

Enhancing Toluene Adsorption on ZnCl₂ One-Step Modified Corn Cob Activated Carbon

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ABSTRACT

Toluene, a hydrocarbon frequently found in water due to human activities and accidents like oil spills, can pose health risks, such as nervous system irritation and liver lesions. This study aimed to develop cost-effective adsorption techniques using activated carbon from corn biomass to remove toluene from water. The activated carbon, synthesized with zinc chloride surface modification and carbonization, was tested in a continuous fluidized bed column. The adsorbents effectively removed toluene, with optimal conditions identified as a bed height of 10 cm, a temperature of 30 °C, and a flow rate of contaminated water at 15 L/h. Operational parameters, like flow rates (15–25 l/h), bed heights (6–10 cm), and temperature (30–40 °C), were varied to assess their impact on toluene adsorption efficiency. Increasing flow rate and temperature reduced toluene removal, while higher bed height improved removal efficiency. However, column adsorption showed lower efficacy due to limited access of adsorbates to surface sites caused by low retention times within the column. On the basis of the breakthrough curve of 0.2 mm AC particles, the maximum adsorption capacity for toluene was 0.15643 mg/g with a total removal efficiency of 44.894%. The analysis, using various kinetic models like Thomas and Adams-Bohart, correlated strongly with the Thomas model ($R^2 > 0.89$), indicating Langmuir isotherm behavior and a second-order kinetic reaction. These findings demonstrate the potential of using the activated carbon from corn biomass in adsorption processes for removing toluene from contaminated water.

Keywords: corncob, zinc chloride, toluene, fluidized bed column.

INTRODUCTION

The global population is growing annually by 1.05%, set to surpass 10 billion by 2057. This growth directly correlates with an increase in per-capita waste generation, resulting in a rise in municipal solid waste (MSW) accumulation, which poses a significant challenge to environmental sustainability (Khan, et al., 2022a; Khan, et al., 2022b). Consequently, the release of MSW into the environment has become a major concern, particularly regarding water pollution, attributed to rapid industrialization and societal progress. Among the hazardous contaminants in water, toluene compounds stand out due to their toxic and carcinogenic nature (Yu et al., 2022; David and Niculescu, 2021; Rouf et al., 2022; Khan et al., 2021; Zhu et al., 2018). Even in minute

concentrations, as low as 0.01 mg/L, they can severely disrupt the biological functions of both terrestrial and aquatic ecosystems. This concentration not only alters the taste of drinking water significantly, but also poses a considerable risk to public health (Bandura et al., 2017; Fayemiwo et al., 2017). Consequently, stringent regulations have been implemented worldwide to limit the toluene concentrations in water and wastewater, necessitating their removal before discharge into the environment (Tursi et al., 2020). The primary sources of toluene contamination in water are typically associated with petroleum leaks from underground storage tanks, pipelines, or tankers (Melaphi et al., 2023; Mohammadi et al., 2020). Other contributing sources include municipal waste, industries such as petrochemicals, chemicals, printing, leather, rubber manufacturing, plastics decomposition, solvent use, agricultural

runoff, exhaust emissions, and petroleum leaks resulting from vehicular accidents (Bandura et al., 2017; Tursi et al., 2020). An effective method for treating the water contaminated with toluene is adsorption, a widely used technique, known for its high efficiency in removing organic contaminants even at low concentration levels (Li et al., 2020; Somma and Reverchon, 2021). Adsorption involves the attachment of contaminants to the surface of a solid material, termed an adsorbent (Anjum et al. 2019; Crini et al., 2019). This technique utilizes interphase transfer to remove surface-active materials and can be implemented by packing the adsorbent into columns or filters through which contaminated water flows. Carbonaceous sorbents are highly regarded as effective adsorbents due to their significant specific surface area, pore size distribution, well-developed microporosity, presence of surface functional groups, degree of modification, and regeneration capabilities, owing to their complex heterogeneous surface nature (Sen, 2017). In the current scenario, utilizing alternative low-cost adsorbents derived from natural sources can address the issues associated with commercial adsorbents, such as cost and the loss of 10–15% during thermal regeneration (Gayatri and Ahmaruzzaman, 2010; Tebbutt, 2013). Moreover, employing natural adsorbents offers environmental benefits, like reducing waste disposal and enhancing soil fertility by acting as nutrient-rich soil additives (Marcinczyk and Ok, 2022; Younas et al., 2021; Diatta et al., 2020). Corn cob is a byproduct that arises from the processing of corn. It represents the husk-like structure of the corn plant, serving as the support for the development of its yellow kernels. Every year, millions of tons of corn cob are discarded as waste, contributing significantly to environmental pollution. Hence, it is crucial to explore cost-effective ways to utilize this plentiful agricultural waste (Iheanacho et al., 2021). Studies indicate that the activated carbon derived from corn cob (CCAC) has demonstrated effectiveness in eliminating various aromatic volatile compounds pollutants from wastewater, including toluene (Zhu et al., 2018; Huang et al., 2024). Corn cobs are a promising and cost-effective option for removing toluene from wastewater, offering several key advantages. Firstly, they are abundantly available as a byproduct of the corn industry, making them sustainable and economical for wastewater treatment (Hien Tran et al., 2022). Their high surface area, reaching up to 903.7 m²/g, is due to their

porous structure, providing ample sites for toluene adsorption (Iheanacho et al. 2021). Moreover, their natural composition, with components like cellulose and hemicellulose, makes them non-toxic and biodegradable, ensuring environmental friendliness (Ashour et al., 2013; Farma et al., 2018). Additionally, corn cobs can undergo various modifications to enhance their adsorption properties, further improving their efficacy in toluene removal (Song et al., 2013). Studies have confirmed their effectiveness as adsorbents, showcasing high adsorption capacity and selectivity, making them a promising option for wastewater treatment processes (Zhu et al., 2018). On the basis of the above characteristics, this study aimed to prepare corn cobs-activated carbon (AC) that effectively adsorb toluene pollutants from contaminated water, mitigating their hazardous effects on the environment (Zhu et al., 2018). The study investigated the impact of different conditions, including temperature, bed height, and flow rate, on the removal performance of contaminated water in the course of the adsorption process. The purpose of this research stems from a comprehensive analysis of the current situation. It aimed to address the pressing need to find sustainable and cost-effective solutions for removing toluene, a toxic and carcinogenic contaminant, from water sources. By developing and optimizing corn cob-activated carbon as an adsorbent, the study intends to contribute to environmental protection, public health improvement, and advancements in wastewater treatment technologies.

MATERIALS AND METHODS

Preparation of the adsorbent

The process begins with the collection of corn cobs from local farmers' homes, specifically selecting the central section of the cobs for sample collection. These recently harvested corn cobs undergo washing and natural sun-drying on the ground to reduce moisture content. After sufficient drying, they are carefully stored in plastic bags and transported to the laboratory, where they are further dried in desiccators (Medhat et al., 2021).

In the laboratory, the corn cob samples are washed with distilled water to remove any remaining debris, dirt, or dust. They are then sun-dried for 48 hours and heated in a hot air furnace at 110 °C

for 2 hours to ensure complete moisture elimination. The dried samples are carbonized in an oven at 300 °C for 1 hour (Marlina and Putra, 2019; Viviani and Yanopa, 2023). This results in carbonized samples that are subsequently crushed and sieved into three sizes: 0.2 mm, 0.4 mm, and 0.6 mm. The carbonized corn cob samples then undergo an activation process, where they are immersed in saturated zinc chloride ($ZnCl_2$) for 8 hours with stirring (Marlina and Putra, 2019). After filtration and washing with distilled water, the samples undergo multiple washing and filtration stages at 50 °C to ensure complete removal of zinc chloride. The recovered activated carbon (AC) is dried in an oven at 150 °C for 2 hours and stored in an airtight container before use. Figure 1 visually represents each step of the manufacturing process of activated carbon from corn cobs, highlighting the detailed procedures followed in this study to produce the activated carbon that is used in subsequent experiments.

Column adsorption setup and studies

The biosorption experiments were conducted using a fluidized bed column. The schematic diagram of the apparatus is illustrated in Figure 2. The setup includes a 70 L feed tank to store the prepared stock solution contaminated with pollutants at a specific concentration for the intended experiment. PVC pipelines were used to connect the system and deliver the wastewater solution.

The column, made from Perspex material, had a height of 80 cm and an internal diameter of 5 cm. A stainless sieve of 1 mm was fixed at the column center to maintain a constant bed height and support the bed during continuous operation. The stock solution with fixed concentrations of 70 mg/ml was allowed to flow through the column using a pump (MARQUIS-MQS128, China). The flow rate was regulated using a valve and measured with a rotameter (Platon, France). Additionally, a second container of 30 L was used to collect the effluent solution.

The concentration measurement of pollutant in the effluents was performed using gas chromatography (GC). The experiments were carried to investigate the effect of changing a common operating parameters by determine the toluene removal efficiency ($Re\%$) which are defined by Eq. 1 (Iheanacho et al., 2021):

$$Re\% = \frac{MPAC}{MPLC} \times 100 = \frac{c_0 Q \int_0^t \left(1 - \frac{c_t}{c_0}\right) dt}{c_0 Q t} \times 100 \quad (1)$$

where: $MPAC$ – mass of pollutant adsorbed in the column (mg); $MPLC$ – mass of pollutant loaded in the column (mg); C_0 and C_t represent the pollutant concentration (mg/l) at entering and at sampling time (t , min) respectively. Q is the flow rate (l/min).

The characteristics of the breakthrough curves were examined under various operational

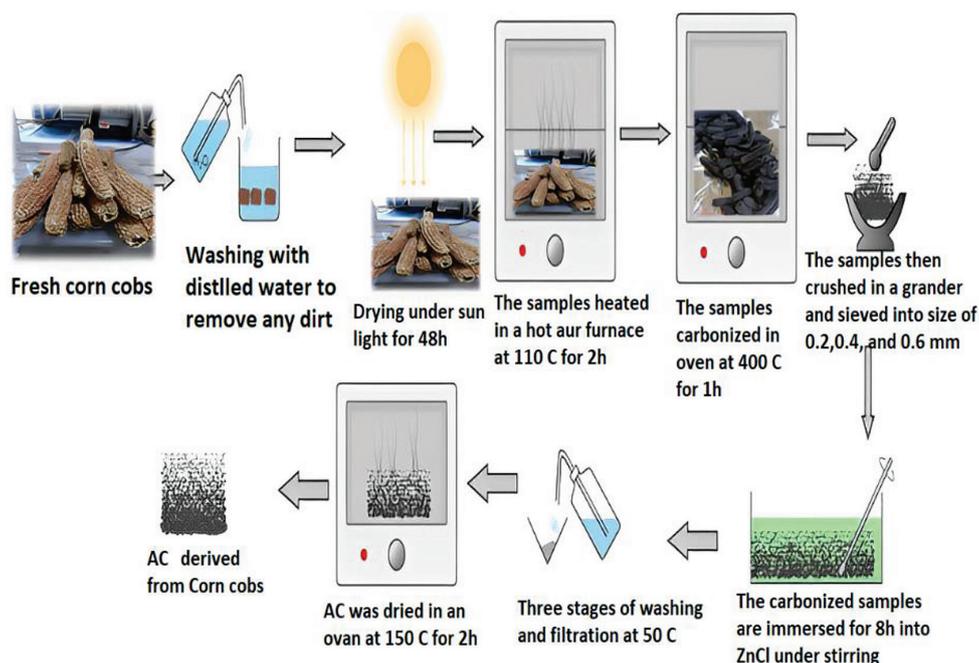


Figure 1. Preparation steps of AC

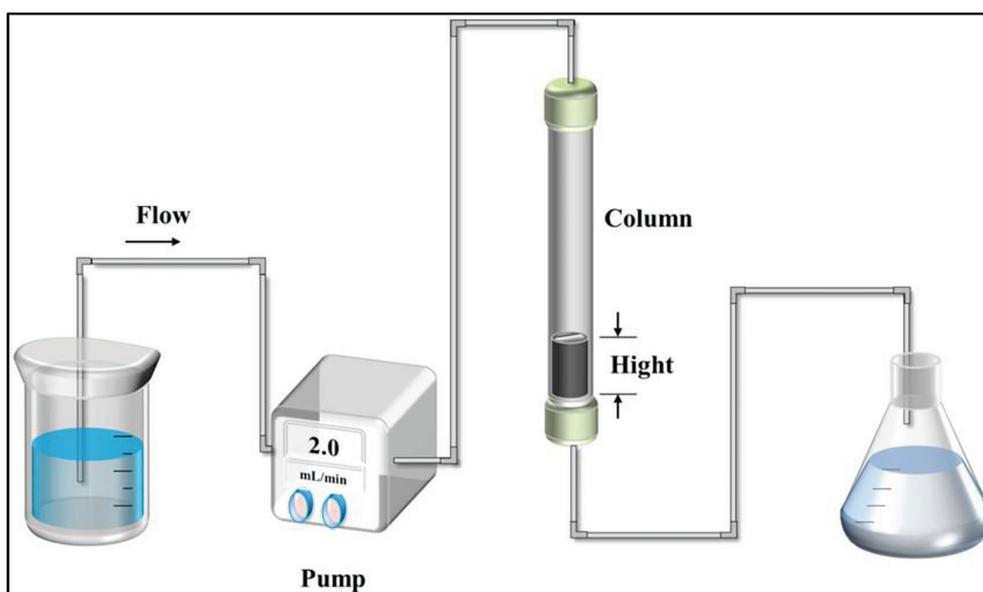


Figure 2. The schematic diagram of the adsorption system (Meina et al., 2024)

conditions by collecting samples at specific intervals until the adsorbents reached saturation. The column study was conducted with different process variables, including flow rates (Q), bed heights (Z), and temperature (T). The effect of particle size was separately investigated at the optimum condition within a range of (0.2–0.6 mm). Table 1 provides a comprehensive overview of the experimental setup and the conditions tested in each experiment regarding toluene adsorption on activated carbon from corn biomass. The experiments were designed to systematically investigate the impact of varying parameters on toluene adsorption efficiency.

RESULTS AND DISCUSSION

Bio-adsorbent characterization

BET analysis was conducted to determine the textural properties of the adsorbents, specifically the specific surface area and pore volume, with the results presented in Table 2. The surface areas for raw corn cobs were measured at $24 \text{ m}^2/\text{g}$, $21 \text{ m}^2/\text{g}$, and $6 \text{ m}^2/\text{g}$ for particle sizes of 0.2 mm, 0.4 mm, and 0.6 mm, respectively. Additionally, the pore volume results were recorded at $0.0031 \text{ cm}^3/\text{g}$, $0.0014 \text{ cm}^3/\text{g}$, and $0.0012 \text{ cm}^3/\text{g}$ for the same particle sizes. In contrast, the activated corn cobs exhibited significantly higher surface areas, measuring $245.12 \text{ m}^2/\text{g}$, $210.25 \text{ m}^2/\text{g}$, and $96.34 \text{ m}^2/\text{g}$

for particle sizes of 0.2 mm, 0.4 mm, and 0.6 mm, respectively. This indicates the successful enhancement of the adsorbents' surface area through the activation process, rendering them more effective in adsorption applications compared to their raw counterparts. The enhanced surface area resulting from the increased temperature (carbonized corn cob at $400 \text{ }^\circ\text{C}$) is attributed to the loss and volatilization of organic compounds, which leads to pore formation (Zhu et al., 2018; Yaashikaa et al., 2020; Yuan et al., 2019; Yahya et al., 2018). This

Table 1. Experimental conditions

Column internal diameter, cm	5
Column height, cm	80
Bed height, cm	6, 8, and 10
Flow rate, mL/min	15, 20, 25
Temperature, $^\circ\text{C}$	30, 35 and 40
Toluene initial feed concentration, mg/mL	70
Particle sizes, mm	0.2, 0.4 and 0.6

Table 2. BET analyses of adsorbents

Adsorbent	Particles size, mm	Surface area, m^2/g	Pore volume, cm^3/g
Raw corn cob	0.2	24	0.0031
	0.4	21	0.0014
	0.6	6	0.0012
Activated corn cob	0.2	245.12	
	0.4	210.25	
	0.6	96.34	

observation highlights the substantial impact of carbonization temperature on the textural properties of the activated carbons (ACs) (Zhu et al., 2018). The addition of ZnCl_2 during the activation process plays a crucial role in inhibiting tar formation (Neme, Gonfa, and Masi 2022). This inhibition prevents particle contraction, resulting in the formation of a wide and open microporosity with the presence of border micro-mesopores. This micro-structure enhances the pore volume and surface area of the AC derived from corn cobs, making it more efficient in adsorption processes. The wider and open micro-mesoporous structure provides abundant active sites for contaminant removal via adsorption, thereby improving the adsorption capacity and overall performance of the adsorbents in water treatment applications. The adsorption capacity of adsorbent materials primarily depends on their surface area and porous structure. A dehydrating agent like ZnCl_2 effectively eliminates volatile compounds from AC adsorbents. Additionally, it facilitates bond cleavage reactions through dehydration and condensation processes (Nahata, 2018). For the following experiment, particles with a size of 0.2 mm were used.

Parametric effect on toluene adsorption

The study on the parametric effect on adsorption focused on how varying operational parameters like flow rates, bed heights, and temperature impact toluene adsorption efficiency on the activated carbon from corn biomass. This analysis aimed to optimize the adsorption process for effective toluene removal from contaminated water, providing valuable insights for water treatment applications.

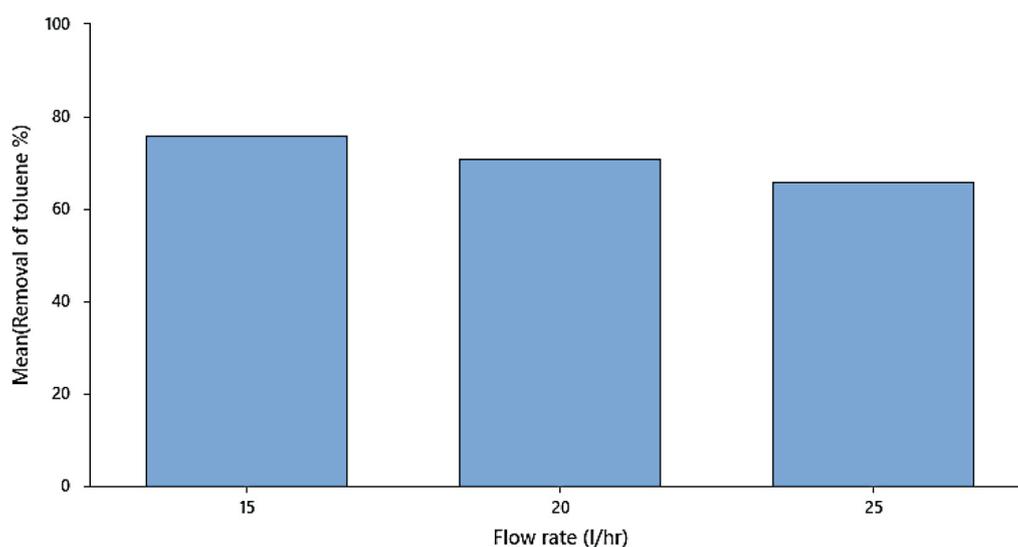


Figure 3. Removal of toluene with respect to feed flow rate using particle size of 0.2 mm.

Effect of feed flow rate

Figure 3 depicts the impact of feed flow rate on toluene adsorption within a fluidized column. Variations in flow rate can exert a substantial influence on the continuous adsorption process. The experimental setup involved conducting adsorption experiments across a range of flow rates, specifically from 15 to 25 liters per hour (l/hr). The findings indicate that a lower flow rate of 15 l/hr exhibited superior performance in toluene removal, achieving a removal rate of 75.8%. Conversely, increasing the flow rate to 20 l/h led to a decrease in toluene removal to 70.83%. Moreover, the highest flow rate of 25 l/h resulted in the lowest removal performance, with a removal rate of 66%. This behavior is attributed to the dynamics of higher flow rates, wherein the flow requires less time to infiltrate the pores of the adsorbent material. Consequently, this leads to reduced mass transfer and inter-particle diffusion. Essentially, the higher feed flow rate impacts the retention time of pollutants in the aqueous phase, diminishing the interaction between the surface of adsorbates and the adsorbents. As a result, this causes higher effluent concentrations prior to reaching equilibrium. Similar observations have been reported by (Iheanacho et al., 2021), (Ma et al., 2020), and (Hong et al., 2021).

Effect of temperature

Figure 4 depicts the effect of temperature on toluene adsorption. Changes in temperature can significantly influence the continuous adsorption process within the fluidized column. The adsorption experiments were conducted across a

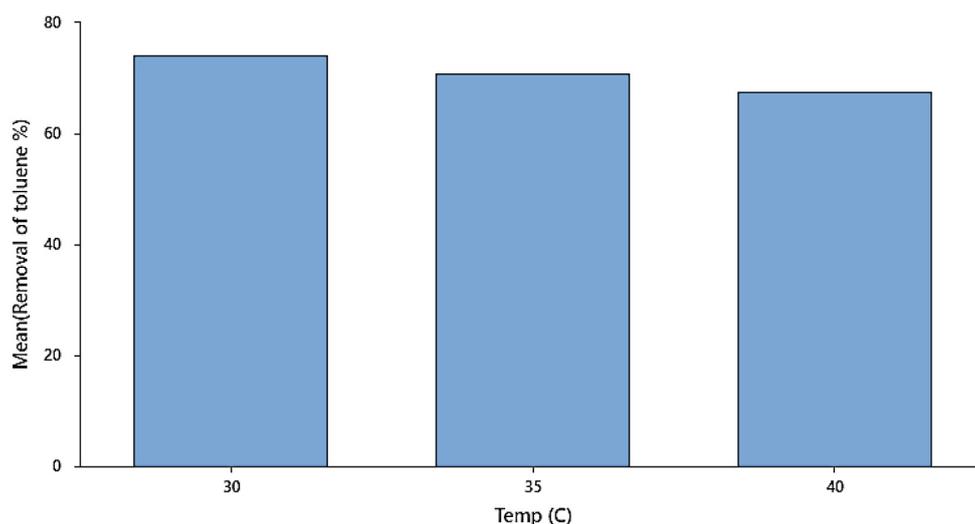


Figure 4. Removal of toluene with respect to temperature change using particle size of 0.2 mm

temperature range of (30–40 °C). The results revealed that the higher temperature (40 °C) exhibited the lowest performance, with a removal efficiency of 67.4667%. Conversely, the adsorption of toluene at (35 °C) increased to 70.933%. Furthermore, the lower temperature (30 °C) showed the best removal performance, with a removal efficiency of 74.23%. Although an increase in temperature enhances adsorption kinetics by providing more thermal energy for molecules to overcome activation barriers and adsorb onto surfaces, the experimental results suggest that a reduction in performance upon increasing temperature indicates that the adsorption processes may be exothermic in nature. In exothermic processes, heat is released as a byproduct of the adsorption reaction, making the adsorption process less favorable and weakening adsorptive forces. Additionally, at elevated temperatures, thermal energy can disrupt the attractive forces between toluene molecules and active sites on the adsorbent surface, leading to reduced interaction and lower adsorption capacity. According to the previous studies, adsorption uptake/capacity increases with the increment of temperature due to decrease affinity and active sites (Jodeh et al., 2015). For organic compounds, an increase in temperature causes a decrease in organic compounds and dissolved oxygen in water, in addition to diffusion transfer increase (Mohammadi et al., 2020). Furthermore, hydrophobic compounds like toluene tend to have lower solubility in the aqueous phase at higher temperatures. This decreased solubility can promote the release (desorption) of toluene back into the liquid phase, reducing the overall adsorption

capacity of the adsorbent. Additionally, as toluene becomes less soluble, other solutes may have a higher chance of adsorbing onto active sites of the adsorbent, leading to competing interactions, especially with water molecules, where organic adsorbents may absorb water as much as toluene, eventually reaching saturation. Similar observations were reported by (Hong et al., 2021).

Effect of bed depth

Figure 5 illustrates the effect of bed depth (amount of AC filled in the column) on toluene adsorption. Changes in bed depth can significantly impact the continuous adsorption process within the fluidized column. The adsorption experiments were conducted at bed depths of 6 cm, 8 cm, and 10 cm, equivalent to 52.98 g, 68.65 g, and 89.30 g of AC, respectively. The results revealed that the lower bed depth (6 cm) exhibited the lowest performance for toluene removal, with a removal rate of 61.633%. However, increasing the bed depth to 8 cm resulted in an increase in toluene removal, reaching 71%. Furthermore, the higher bed depth (10 cm) showed the highest removal performance, with 80%. This behavior can be explained by the fact that a taller bed increases the contact time between the adsorbent and adsorbates, thereby improving adsorption efficiency. Mass transfer can be enhanced by promoting better fluidization. In other words, a deeper bed provides a larger surface area by holding more adsorbent material, leading to a higher adsorption capacity to remove a larger quantity of toluene before the adsorbent material becomes saturated. A deeper bed also increases contact time and extends residence time, allowing more time for toluene molecules to interact

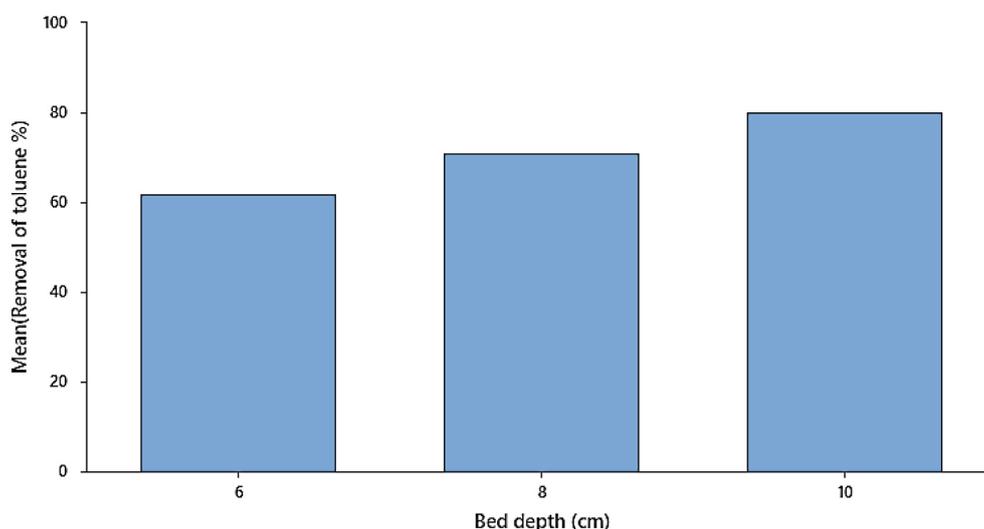


Figure 5. Removal of toluene with respect to bed depth change using particle size of 0.2 mm

with the adsorbent's active sites, which can lead to more comprehensive adsorption. Similar observations have been reported by (Iheanacho et al., 2021) and (Hong et al., 2021). Reaction time will also influence by longer bed height and enhance the adsorption uptake, where the longer contact times generally lead to higher overall adsorption capacities. However, it is important to optimize the contact time to balance efficient adsorption and practical considerations, such as process efficiency and cost (Kong et al., 2020).

Column performance

The breakthrough curves of toluene were used to assess the performance of the column. The breakthrough capacity, exhaustion capacity, and column utilization of the adsorbent column were evaluated

to understand how the column affects the adsorbent's adsorption capability. To analyze changes in the breakthrough curve (plots of C/C_0 versus time), three particle sizes were tested (0.2, 0.4 and 0.6 mm). The experiments were conducted under optimum conditions with a flow rate of 15 l/hr, temperature of 30 °C, and bed depth of 10 cm. Figure 6 presents the breakthrough curves derived from the column tests for toluene. The breakthrough point on the curve is identified as the moment when the effluent concentration (C_t) reaches approximately 10% of the influent concentration (C_0). The time at which this breakthrough occurs is termed the breakthrough time (t_b). The saturation time (t_s) is defined as the point when the effluent concentration reaches 90% of C_0 . Upon observing the behavior of the breakthrough curve

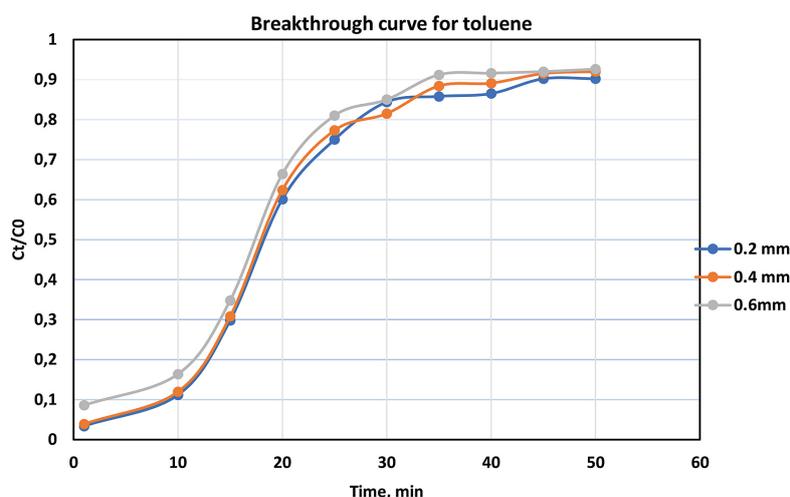


Figure 6. Effect of particle size on breakthrough curve for toluene removal by corn cobs AC adsorbent in continuous fluidized bed column –bed depth: 10 cm, influent concentration: 70 mg/m³; feed flow rate: 15 L/hr; temperature: 30 °C

shown in Figure 6, it can be concluded that both particle sizes of 0.4 mm and 0.6 mm have affected the time needed to achieve breakthroughs and caused a reduction in saturation time. However, the smallest particle size (0.2 mm) exhibits the best performance and may extend the saturation time. These behaviors result from the lower surface area of both 0.4 mm and 0.6 mm particles, which were measured at 210.25 m²/g and 96.34 m²/g, respectively, as indicated by BET analysis. Therefore, both sizes have fewer active sites for sorption due to the reduced surface area of the adsorbent. Furthermore, the 0.2 mm particle size depicts an enhanced surface area (245.12 m²/g) available for the interaction of the adsorbate and the adsorbent. Consequently, the time required to achieve the total capacity of the column was extended, leading to higher adsorption capacity during breakthrough and saturation, increased removal efficiency, and a larger volume of effluent treated at saturation. Table 3 show the parameters observed from breakthrough curve for corn cobs AC adsorbent. The 0.2 mm particles size corn cobs AC has much adsorption capacity for toluene than benzene.

Column kinetics study

Adsorption models have played a vital role in understanding and predicting the behavior of adsorption processes, especially in designing these processes by aligning them precisely with experimental data (Surkatti, Ibrahim, and El-Naas 2021). In this study, adsorption isotherms were employed to characterize the adsorption capacity of toluene on the surface of activated carbon derived from corn biomass. The Langmuir, Adams-Bohart, and Thomas models were utilized to describe the adsorption behavior. Figures 7 and 8 depict the adsorption models for toluene.

Thomas model

The Thomas model is commonly used to describe dynamic systems. It is based on the Langmuir isotherm and second-order kinetic models (Iheanacho et al. 2021). The proposed model for dynamic column adsorption research has the

ability to accurately estimate both the rate constants and the maximum adsorption capacity. The expression suggested by Thomas for the articulation of an adsorption column is presented in Eq. (2) below:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_{Th}q_{Th}M}{Q} - K_{Th}qC_0t\right)} \quad (2)$$

The determination of the adsorption capacity of column q_{Th} and the kinetic coefficient K_{Th} could be attained by analyzing a plot of the natural logarithm of $[(C_0/C_t)-1]$ as a function of time (t) under a specific flow rate condition, as illustrated in Figure 7. In the majority of situations, the analysis generated high correlation coefficient values ($R^2 > 0.89$), suggesting a strong fit between the experimental outcomes and the Thomas model.

Adams-Bohart model

The Adams-Bohart model presumes a direct correlation between the residual capacity, the adsorption capacity, and the initial pollutant concentrations. The Adams-Bohart approach is frequently employed to characterize the initial portion of the breakthrough curve, denoted as C_t/C_0 , as follows (Iheanacho et al., 2021):

$$\frac{C_t}{C_0} = \exp\left(k_{AB}C_0t - k_{AB}N_0\frac{Z}{v}\right) \quad (3)$$

In which, k_{AB} represents the kinetic constant (measured in L/(mg.min)), N_0 refers to the saturation concentration (measured in mg/L), v represents fluid velocity expressed as the volumetric flow rate per bed cross-sectional area (in centimeters per minute), and Z denotes the column bed depth (measured in centimeters).

The time range, denoted as “ t ” is considered from the initial breakthrough to the end. The values of k_{AB} and N_0 were estimated in the linear format by analyzing the slope and intercept of the linear graphs depicting “ $\ln(C_0/C_t)$ ” as a function of time, as illustrated in Figure 8.

By examining Adams-Bohart, the R^2 exhibited lower agreement compared to Thomas model and recorder ($R^2 > 0.749$). In this regard, the Thomas model is the closest to the experimental values, hence it is supposed that the adsorption mechanism

Table 3. Parameters determined from breakthrough curve for 0.2 mm AC particles.

Component	C_b (mg/m ³)	C_s (mg/m ³)	t_b , min	t_s min	Re%
Toluene	7.84	63.14	10	45	44.894

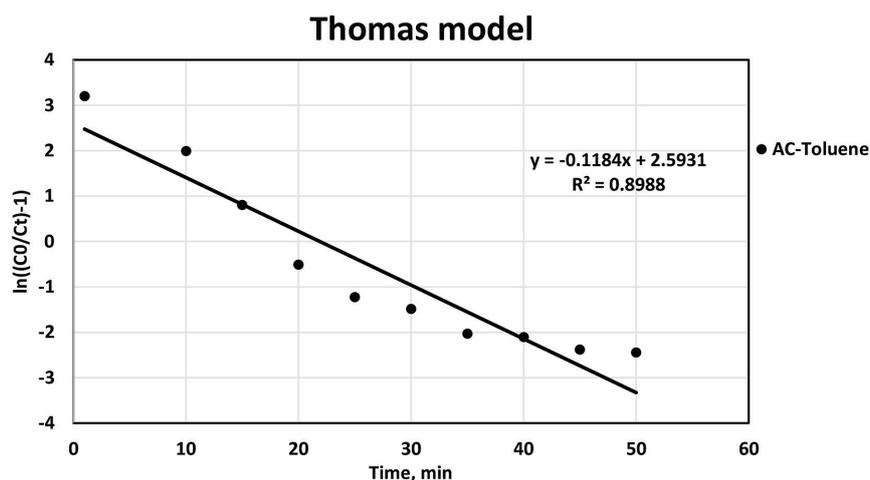


Figure 7. The plot of the measured breakthrough curves according to the linear form of Thomas model for toluene

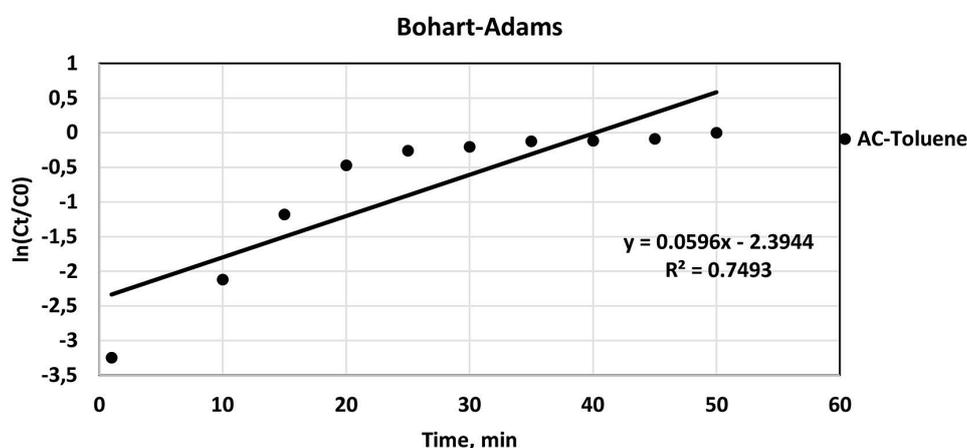


Figure 8. The plot of the measured breakthrough curves according to the linear form of Bohart-Adams model for toluene

was a Langmuir type adsorption followed by a pseudo-second-order chemical sorption (Villabona-Ortiz et al., 2022; Tofan and Suteu, 2023).

CONCLUSIONS

The study successfully developed cost-effective adsorption techniques using activated carbon from corn biomass to remove toluene from water. The activated carbon, synthesized with zinc chloride surface modification and carbonization, effectively removed toluene under optimized conditions: a bed height of 10 cm, a temperature of 30 °C, and a flow rate of contaminated water at 15 L/hr. Variations in operational parameters, such as flow rates, bed heights, and temperatures were systematically evaluated, revealing that increasing flow rate and temperature reduced toluene

removal, while a higher bed height improved removal efficiency. The analysis, employing various kinetic models like Thomas and Adams-Bohart, indicated strong correlation with the Thomas model ($R^2 > 0.89$), demonstrating Langmuir isotherm behavior and a second-order kinetic reaction. These findings contribute significantly to understanding adsorption processes and offer a practical approach for toluene removal from contaminated water using activated carbon from renewable sources.

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