Preparation and Evaluation of *Terminalia catappa* Shell-Based Activated Carbon for Methylene Blue Dye Removal

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Abstract: Tropical almond (*Terminalia catappa*) is a large tree that is widely distributed in coastal environments throughout the tropics. In this study the feasibility of using *Terminalia catappa* shells as a cheap adsorbent for removing methylene blue dye in aqueous solutions was investigated. Two separate samples of activated carbon were prepared from the fruit shells of *Terminalia catappa* via physical and chemical activation, respectively. The specific surface area of the activated carbon prepared using physical activation was found to be 1095 m^2/g, while that prepared via chemical activation was 1613.4 m^2/g. The changes were due to different contact times and the dosage of the adsorbent in the adsorption process were investigated for both samples. The results showed that for both samples, increasing the contact time and adsorbent dosage resulted in a greater percentage of methylene blue dye being removed.
The highest percentage removal was achieved using the chemically activated carbon, which showed an exponential increase from 68.25% to 87.41% at 0 to 40 minutes and a small increment from 89.00% to 90.12% in the last 20 minutes. Similarly, the percentage removal also rose with an increase in the adsorbent dosage from 59.65% to 90.69% at 0.1 to 0.6g of the adsorbent. These findings suggest that *Terminalia catappa* shells is an efficient and cheap adsorbent that be used for the removal of methylene blue dye from aqueous solutions.

Keywords: Terminalia catappa, activated carbon, methylene blue, adsorption, specific surface area, contact time.

إعداد وتقييم الكربون المنشط المستند إلى غلاف *Terminalia catappa* لإزالة صبغة الميثيلين الزرقاء

الملخص: اللوز الاستوائي (*Terminalia catappa*) عبارة عن شجرة كبيرة يتم توزيعها على نطاق واسع في البيئات الساحلية في جميع أنحاء المناطق المدارية. في هذه الدراسة تم دراسة جدوى استخدام قذائف *Terminalia catappa* كمادة ماصة رخيصة لإزالة صبغة الميثيلين الزرقاء في المحاليل المائية. تم تحضير عينتين منفصلتين من الكربون المنشط من قشور ثمار *Terminalia catappa* عن طريق التنشيط الفيزيائي والكيميائي على التوالي. تم العثور على مساحة السطح المحددة للكربون المنشط المحضر باستخدام التنشيط الفيزيائي لتكون 1095 م 2 / جم ، في حين أن المساحة المحضرة عن طريق التنشيط الكيميائي كانت 1613.4 م 2 / جم. كانت التغييرات بسبب أوقات التلامس المختلفة وتم فحص جرعة المادة الماصة في عملية الامتزاز لكلتا العينتين. أظهرت النتائج أنه لكلتا العينتين ، أدى زيادة وقت التلامس وجرعة الممتزات إلى إزالة نسبة مئوية أكبر من صبغة الميثيلين الزرقاء.

تم تحقيق أعلى نسبة إزالة باستخدام الكربون المنشط كيميائيًا ، والتي أظهرت زيادة أسية من 68.25٪ إلى 87.41٪ في 0 إلى 40 دقيقة وزيادة صغيرة من 89.00٪ إلى 90.12٪ في آخر 20 دقيقة. وبالمثل ، ارتفعت نسبة الإزالة أيضًا مع زيادة جرعة الممتزات من 59.65٪ إلى 90.69٪ عند 0.1 إلى 0.6 جم من المادة الممتزة. تشير هذه النتائج إلى أن قذائف *Terminalia catappa* هي مادة ماصة فعالة ورخيصة يمكن استخدامها لإزالة صبغة الميثيلين الزرقاء من المحاليل المائية.

1. Introduction

Due to its significant inter-particulate surface area and a high degree of porosity, activated carbon is a commonly utilized adsorbent. There are several different kinds of activated carbon available, including granular, powdered, spherical, fibrous, and textile forms (Roop and Meenakshi, 2005). In contrast to the powdered form, which has reduced internal surface area and higher pore sizes, the granular form has a large internal surface area and few pores. In comparison, carbon fabric and fibrous activated carbons include a higher percentage of bigger pores and have a larger surface area (Roop and Meenakshi, 2005). (Meena et al., 2022) addresses the value of activated carbon in several environmental applications, including the cleaning of water and air, as well as its part in reducing climate change.
However, the steep price of activated carbon prevents its widespread use. Commercial activated carbon is produced using a variety of carbonaceous sources, including turf, lignite, nutshells, wood, and coal, to cut costs (Adinata et al., 2007). Making activated carbon from inexpensive components like agricultural byproducts could help to further cut its price. Concise research on an overview of the many agricultural waste kinds that can be utilized to create activated carbon, as well as the numerous activation techniques that can be used, has been conducted in recent years (Ahmad et al., 2021).

The article by Yan and Wang (2021) offers a thorough analysis of the uses of activated carbon for reducing air pollution. The potential of activated carbon as a useful remedy for removing several air pollutants, such as particulate matter, sulfur dioxide, nitrogen oxides, and volatile organic compounds, is examined by the authors. The article discusses the difficulties and potential future directions for the development and use of activated carbon in air pollution control and highlights the critical elements influencing the performance of activated carbon.

Research has focused on using synthetic materials to manufacture activated carbon in addition to natural materials. One such substance is *Terminalia catappa*, a big tropical tree found primarily in Asia, Africa, and Australia's tropical regions. Rich in carbon, the *plant Terminalia catappa* has been investigated to be a potential natural precursor for manufacture of activated carbon (Olatidoye et al., 2011). About 700,000 tons of this fruit are produced annually throughout the world (Olatidoye *et al.*, 2011).

Processes involving physical or chemical activation are used to create activated carbon. Using heated gases, the source material is transformed into activated carbon during the physical activation process. The gases are subsequently extinguished with the addition of air, resulting in a well screened, dedusted and fine grade of activated carbon.

(Acharya et al., 2021) offered a thorough analysis of the creation, characteristics, uses, and applications of activated carbon. Additionally, they go over the methods for the characterization of activated carbon and their uses in a variety of industries, including energy storage, wastewater treatment, and the reduction of air pollution. Production of activated carbon from inexpensive resources like agricultural waste has the potential to lower its price and make it more readily available for large-scale applications. It is encouraging that materials like *Terminalia catappa* can be used to make activated carbon.

2.0 Materials and Methods

2.1 Preparation of Adsorbents

Fruits of *Terminalia catappa* plant were gathered from within the campus of Ahmadu Bello University in Zaria. The shells were sun-dried for five days and then broken into smaller pieces. The shells were then burned for one hour in a box furnace at 300 ^{0}C. Smaller pieces of the carbonated materials were crushed. Two samples A and B were collected. Sample A was chemically activated, while sample B was physically activated. In sample A, 10 grams of KOH was dissolved in 40 mL of water to create KOH solution. The carbonized particles were then steeped in the KOH solution for 40 grams. The resulting material was put into a tube furnace and the temperature was raised to 400 ^{0}C, then steam was passed over, and Nitrogen gas to provide an inert environment for 1 h. After carbonization, sample B was physically activated in the same furnace at 600 ^{0}C with steam for a specified time of 1 hour 30 minutes without the addition of KOH.

2.2 Characterization of the adsorbents

Sear's Method for Surface Area Determination;

The Sear's technique was used to estimate the adsorbent's specific surface area (Jawad *et al.*, 2019; Ahmad *et al.,* 2013). 1.5 g of the adsorbent was weighed and acidified with dilute HCl (dropwise) using a burette until the pH was 4.0, then 30 g of NaCl was added to the solution whilst stirring, then water was used to make up the volume to 150 mL. 0.1 M NaOH was used to titrate the solution until the pH was 9. And the specific surface area S (m^2/g) was calculated using the relation;

$$S = 32 * V - 25 \qquad (1)$$

Where V is the volume of NaOH needed to raise the pH of the solution to 9.

2.3 Preparation of adsorbate solutions

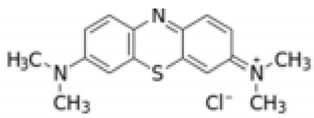

Fig. 1: The structure of Methylene Blue.

In a 1000 mL distilled water, 0.2 g of Methylene Blue was weighed and dissolved to make a 20 mg/L stock solution of Methylene Blue. A series of dilutions were performed to obtain a 10 ml volume of the diluted solution containing specific percentages of water and the original stock solution. The concentration of the new solution was obtained using the dilution formula

$$C_1 \times V_1 = C_2 \times V_2 \qquad (2)$$

A UV-visible spectrophotometer was used to record and measure the absorbance of each diluted solution.

2.4 Effect of operating parameters

The influence of interaction time and dose for the adsorption process of Methylene Blue on activated carbon were examined.

2.4.1 Effect of contact time

120 mL (from the stock solution) was measured and 0.6 g of the adsorbent weighed and dissolved in the new volume at a temperature of 25 ^{0}C. The mixture was stirred constantly using a magnetic stirrer and at different time intervals of 10 min each, 20

ml of the solution was taken, then a UV-visible spectrophotometer was used to record and measure the absorbance.

2.4.2 Effect of adsorbent dose

A volume of 20 mL (from the stock solution) was measured and a contact time of 20 min was kept constant. While the adsorbent doses were varied from 0.1 g, 0.2g, up to 0.6g for each 20mL at a temperature of 25 ^{o}C, and the absorbance was measured using a UV-Visible spectrophotometer.

3.0 Results and Discussion

Calculations show that sample A has a specific area of 1613.4 m^2/g as obtained using sear's method. Similarly, it was also discovered that the specific area of sample B as found to be 1095 (m^2/g).

3.1 Adsorption of Methylene Blue

A plot of Absorbance (nm) against Concentration (mg/L) was done using Microsoft Excel to obtain the Calibration curve as shown in Figure 3.1. It shows a standard curve (calibration curve) with an R^2 = 0.9939. Since the graph shows a linear relationship between absorbance and concentration.

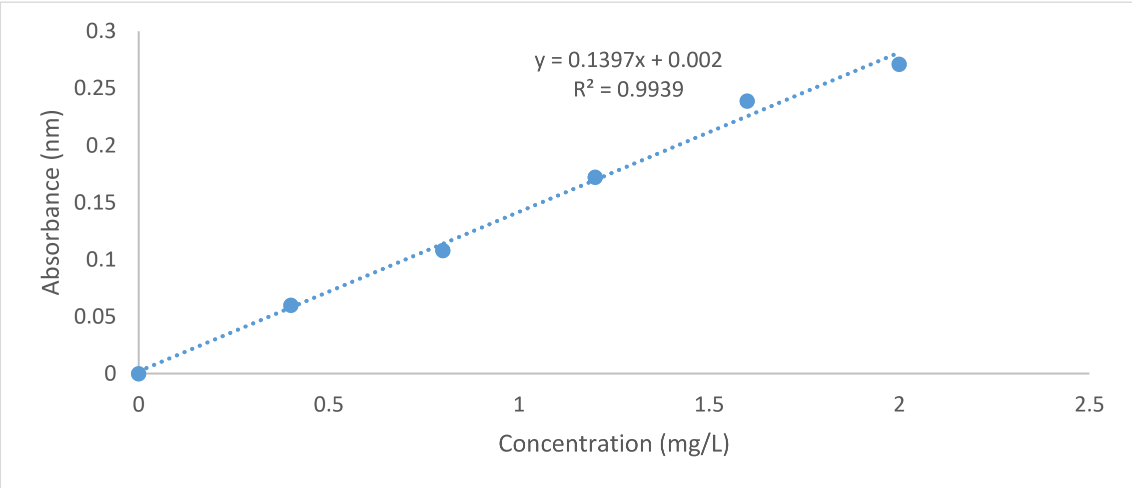

Figure 3.1: Plot showing the Calibration Curve

3.2 Effect of Contact Time on the Adsorption of Methylene Blue Using AC

The impact of contact time is depicted in Figure 3.2 and Figure 3.3, showing similar trend in this variation. It was observed that the rate at which the adsorption occurs rises as contact time increases. Initially, within the first 40 mins, an exponential increase in adsorption was reflected, and thereafter a steady state equilibrium was obtained in the last 20 mins.

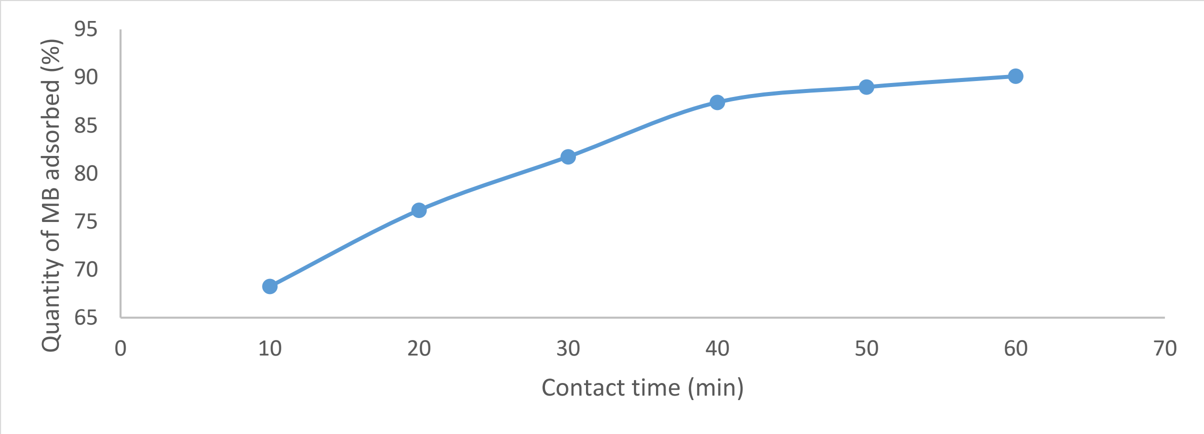

Figure 3.2: Impact of varying contact time on the adsorption process for sample A

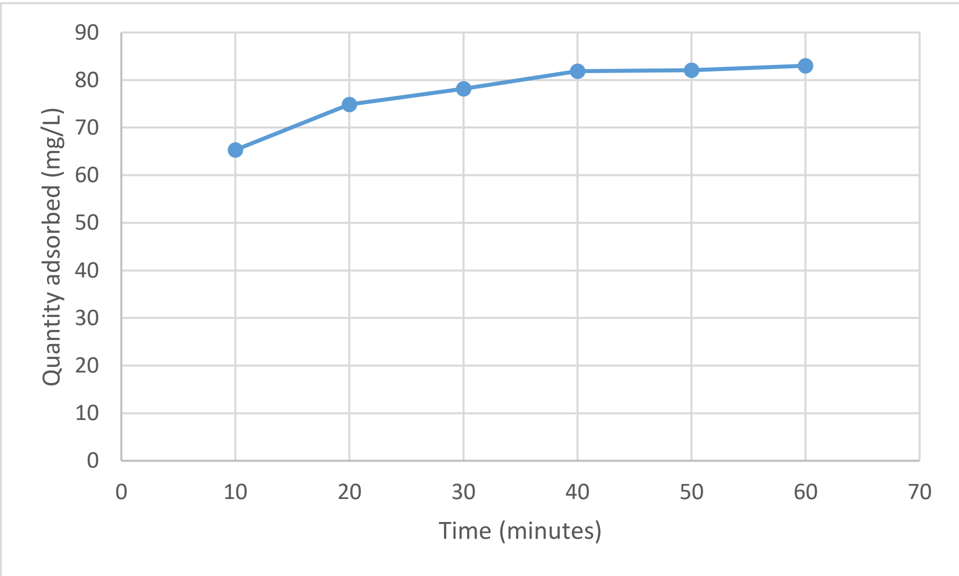

Figure 3.3: Impact of varying contact time on the adsorption process for sample B

The impact of varying contact time on Methylene Blue adsorption onto activated carbon is shown in Figure 3.3. The results show that equilibrium was reached at about 40 minutes, and that the dye elimination increased slightly increased with contact time. This phenomenon might be brought on by the earlier availability of a finite number of available sites, which over time gradually become saturated. Because there was a lot of existing and accessible surface area for the adsorption process at the beginning of the contact time, a high removal rate was seen; however, as time went on, the capacity of the adsorbent gradually became saturated. This is because the few remaining vacant surface sites became difficult to occupy due to the repulsive forces between the solute molecules in the solid and bulk phases. Various researchers have reported this trend in different literature, such as Mondal and Kar(2018).

3.3 Effect of Adsorbent Dosage

The adsorbent effect is depicted in Figure 3.3, which also displays the trend in this variation. Figure 3.3 demonstrates that from 0.1 to 0.3 g of the adsorbent, the amount of Methylene Blue adsorbed increased quickly from 59.65 to 85.23 percent. When the dose was increased from 0.3 to 0.6 g, the amount of Methylene Blue adsorbed became practically constant. The rise in adsorbent dosages may have increased the surface area and the number of adsorption sites, which may have contributed to the rise in the percentages of Methylene Blue adsorbed. The results in Figure 3.5, however, shows how the dosage affected the adsorption of methylene blue in sample B. According to the results, increasing the adsorbent dosage from 0.1g to 0.6g rose the percent removal from 55.23% to 86.96% as a result, more accessible sites are available to bind the methylene blue from the aqueous phase. These results are findings reported by Ai *et al.* (2011) and Li *et al.* (2013).

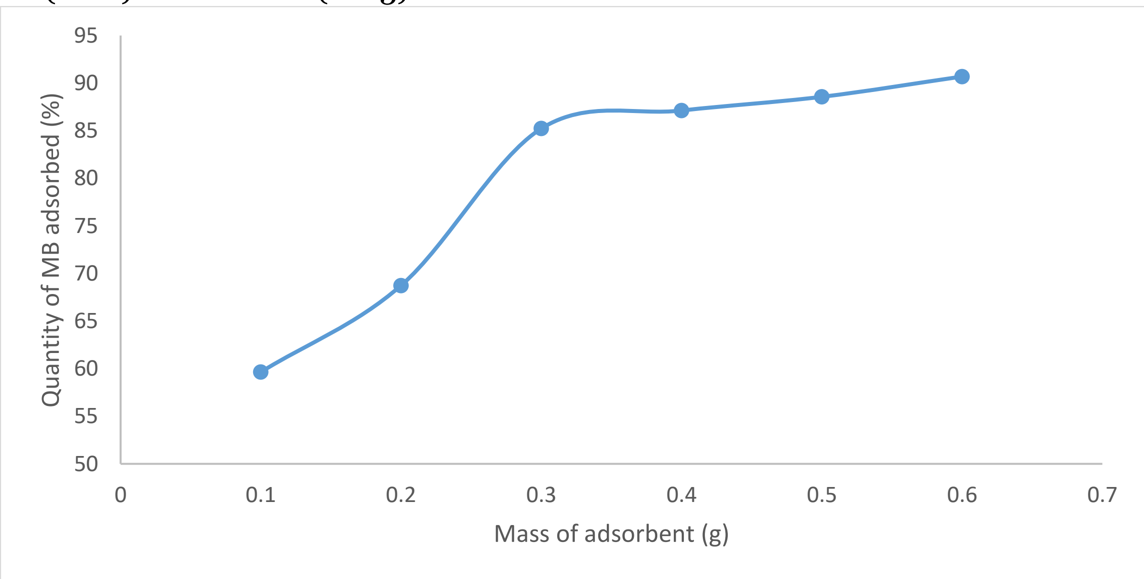

Fig 3.4: Impact of varying AC dosage on the adsorption process for sample A

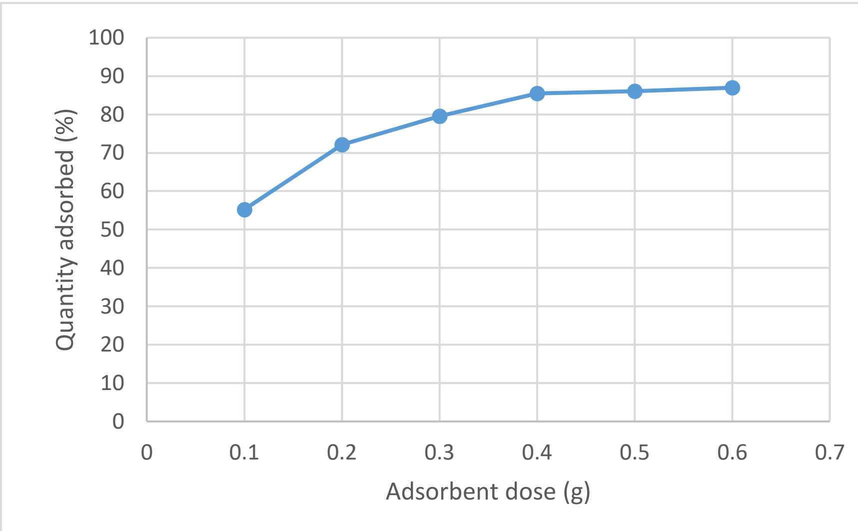

Figure 3.5: Impact of varying AC dosage on the adsorption process for sample B

4.Conclusion

The present work investigated the effectiveness of using *Terminalia catappa* shells as an activated carbon for the removal of Methylene Blue whether it is created using physical or chemical activation. The specific surface area characterization of physical

activation revealed an area of 1095 m^2/g, while the chemical activation demonstrated a specific surface area of 1613.4 m^2/g, which falls within the recommended range for adsorption (500 m^2/g to 3000 m^2/g).
Adsorption tests were performed on both the physical and chemical activated carbon to ascertain the impact of the interaction time and dosage on methylene blue elimination. The results showed that the contact duration generated an increase in removal percent from 65.32 percent to 83.01 percent, while an increase in adsorbent dosage caused an increase in removal percent from 55.23 percent to 86.96 percent.

Additionally, the quantity adsorbed by the activated carbon increased exponentially over the course of the first 40 minutes, from 68.25 percent to 87.41 percent, with a slight increment from 89.00 percent to 90.12 percent in the final 20 minutes. This pattern is explained by the rising adsorbate-adsorbent interaction with increasing contact time.

5.References

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