Optimizing the Removal of Methylene Blue from Aqueous Solution Using *Cucurbita Pepo* and an Analysis of Desorption Efficiency and Material Reusability

Research Article

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Abstract: Approximately 7×10^8 kilograms of dye are produced annually and 15% are released into aquatic bodies, causing global human and environmental health problems. Many conventional purification methods to produce potable water are expensive and inaccessible in under-developed areas. This studys objectives were threefold: low-cost adsorbent was produced from *Cucurbita pepo* and optimized for greatest efficiency of methylene blue (MB) adsorption from water, followed by a study of desorption methods for reuse. A pyrolyzation temperature of 1300°F and 1M NaCl chemical treatment were optimal for adsorbent development. Adsorbent in 0.5 g masses per 50 mL MB solution was most efficient in improving water quality, resulting in 100% dye removal across all treatment groups. The effect of adsorbent size fraction, solution pH, and agitation and adsorbent reusability after desorption (1M NaOH/NaCl with different agitation conditions) were studied and adsorption capacities of self- and commercially produced AC were compared. Mixed size fractions resulted in most efficient removal (100% after 48 hours) due to an interstitial maximization of surface area; however, pH and agitation had no significant effect due to the adsorbent's carbonaceous nature and porous structure. The novel, affordable adsorbent is highly efficient, with 32% greater adsorption capacity than commercially produced carbon, and also environmentally sustainable due to its high reusability as well as accessibility of agricultural waste material and NaCl.

Keywords: Dye pollution ● Activated carbon ● *Cucurbita pepo* ● Methylene blue ● Adsorption ● Desorption

1.   Introduction

Dye pollution, or the release of colored effluents from dyeing and other related industrial processes, is an increasingly severe problem in todays world. More than 10,000 dyes with a total annual production of over 7×10^5

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metric tons are commercially available worldwide, many of which are often improperly disposed of after their use [1]. Of the total global production of dyes, about 15% is lost during the dyeing process, resulting in severe water pollution, especially in Asia and other industry-heavy areas [2]. Due to their low cost and color variety, the use of dyes has increased considerably over the past few years [3].

The release of dyes into the environment harms ecosystems as well as human and organismal health. Firstly, the increased concentration of colored wastes in the water interferes with both the water's aesthetic nature and ability to transmit sunlight, which reduces photosynthetic activity and hinders growth of producers in the water [4]. Secondly, many dyes, especially in aqueous form, are toxic to organisms and render contaminated areas uninhabitable to local biodiversity [1]. Thirdly, dyes are toxic to humans, including those who work directly with them in an industrial setting and those who are exposed to any contaminated water. Dye exposure over long time periods or of acute severity may cause hypertension, vomiting, shock, and tissue necrosis [5].

Methylene blue (MB) is a cationic dye widely used in microbiology, surgery, diagnostics, chemistry, and textile dyeing. Long-term exposure to MB can cause vomiting, nausea, anemia, hypertension, and death [2, 6]. Because MB and other dyes are designed to withhold against time, they degrade very slowly in the environment and effectively resist natural breakdown. Common degrading materials such as sunlight, water, soap, and oxidizing agents are ineffective in removing dye pollution due to the dyes synthetic chemical structures [4]. This presents a significant need for more efficient and effective methods to treat dye pollution.

Many methods of remediation exist for dye pollution, including biodegradation, ozonation, photocatalytic degradation, and ultrafiltration [2]. These methods are costly and inefficient, require large amounts of industrial resources, and produce secondary pollution such as waste catalyst and fouled membrane. As a result, these methods cannot be widely used in many of the regions that suffer from severe dye pollution, since affected areas are often located in underdeveloped or developing countries with limited wealth and industrial resources [7].

Today, adsorption remains one of the most promising methods to efficiently and completely remove dye pollutants. Adsorption is described as a surface phenomenon that involves the increase in concentration of an adsorbate on the surface of an adsorbent via Van der Waals and electrostatic forces. Typically, a solid adsorbent with high surface area and high thermal stability is used to adsorb aqueous or dissolved materials such as dye particles. After the adsorption process reaches equilibrium, the adsorbent can be filtered out and removed, along with it all of the dye particles it has uptaken [8].

Adsorption can be conducted on a wide variety of solid materials, one category of which are biological materials, or biomaterials. Activated carbon (AC), usually charcoal altered to maximize adsorptive power, is a highly efficient adsorbent created from biomaterials and is often used to clean up effluents and wastewater. However, use of AC is currently restricted by its expensive production costs, the need for regeneration after exhausting the material and a loss of adsorption efficiency after regeneration [8]. This has spurred, in part, an increased interest in the use of agricultural waste materials such as corn cobs, rice husks, date pits, and melon rinds - biomaterials that are common and would be thrown away if not used - to create AC. Because of the

cheap and abundant nature of these biomaterials, this form of adsorption is appealing to contaminated areas in underdeveloped or developing countries [9]. This study focused on the use of *C. pepo* as a biomaterial source. *C. pepo* is a gourd species with 9 variations commonly grown around the world and during all seasons, making it widely accessible and a potential biomaterial for AC production.

The activation aspect of AC comes from chemical and physical alterations made to the original biomaterial to allow for efficient adsorption to occur. AC can be created via a two-step process: thermal activation and chemical activation. Thermal activation, also known as pyrolysis, is the burning of materials at high temperatures to purify their structures. Pyrolysis of carbon-based materials removes excess organic matter from their carbon skeletons, producing a cleaner and more porous carbon structure that adsorption can occur on. This decreases the occurrence of unwanted interactions between adsorbate and organic material that may produce harmful byproducts. Pyrolyzation of material also increases pore volume and pore space, thereby increasing the amount of surface area available for adsorption, a surface-dependent process [10]. Chemical activation, which follows pyrolysis, involves the exposure of AC to certain chemicals, such as $ZnCl_2$, to further increase surface area on a microdomain level and optimize surface functional groups to increase adsorption efficiency [11].

The efficiency of dye adsorption depends, in large part, on the properties of the dye and the surface chemistry of the adsorbent [8]. Different interactions such as Van Der Waals, sigma-pi bonding, hydrogen bonding, and other surface phenomena make adsorption possible, and chemical alterations of surface chemistry strengthen these interactions, thereby rendering adsorption more effective [12]. Factors that can alter efficiency of dye adsorption include solution pH, initial dye concentration, adsorbent concentration, and temperature. The specific effects of these factors, however, varies between different materials and should be targeted to optimize AC production and use for treatment of specific types of wastewater [8].

Rahman et al. concluded that greater masses of rice husk-based adsorbent used correlated to higher MB removal rates, indicating that optimal adsorption can be achieved by increasing adsorbent mass [2]. Similarly, Pavan et al. found that higher pH (more basic) dye solutions corresponded to greater MB removal percentages, which may have been a result of interactions between the yellow passion fruit peel-based adsorbents functional groups and the cationic nature of MB [13]. Khodaie et al. found that increasing agitation rate up to 180 rpm also increased MB removal percentages [4].

To further increase usability of AC, decrease AC production costs, and lower AC waste production, desorption of used AC is gaining attention from many environmental engineers in an attempt to further decrease the amount of resources and energy required while maximizing the amount of dye-polluted water that can be cleaned per batch of AC produced. Desorption allows for AC to be reused at a high efficiency and can be carried out with chemical solutions such as HCl and NaOH [6]. The development of an efficient desorption process could vastly increase the efficiency of dye removal via AC.

This study sought to optimize the efficiency of MB removal using AC created from *Cucurbita pepo*. A two-step process to create AC from *C. pepo* was developed, followed by optimization of adsorption efficiency by

examining the effects of factors such as particle size, adsorbent mass, pH, and stirring treatment. Renewability of biomaterial via desorption and reusability efficiencies were also studied.

Based on previous research and literature, it was hypothesized that *Cucurbita pepo* will be most effective at decreasing MB concentrations with $1300°F$ carbonization and $ZnCl_2$ activation. It was also hypothesized that the smallest size fraction, longest period of stirring, acidic pH (pH 5), and highest adsorbent mass (0.5g) will be optimal for highest adsorption efficiency. Lastly, it was hypothesized that 1M NaOH with 100 rpm agitation will be most effective at desorption and the carbonized material will be reusable.

2. Methods

2.1. Experimental Overview

2.1.1. Pilot Studies

Prior to the beginning of experimental trials, an absorption spectrum for MB was created on a spectrophotometer to determine the optimal wavelength at which spectrophotometric analysis should be conducted. A Beers Law Plot was also created to analyze absorbance data for all trials.

2.1.2. Phase 1

Phase 1 examined the efficiency of MB adsorption via *Cucurbita pepo* given different adsorbent masses and activation methods. 50 mL of 4 ppm MB solutions and the largest size fraction (greater than or equal to 3.36 mm) were used in all trials. Three different masses (0.10 g, 0.25 g, 0.5 g) were tested with different chemical pretreatments (none, 0.1M/1M NaCl, 0.1M/1M $ZnCl_2$) in order to assess optimal adsorbent mass and treatment. 3 different thermal activation temperatures were also tested ($500°F$, $1000°F$, $1300°F$). Absorbance data was collected every 5 minutes for the first 30 minutes of the trial, at 24 hours, and at 48 hours.

2.1.3. Phase 2

Phase 2 examined the optimization of MB adsorption via *Cucurbita pepo* by finding optimal pH, adsorbent size fraction, and agitation conditions. 50 mL of 4 ppm MB solution and 0.5 g of adsorbent was used in all trials. The adsorbent was treated with the most efficient chemical treatment (1M NaCl) from phase 1. The pH of MB solutions was altered to 5, 7, and 9 via titration to examine the effects of pH on adsorption efficiency. The adsorbent was sieved into four size fraction variables: x <0.149mm, 0.149 mm <x <0.420 mm, 0.420 mm <x <0.841 mm, and mixed (unsieved). Agitation was altered in duration and vigor: none, in the first 40 minutes at 100 rpm, and throughout the whole trial at 100 rpm. Absorbance data was taken at the end of 30 minutes, at 24 hours, and at 48 hours.

2.1.4. Phase 3

Phase 3 examined and compared the efficiency of MB desorption using NaOH and NaCl and the reusability of desorped biomaterial. 1M NaCl or NaOH solution was utilized to desorp used AC (thermally activated, thermally

and chemically activated, and commercially produced) of the largest size fraction holding known quantities of MB. Agitation conditions were altered (no stirring or 100 rpm stirring) for each desorption medium. The resulting desorbed biomaterial was then reapplied to 30 mL of 20 ppm MB solutions in 0.5 g masses until saturation was reached. Absorbances were measured after 30 minutes, 24 hours, 48 hours, and 72 hours and translated to concentrations. MB removal rates were calculated and compared to initial MB capacities to determine reusability efficiency (%).

2.1.5. Follow-Up Studies

Adsorption capacities of thermally-treated, thermally- and chemically-treated (with and without environmental modifications determined by phase 2), and commercially-produced AC were studied via exposure to continuously renewed 30 mL of 20 ppm MB solution for 72 hours in 0.5g masses. Absorbance measurements were taken at regular 24 hour intervals and converted to concentrations to determine mass (mg) of MB adsorped, up to equilibrium.

2.2. Preparing Biomaterials

2.2.1. Initial Preparation

Squashes of the species *Cucurbita pepo* were obtained from local grocery stores, cut open, and cleaned of seeds inside. The remaining rind was washed and cut into cubes of consistent dimensions using a Mueller Austria onion chopper, obtained from Amazon.

2.2.2. Dehydration and Carbonization

The following procedures described are based on Mahamad et al. and Hussein et al. [7, 14].

The cubed *C. pepo* were separated into batches, spread evenly on trays, and put into the Excalibur dehydrator 3500W, Model Universal Product Code: 029743350029. The biomaterial was dehydrated at 130°F (55°C) for 6.5 hours or until fully dehydrated.

Dehydrated *C. pepo* were placed in evaporating dishes, and four evaporating dishes were placed in the Skutt Firebox 8 (kiln) per carbonization cycle. The kiln was turned to setting 2 and the temperature of the kiln was monitored with a digital pyrometer. When the desired temperature of 500°F, 1000°F, or 1300°F was reached, the kiln was continuously adjusted to maintain the temperature for 2 hours. The kiln was then switched off and left to cool for 30 minutes before opening. The dishes were removed after complete cooling, and the yielded AC was stored in ziploc bags in dark, cool, and dry areas until further processing or use.

2.2.3. Chemical Activation

The following procedures described are based on Satapathy et al. [15].

The 1M and 0.1M $ZnCl_2$ solutions were purchased from Carolina Biological, and 0.1M and 1M NaCl solutions were created from NaCl powder purchased from Sigma Aldrich. The AC was soaked in 50 mL of the appropriate chemical solution in 5 g masses for 2 hours. The mixture was filtered to separate AC from chemical solution, and

the resulting AC was allowed to air-dry for 24 hours.

2.2.4. Size Fraction Sieving

Chemically treated AC was sieved using the Carolina Biological Screen Sieve Set and stored in sorted plastic Ziploc bags in dark areas until their use. AC was separated into three different size fractions: x<0.149mm, 0.149 mm<x<0.420 mm, and 0.420 mm<x<0.841 mm.

2.3. Preparation of MB Solutions

The following procedures described are based on Mahamad et al. [7].

The 1% MB solution, purchased from Fisher Scientific, was diluted to create a MB stock solution of 20 ppm (mg/L). Solutions of 1, 2, 3, and 4 ppm were created by further dilution from the 20 ppm solution and used for pilot studies and trials.

2.4. Pilot Studies

2.4.1. Creation of Absorbance Spectrum

Absorbance spectrums were obtained using the UV-Vis Auto Scanning Spectrophotometer, Model UV-2602 to determine the optimal wavelength at which absorbance values should be taken for MB measurements. MB solutions of concentrations 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 ppm were tested, following protocols detailed in Spectrophotometric Analysis section below.

2.4.2. Creation of Beer's Law Plot

A Beers Law Plot was created using a program on the UV-Vis Auto Scanning Spectrophotometer, Model UV-2602 to correlate absorbance values to concentrations during data analysis. MB solutions of concentrations 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 ppm (mg/L) were used. Three trials were run and data was averaged and graphed on Microsoft Excel in a scatter plot to find a linear regression and corresponding r^2-value indicating fit.

2.5. pH Controls

The following procedures described are based on Han et al. [16].

The pH of 4 ppm MB solution after addition of AC was measured using a Vernier pH Probe. pH was manually titrated to 5, 7, or 9 (as needed in phase 2) using 0.1M NaOH and 0.1M HCl for each individual trial.

2.6. Agitation

The following procedures described are based on Mallampati et al. [17].

Agitation was conducted using a Corning PC-420D Digital Stirring Hot Plate. 50 mL glass beakers containing appropriate MB solutions and biomaterial were placed individually onto stirring plates. Agitation speed was set to 100 rpm. The duration of agitation was controlled by turning off the plate at specific times.

2.7. Desorption

The following procedures described are based on Pathania et al. [6]. Treated AC was repeatedly exposed to batches of 30 mL of 20 ppm MB solution until saturation (when solution color stops changing), and absorbance measurements were taken at 24 hour intervals. After saturation, the used AC, kept in batches from the previous process, were soaked in 1M NaCl or 1M NaOH for one hour. Each desorption chemical treatment was also treated with different stirring conditions (no stirring, 100 rpm). After desorption, AC was filtered and allowed to air-dry for 24 hours. The fully desorped AC, in original batches, was then repeatedly re-exposed to 30 mL of 20 ppm MB solution until saturation, and absorbances were taken at 24-hour intervals.

2.8. Spectrophotometric Analysis

The UV-Vis Auto Scanning Spectrophotometer Model UV-2602 was used to collect absorbance data. Following the device manual, the Spectrophotometer was first blanked with a cuvette of distilled water. Cuvettes containing MB solutions were then placed into the spectrophotometer for analysis. The appropriate program (absorbance spectrum, Beers Law Plot, etc.) was run.

For each sample, an absorbance spectrum was produced by the spectrophotometer and the absorbance value at the predetermined wavelength (668 nm) was recorded. This absorbance value was then matched to a concentration using the Beers Law Plot, produced during the pilot study.

2.9. Data Collection

2.9.1. Trial Set Ups

Trials were conducted in 50 mL glass beakers, and each trial utilized 50 mL of MB solutions of various concentration and appropriate masses of AC. During trials, beakers were sealed with parafilm, kept in constant room temperature, and exposed to normal light conditions.

2.9.2. Experimental Trials - Phase 1, 2, 3

Absorbance values were taken at appropriate time intervals, detailed in Experimental Overview, using the spectrophotometer. At the designated time intervals, samples of the experimental trials were pipetted out in adequate amounts from the surface of the solution. The sample was immediately filtered and the solid portion (AC biomaterial) of the sample was returned to the flask immediately while the liquid portion underwent spectrophotometric analysis before being returned to the flask.

2.10. Data Analysis

2.10.1. Percentage Removal - Phase 1, 2

The absorbance values taken at different times during each trial were converted to concentrations in ppm using the produced Beers Law Plot and recorded.

Percentage removal of MB dye was calculated with the following equation:

$$PE = ((C_0 - C_t)/C_0) * 100, \tag{1}$$

where C_0 and C_t are the initial and final concentrations (ppm) of dye before and after adsorption, respectively. Percentage removal was calculated for each trial for all times at which absorbance data was taken. The percentages were used in further analysis as an indicator of adsorption efficiency.

2.10.2. Desorption - Phase 3

The amount of dye (D) adsorped by AC was calculated per batch, defined as material used within one trial, with the following equation:

$$D = (20n + (C_0 - C_t)) * 0.03L, \tag{2}$$

where C_0 and C_t are the initial and final concentrations (ppm) of dye before and after the final desorption cycle, respectively, and n is the number of times the solution was renewed. MB content was calculated post-saturation and post-reuse for each trial in phase 3 and used to calculate reuse efficiency (R) with the following equation:

$$R = ((D_0 - D_t)/D_0) * 100\%, \tag{3}$$

where D_0 and D_t are the post-saturation and post-reuse MB contents in mg, respectively. The calculated reuse efficiencies were used in further analysis.

2.10.3. Dye Content - Adsorption Capacity Study

Dye content was calculated using the equation detailed above in "Desorption - Phase 3". The calculated dye contents were used in further analysis.

2.10.4. Data Analysis

All calculated percentage removals, final concentrations, phase 3 reuse efficiencies, and adsorption capacities were analyzed within relevant groups. Grouped data was run through a One-Way ANOVA followed by a Post-Hoc Scheffe with $p < 0.05$ on IBM SPSS version 25. All descriptive statistics (mean +/- standard deviation) were graphed with Microsoft Excel and statistical significances were denoted with color-coded asterisks.

3. Results

3.1. Absorption Spectrum and Beer's Law Plot

A spectrophotometric reading was performed and an absorbance spectrum was generated to determine the optimal wavelength at which MB readings should be taken at. Seen in the absorption spectrum displayed in Fig. 1, the peak at 668 nm was selected as the optimal for MB spectrophotometric readings, since low concentrations could still be accurately detected at this wavelength. A Beers Law Plot was generated to convert from absorbance
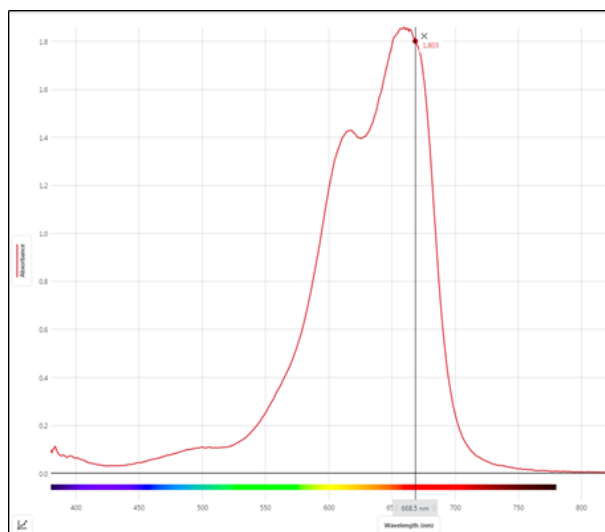
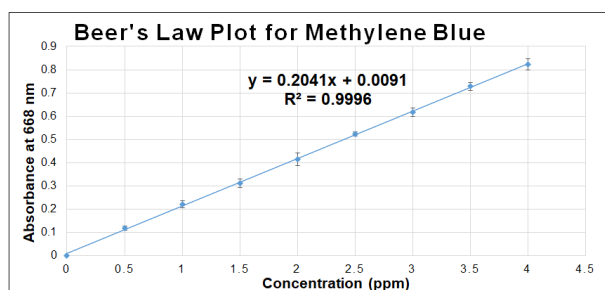**Figure 1.** Absorption spectrum of MB showing 668 nm as a peak.

Figure 2. **Beers Law Plot created by authors to convert absorbance values of MB at 668 nm into concentrations (ppm).**

to concentration (ppm), seen in Fig. 2, allowing equations 1 and 2 to be easily calculated for data analysis. The linear regression generated in Fig. 2 had an R^2 value of 0.9996, indicating a nearly perfect fit between the equation and data points and thus allowing for accurate conversions.

3.2. Phase 1

3.2.1. Thermal Activation

Shown in Fig. 3, which compares MB concentrations during treatment with AC thermally activated at different temperatures, 1300°F was the most effective in removing MB from solution. As denoted by the asterisks ($p < 0.05\%$) in Fig. 3, there is statistical significance between MB concentrations of solutions treated with AC activated at 500°F and 1000°F trials when compared to those of 1300°F during the first 30 minutes. However, as seen in Fig. 4, AC thermally activated at 500°F and 1000°F impart an undesirable color onto the solution and affected absorbance readings. This color impart prevents the process from generating potable water, the goal of
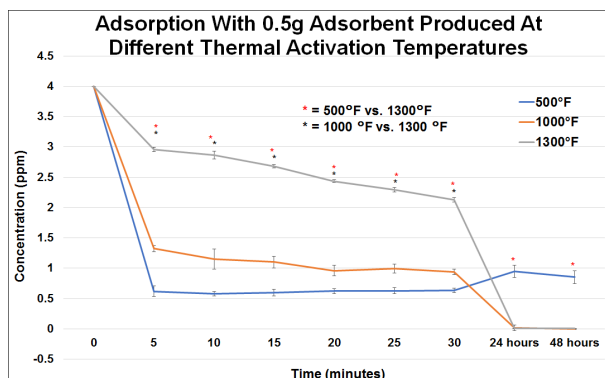
Figure 3. **AC activated at all 3 temperatures resulted in net decreases in concentration, and** $1300°$**F and** $1000°$**F appear equally effective. However, inaccuracies in measurements resulted from solution color changes at** $500°$**F and** $1000°$**F.**
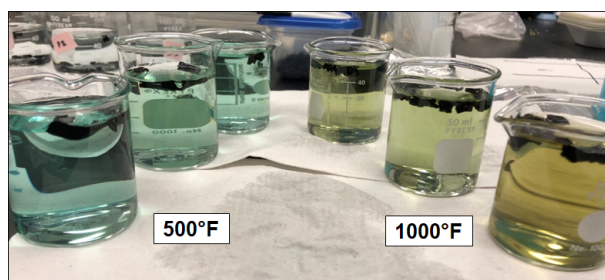

Figure 4. **Carbon activated at** $500°$**F and** $1000°$**F imparted a color into solution overtime (images taken at time** $t = 48$ **hours).**
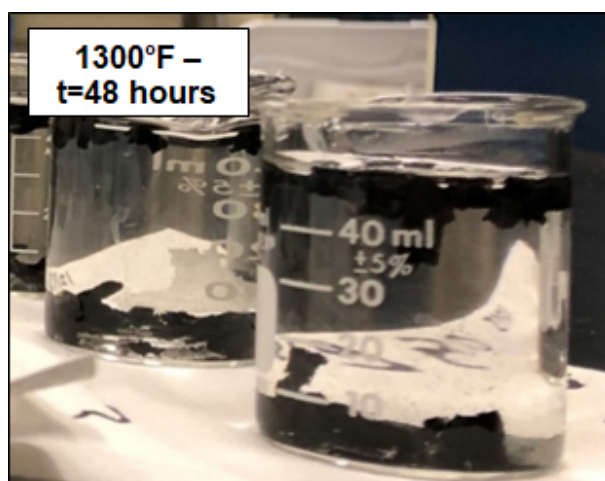

Figure 5. **Carbon activated at** $1300°$**F did not impart color overtime (images taken at time** $t = 48$ **hours).**

this study. Seen in Fig. 5, AC activated at 1300°F did not impart color into solution and reached a concentration of 0 ppm at 24 hours. 1300°F, thus, was selected as the optimal thermal activation temperature.
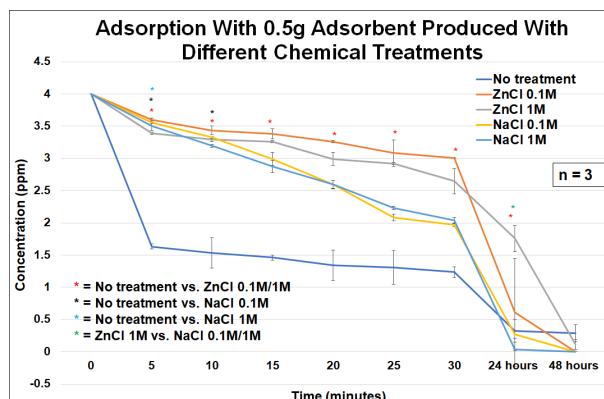
3.2.2. Chemical Activation

Figure 6. **No chemical treatment resulted in an overall trend of lowest MB concentrations but did not reach 0 ppm, however NaCl 0.1M, NaCl 1M, and ZnCl$_2$ 0.1M all reached 0 ppm by 48 hours.**

Fig. 6 compares MB concentrations during treatment with AC chemically activated with NaCl and ZnCl$_2$ at different concentrations. AC that underwent no chemical activation appeared to be most effective over the first 30 minutes of adsorption and displayed significance when compared to 0.1 and 1M ZnCl$_2$ chemical activation. After 24 hours, AC activated with 1M NaCl treatment resulted in 0 ppm MB concentrations (100% removal), which were significantly lower MB concentrations compared to those of AC with no chemical treatment. 1M NaCl appeared the most effective chemical treatment for MB adsorption, able to achieve 100% removal at the fastest rate.
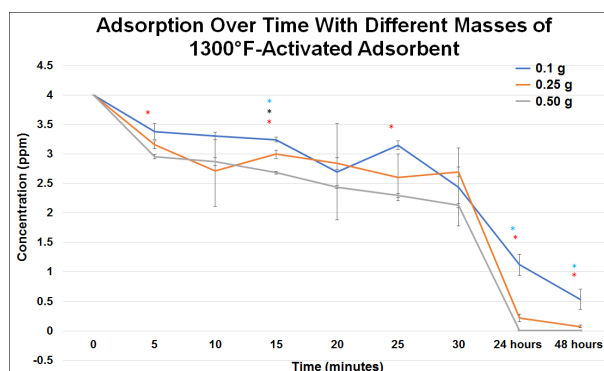
3.2.3. Adsorbent Mass

Figure 7. **Greater AC masses result in more stable removal of MB over time and highest MB removal rate after 48 hours.**

Fig. 7, which compares MB concentrations over time during treatment with different masses of AC, shows inconsistencies in adsorption curves of trials conducted with 0.1g and 0.25g AC but a consistent decline for those conducted with 0.5g AC. This consistent decline eventually reached 0 ppm (100% removal) by the end of 48 hours,

and treatment with 0.5g AC was significantly more effective than treatment with 0.1g and 0.25g AC.
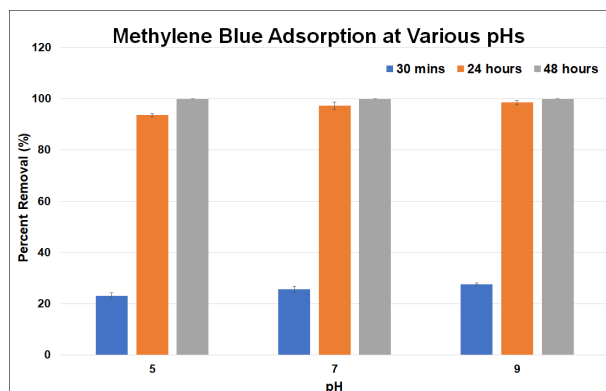
3.3. Phase 2

3.3.1. pH

Figure 8. **The pH 9 showed highest percent removal and pH 5 showed the lowest removal at 30 minutes and 24 hours, however at 48 hours, all pHs result in 100% removal with no deviation.**

Fig. 8, which compares percent removal of MB in solutions with varying pH, shows no significant difference in MB removal between adsorption in acidic, neutral, and basic solutions. After 48 hours, regardless of solution pH, 100% removal rate was reached and no statistical significance was observed between MB concentrations of different solution pH groups at any time during the trials. Hence, pH of the solution appears to have little to no effect on MB removal from solution using AC.
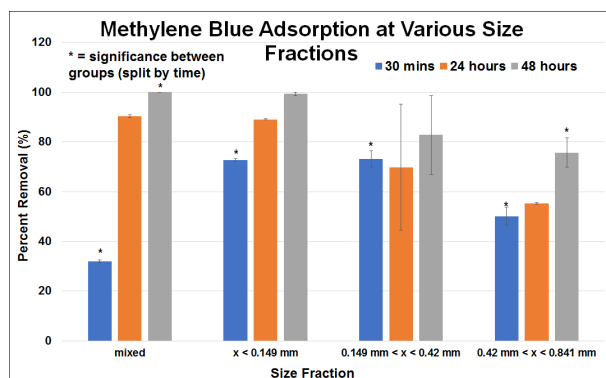
3.3.2. Adsorbent Size

Figure 9. **Mixed size fraction exhibited the highest final percent removal (100%), however significant difference was only observed at 30 minutes and between final mixed and largest size fraction percent removals.**

Fig. 9, which compares MB removal during treatment with AC of different size fractions, shows a significantly higher percent removal when comparing the three particle sizes to the mixed size during the first 30 minutes.

However, by 24 hours there was no significant difference between MB removal achieved by treatment with the three size fractions compared to that with the mixed size. At 48 hours, treatment with both the mixed size fraction and with the smallest size fraction (<0.149 mm) achieved 100% or near 100% MB removal. Treatment with the other two size fractions (0.149 mm<x<0.42 mm and 0.42 mm<x<0.841 mm) did not achieve similar results, with a maximum removal rate of slightly over 80%.
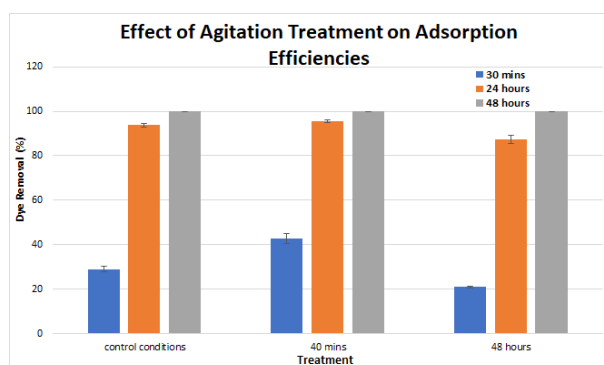
3.3.3. Agitation Duration

Figure 10. **At 48 hours, all agitation treatment groups achieved 100% MB removal.**

Fig. 10, which compares MB removal during treatment with various agitation durations applied, shows differences between different agitation durations within the initial 30 minutes of AC treatment, with the 40-minute treatment faring better than the 48-hour treatment. However, after 48 hours, all treatment groups reached 100% MB removal. Hence, agitation does not appear to have a significant effect on the adsorption of MB using AC.

3.4. Phase 3

3.4.1. Adsorption Capacity

It was determined that 0.5g of AC activated at 1300°F can remove 60 mL of 20 ppm MB solution successfully without any additional chemical or desorption treatments.

3.4.2. Comparison of Adsorption Capacity of Commercially and Self Produced Activated Carbon

Fig. 11 compares adsorption capacities of purchased commercially produced AC with AC produced in this study. No significant difference was observed between the adsorption capacities of only thermally activated AC and the dually thermally and chemically activated AC when compared to the commercial AC. However, there is a significant difference in adsorption capacity when comparing dually thermally and chemically activated AC with other modifications to commercially purchased AC.
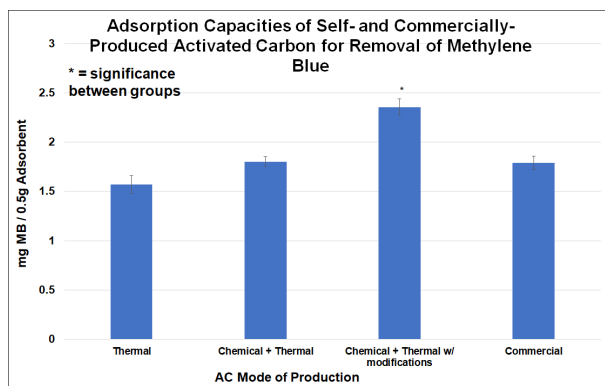
Figure 11. **Chemically and thermally treated AC with phase 2 modifications held the greatest adsorption capacity with significance.**
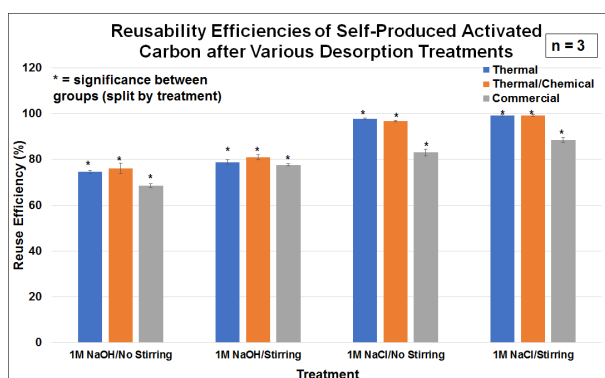

Figure 12. **1M NaCl desorption with stirring produced the most reusable AC, with nearly 100% adsorptive efficiency after reuse.**

3.4.3. Reusability

Fig. 12, which compares the reusability of commercially and self produced AC after different chemical and agitation desorption treatments, shows consistently higher reuse efficiencies of self-produced AC compared to commercially produced AC across all desorption treatments. Between the four treatments, 1M NaCl and agitation present appears to be most effective, with reuse efficiencies for all three AC types at their highest compared to the other three treatments.

4. Discussion

Results of the study partially supported the alternate hypothesis. Goals of the study were achieved, as phase 1 developed a two-step process of first thermal and then chemical activation that created efficient AC from *C. pepo*, phase 2 optimized physical factors for the most efficient use of the AC generated for MB adsorption, and phase 3 developed a desorption process for efficient reuse of the AC generated.

4.1. Phase 1

Results concluded that 1300° was the optimal temperature for thermal activation and NaCl at both 0.1M and 1M were optimal for chemical activation.

4.1.1. Thermal Activation

As the labeled pictures of Fig. 4 and Fig. 5 show, AC produced from pyrolyzation at 500°F and 1000°F imparted a brownish-yellowish-greenish color into solution upon exposure to 4 ppm MB solution. As a result, even though trends in Fig. 3 show 1300°F as corresponding to the highest MB concentrations and suggest that it is the least efficient temperature for adsorption, the apparent trend is likely incorrect. The color changes at 500°F and 1000°F decreased the accuracy of spectrophotometric measurements by adding unwanted color; spectrophotometric measurements rely on stable color to accurately measure absorbance at a selected wavelength. Clearly, 500°F and 1000°F are undesirable for thermal activation, as the color imparted into solution adds unwanted material to the water and creates further problems for purification. With 1300°F thermal activation, the optimal pyrolyzation temperature, 100% MB removal was observed at 24 hours, indicating high removal efficiency.

The color change caused by AC produced at the lower pyrolyzation temperatures can likely be attributed to partial pyrolyzation, which is the incomplete combustion and removal of excess organic material from the carbon-based skeletons of the activated material. The extra organic material present on the AC structures, when exposed to dye, caused unwanted dye-organic material interactions to occur, which manifested as a color change. Partial pyrolyzation is directly correlated to low temperatures, thus the higher temperature of 1300°F was necessary [10]. However, at temperatures that were higher than 1300°F, dehydrated *C. pepo* became ashy and fibrous and easily dissociated in water, unable to be used for adsorption. Thus, 1300°F is the optimal pyrolysis temperature.

4.1.2. Chemical Activation

As Fig. 6 shows, 1M NaCl and 0.1M NaCl treatment resulted in the lowest MB concentrations between 24 hours and 48 hours, with both reaching 100% removal by 48 hours. Compared to this, the untreated group fails to achieve 100% MB removal, and both 0.1M and 1M $ZnCl_2$ treatment are less efficient than the NaCl treatments.

The efficiency of NaCl, which contradicts previous literature reviewed, could be attributed to the activity of Na^+ ions and their possible participation in functional group optimization [4]. Na^+ is located higher on the elemental activity series than Zn^{2+}, the active ion resulting from dissociation of $ZnCl_2$, indicating that Na^+ is more active. Thus, Na^+ likely had greater possibilities and opportunities for interactions with functional groups present on the C. pepo adsorbent, leading to optimization and greater adsorption efficiency.

4.1.3. Adsorbent Mass

In general, greater adsorbent masses correlated to higher MB removal efficiencies and more stable removal of the dye. As shown in Fig. 7, 0.5 g resulted in 100% removal at 48 hours, while 0.25 g was slightly less efficient, though not significantly. This indicates that higher adsorbent masses are more efficient in general, which is likely

due to the adsorbents larger surface area and pore volume. Because adsorption relies on surface-based interactions to occur, greater surface area would increase the efficiency of adsorption.

4.2. Phase 2

In phase 2, results showed that neither agitation nor pH had any significant effect on adsorption efficiencies, while a mixed size fraction was most efficient for adsorption.

4.2.1. pH

As shown in Fig. 8, no significance was observed between MB removal efficiencies at each of the tested pHs when compared within corresponding time intervals. In addition, all pHs resulted in 100 +/- 0 % removal, further supporting the conclusion that pH does not affect adsorption efficiency. This contradicts previous literature reviewed [13]. The AC in this study is carbonaceous in nature, a result of its production from agricultural materials. The dominant presence of carbon, an element that is extremely versatile in bonding and rarely produces polar bonds, suggests that the AC particles are primarily relatively nonpolar. As a result, the presence of ions in solution - in the case of pH, the presence of hydrogen and hydroxide ions - would not interact extensively with the surface of the AC and thus would not have a great effect on adsorption efficiency. In comparison, if siliceous material were to be utilized, the dominant presence of -OH hydrogen bonds - a natural part of $SiOH_2$, which defines siliceous - would lead the material to be greatly influenced by changes in pH [18].

4.2.2. Size Fraction

As shown in Fig. 9, a mixed size fraction treatment produced the highest average MB percent removals at each time interval compared to that of all other size fractions. In addition, significance between MB percent removals of treatment with the mixed size fraction and other size fractions were observed. Large particle sizes have lower surface area due to less pore volume and lower pore counts, which does not favor adsorption, a surface-based interaction. However, as particle sizes decrease, the effect of the cohesion of individual AC particles becomes much more apparent, since the particles can adhere to each other much more efficiently as a result of finer particle sizes and more uniform shape. Dye particles are not able to efficiently interact with the surfaces of the AC, resulting in lower adsorption efficiencies. The mixed size fraction, with both large and small particle sizes present, reaches an interstitial optimization of both volume and surface area while simultaneously preventing excessive cohesion.

4.2.3. Agitation

Shown in Fig. 10, agitation treatment has no significant effect on MB adsorption efficiencies compared within time intervals. This contradicts previous literature reviewed [4]. Agitation is most necessary during adsorption when the AC used is completely solid and settles easily, causing clumping and a loss of accessible surface area. Because AC produced from carbonaceous material has a porous structure, as the material developed in this study most likely does, agitation is unnecessary to disrupt settling and allow for maintenance of accessible surface area for adsorption.

4.3. Phase 3

In phase 3, results showed that desorption could be applied to AC of 3 types (thermally activated only, thermally and chemically activated, and commercially produced) with near 100% reuse efficiency when conducted with 1M NaCl and stirring at 100 rpm.

Shown in Fig. 12, all treatments produced reuse efficiencies of at least 70%, with 1M NaCl and 100 rpm stirring treatment resulting in almost 100% reuse efficiency. The effectiveness of desorption is likely due to the altering of surface properties on the adsorbent by NaCl. Functional groups can be slightly further optimized on the adsorbent surface, which increases adsorption capacity beyond saturation [18]. The physical detachment of dye particles from adsorbent is not present or is negligible during desorption, because the desorption solution does not experience any color change. The increased effectiveness of NaCl compared to NaOH could, once again, be attributed to the greater suitability of Na^+ and Cl^- specifically for the surface functional groups of AC utilized in this study.

4.4. Adsorption Capacity

Comparing adsorption capacities of commercially and self produced AC from this study, it was found that though all ACs were effective, the capacities of thermally and chemically treated AC with extrinsic/environmental modifications (phase 2) was the highest, followed by only thermally and chemically treated AC, which had a comparable adsorption capacity to commercially produced AC. This indicates the extent of optimization provided by chemical activation, thermal activation, and any extrinsic/environmental modifications. The AC produced in this study clearly shows potential as an efficient adsorbent and usability for dye removal from water.

4.5. Implications of Cost and Accessibility

Cost efficiency is a significant factor in pollution control. Around the world, areas with the severest pollution are often located in underdeveloped or developing countries that lack the wealth and resources to afford sophisticated decontamination methods. The AC adsorbent produced in this study is highly cost efficient. NaCl, which was shown to be most effective for both chemical activation and desorption, is commonly known as table salt and is widely used globally with easy accessibility. The use of agricultural carbon-based waste material as the parent material of the AC accomplishes the goal of repurposing waste into more useful materials, thereby also increasing cost efficiency of AC production. Moreover, *C. pepo* has many varieties grown worldwide, which allows adsorbent production to not be limited by season or area and potentially be applicable for both large-scale industrial and household use.

4.6. Limitations

Due to the fluctuating nature of the kilns functioning, carbonization temperature was unable to always be controlled steadily - instead, a range of temperatures around the target temperature was achieved, which

may have caused error in precision. However, this makes the process more usable in an everyday setting, since an exact temperature is clearly not needed for efficient AC to be produced. A range of temperatures is much more easily achieved than a specific temperature. Moreover, the inability to directly examine pore structure and surface chemistry properties on the adsorbent severely limited the level of optimization that could be achieved. If chemistry properties or pore structure were better known, the processes of development and optimization (phase 1 and 2) could be altered for greater efficiency.

5. Conclusion

C. pepo is effective as a parent material for dye adsorbent, and results of the study also indicate potential for effective desorption and reuse. A pyrolyzation temperature of 1300°F and 1M NaCl chemical activation produced the most efficient adsorbent and were both necessary to create and optimize the porous structure of the adsorbent, which is extremely important for adsorption to occur. Alterations in pH and agitation did not significantly affect adsorption efficiency, while a mixed size fraction produced the highest adsorption efficiency. Overall, the adsorbent produced in this study is highly cost efficient, environmentally sustainable, and efficient for dye removal.

Conflict of Interest

Authors of this article declare that they have no conflict of interest.

Human Studies/Informed Consent

No human studies were carried out by the authors for this article.

Animal Studies

No animal studies were carried out by the authors for this article.

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