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# THE EFFECT OF HCl ACTIVATOR CONCENTRATION ON THE EFFECTIVENESS OF ACTIVATED CARBON DERIVED FROM CORNCOBS FOR METHYLENE BLUE ADSORPTION

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**ABSTRACT**

*This study aimed to investigate how activator hydrochloric acid (HCl) concentration affects the adsorption capacity of corncob-activated carbon in Methylene Blue (MB) dye. This was followed by immersion in HCl solutions with various concentrations (2.5 M; 3M; 3.5 M; and 4 M) as chemical activating agents. Next, FTIR and XRD were used to characterize the activated carbon that had been activated and unactivated. The study analyzed the reduction of methylene blue dye concentration in the air to evaluate the effectiveness of activated carbon as an adsorbent. It examined various factors influencing the adsorption process, including different initial concentrations of the azo dye (20 ppm, 30 ppm, 40 ppm, 50 ppm, and 60 ppm) and contact times (15, 30, 45, and 60 minutes). The experimental results indicated that a 3 M concentration of HCl was the most effective activator, leading to a maximum dye removal rate of 80.77%. For an initial concentration of 20 ppm of the azo dye, the highest adsorption results were achieved at 85.67%. Furthermore, the optimal contact time for maximum adsorption was found to be 30 minutes, with a peak adsorption rate of 70.08%. The Langmuir adsorption isotherm model demonstrated a better fit for the adsorption of methylene blue onto corncob-activated carbon. It can be concluded that activated carbon produced from corn cobs and treated with HCl is an effective adsorbent for reducing methylene blue levels in the solution.*

**ABSTRAK**

Penelitian ini bertujuan untuk mengetahui bagaimana konsentrasi aktivator asam klorida (HCl) mempengaruhi kapasitas adsorpsi karbon aktif tongkol jagung pada pewarna metilen biru. Metode yang dilakukan adalah dengan perendaman dalam larutan HCl pada berbagai konsentrasi (2,5 M; 3 M; 3,5 M; dan 4 M) sebagai bahan pengaktif secara kimiawi. Selanjutnya, FTIR dan XRD digunakan untuk mengkarakterisasi karbon aktif yang telah diaktivasi dan belum diaktivasi. Analisis penurunan konsentrasi zat warna metilen biru dalam air dilakukan untuk menentukan efektivitas karbon aktif yang dihasilkan sebagai adsorben. Faktor yang mempengaruhi proses adsorpsi, misalnya variasi konsentrasi awal pewarna azo (20 ppm, 30 ppm, 40 ppm, 50 ppm, dan 60 ppm) serta variasi waktu kontak (15, 30, 45, dan 60 menit), juga dibahas dalam penelitian ini. Hasil percobaan didapatkan konsentrasi HCl 3 M sebagai agen aktivator terbaik untuk menghilangkan metilen biru secara maksimal (80,77%). Untuk konsentrasi awal pewarna azo 20 ppm diperoleh hasil adsorpsi terbaik (85,67%), sedangkan pada waktu kontak 30 menit diperoleh adsorpsi maksimum (70,08%). Model isoterm adsorpsi Langmuir memberikan korelasi yang lebih baik untuk adsorpsi MB ke dalam karbon aktif tongkol jagung. Berdasarkan hasil tersebut, disimpulkan bahwa sampel karbon aktif dari tongkol jagung yang diaktivasi dengan HCl dapat menjadi adsorben yang baik untuk menurunkan kadar methylene biru dalam larutan.

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## INTRODUCTION

The textile industry and its products have experienced significant growth in early 2024. However, this growth has led to an increase in the production of organic waste from industrial processes, especially in the azo-dye group. The azo-dye group is known to have serious environmental impacts.

Most azo-dyes have complex and stable structures, often including aromatic compounds, making them highly resistant to decomposition through either chemical, physical, or biological treatment (Choi, 2019). Untreated disposal of azo- dye can lead to chromaticity, causing aesthetic discomfort (Ali *et al.*, 2023). In addition, these azo-dyes can hinder the penetration of sunlight through the water surfaces, resulting in decreased photochemical and biological activity of aquatic plants (Choi, 2019). Furthermore, azo-dyes have the potential to contaminate groundwater, posing a significant threat to the assimilation of organisms (Choi and Kim, 2016). A commonly used cationic azo-dye used for colouring in the textile industry and its products is methylene blue (MB). It is relatively affordable. It is known that cationic azo-dyes are more toxic than other types of azo-dyes. Prolonged exposure can cause life-threatening conditions such as increased heart rate, nausea, shock, cyanosis, jaundice, limb paralysis, confusion, eye burns, and necrosis of affected tissue (Fito *et al.*, 2023). Waste water containing MB must be treated before discharged into the aquatic environment to reduce the effects of MB on the environment.

The treatment of wastewater containing azo-dyes can be done through the highly effective adsorption process (Choi, 2019; Fajarwati *et al.*, 2020; Medhat *et al.*, 2021; Fito *et al.*, 2023) . Expensive commercial activated carbon is commonly used, but its cost is a drawback. Activated carbon from natural materials is more affordable, due to abundant availability of raw materials. In recent years, scientists have developed an interest in repurposing leftovers or by-products to make environmentally beneficial products. As a result, some industrial and agricultural leftovers have been converted into activated carbon. One of the raw materials for activated carbon developed is derived from corncobs. For the production of activated carbon used in industrial applications, corncobs are an attractive and sustainable resource (Marsh and Reinoso, 2006).

A number of variables, such as the raw materials used, activation procedure, and process parameters, affect the physical and chemical characteristics of activated carbon (Marsh and Reinoso, 2006). The preferred method is chemical activation as it requires lower temperatures and shorter activation times. For chemical activation, many different activating agents can be used, such as potassium hydroxide, sulfuric acid, phosphoric acid, and sodium hydroxide. Chemical reactions between the acid and the elements are a part of acid treatment. Changes in surface functioning, adsorption capacity, and structure result from the treatment (Wolak and Orzechowska-Zięba, 2024). Ash and other inorganics fill may decrease, inhibit of the surface or block the micropores of the existing network. Even before treatment, plenty of functional groups are present in a lot of Activated Carbon (AC). Even though some functional groups are destroyed during treatment, acid treatment may introduce new functional groups. The behavior of adsorption will also be altered

by these modifications to the surface functional groups (Ahmad *et al.*, 2013).

It has been proven that this modification is helpful in the removal of hazardous substances in the environment that have variety of chemical characteristics. Textural characteristics and surface functional groups, which are in turn substantially impacted by precursor type and activation method, have significant impact on the adsorption capabilities of AC (Charmas, Zięzio and Jedynak, 2023). Depending on the ash concentration and the available functional groups, different acid treatments will react in different ways, leading to varying outcomes. Oxygen functional groups including phenols, ethers, and lactones were observed to rise when AC was treated with HCl (Saadattalab *et al.*, 2023), and also increasing the BET surface area (Nuithitikul, Srikhun and Hirunpraditkoon, 2010). For some samples, such as coal treated with HCl solutions, this could also increase the capacity of $SO_2$ adsorption (Paluch, Bazan and Robert, 2023).

Based on the above, creating an affordable and environmentally friendly adsorbent for higher MB adsorption is essential. The aim of this study was to investigate how the effect of activator hydrochloric acid (HCl) concentration affects the adsorption capacity of corncob-activated carbon (CAC) on MB dye.

## METHOD

### Materials

The tools used in the research were an analytical balance (Electronic Balance JA3003), a 100 μm sieve, a porcelain grinder, a magnetic stirrer (Cimarec), a beaker (Herma), a measuring flask (Iwaki), a dropper pipette, a Mohr pipette (Iwaki CTE33 ashahi glass, made in Indonesia), a suction ball (D&N, made in Germany), a spatula, a UV-Vis spectrophotometer (722 Vis Spectrophotometer), a furnace (B-One operation manual mini muffle furnace mini 1210), an X-ray diffractometer (Bruker D2 Phaser), and filter paper. Then it was characterized using A Thermo Nicolet iS10FT-IR spectrophotometer was used to investigate the functional groups of corncob-activated carbon. The spectrophotometer was monitored between 4000 till 400 $cm^{-1}$. A X-Pert PRO PANalytical X-ray diffractometer (XRD) with a diffraction angle in the range of 5° - 60° was used to examine the crystal structures of corncob-activated carbon.

The research uses corncobs, an agricultural waste collected from local farm areas in Bojonegoro, using gloves and polyester bags. The corncobs used have a moisture and ash content of 6% and 2.89% by weight, meeting the Indonesian National Standard (SNI). First, the raw materials were washed with distilled water to remove surface dirt. Then, they were dried in the sun for 2–3 days, followed by dehydration in an oven at 120°C for 2 hours. The dried materials were then chopped, crushed, and sieved to a particle size of less than 2 mm. The activator agent in this study is E-Merck 37% hydrochloric acid, used without further purification. The other materials used in this research were methylene blue, and aquadest, filter paper whatmann.

### Methods

### Stages Of Making Corncob-Activated Carbon

Corncobs were washed with water. Then, they were cut into small pieces and heated in the sun. This was followed by heating in a furnace at 120ºC for 2 hours. This stage was called the dehydration stage. Next, the corncobs were carbonized by heating them in a furnace at a temperature of 600ºC. The dried carbons then crushed

and sieved with a 100 mesh size. This was followed by immersion in HCl solutions with various concentrations (namely 2.5 M; 3M; 3.5 M; and 4 M) as chemically activating agents. The mixture was filtered and washed with distilled water until the filtrate pH was neutral. After that, it was dried in an oven at 120ºC and placed in a desiccator (Medhat *et al.*, 2021; Wardani *et al.*, 2022). Next, the activated carbon was analyzed by XRD (X'Pert PRO PANalytical) and FTIR (Thermo Scientific Nicolet iS10).

**Stage of Activated Carbon Surface Area Analysis using Methylene Blue Dye Adsorption**

In this experiment, MB stock solution was prepared by dissolving 0.02 g MB in 1 L distilled water. Batch studies were conducted to investigate the effects of contact time and initial concentration of MB dye on the adsorption efficiency for MB. The contact times were controlled from 15, 30, 45, and 60 minutes to determine the effect of MB adsorption onto corncob. 0.5 g of corncob-activated carbon was placed in 25 mL of 20 ppm MB dye solution and the mixture was stirred with a magnetic stirrer with varying initial concentrations of 20 ppm, 30 ppm, 40 ppm, 50 ppm and 60 ppm MB solution. Furthermore, each mixture was filtered with Whatman paper No. 42. The concentration of MB dye remained in the sample then filtered and analyzed using spectrophotometric methods. An established MB calibration curve was used to calculate the concentration of MB. All experiments were repeated 3 times. This treatment was conducted following prior research by (Choi, 2019)

The amount of MB adsorbed by corncob was measured using a UV-Vis spectrophotometer (Shimadzu, MINI-1240) at 660 nm, which is the maximum absorption wavelength of MB. The amount of adsorption (q) was calculated using the formula (1) as following equation:

$$q = \frac{(C_0 - C_t)V}{m} \quad \ldots(1)$$

Here, $C_0$ (mg/L) was represent the initial concentration of the solution, $C_t$ (mg/L) was the concentration of the solution at time t, $V$ (L) was the volume of the solution, and $m$ (g) was the amount of corncob used.

The percentage removal of MB dye was calculated using the formula (2) as following equation:

$$\%\ Removal = \frac{(C_0 - C_F)}{C_0} x100 \quad \ldots(2)$$

Respectively, $C_0$ (mg/L) and $C_F$ (mg/L) were the initial and final concentration of MB dye in the solution.

## RESULT AND DISCUSSION

**Synthesis of Corncob-Activated Carbon (CAC)**

In this research, corncobs were used as raw material for the production activated carbon. Corncobs were previously carbonated using furnace at a temperature of 600ºC for 2 hours. This goal was to eliminate the volatile elements present in the corncob. Carbonization broke down organic compounds and resulting water, acetic acid vapour, tar, and hydrocarbons. After carbonization, the remaining solid material was transformed into coal with narrow pores. The reduction in mass before and after carbonization was significant, decreasing from 422.71 grams to 123.03

grams (a 70% reduction), indicating the decomposition of compounds.

The most important factor influencing the quality of activated carbon is its yield of carbonization. It is well known that a high yield of carbonization content is necessary for activated carbon to absorb multipollutants from wastewater efficiently and effectively. Because carbonous materials that can significantly contribute to the adsorption of various contaminants are referred to yield of carbonization. According to the research that has been done by (Fito *et al.*, 2023), for the adsorption, the yield of carbonization prepared content needs to be at least 60%. As a result, the yield of carbonization in present study as mentioned above.

The pore structure of the carbonization yield of activated carbon consists of various pore size distributions, including micropores, mesopores, and macropores. The distribution and connectivity of these pores directly influence the rate at which adsorbates diffuse to the adsorption sites. Additionally, the specific surface area and pore volume of activated carbon determine its capacity to adsorb specific substances. The pore structure also impacts the kinetics and equilibrium processes of adsorption. Furthermore, the surface chemistry of activated carbon is crucial in determining the selectivity and specificity of particular adsorbates (Li *et al.*, 2020; Phothong, Tangsathitkulchai and Lawtae, 2021).

To activate the carbon powder, we used varying concentrations of HCl (2.5 M, 3 M, 3.5 M, and 4 M). The activation process involved immersing the carbon powder in 200 ml of HCl solution and stirring it with a hot plate at a temperature of 200°C and a speed of 300 rpm for 4 hours. This process was carried out to enhance the interaction between the HCl solution and the carbon by providing heat energy, which increases the kinetic energy and facilitates HCl absorption into the carbon.

## Characterization of Corncob-Activated Carbon

### XRD

Crystalline materials hae a higher density than amorphous ones due to less free space and cavities. The extra space in amorphous materials increases their capacity for gas and liquid adsorption (Fito *et al.*, 2023). X-ray diffraction can used to describe the crystal structure of the activated carbon made from corncobs through the carbonization and acidic activation procedures, as shown in Figure 1. Both, unactivated carbon and activated carbon samples are broad peaks and the absence of sharp peaks indicates a dominant amorphous structure, possessing beneficial properties for well-defined adsorbents (Oday and Al-jendeel, 2024). The broad peak that was found in the diffractogram confirmed that the activated carbon has a high microstructure. This pattern is known to be the characteristic of amorphous carbon structures such as irregular graphite (Ramesh, Rajalakshmi and Dhathathreyan, 2017). According to (Prabu and Raghu, 2017), carbon with an amorphous compound structure has a turbostratic structure originating from graphite layers with a microcrystalline network (Prabu and Raghu, 2017). Also, the graphitic nature of the carbon material decreases as the chemical agent ratio increases, leading to an increase in material porosity (Ramesh, Rajalakshmi and Dhathathreyan, 2017).

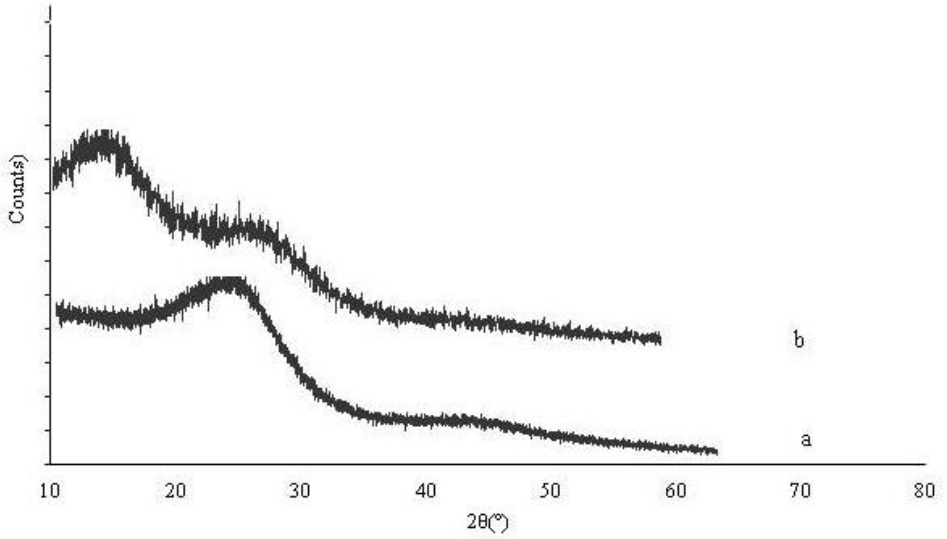


**Figure 1. XRD analysis of Corncob-Activated Carbon (a. before activation; b. after activation)**

The activated carbon made from corncob shown in Figure 1, both before (a) and after activation (b), has an amorphous form mostly due to the broadening of the background diffraction. The two broad peaks shown in the XRD test before activation (Figure 1.a) are located at 2-theta values of about 23.6° and 9.7°, respectively. while the broad peak of activated carbon after activation (Figure 1.b) has shifted with a 2-theta value of about 23.7°. This shift indicates the difference in the interfacial distance of carbon crystals. This interfacial distance is caused by the HCl activator (MFJDP Tanasale, Latupeirissa and Letelay, 2014). Acid treatments created a new porous structure. HCl can extract the primary metallic contaminants from the Corncob-Activated Carbon that dissolves in the acidic solution. The dispersion of the mineral affects how reactive the material is.

## FTIR

The surface functional groups of Corncob-Activated Carbon were analyzed by FTIR. This analysis aimed to determine the impact of unactivated corncob and the impact of employing HCl to corncob-activated carbon (Figure 2). According to the literature, the bands that appeared were associated with the stretching vibration peak of cellulose and hemicellulose. The peak at 1600, 1500, 1420, and 850 $cm^{-1}$ were typically for aromatic macromolecules (Jawad *et al.*, 2016; Oday and Al-jendeel, 2024). After activation, some of the reported bands have disappeared, which could be due to the carbonization or acid treatment of the corncob during the carbonization and/or activation processes (Figure 2 and Table 1).

The collected FTIR data generally signifies that the corncob-based activated carbon is plentiful with surface functional groups (Figure 2 and Table 1). The comparison of charcoal and activated carbon in Figure 2 also Table 1 reveals their remarkably similar properties. The FTIR analysis indicated the presence of OH and C-O bonds suggests that activated carbon tends to be more polar (Maulina and Anwari, 2019). Consequently, as a polar adsorbent, the polar groups usually facilitate water cluster formation that can be employed for water purification, sugar, alcohol, or as a formaldehyde emission absorber (Ahmad *et al.*, 2013). Also based on the literature, said that porous structure growth can be aided by a thorough debris removal using HCl pretreatment.

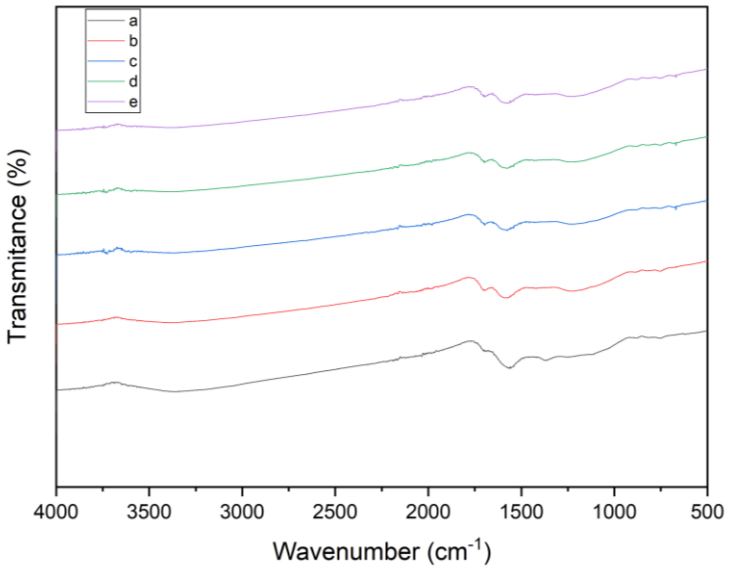


**Figure 2. Spectrum FTIR of Unactivated Carbon (a); Corncob-Activated Carbon HCl 2,5 M (b); Corncob-Activated Carbon HCl 3 M (c); Corncob-Activated Carbon HCl 3,5 M (d); Corncob-Activated Carbon HCl 4 M (e)**

**Table 1. Comparison of Functional Groups of Carbon Before Activation With Corncob-Activated Carbon**

| FT-IR Peaks ($cm^{-1}$) | | | | | Functional Group |
|---|---|---|---|---|---|
| Unactivated Carbon | HCl 2,5 M | HCl 3 M | HCl 3,5 M | HCl 4 M | |
| 666,67 | 667,72 | 666,98 | 667,95 | 668,10 | O-H bending |
| | 1227,76 | 1231,45 | 1230,86 | 1230,66 | C-O stretching |
| 1373,20 | | | | | C-H stretching |
| 1557,91 | 1574,36 | 1576,23 | 1575,09 | 1574,55 | C=C aromatic |
| | 1697,68 | 1694,54 | 1697,59 | 1697,62 | C=O stretching |
| | | 1979,14 | | | C=O stretching |
| 3363,30 | 3382,47 | 3370,15 | 3420,31 | 3419,56 | O-H stretching |
| | | 3649,15 | | | O-H stretching |
| | | 3725,98 | 3734,98 | 3734,53 | O-H stretching |
| | | 3839,79 | 3839,22 | | O-H stretching |

The impact of acid treatment on the structure of a certain material was investigated. Low concentration acid treatment did not create a new structure but did increase microporosity (Oday & Al-jendeel, 2024). The characteristic bands of carbonates at 1400$cm^{-1}$ were significantly reduced after the acid treatments, indicating the removal of carbonate impurities. Treatment at low concentration did not cause major changes to the structure of material but did eliminate carbonate impurities, thus increasing the surface area and pore volume. Also, the existence of various functional groups on the surface of the activated carbon is the significant condition for the successful adsorption of MB from industrial eluent (Fito et al., 2023).

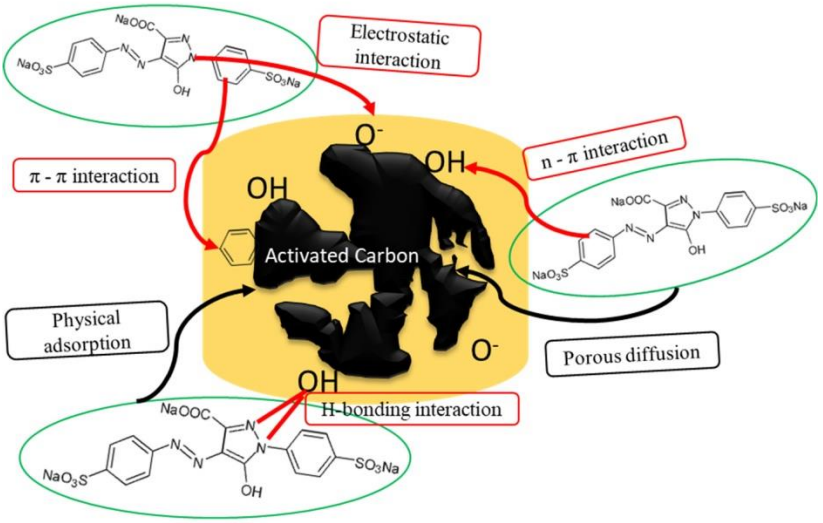


**Figure 3. Mechanism of Adsorbing Azo-Dye into Activated Carbon**

The initial stages of the interaction between activated carbon and poisonous dye particles involve surface contact and intra-particle diffusion mechanisms. On the surface of the activated carbon, a variety of absorption processes, including acid-base reaction, hydrophobic contacts, hydrogen interactions, π – π interaction, electrostatic interactions, and van der Waals forces may occur (Inagaki *et al.*, 2014). When employing activated carbon for dye adsorption, the most prevalent mechanisms are usually ion exchange and electrostatic attraction (Ali *et al.*, 2023). Ions in the azo-dye solution and the functional groups on the surface of activated carbon have the greatest impact on the adsorption mechanism. As a result, activating carbon's surface will enhance reactivity and boost azo-dye particle adsorption. Typically, throughout the adsorption process, several adsorption mechanisms take place concurrently. Possible dye adsorption instances are shown in Figure 3.

## Corncob-Activated Carbon for Methylene Blue Adsorption

### Adsorption Capacity

Determination of the adsorption capacity of corncob-activated carbon was carried out on samples without activation, sample with 2.5 M HCl, sample with 3 M HCl, sample with 3.5 M HCl and sample with 4 M HCl. Each sample was prepared for absorbance reading and have been done with triplo. test results are presented in the histogram of Figure 4.

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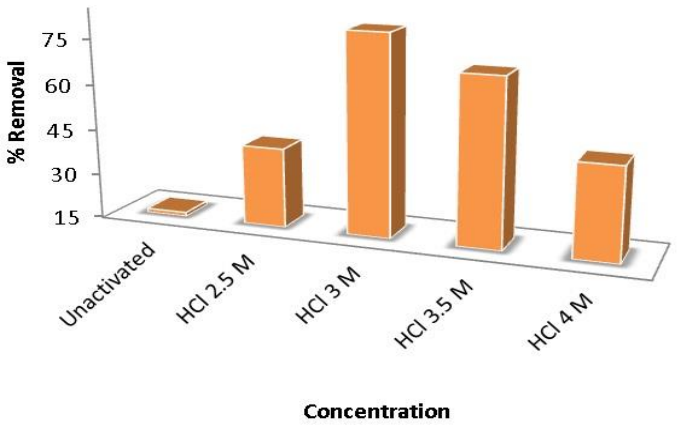


**Figure 3. Histogram of Adsorption Capacity of Activated Carbon Corncobs**

Based on the absorbance value of each sample, all of them tend to decrease in absorbance. This means that mass ratio and contact time influence the measurement of the adsorption of corncob on methylene blue dye. At 3 M HCl activation, the highest surface area was obtained, resulting in high adsorption as well.

## Effect of Contact Time

The contact time resulting in the maximum adsorption capacity is the equilibrium time. According to the collision theory, the speed of a reaction depends on the number of collisions at a contact time (Jawad et al., 2016). More collisions lead to a faster reaction until equilibrium is reached. The equilibrium state is when there is a balance between the rates of adsorption and desorption (Fito et al., 2023). Adsorption studies were conducted on corncob-activated carbon with respect to the uptake of Methylene Blue (MB). The impact of contact time on concentration differently prepared samples of activated carbon was studied for MB adsorption (Fig. 5).

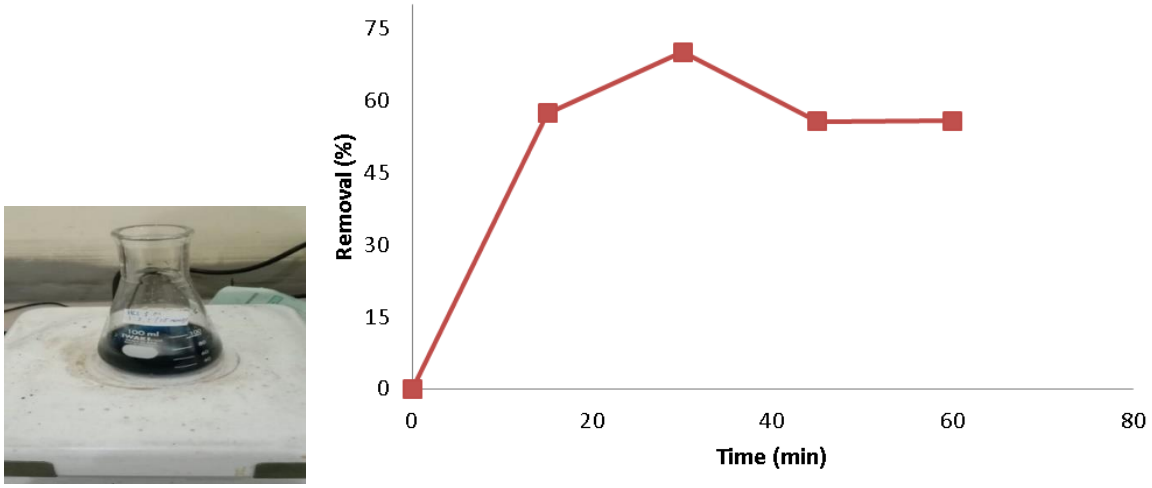


**Figure 4. The relation between percentage of MB removal vs adsorbent contact time (minutes)**

Figure 5 depicts the relationship between the percentage of MB removal and contact time. The results indicated rapid dye removal within the first 20 minutes, followed by a gradual increase in adsorption percentage until reaching the maximum slope. Subsequently, adsorption slowed down, reaching saturation within 45 minutes. The maximum removal efficiency for the samples was 57.3%, 70.08%, 55.61%, and 55.72%, respectively. Consequently, the best contact time on adsorption capacity and MB removal percentage was 30 minutes.

## Effect of Initial Concentration

The initial concentration of MB dye is a crucial factor in reducing the resistance to mass transfer between the corncob surface and the MB dye solution (Priyantini *et al.*, 2019). The rate of adsorption, adsorption capacity, and the cost of the adsorbent are all critical factors in choosing an adsorbent (Choi, 2019). The quantity of adsorbent used is also important in terms of cost. Having the ability to adsorb and eliminate large amounts of harmful substances using a small amount of adsorbent offers numerous economic advantages (Fito *et al.*, 2023). As a result, this experiment aimed to investigate the

concentration of MB that could be removed by the corncob adsorbent.

The impact of the initial dye concentration on the removal of MB dye by corncob is illustrated in Fig. 6. The results indicated that the corncob was capable of adsorbing a sufficient amount of MB dye at low concentrations, but its adsorption capacity decreased at higher concentrations. As a result, the percentage of MB removed decreases as the concentration of MB dye increases.

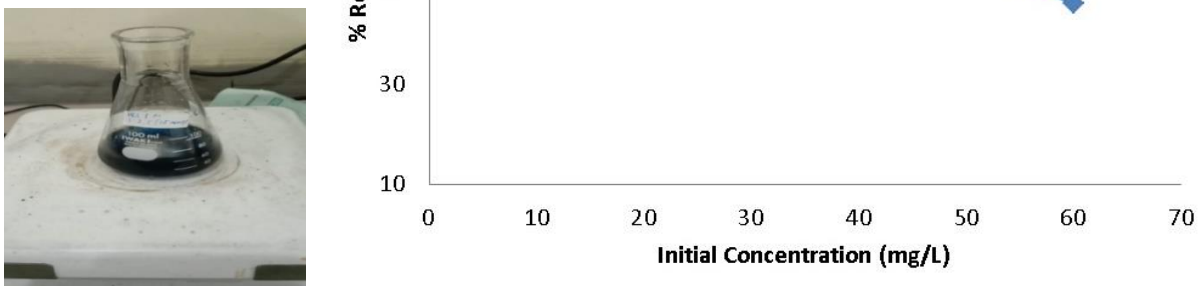


**Figure 5. The relation between the percentage of MB removal vs initial concentrations (mg/L)**

Figure 6 depicts the relationship between the percentage of MB removal and initial concentrations. At lower concentrations, fewer particle bonds among waste particles make the adsorption of waste particles to activated carbon more optimal. The adsorption process works best in gas and thin solutions, so lower solution concentrations lead to more optimal adsorption. The maximum removal efficiency for the samples was 85.67%, 77.67%, 64.39%, 55.58%, and 46.13%, respectively.

## Adsorption Isotherm

The interaction between the adsorbate and the adsorbent surface, maximum adsorption capacity, and dynamic equilibrium were studied using the adsorption isotherm model (Jawad et al., 2016). The best-fitted model provides information about the nature of the adsorption system. In this study, two models of parameters were used (Langmuir and Freundlich), to estimate the best adsorption isotherm model.

According to the $R^2$ value ($R^2 \approx 1$), the adsorption isotherm study indicated that the Langmuir isotherm model fitted better than the Freundlich isotherm model, suggesting monolayer heterogeneous surface of the adsorption active sites. It can be seen in Figure 7.

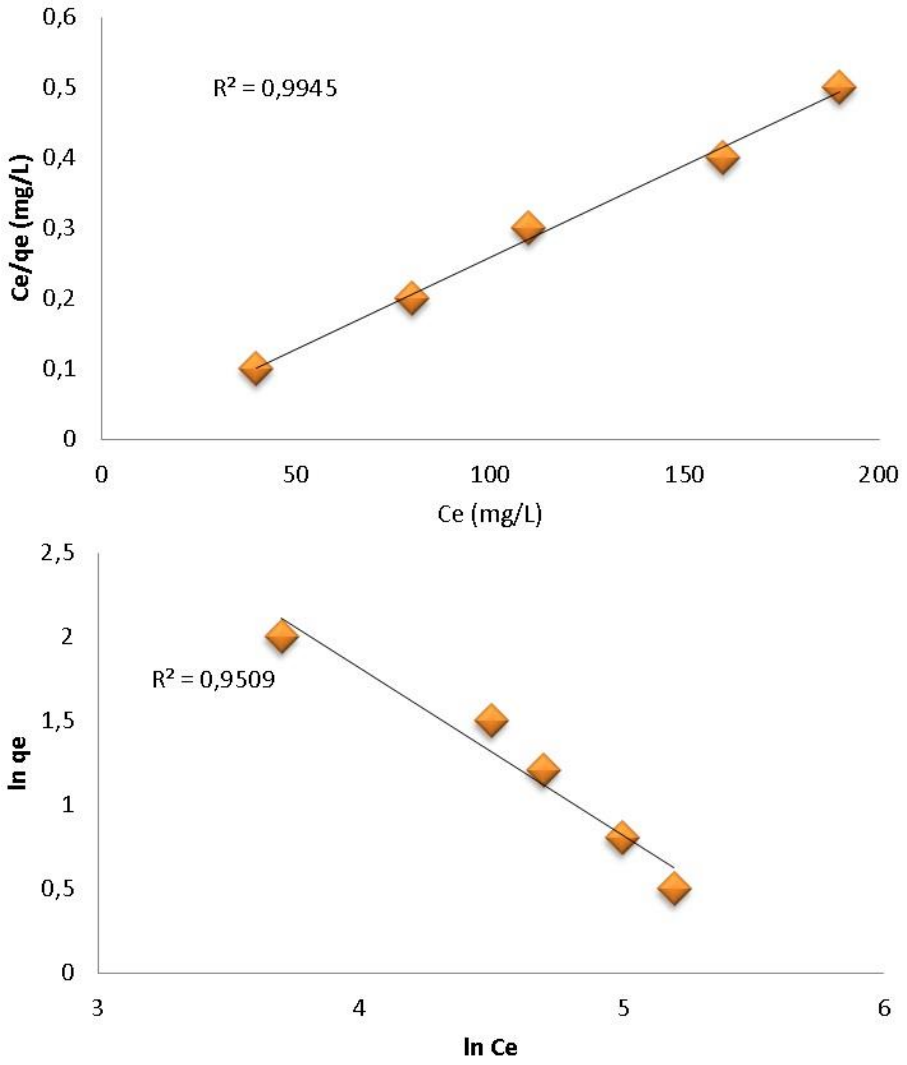


**Figure 6. MB adsorption with activated carbon (a) Langmuir isotherm plot; (b) Freundlich isotherm plot**

In the comparison of the maximum adsorption capacity of MB dye by agricultural byproduct adsorbents, the corncob showed higher adsorption than others. It was reported by (H. Choi, 2019)(Paluch et al., 2023)(Fito et al., 2023) . When agricultural byproducts were modified for dye removal, the efficiencies were higher than natural materials.

## CONCLUSION

In this study, activated carbon was successfully prepared with well-developed surface and adsorption capacities from agricultural waste, corncob. Using HCl as an activator agent. XRD and FTIR have been used to characterize the prepared samples. Experimental results showed that 3 M HCl activation attained a maximum removal of MB (80,77%). The contact time attained maximum removal at 20 mg/L (85,67%) and also initial concentration of the azo-dye attained maximum removal at 30 min (70,08%). The Langmuir adsorption isotherm model provided a better correlation for the adsorption of MB onto Corncob Activated Carbon. Based on these results, it was concluded that the activated carbon samples from corncob activated with HCl could be a favorable adsorbent for reducing Methylene Blue in solution.

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