STUDY OF ELIMINATION OF METHYL ORANGE FROM AQUEOUS SOLUTIONS BY NATURAL AND COMMERCIAL ADSORBENTS

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ABSTRACT

The aim of our study is to explore the feasibility of natural and synthetic adsorbents to adsorb methyl orange dye. The effect of contact time, adsorbent dosage, initial pH and initial dye concentration were investigated for these adsorbents. Adsorption isotherms were interpreted from various isotherm models like Langmuir and Freundlich.

The adsorption kinetics were studied using first and second–order kinetic models. The rate of dye removal follows pseudo-second-order kinetic model, with correlation coefficients when experimental data were fitted in the model.

The obtained results showed that the silicagel and peanut shells did in fact improve the adsorption capacity of methyl orange.

Keywords: Adsorption–Methyl orange –Isotherm–Kinetic

1. INTRODUCTION

Progress in industrialization in particular textile industries has led to discharge of unprecedented amount of wastewater containing synthetic dyes, which pollutes the rivers and consequently causes harm to human and other living organisms (Venoth M et al). A majority of the used dyes are azo reactive dyes which are bright in color due to the presence of one or several azo (─N═N─) groups associated with substituted aromatic structures (Leechart P et al,2009). These dyes are designed to be chemically and photolytically stable. They exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life (Bahatngar A et al, 2005).

Conventionally, chemical coagulation/flocculation, ozonation, adsorption, oxidation, electrochemical treatment, filtration and floatation, all of them are used for the removal of dyestuffs. Although they can remove dyes partially, their initial investment and operational costs are so high that they can be widely used in dyeing and finishing industries, especially in developing countries (Chung KT et al, 2005). Among these processes, adsorption has been found to be superior than other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity of toxic substances. In this work the adsorption process took place on peanut shells. These natural materials are available in large quantities and they can be used as inexpensive sorbents. Due to their low-cost, after these materials have been used .The abundance and availability of agricultural byproducts makes them good sources of raw material. The other adsorbent was used is Silica gel which is prepared by the coagulation of colloidal silicic acid (Irina ). Silicic acid, Si(OH)₄, has a tendency to polymerize and form a network of siloxane (Si-O-Si). At the same time, some of the Si-O-H groups remain free and become functional groups. Silica gel is used in many industries as adsorbent desiccant and purifying agent.
(Gupta VK et al., 2009; Backaus W K et al., 2001). After the drying procedure, silica is easily regenerated at 150 °C. In this study, new adsorbent like silicagel and eanut shells are used for the removal of methyl orange from aqueous solution. The effect of different parameters such as temperature, contact time, adsorbent dose and initial dye concentration were investigated. The kinetic and equilibrium data were collected from batch adsorption studies that were carried out in order to study the adsorption process. Two different adsorbents were used, natural and commercial, for the removal of methyl orange dye from aqueous solutions. The effect of different parameters such as, contact time, adsorbent dose and initial dye concentration were investigated.

2. MATERIALS AND METHODS

2.1 Sorbents

a. Silicagel
Commercial porous silica gel was supplied by PROLABO as spherical particles with diameters ranging from 63 to 200 µm, specific area of 500 m²/g and a porous volume of 75 cm³/g. Due to the presence of some trace impurities, mainly carbon and chlorine, silica gel was washed with hydrochloric acid and rinsed with distilled water. The product was dried and stored in a desiccator, ready for further use.

b. Peanut shells
The used peanut shells are agricultural by-products, which were well washed and dried in an oven brand BINDER at a temperature of 105 °C for 48 hours. Then they were ground by a mortar to obtain fine particles heterogeneous. These particles were passed through a sieved electric (using RETSCH siever) in order to obtain fine particles of homogeneous sizes, characterized by a diameter between (0.315 mm ≤ d < 0.355 mm). They were kept in a desiccator until use.

2.2 Adsorbate
Methyl Orange, 4-dimethylaminoazobenzene-4'- sulfonic acid (MO), is a bright orange crystalline powder with a molecular weight of 327.34 and melting point around 300°C. It was purchased from LABOSI and used without further purification. The molecular structure of MO a water soluble dye is shown in Figure 1. MO is dark red in aqueous solution below pH 3 and the color brightens to orange as pH increases. A stock solution of MO (500 mg/L) was prepared by dissolving 0.3 g of the dye in 1 L of distilled water and filtered via Whatman filter paper. The prepared stock solution was then wrapped with aluminum foil and stored in a dark to prevent exposure to direct light.

![Molecular structure of Methyl Orange](image)

**Figure 1.** Molecular structure of Methyl Orange

2.3 Methods
The elimination of methyl orange was carried out batchwise at ambient temperature by means of adsorption onto silica gel and peanut shells, introducing a fixed mass of solid support into a known volume of colored solution, under set operating conditions (shaking time, concentration, pH and agitation speed). For the kinetic and the
adsorption isotherm studies, the contact time between the solid support and the solution and the solution concentration were varied, respectively.

A mother solution of a methyl orange concentration of 0.3 g/l was prepared by dissolving the coloring agent in distilled water (the pH of solution is equal 6). The other solutions were prepared from the mother one by dilution.

The solid support did not undergo any pretreatment; they were just kept in a dissicator, ready for use. The pH of the obtained solution was adjusted by nitric acid (1.5 N) and sodium hydroxide (1.5 N), using a JENWAY 3510 pH meter. All the glassware was rinsed and washed using nitric acid and distilled water. A mass of 30mg (± 0.2mg) of solid support and 30 ml of colored solution were mixed in a 50 ml erlen Meyer, and agitated for a contact time varying between 5 and 180 min. The solid-liquid separation was carried out by filtration by means of filter paper. The dosage of the filtered solution was performed by UV-vis Spectroscopy using a Shimadzu UV-160A spectrophotometer.

The adsorption capacity can be calculated as follows

\[ q = \frac{(C_0 - C_f)}{r} V \]  

where \( q \) is the adsorption capacity (mg de coloring agent/g adsorbent), \( C_0 \) and \( C_f \) are the initial and final adsorbate concentrations, respectively (mg/l), \( m \) the mass of adsorbent (g), \( V \) the volume of the solution (l) and \( r \) the solid to liquid ratio (g/l).

3. RESULTS AND DISCUSSIONS

3.1 Effect of contact time

The effect of contact time on the percentage removal of methyl orange dye was investigated at initial dye concentration of 10mg L⁻¹, as shown in Figure 2. The percentage removal of dye by Silicagel and peanut shell support was rapid in the beginning but it gradually decreased with time until equilibrium was reached.

![Figure 2. Effect of contact time in the MO retention onto silica gel and peanut shell.](image)

(Experimental Conditions: \( C_0=10\)mg/l, \( v=600\) rpm, \( T=22^\circ\)C, \( r=10\)g/l, \( pH=6\))
3.2 Effect of initial concentration

The effect of initial concentration of dye on the removal of methyl orange (in terms of percentage removal) on adsorbent was studied as shown in Figure 3. The initial concentration of the methyl orange has an important effect on the retention process where values of 5, 10, 20, 40, 60, 80 and 100mg/l were considered. The results are shown in the following figure. From the above figure it can be seen that the initial concentration has an important effect on the MO retention where an increase leads to an increase of the pollutant adsorption up to saturation where all the sites are occupied.

![Figure 3](image1.png)

**Figure 3.** Effect of initial concentration of MO retention onto silica gel (v=600 rpm, T=22°C, r=10g/l, pH≈6)

![Figure 4](image2.png)

**Figure 4.** Effect of initial concentration of MO retention onto peanut shell (v=600 rpm, T=22°C, r=10g/l, pH≈6)
Table 1: Percentage of elimination of MO on Silica gel

<table>
<thead>
<tr>
<th>Contact time</th>
<th>C₀=20mg/l</th>
<th>C₀=40mg/l</th>
<th>C₀=60mg/l</th>
<th>C₀=80mg/l</th>
<th>C₀=100mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>5min</td>
<td>4.4</td>
<td>78</td>
<td>85.83</td>
<td>87.4</td>
<td>90.22</td>
</tr>
<tr>
<td>30min</td>
<td>19.25</td>
<td>80.77</td>
<td>86.38</td>
<td>87.77</td>
<td>90.93</td>
</tr>
<tr>
<td>90min</td>
<td>23.3</td>
<td>82.5</td>
<td>88.8</td>
<td>88.93</td>
<td>90.96</td>
</tr>
<tr>
<td>180min</td>
<td>24.4</td>
<td>84.35</td>
<td>87.53</td>
<td>89.02</td>
<td>91.06</td>
</tr>
</tbody>
</table>

Table 2: Percentage of elimination of MO on peanut shell

<table>
<thead>
<tr>
<th>Contact time</th>
<th>C₀=20mg/l</th>
<th>C₀=40mg/l</th>
<th>C₀=60mg/l</th>
<th>C₀=80mg/l</th>
<th>C₀=100mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>5min</td>
<td>4.85</td>
<td>76.22</td>
<td>68.46</td>
<td>75.66</td>
<td>80.33</td>
</tr>
<tr>
<td>30min</td>
<td>6.05</td>
<td>76.57</td>
<td>68.58</td>
<td>76.38</td>
<td>81.02</td>
</tr>
<tr>
<td>90min</td>
<td>48.25</td>
<td>76.62</td>
<td>68.65</td>
<td>76.78</td>
<td>81.13</td>
</tr>
<tr>
<td>180min</td>
<td>49.05</td>
<td>76.7</td>
<td>68.68</td>
<td>76.93</td>
<td>81.18</td>
</tr>
</tbody>
</table>

3.3 Effect of pH on adsorption
The efficiency of sorption is dependent on the pH of the solution (Aksu Z. et al, 2003) because variation in pH leads to variation in the surface properties of the sorbent and the degree of ionization (Gupta V K et al, 2007). Thus, comparative experiments were performed for pH values ranging from 2 to 10 in order to obtain the optimum pH for dye adsorption. The result depicted in Figure 5 shows that the sorption of MO increased from the initial pH 2 up to pH 4.0 and then decreased over the pH range of 4 – 10.

Electrostatic attraction between the fibers surface and the dye molecules leads to maximum adsorption. However, at pH values higher that 4, the surface of the sorbents will be less which results in the decrease in diffusion and adsorption thereby due to electrostatic repulsion. The lower adsorption of the direct dyes in alkaline medium can also be attributed to the competition from hydroxide ions (OH⁻) with the anionic dye molecules for the adsorption sites (Gupta VK 2009).

Figure 5. Effect of pH on retention of MO onto silica gel (v=600 rpm, T=22°C, r=10g/l, C₀=10mg/l)
Figure 6. Effect of pH on retention of MO on peanut shell (v=600 rpm, T=22°C, r=10g/l, C₀=10mg/l)

4. THE ADSORPTION ISOTHERMS

To plot the adsorption isotherms, the evolution of the equilibrium capacity was followed, based on residual concentrations in the aqueous phase. We use different values of concentration.

By observing the curve, we can see that the shape of this isotherm is a Langmuir isotherm, and to identify the real nature of the adsorption process we tested models of Langmuir, Freundlich.

The linear forms of each model are given by the following expressions:

**Freundlich:**
\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

**Langmuir:**
\[
\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K q_{max}} C_e
\]

Analysis of experimental results using these two models allowed us to have the following results.

Table 3: Isotherm adsorption of MO onto silica gel and peanut shell

<table>
<thead>
<tr>
<th>Models</th>
<th>Equations</th>
<th>Linear forms</th>
<th>Constants</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicagel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td>Q_{max}=10.81 K=17.5</td>
<td>0.14175</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td>K_{f}</td>
<td>0.99961</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/n=0.3623</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Peanut shell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td>Q_{max}=9.165 K=0.027</td>
<td>0.57329</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td>K_{f}</td>
<td>0.73797</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/n=1.24049</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results of table 3 show clearly that the retention of methyl orange on silicagel and peanut shells are well described with Freundlich Model. These results are confirmed with correlation values with: \( R^2 = 0.99961 \) for silicagel and \( R^2 = 0.73797 \) for peanut shell

5. ADSORPTION KINETIC STUDY
The adsorption of a solute by a solid in aqueous solution is a phenomenon with often complex kinetics.

a. Pseudo-first-order model
The pseudo-first-order model was described by eqn
\[
\log (q_e - q_t) = \log (q_e) - k_1 t/2.303
\]
where \( q_e \) and \( q_t \) refer to the amount of dye adsorbed (mg g\(^{-1}\)) at equilibrium and at any time, \( t \) (min), respectively and \( k_1 \) is the equilibrium rate constant of pseudo-first-order adsorption (min\(^{-1}\)).

b. Pseudo-second-order model
The pseudo-second-order model is represented by eqn (5).
\[
t/qt = 1/k_2 q_e^2 + t/q_e
\]
where \( k_2 \) is the equilibrium rate constant of pseudo-second-order adsorption (g mg\(^{-1}\) min\(^{-1}\)). Experimental kinetic data were adjusted according to the indicated models. Table 4 showed that the second order equation model provided the best correlation with experimental results. This fact indicates that the sorption of methyl orange dye on adsorbent follows the pseudo-second order kinetics.

Table 4: The correlation factors and the kinetics constants of the two kinetic models of MO

<table>
<thead>
<tr>
<th>Supports</th>
<th>First order kinetic</th>
<th>Second order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1(\text{min}^{-1}) )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td><strong>Silicagel</strong></td>
<td>0.0224</td>
<td>0.83385</td>
</tr>
<tr>
<td><strong>Peanut shell</strong></td>
<td>0.05</td>
<td>0.98893</td>
</tr>
</tbody>
</table>

6. CONCLUSIONS
The use of silicagel and peanut shell for the removal of MO from aqueous solutions was investigated. The effect of various parameters such as pH, contact time and dye concentration was studied. The direct dye adsorption of MO on these two supports followed the pseudo-second-order kinetics. The equilibrium data fitted well in the Freundlich model of adsorption. The present work demonstrates that these sorbents can be utilized as efficient sorbents for the removal of MO from aqueous solutions.

REFERENCES


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