Removal of Methylene Blue Using Mango Seed Derived Carbon

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Abstract

When mangoes are consumed or processed, their peels and seeds are generated as waste. The waste is an environmental concern, but it is a natural and renewable resource. In this project, a process was developed to convert mango seeds into carbonized adsorbents. The effectiveness of mango seed-derived carbon in removing a dye from water was evaluated. Water containing methylene blue was treated with mango seed-derived carbon. The concentration of methylene blue in the water before and after the treatment was monitored by a do-it-yourself "spectrophotometer".

Keywords

mango seeds, carbon, methylene blue, water, adsorption

1. Introduction

Mangoes are consumed worldwide, and there has been an increasing demand in the past few decades.[1] However, fruits have the highest wastage rate of all foods.[2] A mango's peel and seed consist up to forty percent of its total fruit weight. Since mangoes are abundant in a multitude of countries, a large amount of waste is produced and difficult to dispose of.[3] Places such as Africa face economic issues, and do not have sufficient clean water. Nevertheless, Africa has become one of the biggest producers of mangoes due to its geographical advantage.[4] The mango industry has been growing rapidly in many other places as well. In areas like Thailand, mangos are the most popular tropical fruit.[5] Although Thailand's water quality is generally fine, agricultural and industrial pollutants resulting from human activity can lead to the deterioration of water quality.[6]

One possible solution to the agricultural waste and polluted water issues is to convert mango seeds into activated carbon, and use the resulting carbon to remove contaminants from water. Many past experiments have involved the removal of methylene blue from water with materials such as: acorn shells, dehydrated peanut hulls, and tea seed shells.[13] Equilibrium adsorption, thermodynamic and kinetic study results were compiled from all the experiments and indicated that such materials are renewable resources, and can potentially be used as adsorbents for removing methylene blue.

2. Materials and Methods

2.1 Absorption Measurement Setup

The absorption measurement setup consists of a sheet of orange construction paper, a cardboard box, a light source and a phone with an installed spectrophotometer app. There were three holes in the box: one to hold the glass vial during the measurement, one to restrict light that enters the cardboard box to shine on water solution, and one for the spectrophotometer to measure the light going through the water solution. The orange construction paper was folded in half and placed behind the cardboard box with a light source facing the paper. The spectrophotometer app measures the intensity of red, green and blue components of the light in a specific section of the camera's view. The amount of absorption in each solution sample can be calculated from the intensity of the red component. The absorbance for standard solutions 26.2, 20.0, 15.0, 10.5, 5.20, and 2.60 mg/L were used to generate a calibration curve which resulted in the following equation:

$$y = 0.04x + 0.01 \quad (1)$$

where y represents absorbance (the amount of red light that came through the vial) and x represents the concentration (mg/L).

Figure 1. Photo of the absorption measurement setup

2.2 Carbonization of Mango Seeds

Mango seeds were dried for at least one week at room temperature. The seeds were chopped and placed into a tube furnace at 500℃ for two hours, with nitrogen flowing through at two liters per minute. Once completed, the carbon was grounded and ready to be placed into the methylene blue solutions.

Figure 2. Carbonization process of mango seeds

2.3 Adsorption Equilibrium

Four beakers contained 50mL of different concentrations of methylene blue solution: 2.6, 5.2, 10.5 and 26.2mg/L, respectively. Each beaker had 0.20g of carbon in it. The beakers were then placed onto the stirrer, and the mixture was stirred with a Teflon-coated magnetic bar for forty eight hours. After mixing, the solutions were set inside a centrifuge to separate the carbon and methylene blue solution. The solutions later were transferred into vials. To measure the intensity of red light, each vial was placed into the absorption measurement setup and the spectrophotometer measured the intensity of red light. The equilibrium concentration for each solution was calculated from the absorbance using the Calibration Curve equation.

The equilibrium amount of methylene blue adsorbed per unit mass of carbon (Q_e) values was calculated with the following equation:

$$Q_e = \left(\frac{C_0 - C_e}{m}\right) V \qquad (2)$$

where C_0 (mg/L) represents the concentration before the adsorption, while C_e (mg/L) represents the concentration after adsorption, *m* (g) represents mass of carbon, and *V* (L) represents the volume of methylene blue solution.

2.4 Effect of Amount of Adsorbent

This experiment followed the similar procedure as described in section 2.3. The six beakers each contained 50mL of methylene blue solution with a concentration of 10.5mg/L. Different amount of the carbon adsorbent was added into each solution: 0.05, 0.10, 0.15, 0.20, 0.30 and 0.40g. The percent removal of the methylene blue was calculated using the equation below:

$$\%removal = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad (3)$$

3. Results and Discussions

3.1 Carbonization Process

The thermal activation method was used to carbonize the mango seeds. While the two general consecutive steps of thermal activation are carbonization (heating to a high temperature) and activation (gasifying the seeds with an oxidizing agent)[7]. Extreme pyrolysis, the process of heating for carbonization, results in extremely porous activated carbon particles as residue. The reaction causes larger molecules to break down into smaller molecules in the presence of heat. The frequency of vibration in the molecules are proportional to the temperature of the molecules, therefore, at a high temperature, molecules are shaking so frequently, that they are being stretched and breaking down. After the porous carbon particles are obtained, they need to be oxidized by gas or chemical treatment. However, the procedure used in this project only followed carbonization due to unavailability of equipment.

During the carbonization process, mango seeds were heated to 500 ºC in nitrogen for two hours. Some molecules in the seeds broke down into small molecules, which were carried out of the tube furnace by nitrogen. Many pores were created in the residue material, carbon. The size of these pores ranges from nanometers to micrometers. The surface area increases because of the presence of large quantity of pores.[7] One important property of the activated carbon is its high surface area. Impurities, in this case methylene blue, adsorbs on the active sites on the surface of the pores inside the carbon particles; whereas, water is able to pass through the activated carbon and is cleansed. The high surface area of carbon allows the carbon to adsorb more methylene blue. Carbon continues to take up methylene blue molecules until its active sites on the surface in the pores are completely occupied. If there is too much methylene blue, the methylene blue will remain floating in the solution. If there is too much carbon to adsorb a small amount of methylene blue, almost all of the methylene blue will be adsorbed with some active sites available on the surface area of the carbon to adsorb more.

3.2 Calibration Curve

Table 1 shows the diluted solutions that were used to create the calibration curve. The calibration curve was used to determine the concentration of methylene blue after the carbon adsorbents were mixed in. As seen in both Table 1 and Figure 3, the greater the concentration, the higher the absorbance is (less red light passes through the methylene blue solution). In Figure 3, the linear regression model on the calibration curve has a high R^2 value of 0.97, meaning that the curve is fairly accurate. The linear relationship between absorbance and concentration follows the Beer-Lambert's law. Since 10.5mg/L was an outlier, it was not used in the creation of the calibration curve. This could be due to the inaccuracy of the spectrophotometer that was used in the process of calculating the absorbance. If the accuracy of the spectrophotometer is improved, the calibration curve can improve.

Table 1. Standard solutions used for calibration curve

Solutions	1	2	3	4	5	6
Concentration (mg/L)	26.2	20.0	15.0	10.5	5.20	2.60
Absorbance	1.16	0.720	0.659	0.792	0.236	0.119

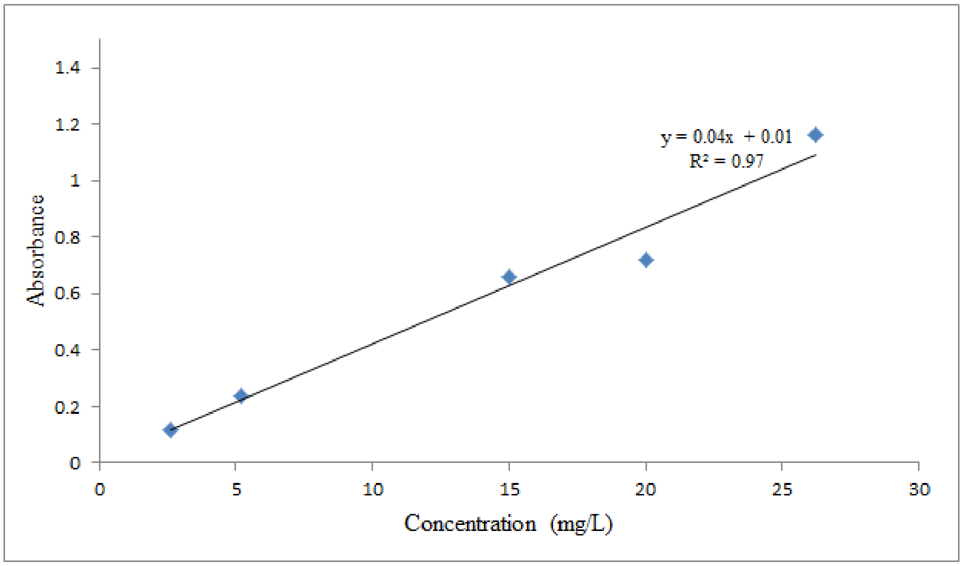

Figure 3. Calibration curve displaying linear relationship between concentration and absorbance

3.3 Adsorption Equilibrium

Figure 4 depicts a comparison of different methylene blue solutions before (left) and after carbon (right). As seen, the finishing solution is lighter and therefore less concentrated since the carbon successfully adsorbed the methylene blue. In Table 2, the absorbance value after the carbon is mixed is much lower compared to the initial absorbance values, as more red light pass through the solution without absorption. In addition, the concentration equilibrium (C_e) was calculated (Table 3). The concentration after the adsorption experiment (Table 3) is much smaller the initial concentration (Table 2). For example, a methylene blue solution that started with a concentration of 5.20 mg/L had a concentration of 0.277 mg/L after experiment. The data show that the carbon successfully absorbed methylene blue from water solution. However, there are two C_e values that are negative. This could be due to the values substituted into equation (1).

The absorbance values after carbon adsorption are the *y* values, and if less than 0.01, the *x* value (C_e) becomes negative. This error mainly stems from the inaccuracy of the spectrophotometer.

In Table 3, the amount of methylene blue adsorbed per mass unit of carbon, Q_e , was calculated using equation (2). The Q_e continues to increase as the C_e, as observed in Table 3 and Figure 5. Through the graph, 12.2mg/g is the limit of the adsorption capacity (Q_e) as measured in the experiment; however, the capacity may be greater as the trend line continues to rise.

Figure 4. Methylene blue solutions before and after experiment

Table 2. Adsorption equilibrium data (same amount of carbon and different concentrations)

Solution Number	1	2	3	4	5	6
Initial Concentration (mg/L)	2.60	5.20	10.5	15.0	20.0	26.2
Initial Red Intensity	187	143	17	54	47	13
Initial Absorbance	0.119	0.236	1.16	0.659	0.720	1.27
Red Intensity	249	241	212	220	76	30
Absorbance	0.00692	0.0211	0.000150	0.0407	0.504	0.925

Table 3. C_e (mg/L) and Q_e (mg/g) Values

Solution Number	1	2	3	4	5	6
C_e (mg/L)	-0.0769	0.277	-0.246	0.768	12.3	22.8
Q_e (mg/g)	0.630	1.36	2.56	3.94	8.09	12.2

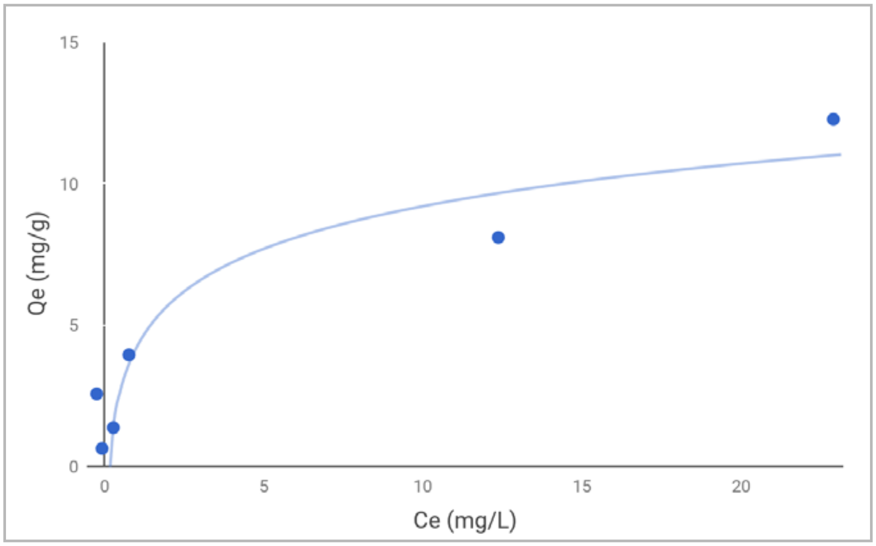

Figure 5. Trend line for C_e and Q_e

3.4 Effect of Amount of Adsorbent

Table 4 and Figure 6 give numerical and visual evidence that the solution becomes clearer. Table 4 displays the red intensity values and the absorbance values for 10.5 mg/L of methylene blue solution with different amounts of carbon. As more carbon is placed into the solutions, the red intensity values increase and the absorbance values decrease. Figure 7 uses the values from Table 4 to form an exponential trend line that also shows that the solutions become clearer with as greater amounts of carbon are placed, also pictured in Figure 6, where 0.051g of carbon is on the left and 0.4g of carbon is on the right.

The concentration equilibrium, C_e, was calculated using equation (1) and compared to the initial concentration of 10.5mg/L. As seen in Table 5, the concentration decreased dramatically from the initial. To determine the percent removal of methylene blue in the solution, equation (3) was used.

As shown in Table 5, the percent removal values increase as the amount of carbon increase. The carbon removes more methylene blue, allowing the solution to be clearer. The values gathered in Table 5 are plotted in Figure 8. The graph first begins steep but later evens itself out to a flatter line. As the amount of carbon increases, the surface area increases; therefore, the adsorption capacity is greater, but the solution stays the same. Therefore, almost all of the methylene blue is removed from the solution. When the adsorbent is 0.2g and above, the percent removal is lower and the value reaches its maximum[17].

Table 4. Effect of Amount of Adsorbent (different amount of carbon and same concentration)

	1	2	3	4	5	6
Amount of Carbon (g)	0.051	0.103	0.151	0.200	0.302	0.401
Red Intensity	154	195	208	221	222	227
Absorbance	0.2109	0.0892	0.0790	0.0580	0.0567	0.0458

Figure 6. Methylene blue solutions after effect of amount of adsorbent experiment

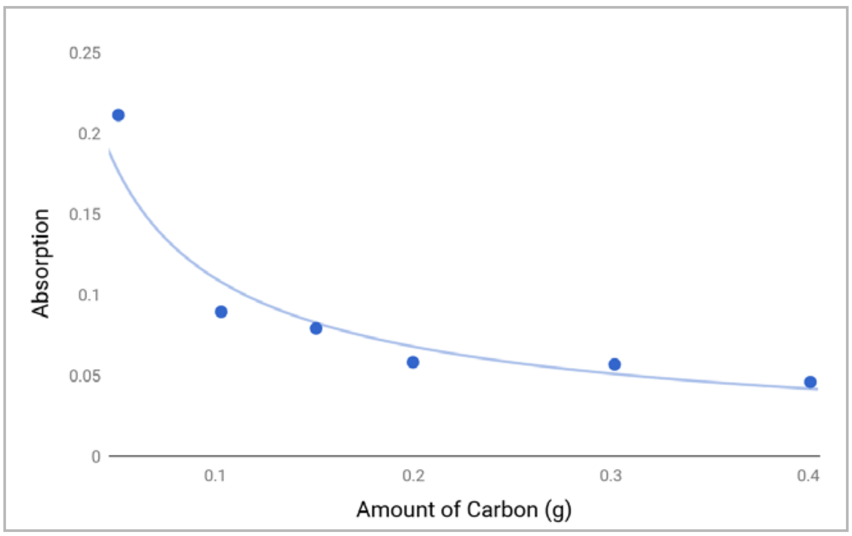

Figure 7. Absorption in relation to amount of carbon

Table 5. Percent removal of methylene blue

Concentration After Carbon (mg/L)	5.02	1.98	1.72	1.20	1.16	0.895
% Removal (%)	52.1	81.1	83.5	88.5	88.8	91.4

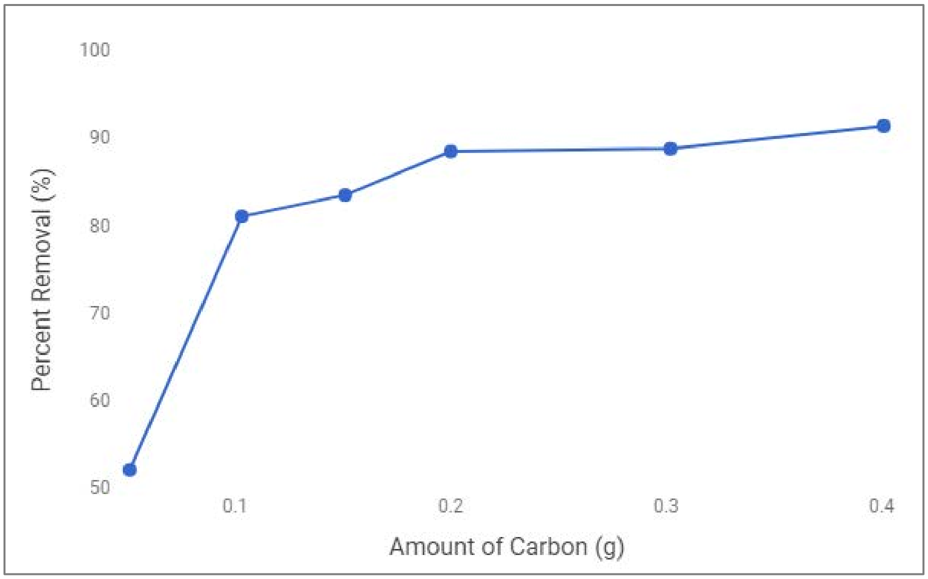

Figure 8. Percent removal of methylene blue in relation to amount of carbon

4. Conclusion

A carbonization was used to convert mango seeds into carbon at 500 °C under nitrogen protection. Two adsorption experiments were conducted with changed variables, and the results show that the mango seed derived carbon can remove methylene blue from water. Surface atoms of the adsorbent are partially exposed so the adsorbate molecules can be attracted. Methylene blue molecules can adhere physically to the surface of the carbon, and are separated from water.

Through the adsorption equilibrium experiment, the results concluded that the solutions with lower concentrations of methylene blue became clearer, almost like water. The equilibrium relationship between the amount of methylene blue adsorbed per unit mass of carbon (Q_e) and the equilibrium concentration (C_e) showed that Q_e increases with C_e initially, and it gradually levels off. Eventually when the concentration is so large, the amount of methylene blue adsorbed by the carbon stays relatively the same. The carbon has reached its adsorption limit and is no longer able to adsorb more methylene blue.

Through the effect of amount of adsorbent experiment, the data and graphs show that as larger amounts of carbon were used in the experiment, more methylene blue was adsorbed, and the water became clearer. As the amount of carbon increases, the % removal gets more steady and flat as it slowly approaches 100%. After a certain amount of carbon was added, the line became completely straight. These two experiments show that the methylene blue concentration and the amount of carbon in the solution play a big role in the process of removing methylene blue from water.

In the future, the accuracy of the spectrophotometer needs to be improved. Different methods of carbonization and activation will be investigated.

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Biography

Emily L. Chen is an incoming sophomore at Dublin High School. She desires to pursue a career in computer science or biology. She especially loves computer coding and networking. She became an IBM Certified Specialist of SPSS Statistics level one in January 2017. She is a founding member and currently holds a position as co-Webmaster of the IEOM Society Bay Area Student Chapter. She is involved in her school's Interact club, and holds a position as a board member. On her free time, she enjoys reading and going outside. She also enjoys traveling the world and sightseeing.

Alicia H. Chen is an incoming junior at Dublin High School. She holds a large interest in the STEM field and wishes to enter either the medical or technology field. She is founding member and co-Webmaster of the IEOM Society Bay Area Student Chapter and is a board member of her school's Interact club. She is also an Engineering Academy student at her school. She enjoys doing volunteer work in her community some of which include volunteering at a local hospital and volunteering for the city for summer camps. On her free time, she enjoys listening to music, dancing, reading, drawing, and socializing.