A novel low-cost plant-based adsorbent from Red Oak (Quercus rubra) Acorns for wastewater treatment: Kinetic study on removal of dye from aqueous solution

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Abstract. Oak species are a successful plant group that have colonized the world's largest areas of forest. Oak trees are also prevalent in urban green spaces in the United States and Canada. As a result, these trees produced an abundance of acorns each year. In urban areas, these acorns are frequently discarded as solid waste. Alternative uses for this forest/plant waste are highly desirable because they will not only be valorized but will also contribute to the reduction of solid waste. The purpose of this work was to manufacture low-cost activated carbon using Red Oak (Quercus rubra) acorns and utilize it to remove methyl blue colors in aqueous solutions. The results of experiments indicated that prepared carbons were effective at removing pollutants from water. The pH, starting dye concentration, temperature, duration of the adsorption process, and shaking rate all had an effect on the adsorption process. The basic pH system was found to have the most favourable conditions for dye removal after a 3-hour contact time. The starting concentration of adsorbate has a detrimental influence on the removal rate, while the other factors also may have effect. A kinetic analysis revealed for the first 2 hours, the dye adsorption was better characterized by a pseudo-second order kinetic model with an equilibrium concentration (q_e) of 0.9756 mg/g and an equilibrium rate constant (k_2) of 16.81 g/mg min. Given that Red Oak acorns are largely regarded as solid waste due to their low monitory value and their widespread availability, the resulting carbons are anticipated to be economically feasible for the treatment of wastewater. The study's various findings indicate that this novel material is an excellent biosorbent for dye removal from contaminated waters.

Key word: Waste, Dye removal, Red Oak Acorn, Adsorption

1. Introduction
Organic synthetic dyes are substances that are employed in a variety of industries, including automotive, chemical, paper, and most notably, textiles. Once discharged with liquid effluents [1], these products offer considerable dangers to aquatic ecosystems; thus, they are classed with all other hazardous organic compounds as important pollutants that cause environmental damage [2]. In the industrial sector, methylene blue (MB) is one of the dyes that is most often employed in a number of applications (for example, the tanner and textile industries) [3]. As MB is used extensively, it is found at high concentrations in wastewater [4]. Due to the absence of an effective treatment method for these
wastewaters, MB is recognized as a major source of aesthetic pollution. When dyes are absorbed via polluted water, these have a serious impact on human body, resulting in an elevated heart rate, vomiting, jaundice, tissue destruction, and quadriplegia [5]. Additionally, this has a harmful impact on the aquatic ecology by preventing penetration of light into the water, decreasing photosynthesis rate, and decreasing the water’s dissolved oxygen [6].

Numerous physical and chemical techniques for reducing dye pollution have been developed, including membrane separation, rapid oxidation, and adsorption [7]. However, the majority of these techniques have inherent constraints, including operational complexity and a high cost. Adsorption, in compared to other technologies, is a more straightforward and practical method of successfully eliminating color contaminants [6]. The expense and regeneration of activated carbon, on the other hand, are significant impediments to its usage. As a result of their low cost, renewable nature, and efficacy, researchers have concentrated their efforts on dye removal using waste-based adsorbents. Additionally, by reusing waste materials such as forestry wastes and farming by-products, ecological impact may be minimized while increasing the value of waste resources [7]. This is why, in recent years, adsorbent materials have been synthesized using a range of low-cost natural materials, such as: Bamboo [8], sludge [9], Argan shells [10], industrial wastes [11], gulfweed [12], various nuts [13], coconut shells [14–16], eggshell [17,18], eggplant [19], apple pulp [20]. Previous reports of dye removal (%) with various adsorbents are presented in table 1 below. A single low-cost adsorbent would be incapable of removing all pollutants effectively. Additionally, a greater quantity of adsorbents is required during the removal process, as the majority of inexpensive adsorbents have limited adsorption capacity. As a result, it is necessary to develop innovative, readily available, low-cost, ecologically acceptable, and highly effective adsorbents.

| Adsorbent                        | Dye                                      | Removal %                             | References |
|----------------------------------|------------------------------------------|---------------------------------------|------------|
| Raw maize cob agricultural waste | Bromothymol blue and bromophenol blue    | 96.39%, and 94.53%, respectively      | [1]        |
| Fly ash from coal                | Crystal violet (CV) and MB                | CV>90% and MB<85%                     | [2]        |
| Bio-adsorbents Spirulina platensis | FD&C Red No. 40 and Acid blue 9         | 95% for both                          | [3]        |
| Activated carbon from ZnO-NP-loaded Parthenium weed (ZnONPs-PWAC) | MB                                       | Around 99%                            | [4]        |
| Agricultural waste/graphene oxide 3D | MB                                       | The removal was >90% after five cycles | [5]        |

In this investigation, acorns grown on a red oak (Quercus rubra) tree were used. Red oaks are native to southeast and south-central Canada, as well as eastern and central United States. [26]. It is readily available and abundant in nature. The adsorbent in this study is activated carbon derived from red oak (RAC) acorns, and the adsorbate is methylene blue (MB). Given the promising results obtained for the adsorption of MB in Author’s previous paper, more extensive study for different level of system parameter (i.e. pH, starting dye concentration, mixing time, temperature, and shaking rate) was conducted for this paper to have a better idea of the influence of these variables. Additionally, it is critical to correctly define the adsorption kinetics. Determining the adsorption parameters of the models enables optimization of the adsorption mechanism and successful design of adsorption systems [15]. The investigation of the kinetics of MB removal by RAC from an aquatic media is one of the objectives of this research project.
2. Materials and methods

2.1. Precursors and activation carbon preparation
From the Dartmouth area of Nova Scotia, Canada, acorns were gathered from fallen pieces under red oak trees. Prior to the start of the investigations, the materials were dehydrated and processed using a high-speed rotational milling machine. The crushed acorn is then heated to 500°C for one hour in a muffle furnace. The activated material was sieved to divide it into distinct size fractions. This study implements a portion of Red Oak Acorn Activated Carbon (RAC) with a diameter of 0.5 to 1.00mm (RAC). Specification of the material is summarized in Table 2 below:

| Precursor                      | red oak (Quercus rubra) acorn |
|-------------------------------|-------------------------------|
| Location collected            | Nova Scotia, Canada           |
| Activation Method             | Thermal                       |
| Activation temperature        | 500°C                         |
| Activation time               | 1 Hour                        |
| Particle size                 | 0.5 to 1.00 mm                |

2.2. Dye used as in this study
Methylene blue (MB), dye acquired from Fisher Scientific in the United States of America, was employed in this work. It has a molecular mass of 373.896 g/mol and the chemical formula is C₁₆H₁₈ClN₃S₄H₂O.

2.3. Reagents used
All compounds utilized in this study were analytical reagent grade. Fisher Scientific, USA, supplied sodium hydroxide (NaOH), hydrochloric acid (HCl), and sodium chloride (NaCl).

2.4. Adsorption experiment
To evaluate the effect of pH, starting dye concentration, temperature, stirring time, and rate on Methylene Blue dye adsorption, batch experiments were done with polypropylene tubes with covers. A 1000 mg/L concentration stock solution of MB was prepared and diluted to the desired concentrations. 0.1 M NaOH or 0.1 M HCl acid was used to adjust the final pH of the working solution. Following pH adjustment, prepared activated carbon (RAC) was added as required. After RAC addition, the mixture was shaken in a rotary mixer (Barnstead/Lab-Line MaxQTM 2000) at a temperature, time, and rate of mixing that were predetermined. Following the adsorption period, the samples (suspensions) were spun for 10 minutes at a speed of 25,000 rpm using a centrifugal machine (Thermo Electronic Corporation). Aliquots of the solution were decanted from the supernatant, which is used to determine the concentrations of MB dye using a DR-5000 (HACH Co) UV Visible Spectrophotometer at a wavelength of 660 nm. Equilibrium adsorption capacity (in mg/g) was calculated using the following equation:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  \hspace{1cm} (1)

Where equilibrium adsorption capacity (mg/g) is denoted by \( q_e \) and starting and equilibrium concentrations (mg/L) of dye are denoted by \( C_0 \) and \( C_e \) respectively; the solution volume (mL) is denoted by \( V \); and \( m \) denotes the adsorbent's dry weight (g). The adsorbate removal efficiency (R%) was calculated according to using the following equation.

\[ R(\%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \]  \hspace{1cm} (2)

Where starting and ending concentration of MB dye (mg/L) are denoted by \( C_i \) and \( C_f \) respectively.
2.5. Kinetic sorption studies

The kinetic study is critical for the adsorption process because it determines the absorption rate of the adsorbate and regulates the residual time throughout the adsorption process, both of which are important parameters. It is proposed in this paper to employ pseudo-first order and pseudo-second order kinetic models. The pseudo-first order equation is shown in equation 3 below [27][28].

\[
\ln(q_e - q_t) = ln q_e - k_1 t \tag{3}
\]

Equation 4 also shows the pseudo-second order equation [29].

\[
\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \tag{4}
\]

Where, \(q_t\) and \(q_e\) are amount of MB adsorbed on unit mass of RAC at time, \(t\) and at equilibrium respectively. Rate constant for pseudo-first order kinetics is denoted by \(k_1 (\text{min}^{-1})\). Pseudo-second order kinetics rate is represented by \(k_2 (\text{g/mg min})\).

For Kinetic studies, 5gm of RAC is added to 1L MB solution with initial concentration 50mg/L in a glass jar. The content of the jar is continuously mixed at 20°C. Liquid samples were collected from the glass jar at regular interval. Total sample volume removed was kept less than 10% of the starting volume. MB concentration of the collected sample was measured following the methods described in section 2.4 previously.

2.6. Sample characterization

Scanning electron microscopy (SEM) was employed to capture images of and examine the morphology of the activated carbon that had been synthesized. The SEM pictures were acquired using a Hitachi S4700 cold field emission at a 10-kV acceleration voltage before and after adsorption with MB. Conductive glue or tape was used to secure the sample on a metallic stub during this process.

3. Results

3.1. Starting dye concentration effect

Starting adsorbate concentration effect is shown in Figure 1. Below. It can be observed, the dye removal rate (i.e., %) reduces as the starting adsorbate (i.e., dye) concentration increases. At low concentration levels, all dye molecules in the mixture engage with the adsorbent’s receptors, resulting in about 99 percent adsorption. On the other hand, the adsorbent has a limited number of receptors that reach saturation at a certain concentration,[30]. As a result of the saturation of binding sites at greater concentrations, more MB molecules remain unabsorbed in the solution, resulting in a lower dye removal %.

![Figure 1. Effect of starting adsorbate concentration on MB removal (%).](image-url)
3.2. pH effect
One of the critical components, impacting the adsorption process is the system pH. It has the potential to influence the adsorption process by influencing the adsorbent's surface charge, adsorbate speciation diversity, and the extent of ionization. Additionally, it is highly correlated to the hydrogen ion's capacity to compete for functional sites on activated carbon molecules. In this paper pH rang of 5.0 – 10.0 was investigated. The elimination of MB increased dramatically when the solution pH was shifted to 8.0(Fig. 2). Additional increases in the pH of the solution were minor. MB is a cationic dye that exists as positively charged ions in aqueous solution. As a charged species, its affinity for the surface of the adsorbent is mostly dictated by the adsorbent's surface properties, which is controlled by the solution pH.

![Figure 2. Effect of pH on MB removal (%).](image)

As the system's acidity drops, the surface functional groups deprotonate, raising the negative charge concentration, thereby boosting dye cation linkage. Increased adsorbate removal capacity at elevated pH might possibly be a result of a reduction in H⁺ ions, which competes with other cations (i.e., adsorbate) for available binding sites on the carbon surface at lower pH. The competition between H⁺ and adsorbate ions adhering to adsorbent surface, lessens when the pH rises, resulting in increased dye absorption.

3.3. Temperature effect
Figure 3 displays the temperature effect on removal rate (R%). At higher temperature the water viscosity reduces, and adsorbent pore structure may expand. In this study system temperature was increased from 20 to 45°C. The removal rate was observed to be 94 to 96% in the temperature range. So, temperature effect on MB removal was not significant in this range.

![Figure 3. Effect of Temperature on MB removal (%).](image)
3.4. Mixing rate effect
Adsorption process is affected by mixing rate of the system. Impact of Mixing effect on adsorbate removal is shown in Figure below (i.e., Figure 4). Throughout the experiment, increasing the mixing rate resulted in a rise in the removal efficiency, which eventually reached a plateau. The highest mixing rate (175 RPM) shows little lower removal rate (76%) then removal for mixing in 100 to 150 rpm range. This impact might be linked to greater vibration and a reduction in boundary layers surrounding the adsorbent particles as a consequence of an increase in the amount of stirring. However, at 175 rpm increase turbulence might reduce the contact between the MB and binding site on adsorbent surface.

Figure 4. Effect of Mixing rate on MB removal (%).

3.5. Mixing time effect
Adsorbate removal after various mixing time was tested from 5min to 3 hours. Mixing time effect on MB removal (R%) is shown graphically in Figure 5. The removal rate increases drastically up to the 80 minutes of mixing probably because at the beginning, all receptor site on activated carbon surface were not occupied and more functional groups are accessible for linkage. Also, at longer mixing time the MB molecules got more opportunities to be attracted to the binding site of the adsorbent surface resulting in higher removal rate. For 3 hours of mixing almost (96%) all of the Dye was removed.

Figure 5. Effect of time on MB removal (%).

3.6. Adsorption kinetics
Various kinetic models (i.e., pseudo 1st order, pseudo 2nd order) are used to describe the adsorption process. Results of the kinetics adsorption experiment is shown in Table 3. below:
Table 3. Results of Adsorption Kinetics experiments

| Model          | Intercept | Slope  | Equilibrium Conc. | Equilibrium rate constant | R²  |
|----------------|-----------|--------|-------------------|---------------------------|-----|
| pseudo 1st order | 0.385     | -0.0026| 1.46961           | -0.0026                   | 0.9518 |
| pseudo 2nd order | 0.0625    | 1.025  | 0.97561           | 16.81                     | 0.9999 |

Figures 6 and 7 graphically show the pseudo 1st and 2nd order kinetic model. R² value indicates that adsorption process for Methylene blue on RAC could be better explained using pseudo 2nd order kinetics than the other. Suitability of this model revealed that adsorption occurs via chemical reactions (chemisorptions), which involve electrons exchange of between the MB and RAC. Chemisorptions occur when MB ions form a chemical connection with the adsorbent surface and migrate toward spots that maximize their coordination number with the surface.

Figure 6. Pseudo 1st order kinetic model

Figure 7. Pseudo 2nd order kinetic model
3.7. SEM analysis

Scanning electron microscopy (SEM) was utilized to examine the morphological and surface characteristics of the produced activated carbon. Figures 8(a) and (b) illustrate the RAC surface before and after adsorption experiment.

![Figure 8(a) RAC surface before adsorption](image)

![Figure 8(b) RAC surface after adsorption](image)

Figure 8. Photographs taken with a scanning electron microscope of activated carbon (a) before and (b) after the adsorption process.

Overall morphology of these photographs demonstrates an extraordinary degree of variation. Before adsorption, the surface of the RAC was spongy, rough, and fragmented, with voids on the surface structure that could be seen. However, after the adsorption of MB on RAC, the surface appeared smooth and intact, and the number of holes reduced as the dye filled the majority of the holes on the surface.

4. Conclusion

The acorns of Red Oak (Quercus rubra) trees, which are typically regarded as solid waste due to their low monetary value and widespread availability, was used to yield carbons that are economically viable for wastewater treatment. The SEM analysis of the synthesized activated carbon both before and after the adsorption process reveals that it has the potential to be used in the effective adsorption of MB dye. Pre- and post-adsorption characteristics of the RAC are determined using scanning electron microscopy (SEM), verifies its potential for effective adsorption of the MB dye.

The results of the present investigation can be summarized below:

- a) Initial dye concentration has an antagonistic relationship with dye removal
- b) Mixing time and rate is has synergistic effect on removal rate
- c) Dye removal rate for the temperature range (20 to 45°C) investigated was 94 to 96%
- d) Dye removal rate observed during different condition is quite comparable to the previous reports presented on Table 1.
- e) Pseudo 1st order rate constant was -0.0026 (min⁻¹), equilibrium concentration 1.46961 mg/gm and R² value was 0.9518
- f) Pseudo 2nd order rate constant was 16.81 gm/gm min, equilibrium concentration 0.9756 mg/gm and R² value was 0.9999
- g) Adsorption process for Methylene blue on RAC follow pseudo 2nd order kinetics more closely than the pseudo 1st order, so MB adsorption onto RAC occurs via chemical reactions (chemisorptions).

The outcomes of the study indicate that this innovative material is a good biosorbent for the removal of dyes from contaminated water system.
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