Removal of Methylene Blue by Modified Carbon Prepared from the Sambucus Nigra L. plant

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Abstract
An increase in population initiating rapid industrialization was found to consequently increase the effluents and domestic wastewater into the aquatic ecosystem. In this research the potentialities of Sambucus nigra L. (SNL) plant in the remediation of water, contaminated with methylene blue (MB), a basic dye were investigated. SNL was chemically impregnated with KHCO₃. Operating variables studied were pH, amount of adsorbent and contact time. In general, pH did not have any significant effect on colour removal and the highest adsorption capacity was obtained in 0.035 g MB/g-activated carbon. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption models were applied to describe the equilibrium isotherms. The adsorption isotherm data were fitted to the Temkin isotherm. The mass transfer property of the sorption process was studied using Lagergren pseudo-first-order and chemisorption pseudo-second-order kinetic models. The sorption process obeyed the pseudo-second-order kinetic model. The surface area, pores volume and diameter were assessed by the Brunauer-Emmett-Teller and Barrett-Joyner-Halenda methods. The results were compared to those from activated carbon (Merck) and an actual sample. The results indicate that SNL can be employed as a natural and eco-friendly adsorbent material for the removal of dye MB from aqueous solutions.

Key words: adsorption, industrial effluent, activated carbon, methylene blue, Sambucus nigra L.

1. Introduction
Dyes are synthetic aromatic water-soluble dispersible organic colorants with potential applications in various industries. The use of dyestuff materials has increased gradually due to the tremendous increase in industrialization and due to the general desire for color in everyday objects [1]. Dyes are used extensively in the paper, textile, leather, pharmaceutical, food, cosmetics, and printing industries [2,3]. The discharge of colored waste is not only damaging the aesthetic nature of the receiving streams, but also it may be toxic to the aquatic life in those streams. In addition, color interferes with the transmission of sunlight into a stream and therefore reduces the photosynthetic action [4]. Various treatment methods, such as physical, physic-chemical, biological and chemical processes have been investigated for treating dye-bearing effluents [5]. The adsorption technique has proved to be an excellent method to treat effluents, offering advantages over conventional processes, especially from an environmental point of view [6,7]. Adsorption is considered to be superior to other techniques owing to its low cost, simple design, good availability, and its ability to treat dyes in more concentrated form. Activated carbon is the most widely used adsorbent, showing great success due to its high adsorption capacity. However, its use is limited due to its high cost, and this has led to a search for cheaper substitutes. In terms of environmental protection, the utilization of these types of waste has sparked the development of processes for the production of carbon adsorbents based on plants and...
agricultural waste. Both the nature of the precursors and the production process strongly influence the porous structure and adsorption properties of the resulting activated carbons. The adsorption characteristics of activated carbon are determined by its pore structure (magnitude and distribution of pore volume) and surface chemistry (type and quality of surface-bound heteroatomic functional groups) [8]. Activated carbon can be prepared from a large number of sources, such as palm shells, wood, coconut shells, coal, carbon fibers and pitch [9]. Activated carbon can adsorb molecules from both liquid and gaseous phases depending on the specific surface area, pore size distribution, and surface functional groups (also denoted as surface complexes). Applications of activated carbon include drinking water purification, wastewater treatment, sweetener discoloration, food and chemical processing, solvent recovery, gasoline emission control, cigarette filters and as a treatment for industrial emission gas [10].

The aim of this research was the investigation of the methylene blue (MB) removal ability from aqueous solutions by activated carbon prepared from Sambucus nigra L. (SNL) that was chemically impregnated with KHCO₃. The pH, amount of adsorbent, and time of contact of activated carbon from SNL were investigated and results were compared to Merck activated carbon and an actual sample.

2. Material and Methods

2.1. Preparation of modified activated carbon

The SNL plant was used as the starting material. It was collected from the north of Iran. The stem of plant was burnt and then screened though a 120 nm sieve. The produced carbon (1 g) was chemically impregnated with KHCO₃ (20%). The mixture was activated in five different furnaces (Table 1). The obtained carbon was then washed with hot distilled water. They were dried at 50-80°C in a thermostatically controlled oven and were then filtered and analyzed using a UV spectrophotometer (Shimadzu, UV1101, Japan).

The highest adsorption capacity of MB observed in a furnace with three continuous time and temperature steps (Fig. 1) was found in No. 5. These values were 30 min at 200°C, 60 min at 500°C, 30 min at 800°C.

Therefore, the remaining adsorption experiments were carried out using these optimum times and temperatures in a furnace.

| Table 1. Three-step preparation process at different times and temperatures |
|---|---|---|---|---|---|---|
| 1   | 30 min | 200°C | 60 min | 400°C | 15 min | 700°C |
| 2   | 30 min | 200°C | 60 min | 500°C | 15 min | 700°C |
| 3   | 30 min | 200°C | 60 min | 600°C | 15 min | 700°C |
| 4   | 30 min | 200°C | 60 min | 500°C | 30 min | 700°C |
| 5   | 30 min | 200°C | 60 min | 500°C | 30 min | 800°C |

2.2. Preparation of the adsorbate

MB (Fig. 2), a basic dye used as the model adsorbate in the present study, is a monovalent cationic dye. It has a molecular formula of C₁₆H₁₈N₃SCl and a molecular weight of 319.86 (g/mol). It was used as an adsorbate without any purification. A stock solution of 1000 mg/L was prepared by dissolving an appropriate quantity of MB. The working solutions were prepared by diluting the stock solution with distilled water to procure the appropriate concentration of the working solutions. The chemical structure of MB is shown in Fig. 2. The concentration of MB was determined using a UV-Vis spectrophotometer at a wavelength of 620 nm.

2.3. Effect of pH

The pH of the solution from which adsorption occurs may influence the extent of adsorption. The pH affects adsorption in that it governs the degree of ionization of the acidic and basic compounds. In general, the initial pH value may enhance or depress the uptake. This is attributed to the change in the charge of the adsorbent surface with the change in the pH value [8]. In this work, the effect of the pH on the adsorption of MB by activated carbon derived from SNL was studied over a pH range of 3 to 12. In the experiments, 0.035 g of activated carbon was added to 50 mL volumes of MB aqueous solution having an initial concentration 25.35 mg/L for a constant sorption time of 10 min. The adsorption behavior of the activated carbon of SNL was studied by $q_e$ (mg/g) and was calculated by the following mass balance relationship:

$$q_e = \frac{(C_0 - C_e) V}{W}$$

(1)

Here, $C_i$ and $C_e$ are the initial and equilibrium liquid-phase concentrations of dyes, respectively (mg/L), $V$ the volume of the solution (L), and $W$ the weight of the dry SNL used (g).
0.035 g of activated carbon derived from SNL was added to 50 mL of MB solution (25.35 ppm) and the mixture was agitated in a shaker for different times, after which it was filtered. The remaining MB concentration filtrates were analyzed with a spectrophotometer at 620 nm. This experiment was also carried out using Merck activated carbon.

### 2.8. Adsorption isotherm

Equilibrium adsorption isotherm studies are required in the screening of a sorbent for potential use as a form of wastewater treatment. This process can help to evaluate the affinity of a sorbent for a particular sorbate [12].

The experimental data results were analyzed by means of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm equations. The Langmuir equation can be applied for the monolayer sorption onto a surface of a finite number of identical sites. The linearized form of the Langmuir isotherm is presented by the following equation [13]:

\[
\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{K_L q_{max}}\right)\left(\frac{1}{c_e}\right)
\]

Here, \(c_e\) is the equilibrium concentration (mg/L), \(q_e\) is the adsorption capacity at equilibrium (mg/g), \(K_L\) denotes the Langmuir adsorption constant (L/mg) and \(q_{max}\) is the theoretical maximum adsorption capacity (mg/g) [14].

The sorption of MB was carried out at different initial MB concentrations ranging from 8.45 to 59.15 ppm; optimum conditions of all pertinent factors were used.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor \(R_L\), as determined by the following equation:

\[
R_L = \frac{1}{1 + K_L c_0}
\]

The BET surface area of activated carbon fiber derived from SNL as used in this paper was 426.9 (m²/g) with a total pore volume of 0.126 (cc/g). The average pore diameter of SNL was found to be 1.186 nm. Table 2 shows the characteristics of the activated carbon derived from SNL.

#### 2.6. Effect of contact time

The effect of the contact time on the adsorption of MB on the activated carbons from SNL and Merck was studied. A 0.035 g sample of activated carbon derived from SNL was added to 50 mL of MB solution and agitated in a shaker in 1-30 min. The experiments were carried out at an initial MB concentration of 25.35 ppm. The samples were withdrawn at a suitable time interval, filtered, and centrifuged and the filtrate was analyzed for the remaining MB concentration spectrophotometrically at 620 nm.

#### 2.7. Adsorption kinetics

The adsorption kinetics of MB on activated carbon derived from SNL can be studied by applying a pseudo-first-order and pseudo-second-order rate equation of the types typically used to determine the adsorption of an adsorbate from an aqueous solution. These are expressed below:

\[
\ln(q_e - q_t) = \ln q_e - k_w t
\]

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

In these equations, \(q_e\) and \(q_t\) are the amount of dye adsorbed per unit mass of the adsorbent (mg/g) at the equilibrium time and at time \(t\), respectively, and \(k_w\) is the rate constant [11].

### Table 3. Comparison of the coefficients isotherm parameters by MB adsorption onto SNL and Merck AC

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Constant parameters</th>
<th>Sambucus nigra L. (AC)</th>
<th>Merck (AC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(K_L) (L/mg)</td>
<td>266.67</td>
<td>33.33</td>
</tr>
<tr>
<td></td>
<td>(R_L)</td>
<td>1.48 \times 10^{-4}</td>
<td>1.18 \times 10^{-3}</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.673</td>
<td>0.936</td>
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<tr>
<td>Freundlich</td>
<td>(N)</td>
<td>3.98</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.774</td>
<td>0.555</td>
</tr>
<tr>
<td>Temkin</td>
<td>(A) (L/mg)</td>
<td>3229.23</td>
<td>1317.9</td>
</tr>
<tr>
<td></td>
<td>(b) (J/mg)</td>
<td>232.64</td>
<td>94.67</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.926</td>
<td>0.739</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>(Q_m) (mg/g)</td>
<td>77.71</td>
<td>304.6</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.771</td>
<td>0.604</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Effect of the pH

Fig. 4 shows the effect of the pH on the removal percentage of MB dye for the activated carbon derived from SNL and from Merck activated carbon. The sorption at pHs ranging from 3 to 11 was remarkable, and there was no significant difference in the dye concentration remaining when the pH was increased because the solution pH was higher than the pHzpc value [17].

3.2. Effect of the adsorbent dosage

Fig. 5 shows the effect of the adsorbent dosage on the adsorption of MB for activated carbon derived from SNL and for the Merck activated carbon. It was observed that the removal of MB increased to 0.045 and then remained nearly constant. The increase in the color removal percentage was due to the increase in the size of the available sorption surface.

3.3. Effect of the contact time

Equilibrium levels were mostly achieved in 10 min. A slight increase occurred during the next 10 min. Fig. 6 shows the effect of the contact time on the adsorption of MB for activated carbon derived from SNL and for the Merck activated carbon.
Removal of Methylene Blue by Modified Carbon

3.4. Adsorption kinetics

Figs. 7 and 8 show the pseudo-first-order and pseudo-second-order plots, respectively. As shown, the pseudo-second-order plot gives a straight line with a correlation coefficient $R^2$ of 1 for SNL (activated carbon) and 1 for Merck (activated carbon), indicating that the applicability of the pseudo-second-order equation was better than that of the pseudo-first-order plot, with $R^2 = 0.376$ for SNL (activated carbon) and $R^2 = 0.272$ for Merck (activated carbon) only. Table 5 shows the kinetics constants for the pseudo-first and pseudo-second-order models.

3.5. Adsorption isotherm

According to the $R^2$ values, the fitting of the Temkin isotherm to the experimental data is better than that of the other isotherms in this study for SNL. In addition, the fitting of the Langmuir isotherm to the experimental data is better than that noted with

| Table 5. Kinetics constants for pseudo-first and pseudo-second-order models |
|---------------------------------|---------------------------------|---------------------------------|
| Activated carbon | Methylene blue | Pseudo-first-order | Pseudo-second-order |
|                  |                  | $K$ (1/min) | $q_e$ (mg/g) | $R^2$ | $K$ (g/mg min) | $q_e$ (mg/g) | $R^2$ |
| SNL              | Methylene blue  | 0.291      | 0.0936       | 0.376 | 10.41          | 37.04        | 1 |
|                  | SNL              | 0.328      | 0.0196       | 0.272 | 24.29          | 37.04        | 1 |

SNL: Sambucus nigra L.
the other isotherms in this study for the Merck activated carbon. Figs. 3, 9-11 show the Langmuir, Freundlich, Temkin and D-R models, respectively, for the adsorption of MB by SNL and Merck activated carbon.

**4. Conclusions**

This study investigated the adsorption mechanism of MB (a cationic dye) on activated carbon samples from an aqueous solution as a function of the pH, amount of adsorbent, contact time, adsorption kinetics and adsorption isotherm. The results were compared to those using Merck activated carbon and a real sample. According to the results, prepared activated carbon can be used as a low-cost adsorbent comparable to commercial forms of activated carbon for the removal of textile dyes from textile wastewater processes. The cost is low because SNL is a weed in the north of Iran. The highest adsorption capacities were observed in three continuous steps at the times and temperatures of 30 min at 200°C, 60 min at 500°C, 30 min at 800°C. According to the results, the pH did not have a significant effect on the color removal activity. The highest adsorption capacity was obtained when 0.035 g of adsorbent. The adsorption equilibrium for color removal was reached within 10 min. The isotherm data was well fitted to the Temkin model, and the sorption process obeyed the pseudo-second-order kinetic model.

**References**


