adsorbate in solution is described (LETTERMAN, 1999).

Considering a steady-state process, the mass balance allows to equate the amount of adsorbate per unit mass of adsorbent material as follows:

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

where:
- \( C_0 \) – initial adsorbate concentration \([\text{mg/L}]\);
- \( C_e \) – final adsorbate concentration or equilibrium concentration \([\text{mg/L}]\);
- \( V \) – batch volume \([\text{L}]\);
- \( m \) – adsorbent mass \([\text{g}]\).

According to Cheremisinoff and Ellerbusch (1978), adsorption isotherms are usually constructed with the purpose of evaluating the adsorptive capacity of a material when in contact with the fluid of interest. Thus, they act as a way of determining which adsorbent is the most appropriate for a desired application.

As stated by Valencia (2007), the main mathematical models in the study of adsorption isotherms in solid-liquid systems are those of Langmuir and Freundlich.

The Langmuir isotherm is based on the following assumptions: the surfaces are homogeneous and all active sites have equal affinity for the adsorbate. Mathematically, the Langmuir isotherm can be defined by the equation:

\[
q_e = \frac{q_{\text{max}}bC_e}{1 + bC_e}
\]

Or its linearized form:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}b} + \frac{1}{q_{\text{max}}}C_e
\]

where:
- \( q_e \) – adsorbed mass per units of adsorbent mass \([\text{mg of adsorbate/g of adsorbent}]\);
- \( C_e \) – equilibrium concentration of adsorbate in solution \([\text{mg/L}]\);
- \( q_{\text{max}} \) – constant that indicates the adsorption capacity in the monolayer \([\text{mg/g}]\);
- \( b \) – equilibrium adsorption constant.

The Freundlich isotherm, however, is empirical and generally can accurately describe the
adsorption test data in aqueous systems. Furthermore, in this model the equilibrium is described on heterogeneous surfaces and it is not assumed that adsorption occurs in monolayer (DINESH; PITTMAN, 2006). Its mathematical form is given by:

\[ q_e = k_f C_e^{1/n} \]  

(07)

Linearising:

\[ \log(q_e) = \log(k_f) + \frac{1}{n} \log(C_e) \]  

(08)

Where \( k_f \) and \( n \) are coefficients to be determined empirically. \( k_f \) refers to the ability of the molecules of the fluid to be adsorbed, while \( n \) depends on the adsorption characteristics. By setting the values of \( k_f \) and \( C_e \), the value of \( 1/n \) determines whether the binding of the adsorption will be weak (when \( 1/n \) is a high value) or strong (\( 1/n \) low).

2. EXPERIMENTAL

2.1. Materials

For the adsorbent production, dry sludge was initially collected at the Sewage Treatment Station of the Federal University of Rio Grande do Norte; then the sample went through grinding and sifting, resulting in a fine powder. Methylene blue (CAQ) was supplied by the Laboratory of Environmental Engineering and Quality Control.

2.2. Synthesis and activation of coal

According to the methodology adopted by Bezerra (2017), the sludge impregnation in KOH (85%) was carried out at a base/sludge mass ratio of 50%. After mixing, the material received a heat treatment in a tubular reactor for 45 min at 550 °C (at a rate of increase of 10 °C.min\(^{-1}\)), with nitrogen flow of 100 mL.min\(^{-1}\).

Thereafter, HCl was mixed with the charcoal at 70 °C and constant stirring for two hours in order to promote the separation of unwanted ashes and minerals. The charcoal was vacuum filtered, washed with distilled water at 90 °C until obtaining an approximately neutral pH, and finally kept in an oven at 105 °C for 24 hours.

2.3. Determination of the calibration curve

Starting from solutions with concentrations ranging from 1 to 5 ppm, the absorbances of each solution were obtained through a UV/VIS spectrophotometer at a wavelength of 663 nm. The plot of the absorbance (y-axis) by concentration (x-axis) yielded to the equation \( y = 0.11634x \), with \( R^2 = 0.9944 \).

2.4. Kinetic and equilibrium tests

The experiments were carried out at the TECNAL TE-420 orbital shaker at 27 °C and rotation of 150 rpm.

To evaluate adsorption kinetics, 0.04 g of charcoal and 50 mL of 10 mg/L methylene blue solution were added in 125 mL erlenmeyers. After stirring, two erlenmeyers were removed at each specified time: 2, 5, 10, 30, 60, 90, 120, 150, 180, 210, and 240 min. The samples were then vacuum filtered and analyzed in a UV/VIS spectrophotometer, allowing the calculation of adsorption capacity. With these results, three kinetic models (pseudo-first order, pseudo-second order and intraparticle diffusion) were tested to verify the model that best fits the experimental data.

In the adsorption isotherms, concentrations of 10, 12.5, 15, 17.5, and 20 mg/L. In triplicate, the erlenmeyers were shaken for 210 min, which was the equilibrium time found from the kinetic experiments. With the spectrophotometric data collected, it was possible to determine which adsorption isotherm model best represents the dye adsorption process, whether Langmuir or Freundlich.

3. RESULTS AND DISCUSSION

3.1. Kinetics of adsorption

The rate and adsorption mechanism can be elucidated from kinetic experiments. Pseudo-first order (P1), pseudo-second order (P2) and intraparticle diffusion (ID) models are used in order to interpret them. Starting from solutions containing 10 mg of dye / L, the results obtained for the adsorbed amount and percent removal of methylene blue can be visualized in Table 1.
Table 1. Concentration data, amount of adsorbed dye and adsorption process efficiency over time for the methylene blue dye

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Conc. (mg/L)</th>
<th>Adsorbed mass (mg dye/mg adsorbent)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.854</td>
<td>0.01029</td>
<td>62.91</td>
</tr>
<tr>
<td>5</td>
<td>1.769</td>
<td>0.01158</td>
<td>64.63</td>
</tr>
<tr>
<td>10</td>
<td>1.401</td>
<td>0.01189</td>
<td>71.97</td>
</tr>
<tr>
<td>30</td>
<td>0.734</td>
<td>0.01200</td>
<td>85.31</td>
</tr>
<tr>
<td>60</td>
<td>0.490</td>
<td>0.01217</td>
<td>90.21</td>
</tr>
<tr>
<td>90</td>
<td>0.410</td>
<td>0.01199</td>
<td>91.80</td>
</tr>
<tr>
<td>120</td>
<td>0.398</td>
<td>0.01200</td>
<td>92.04</td>
</tr>
<tr>
<td>150</td>
<td>0.263</td>
<td>0.01217</td>
<td>94.74</td>
</tr>
<tr>
<td>180</td>
<td>0.098</td>
<td>0.01238</td>
<td>98.04</td>
</tr>
<tr>
<td>210</td>
<td>0.061</td>
<td>0.01242</td>
<td>98.78</td>
</tr>
<tr>
<td>240</td>
<td>0.049</td>
<td>0.01244</td>
<td>99.02</td>
</tr>
</tbody>
</table>

The results above show that the coal produced from sludge from the STP/UFRN removes the dye with an efficiency of 98.04%. The balance is reached in approximately 210 min, with no significant change in concentration after that. In the following graph, it is possible to see how the removal occurs.

The model P1 did not present much linearity, with $R^2 = 0.8990$, making it incompatible with the process. In the linearity analysis based on the model P2, it was observed that the results were more satisfactory, as shown in Figure 3, plotted from Equation (02).

![Figure 2](image1.png)

**Figure 2.** Adjustment to the kinetic model P1 for the methylene blue dye

![Figure 3](image2.png)

**Figure 3.** Adjustment to the kinetic model P2 for the methylene blue dye

From the graph, the adjustment for the P2 model is accurate with the methylene blue’s sorption kinetics description, so a $R^2$ constant equal to 0.9997 is obtained. By also testing the ID...
model, the graph shown in Figure 4 is obtained with the Equation (03).

![Graph showing the kinetic model ID for the methylene blue dye](image)

**Figure 4.** Adjustment to the kinetic model ID for the methylene blue dye

The graphs for the ID model did not show good linearity results for the methylene blue, as shown by $R^2 = 0.9059$. A summary can be seen in Table 3, which shows kinetic parameters, theoretical $q$ values, and the correlation coefficients of the dye for each model.

**Table 3.** Kinetic parameters of methylene blue sorption

<table>
<thead>
<tr>
<th>Methylene blue</th>
<th>P1</th>
<th>P2</th>
<th>ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{e1}$</td>
<td>0.0020</td>
<td>0.0124</td>
<td>$k_{d1}*10^4$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.0175</td>
<td>41.67</td>
<td>$C*10^{-4}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.8990</td>
<td>0.9997</td>
<td>$R^2$</td>
</tr>
</tbody>
</table>

Regarding the ID model, it is noted that the value of $C$ is nonzero in the case under study and, therefore, the straight line of the graph $q_t$ versus $t^{0.5}$ does not pass through the origin. Thus, it can be concluded that the ID mechanism is not the speed determining step, so there are certainly other mechanisms acting simultaneously in the adsorption process control (WEBER; MORRIS, 1963).

The results show that, for methylene blue, the model that best describes its adsorption kinetics is P2, suggesting that the speed determining step may be the chemisorption involving attraction forces through electron sharing between adsorbent and adsorbate (HO, McKAY, 1998). The model was able to accurately describe the $q_e$ value: the experimental value was 0.01238 mg dye/mg adsorbent; or theoretical, 0.01243 mg dye/mg adsorbent.

### 3.2. Adsorption isotherms

Adsorption equilibrium experiments were performed with the objective of determining the coal’s maximum adsorption capacity. The adsorption isotherm is an important tool in understanding the adsorption systems. The most common models in solid-liquid systems are those of Langmuir and Freundlich. Table 4 shows the adsorption isotherms data for methylene blue.

**Table 4.** Data for the construction of the adsorption isotherm of methylene blue

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$C_e$ (mg/L)</th>
<th>$q_e$ (mg dye/mg adsorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.049</td>
<td>0.0124</td>
</tr>
<tr>
<td>12.5</td>
<td>0.153</td>
<td>0.0156</td>
</tr>
<tr>
<td>15</td>
<td>0.998</td>
<td>0.0187</td>
</tr>
<tr>
<td>17.5</td>
<td>3.164</td>
<td>0.0218</td>
</tr>
<tr>
<td>20</td>
<td>4.994</td>
<td>0.0249</td>
</tr>
</tbody>
</table>

Plotting the values of $q_e$ as a function of $C_e$ gives the experimental isotherm of the dye, as shown in Figure 5.

![Isotherm of adsorption of methylene blue](image)

**Figure 5.** Isotherm of adsorption of methylene blue

The curve shows that the adsorption isotherm obtained is favorably concave, which indicates, in consonance with McCabe et al. (2000), that the adsorption process will occur even at low concentrations of adsorbate.

Linearizing the data in Table 4, it is possible to test the Langmuir and Freundlich
models in order to verify which one best represents the dye removal process under analysis.

To evaluate the suitability of the experimental data to the Langmuir model, following Equation (06), a curve of the ratio between the equilibrium concentration and the adsorbed mass versus the equilibrium concentration is plotted, as shown in the following graph.

Figure 6. Linear Langmuir isotherm for the methylene blue dye

Regarding the Freundlich model, according to Equation (08), the logarithm of the adsorbed mass versus the concentration at equilibrium is plotted, as shown in Figure 7.

Figure 7. Linear Freundlich isotherm for methylene blue dye

The equilibrium parameters obtained for the two models evaluated, calculated from the linearized equations, are shown in Table 5, from which it is possible to conclude that the two models provided a good fit, as they express the linearized equations’ correlation coefficient values. In the case under analysis, the best fit occurred with the Langmuir model. This conclusion is reinforced by Figure 8, in which the isotherm formed by the experimental data is compared with the theoretical isotherm constructed from the equilibrium parameters calculated in Table 5. In Figure 8, the Langmuir isotherm is represented by a blue dotted line, the Freundlich one by an orange solid line, and the experimental data by gray square markers.

Table 5. Balance parameters for the removal of methylene blue by Langmuir and Freundlich models

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>5.540</td>
<td>0.0193</td>
</tr>
<tr>
<td>qmax</td>
<td>0.0249</td>
<td>7.265</td>
</tr>
<tr>
<td>R²</td>
<td>0.9917</td>
<td>0.9803</td>
</tr>
</tbody>
</table>

Figure 8. Comparison between the experimental data and the theoretical isotherms for methylene blue dye

A fundamental property of the Langmuir isotherm is the separation factor, a dimensionless parameter given by the equation:

\[
R_L = \frac{1}{1 + bC_0}
\]

The values of \(R_L\) indicate whether the isotherm is reversible (\(R_L = 0\)), favorable (0 < \(R_L < 1\)), linear (\(R_L = 1\)) or unfavorable (\(R_L > 1\)), according to Derakhshan et al. (2013). Table 6 shows the \(R_L\) values for the methylene blue.

Based on the tabulated values, it can be confirmed that the methylene blue dye adsorption on charcoal produced from STP sludge is favorable, since all calculated values were within the range between 0 and 1.
Table 6. Separation factor of Langmuir isotherm for methylene blue dyes

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.01773</td>
</tr>
<tr>
<td>12.5</td>
<td>0.01423</td>
</tr>
<tr>
<td>15</td>
<td>0.01189</td>
</tr>
<tr>
<td>17.5</td>
<td>0.01021</td>
</tr>
<tr>
<td>20</td>
<td>0.00894</td>
</tr>
</tbody>
</table>

Also, the adsorption capacity of methylene blue by coal was 0.02488 mg dye/mg adsorbent, which converted to approximately 24.88 mg/g. The results obtained in the literature show that the value of $q_{max}$ was lower than the one for the removal with sawdust powder (VALCARENGHI et al., 2014) or sugarcane bagasse (JORGE; TAVARES; SANTOS, 2015), about 70 mg/g for both adsorbents. Regarding the Freundlich isotherm, an important parameter to evaluate is the coefficient $n$, equivalent, in this case, to 7.265. As this value is between 1 and 10, there is one more indication that the adsorption process is favorable in the system (NEVES, 2015).

3.3. Efficiency of the adsorptive process

It has been seen that at the concentration of 10 mg/L, it is possible to remove the dye’s visible color. This is achieved with 0.04 g of charcoal. After the equilibrium time, the dye removal efficiency is approximately 99%. Table 7 shows the removal efficiency values by varying the initial concentration of dyes.

Table 7. Initial and final concentrations and adsorptive efficiency for the methylene blue dyes in the presence of coal made with STP sludge

<table>
<thead>
<tr>
<th>Methylene blue</th>
<th>$C_0$ (ppm)</th>
<th>$C_e$ (ppm)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.049</td>
<td>99.51</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>0.153</td>
<td>98.78</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.998</td>
<td>93.35</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>3.165</td>
<td>81.92</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4.994</td>
<td>75.03</td>
<td></td>
</tr>
</tbody>
</table>

It can be noticed that increasing the initial methylene blue concentration from 10 mg/L to 20 mg/L resulted in an efficiency drop from 99.51% to 75.03%.

Thus, it is evident that, by increasing the concentration of the dye in solution, the number of available sites on the surface of the adsorbent decreases. This means that, with the reduction of the dye concentration in the medium, the probability of reaction between the adsorbate molecules and the active sites of the adsorbent increases, favoring the rate of adsorption. Therefore, an alternative to increase the percentage of removal of methylene blue dye in coal produced from STP sludge is to promote dilution of the effluent before adsorption is performed.

4. CONCLUSION

Based on the results, the authors conclude that the charcoal produced from STP sludge is an alternative to be used in the removal of methylene blue in aqueous solutions. At a concentration of 10 mg/L, elimination of visible color was obtained by using 0.04 g of charcoal.

Analyzing the dye removal as a function of time, it was found that the pseudo-second order model describes the kinetics of methylene blue sorption. The equilibrium study showed that the Langmuir model provided a better fit to the experimental data.

As suggestions for future work, the authors cite the need to: investigate the effect of pH and temperature on dye removal; evaluate other kinetic and equilibrium models; test the adsorption capacity of coal against other dyes; evaluate the efficiency of the coal in the removal of more than one parameter at the same time, for example, color and heavy metals; and use industrial effluents.

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