Comparison Studies for the removal of Methylene Blue from aqueous solution using Tea and Coffee powder

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Abstract: The adsorption studies were carried out in batch scale to evaluate the different adsorption parameters vis-à-vis the efficiencies of dye removal from aqueous solutions. The contact time data obtained from the adsorption of methylene blue on the Tea powder and Coffee powder showed that a contact time of 16 min and 22 respectively and there was no significant change in concentration of the dye with further increase in contact time. The plot of pH versus percentage adsorption shows the significant adsorption takes place with Tea powder and Coffee powder for dye at 6 only. The equilibrium uptake was increased and percentage adsorption was decreased with increasing the initial dye concentration for both the adsorbents. The percentage adsorption of dye increases with increasing the adsorbent dosage of Tea powder and Coffee powder. The percentage adsorption of dye decreases with increasing Tea powder and Coffee powder particle size. The percentage adsorption and dye uptake of dye increases with increasing the temperature of solution with both Tea powder and Coffee powder. The Langmuir isotherm for both the adsorbents proved to be the best adjustment of the experimental data than the Freundlich Isotherm.

Keywords: Adsorption, Langmuir Isotherm, Freundlich Isotherm, Methylene Blue Dye.

1. Introduction

Dyes are frequently used in different industries, such as textile, rubber, paper, plastic, leather, food, and cosmetics, and may generate large amount of aqueous, colored effluents. It is estimated that there are currently more than 10,000 commercially available dyes with an annual production of over 0.7 million tons worldwide, of which 10 to 15% is lost in industrial effluents during manufacture and processing operations\(^1\). Releasing colored effluent into natural bodies of water has become a major source of water pollution, causing many significant problems. The presence of very small amounts of dye in water (< 1 ppm for some dyes) causes aesthetic deterioration and diminishes the solubility of dissolved oxygen, water transparency, and sunlight permeability, affecting aquatic life and the food chain\(^2\). In addition, some dyes and/or their degradation products (e.g., aromatic amines) may have toxic, carcinogenic, mutagenic, or teratogenic effects on the health of humans and aquatic organisms.
Although varieties of adsorbents are available commercially, they are very costly. Therefore, the use of new and inexpensive adsorbents for Zn (II) removal of metals from wastewater seems necessary. In recent years, several low-cost materials such as industrial by-products and agricultural wastes have been used as plant biomass precursor for the Zn (II) removal as well as other metal ions from water systems.

Methylene blue (MB) is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}N_3SCl$. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water. MB is an important basic dye widely used for coloring paper, temporary hair colorant, coating for paper stock, dyeing, printing cotton and tannin, dyeing leather, used as an antiseptic and for other medicinal purposes. Textile effluent characteristics vary, so that the treatment for color removal include many different physical, chemical, and biological treatment methods, such as coagulation-flocculation, adsorption on activated carbon ozonation, membrane processes, electrochemical treatment, and aerobic or anaerobic biodegradation. The advantages and disadvantages of each technique have been extensively reviewed.

Adsorption is an efficient and economical method for removing dyes from industrial effluents. In this process, a substance (soluble dye) from the liquid phase (wastewater) is transferred to the surface of a solid, highly porous material (adsorbent), to which it binds physically or chemically. The adsorption technique is preferable to other wastewater treatment techniques in terms of efficiency, low cost, simplicity, ease of operation, and inactivity towards toxic substance. Moreover, the specific advantage of method is that the adsorbent can be chosen from a large variety of material. These adsorbent, used in batch or dynamic condition, can be naturally occurring material (wood, peat, coal, chitin and chitosan, biomass, clays, etc.), as well as industrial/agricultural wastes or byproducts (fly ash, red mud, blast furnace slag, dye hydroxide sludge, sawdust, bark, lignin, sunflower stalks, maize cob, rice husk, hazelnut shell, olive stones, seashell, etc.).

The aim of this work is to evaluate the efficiency of using (Tea powder and coffee powder) as adsorbent for removal of methylene blue (MB) from an aqueous environment. The obtained result gives some insight with respect to utilization of (Tea powder and coffee powder) as an eco-friendly adsorbent in textile industry wastewater treatment. Thus, these results may be applied for predicting the adsorption mechanism, for characterization and optimization of the process, and equipment and process design.

2. Materials and Methods

2.1. Preparation of adsorbent

The used Tea and Coffee powder in the present study were collected from the kitchens. The collected powders were washed with deionised water several times to remove dirt and color. The washing process was continued till the wash water contains no dirt. The washed powders were then completely dried in oven for 20 hr. The dried powders were then ground into small size of powder using blender. In the present study the powdered materials in the range of 0.3-1.5 mm particle size were directly used as adsorbent without any pretreatment.

2.2. Chemical

Stock solution of methylene blue of 5, 10, 15, 20, 25, 30 mg/L was prepared by dissolving 5, 10, 15, 20, 25, 30 mg of methylene blue in 1000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared dye solutions varied between 5 and 30 mg/L.

2.3 Apparatus

An UV Spectrophotometer was used for the determination of methylene blue concentration. Adsorbate pH and adsorbent weight were measured using a Systronics pH meter and a Shimatzu electronic balance.

2.4 Batch Adsorption Experiments

Biosorption experiments were performed at room temperature (30 ± 1°C) in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 50 mL of different dye concentrations. After 1 hr of contact (according to the preliminary sorption dynamics tests), with 0.05 g Tea and coffee Powder, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The dye content in the supernatant was determined using UV Spectrophotometer after filtering the adsorbent with 0.45 μm filter paper. The amount of dye adsorbed by Tea
and coffee Powder was calculated from the differences between dye quantities added to the adsorbent and dye content of the supernatant using the following equation:

\[ q = \frac{C_0 - C_f}{M} \frac{V}{ } \]  

(1)

Where \( q \) is the dye uptake (mg/g); \( C_0 \) and \( C_f \) the initial and final dye concentrations in the solution (mg/L), respectively; \( V \) the solution volume (mL); \( M \) is the mass of adsorbent (g). The pH of the solution was adjusted by using 0.1N HCl and 0.1N NaOH.

The Langmuir\textsuperscript{12} sorption model was chosen for the estimation of maximum dye sorption by the adsorbent. The Langmuir isotherm can be expressed as

\[ q = \frac{Q_{\text{max}} b C_{eq} }{1 + b C_{eq} } \]  

(2)

Where \( Q_{\text{max}} \) indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant \( b \) (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

\[ \frac{1}{q} = \frac{1}{Q_{\text{max}}} + \frac{1}{b Q_{\text{max}} C_{eq}} \]  

(3)

The Freundlich\textsuperscript{13} model is represented by the equation:

\[ q = K C_{eq}^{\frac{1}{\gamma}} \]  

(4)

Where \( K \) (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and \( 1/\gamma \) is the Freundlich exponent related to adsorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows:

\[ \ln q = \ln K + \frac{1}{\gamma} \ln C_{eq} \]  

(5)

3. Results and Discussion

3.1. Effect of contact time

Time course profiles for the adsorption of methylene blue from 5 mg/L concentrated solution are shown in Figure-3.1. The data obtained from the adsorption of methylene blue on the Tea Powder and Coffee Powder showed that a contact time of 16 min (95.9%, 4.79 mg/g) and 22 min (85.8%, 4.294 mg/g) respectively was required to achieve an optimum adsorption and there was no significant change in concentration of the methylene blue with further increase in contact time. Therefore, the uptake and unadsorbed methylene blue concentrations at the end of 16 min with tea powder and 22 min with coffee powder were given as the equilibrium values, \( q_{eq} \) (mg/g) and \( C_{eq} \) (mg/L). For further studies of adsorption with other variable parameters, with these two adsorbents, the optimum time of 16 min for tea powder and 22 min for coffee powder has been chosen for contact period.
3.2. Effect of pH

It is well known that the pH of the medium affects the solubility of dye and the concentration of the counter ions on the functional groups of the adsorbents cell walls, so pH is an important parameter on adsorption of methylene blue from aqueous solutions.

As shown in Figure- 3.2 the % Adsorption of dye increased with the increase in pH from 2.0 to 6.2 and decreased from 6 to 10 for both the tea and coffee powders. Similar results were also reported in literature for different adsorbent systems. As a result, the optimum pH for methylene blue adsorption was found as 6 for both the adsorbents and the other adsorption experiments were performed at this pH value.

![Graph of pH vs % Adsorption](image-url)
3.3. Effect of Initial dye concentration

Figures- 3.3 and 3.4 show the effect of methylene blue concentration on the adsorption of methylene blue by Tea and Coffee Powder. The data shows that the methylene blue uptake increases and the percentage adsorption of methylene blue decreases with increase in dye ion concentration. This increase (4.79 – 17.68 mg/g with tea powder and 4.29 to 15.93 mg/g with coffee powder) for 5 mg/L solution is a result of increase in the driving force, i.e. concentration gradient. However, the percentage adsorptions of methylene blue on Tea and Coffee Powder were decreased from 95.9 to 58.96% with tea powder and from 85.88 to 53.12%. Though an increase in dye uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more dye available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of methylene blue displays an opposite trend. At lower concentrations, all methylene blue present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher methylene blue concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high methylene blue concentrations.

![Figure 3.3](image1.png)

Figure 3.3. Effect of Initial Concentration ($C_i$) on % Adsorption and Dye Uptake of methylene blue by using Tea Powder with 0.05g/50ml adsorbent concentration.

![Figure 3.4](image2.png)

Figure 3.4. Effect of Initial Concentration ($C_i$) on % Adsorption and Dye Uptake of methylene blue by using Coffee Powder with 0.05g/50ml adsorbent concentration.
3.4. Effect of adsorbent dosage

The effect of adsorbent concentration on the dye uptake at equilibrium conditions was observed that the amount of dye adsorbed varied with varying adsorbent concentration. The amount of dye adsorbed increases with an increase in adsorbent concentration from 0.05 to 0.3g. The percentage of dye removed was increased from 95.9 to 97.76 % with tea powder and from 85.88 to 97.15 % with coffee powder for an increase in adsorbent concentration from 0.05 to 0.3 g at initial concentration of 5 mg/L. The increase in the adsorption of the amount of solute is obvious due to increasing adsorbent surface area. Similar trend was also observed for dye uptake using Tea and coffee powder as adsorbent.

3.5. Effect of adsorbent particle size

The effect of different adsorbent particle sizes on percentage removal of dye is investigated and showed in Figure-3.5. It reveals that the adsorption of dye on tea powder decrease from 95.9 to 85.7% and from 85.88 to 67.15 % on coffee powder with the increased particle size from 0.3 to 1.5 mm at an initial concentration of 5 mg/L. The smallest size obtained was 0.3 mm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

![Figure3.5. Effect of Adsorbent size on % Adsorption of methylene blue by using Tea and Coffee Powder with 0.05g/50ml adsorbent concentration.](image)

3.6. Effect of temperature:

As we increase the temperature from 30 to 65°C by making all the parameters constant using 5 mg/l dye solution the dye uptake gradually increases.

3.7. Adsorption Isotherms

3.7.1. Langmuir model

The linear plot of specific sorption ($C_e/q_e$) against the equilibrium concentration ($C_e$) shows that the adsorption obeys the Langmuir model with the experimental data for the sorption of methylene blue onto Tea powder and Coffee powder at various temperatures as shown in Figure 3.6 and 3.7. Values of the Langmuir constants, the saturated monolayer sorption capacity, $Q_{max}$, and the sorption equilibrium constant, $K_r$, are presented in Table-3.1 for the sorption of methylene blue onto Tea powder and Coffee powder at 30, 35, 40, 45, 50, 55, 60 and 65°C. The values of the coefficient of determinations, $r^2$, obtained from Langmuir model indicates that there is strong positive evidence that the sorption of methylene blue onto Tea powder and Coffee powder follows the
Langmuir isotherm. The maximum dye uptake $Q_{\text{max}}$ was calculated as 19.13 mg/g with tea powder and 15.92 with coffee powder.

![Langmuir Equation with Tea powder](image1)

**Figure 3.6.** Langmuir Isotherm equation for adsorption of methylene blue by using Tea Powder.

![Langmuir Equation with Coffee powder](image2)

**Figure 3.7.** Langmuir Isotherm equation for adsorption of methylene blue by using Coffee Powder.

### 3.7.2. Freundlich model

The logarithmic plot of the Freundlich expression for the amount of dye adsorbed per unit mass of the adsorbent ($q_e$) and the concentration of dye at equilibrium ($C_e$). The values of $K_F$ and $n$ were calculated from the slope and intercept of the plot. Table 3.1 shows the Freundlich constant and linear correlation coefficient.
Table 3.1. The values of parameters and correlation coefficients for Langmuir, Freundlich isotherm model for methylene blue adsorption with Tea and Coffee Powder.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$, mg/g</td>
<td>$b_L/mg$</td>
</tr>
<tr>
<td>Tea Powder</td>
<td>19.13</td>
<td>0.0813</td>
</tr>
<tr>
<td>Coffee Powder</td>
<td>15.92</td>
<td>0.421</td>
</tr>
</tbody>
</table>

4. Conclusion

The adsorption performances are strongly affected by parameters such as Contact time, pH, initial dye concentration, adsorbent dosage, adsorbent particle size and temperature. The contact time data obtained from the adsorption of methylene blue on the Tea powder and Coffee powder showed that a contact time of 16 min and 22 respectively and there was no significant change in concentration of the dye with further increase in contact time. The plot of pH versus percentage adsorption shows the significant adsorption takes place with Tea powder and Coffee powder for dye at 6 only. The equilibrium uptake was increased and percentage adsorption was decreased with increasing the initial dye concentration for both the adsorbents. The percentage adsorption of dye increases with increasing the adsorbent dosage of Tea powder and Coffee powder. The percentage adsorption of dye decreases with increasing Tea powder and Coffee powder particle size. The percentage adsorption and dye uptake of dye increases with increasing the temperature of solution with both Tea powder and Coffee powder. The Langmuir isotherm for both the adsorbents proved to be the best adjustment of the experimental data when compared to the Freundlich Isotherm.

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References


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