

Removal of Organic Pollutants from Wastewater by Column adsorption process using Corncob activated carbons as adsorbents

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Abstract

This study focuses on using corn biomass-derived activated carbon to remove benzene and toluene (BT) from water, pollutants that are commonly found due to human activities and accidents like oil spills. The study explores cost-effective adsorption techniques and tests the activated carbon in a continuous fluidized bed column. Toluene is better adsorbed due to its lower solubility. Optimal conditions were identified: 10 cm bed height, 15 mL/min flow rate, and 30°C temperature. According to the breakthrough curve, the maximum adsorption capacity was 0.1447 and 0.15643 (mg/g) with total removal efficacies of 46.72% and 44.894% for benzene and toluene, respectively. The study shows the potential of this method for efficient BT removal, offering insights for water purification and environmental cleanup. Keywords: Adsorption, Corn cobs, Bio-adsorbent, Benzene, Toluene, Wastewater Treatment.

1. Introduction

Freshwater is a vital resource that is interconnected with various aspects of our world. Its availability is essential for human existence and the sustainability of the planet. Quantity and quality are crucial factors for freshwater, but despite water covering about 70% of the Earth, only 2.53% is freshwater, with less than 0.1% accessible for human consumption [1]. In recent decades, the world has witnessed serious challenges that threaten life, environmental diversity, and socioeconomic development, including water scarcity [2]. The rapid pace of urbanization and industrialization, and climatic changes has severely affected the amount of potable water around the world [3]. Considering an increase in the population growth rate, there is a severe concern that 3.5 billion people, or 48% of the world's population, may have insufficient access to water in the upcoming years and the amount of fresh water availability is expected to reduce with time, which will negatively affect the development in many countries [4]. Furthermore, there are various classes of contaminants found in water that contributed to worsen its quality. Thuse, consumption of untreated or partially treated wastewater contains harmful contaminants is primary reasons for the loss of human lives [1,5].

Mono-aromatic Volatile Organic Compounds (VOCs) such as Benzene and Toluene (BT) has involved in various industrial sectors due to their similarity characteristics and properties including the ability to quickly dissolve a wide range of organic compounds, the poor reactivity, the high evaporation rate, low or absence of corrosion against metals. However, discharge these compounds into the environment can cause dangerous effects on human health that make them considered by different national and international institutions priority cancer [12–14].

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contaminants [6]. Sources of water contamination with BT include petroleum spills or leaks, improper disposal of petroleum products, and industrial processes that use or produce petroleum products [7–9]. Groundwater and surface water can be contaminated by BT, and contamination can spread to nearby bodies of water, including lakes, rivers, and oceans [10,11]. Exposure to BT compounds can be inhaled through the air, ingested through drinking water, or absorbed through the skin [12]. Exposure to BT can cause a range of health problems, including damage to the nervous system, liver and kidneys, and increased risk of

Water contaminated with BT can be treated using a variety of methods, including activated carbon filtration, air stripping, and bioremediation [15-17]. The specific method used will depend on the type and concentration of contaminants, as well as the location and accessibility of the contaminated water [18]. Effective treatment of water contaminated with BT is important for protecting human health and the environment.

An effective method for treating water contaminated with BT is adsorption. Adsorption is a widely used and popular technique due to its high efficiency in removing organic contaminants at low-concentration level [19,20]. Adsorption has several advantages for BT removal, including high removal efficiency, low operating costs, and ease of use. Also, it is a physical process that does not require the use of chemicals or the production of harmful byproducts. Adsorbents can also be regenerated and reused, reducing waste and costs [6,21]. Therefore, this method is popular for both small-scale and large-scale water treatment systems [22,23]. Adsorption involves the attachment or adhesion of the contaminants onto the surface of a solid material called an adsorbent [17,24]. It is basically employing interphase transfer to removes surface active material. The adsorbent can be packed into columns or filters through which the contaminated water is passed.

As the water flows through the adsorbent, the BT molecules adhere to the carbon surface, effectively removing them from the water [22,25,26].

Carbonaceous sorbents are recognized as the most effective adsorbents for adsorption process due to their profound specific surface area, pore size distribution, well-developed microporosity, the presence of surface functional groups, degree of modification, regeneration, the complex heterogeneous surface nature [15]. Activated carbon (AC) is particularly favored for BT adsorption due to its excellent adsorption capacity and versatility [27]. It is commonly available in granular, powdered, or fiber forms [15,28–30]. Commercial activated carbon is commonly used as adsorbent due to high adsorption capacity with mean of (298.62 mg/g for organic pollutants) as result of highly porous nature with mean pore volume of $(0.71 \text{ cm}^3/\text{g})$ and high surface area with mean of $(844 \text{ m}^2/\text{g})$ [31]. However, using commercial activated carbon is costly and loss 10-15% during thermal regeneration [32,33].

In present scenario, alternative low-cost adsorbents derived from natural sources can solve many problems associated commercial adsorbents. The use of adsorbents derived from natural sources is gaining popularity due to several advantages over commercial adsorbents. Natural adsorbents are derived from renewable sources and are readily available, making them costeffective and environmentally friendly. They can be easily produced and can replace synthetic materials, reducing the dependence on non-renewable resources [24,30,34,35]. Natural adsorbents can be obtained from various sources, such as plant-based materials, agricultural waste, and animal by-products [31]. These materials have been found to have excellent adsorption properties, and their use can be optimized by modifying their surface properties through various treatments [27,36,37].

For instance, agricultural waste-derived ACs such as stones, husk, peels, leaves, shells, have been shown to have good adsorption capacity for organic and inorganic pollutants from wastewater including BT pollutants. These materials are abundant, rich in carbon content,

and can be easily processed into adsorbents with high surface area and porosity [31]. Similarly, natural clays, zeolites, fly ash, sawdust, miscellaneous, sludge have also been found to be effective adsorbents for BT [27,31,32]. Moreover, the use of natural adsorbents can also provide additional benefits, such as reducing disposal waste and improving soil

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fertility as a nutrient-rich soil amendment [32,38]. This study focuses on utilizing corn cobs, which are a readily available, low-cost, and underutilized plant material, as a biosorbent for the removal of BT compounds from aqueous solutions in a column system. The study examines the impact of different operating parameters, including temperature, bed height, flow rate and activated carbon particle size on adsorption process removal performance of contaminated water.

2. Materials and Methods

An agricultural solid waste (corn cobs) was collected from local farmers' households, deionized distill water, $ZnCl_2$, C_6H_6 , and $C_6H_5CH_3$, with high purities, were purchased from local market and used in this work. Table 1 illustrate the chemicals used in the present work. Table 1: Chemicals used in the present study

NO	Compound	ompound Purity		Supplier		
1	Zinc chloride	98%	ZnCl ₂	Thomas baker		
2	Distilled water		H ₂ O	Iraq		
3	Benzene	99.7%	C6H6	Alpha chemika, India		
4	Toluene	99.9%	C ₆ H ₅ CH ₃	Alpha chemika, India		

2.1 Preparation of adsorbents

The corn cobs are sourced directly from local farmers' households. For sample collection, the middle part of the corn cob is specifically chosen. To decrease the moisture content, the newly harvested corn cobs are naturally dried under sunlight on the ground floor. Once adequately dried, the cobs are sealed in plastic bags and sent to the laboratory, where they are stored in desiccators.

In the laboratory, the corn cob samples undergo washing process with distilled water to remove any remaining debris, dirt, or dust and followed with naturally drying under sunlight for 48h and then heated in a hot air furnace at 110 °C for 2 h to ensure the elimination of any moisture content. After drying, the samples are carbonized in oven at 400 °C for 1h. The samples then crushed in a grinder and sieved into three sizes 0.2 mm, 0.4 mm, and 0.6 mm mesh. The entire samples can be utilized as a substrate in the subsequent experiment.

Next, the carbonized corn cob samples were goes through activation process. Detailed procedures are described as follows. The carbonized samples are immersed for 8h into the saturated Zinc chloride, $ZnCl_2$, under simple stirring. Then the samples recovered by filtration and washed with distilled water at room-temperature. In order to ensure the zinc chloride was completely removed, the samples go through three stages of washing and filtration at 50 °C. The recovered activated carbon (AC) was dried in an oven at 150 °C for 2 h, then stored in an airtight container before use. The final product of each step is presented in Figure 1.

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Figure 1: Macrostructural images of corn cob in different forms (a) dried-bulk corn cobs; (b) carbonized corn cob at 400 °C; (c) ground carbonized corn cobs; and (d) activated carbon from carbonized corn cob.

2.2 Preparation of Adsorbate

A stock solution of Benzene and Toluene was prepared by dissolving a measured amount of organic pollutants in distilled water. Concentration of 70 mg/m³ was prepared and used for the column experiments.

2.3 Column adsorption setup and studies

Fluidized bed column was employed to performed biosorption experiments. The schematic diagram of the apparatus and the setup are illustrated in Figure 2. The setup has a 70 L feed tank to store the prepared stock solution contaminated with pollutants at a specific concentration for the intended experiment. A PVC pipe lines were used to connect the system and to deliver the wastewater solution. The column was made from Perspex material with a height of 80 cm and a 5 cm internal diameter. A stainless sieve of 1 mm was fixed at the column center to keep constant bed height and support the bed during the continuous operation process. The stock solution was introduced into the column with the aid of a pump (MARQUIS-MQS128, China). The flow rate was regulated with the aid of valve and measured with a rotameter (Platon, France). In addition, a second container of 30 L was used to collect the effluent solution.

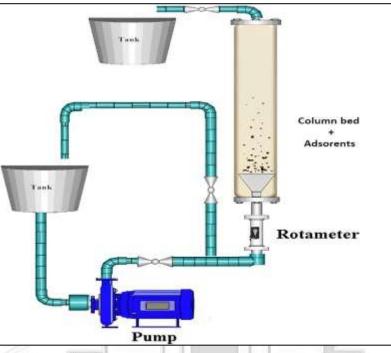
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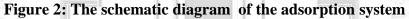
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The breakthrough curves' characteristics were examined under various operational conditions by gathering samples every specific period, until the adsorbents reached saturation. The column study was conducted at different process variables, including flow rates (Q), bed heights (Z), and Temperature (T). The effect of particles size was investigated separately at the optimum condition with a range of (0.2-0.6 mm). Table 2 shows the set of experiments under different conditions.

No	Temp, C	Flow rate, (l/hr)	Bed depth, cm
1	30	15	6
2	30	20	8
3	30	25	10
4	35	15	8
5	35	20	10
6	35	25	6
7	40	15	10
8	40	20	6
9	40	25	8

Table 2: Set of experiments and	d conditions of each experiment.
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Table 3 illustrates important definitions to investigate the performance of column,adsorption capacity, and total removal percentage.

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Table 3: Characteristic parameters of the breakthrough curves [22]

Parameters	Description	Formula		
Breakthrough time (t _b), min	The time it takes for the solute tot_b can determine at $C_b = 0.1 C_0$ first appear at the outlet of the porous media.			
Saturation (exhausted) time (t, min), The time to achieve saturation concentration of solute at th outlet of the porous media.			
Breakthrough b), concentration (C mg/ml	The concentration of solute at th outlet of the porous media a breakthrough time.			
Saturation (Cs concentration mg/ml), The maximum concentration o solute observed in the effluent	fCs=0.9 C ₀		
qb, mg	The adsorption capacity a breakthrough.	$ \begin{array}{cccc} \text{at} & \int & (1)c \\ & tb & dt \\ \text{qb=}C_0 & Q \end{array} $		
qs, mg	The adsorption capacity at a saturation, also denoted as q representing equilibrium adsorption capacity (mg/g),	e dt		
m _{total} , mg		$tm in = CoQt_s$		
m out, mg	The amount of BT that left th column unadsorbed at saturation.			
m adsorbed , mg	The amount of BT adsorbed in the column at saturation.			
Removal percentage (RE%)	Total adsorbed molecules in th column to the total amount of molecules sent to the column	eRE (%) = m ads/ m in × 100		

2.4 Characterization and Analytical Measurements

A Brunauer-Emmett-Teller (BET) analysis was performed to investigate a specific surface region's properties, including specific surface area, pore size, and pore volume. The analysis took place at the Ministry of Science and Technology Building Research Center using an automated Quantachrome Autosorb-6Isa system from the USA.

To measure the concentration of BT in the experiment's effluent, Gas Chromatography (GC) analysis was conducted using a Thermo Scientific FOCUS GC device. This analysis also occurred at the Ministry of Science and Technology-Building Research Center.

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3. Results and Discussion

3.1 Adsorbents Characterisation

BET analysis was used to determine the textural properties of the adsorbents (specific surface area and pore volume), the results presented in Table 4. The surface areas for raw corn cobs were 24, 21, and 6 m^2/g for particles size of 0.2, 0.4, and 0.6 mm, respectively. Furthermore, the results of pore volume recorded 0.0031, 0.0014, and 0.0012 for particles size of 0.2, 0.4, and

0.6 mm, respectively.

However, compared to raw corn cobs, the activated corn cobs show higher surface area and recoded 245.12, 210.25, and 96.34 for particles size of 0.2, 0.4, and 0.6 m^2/g , respectively. This indicates that the activation process has successfully enhanced the surface area of the adsorbents, making them more effective in adsorption applications compared to their raw counterparts.

The increase in the surface area with higher temperatures (carbonized corn cob at 400 $^{\circ}$ C) can be due to volatilization and loss of organic compounds which results in pore fabrication [39,40]. This observation indicates that the carbonization temperature has a substantial impact on the textural properties of the activated carbons (ACs) [40].

The addition of ZnCl₂ during the activation process plays a crucial role in restricting tar formation [41]. By inhibiting tar production, the contraction of the particle is prevented, leading to the formation of a wide and open microporosity, with the presence of border micro-mesopores [41]. This unique microstructure enhances the surface area and pore volume of the activated carbon derived from corn cobs, making it more efficient in adsorption processes. The wider and open micro-mesoporous structure provides ample active sites for the adsorption of contaminants, further improving the adsorption capacity and overall performance of the adsorbents in water treatment applications. The adsorption capacity of activated carbon primarily relies on its porous structure and surface area. ZnCl₂ serves as a dehydrating agent, effectively eliminating volatile compounds from the activated carbon. Additionally, it facilitates bond cleavage reactions through dehydration and condensation processes [14]. For the following experiment the particles with size of 4 mm were used.

Table 4. Surface pr	oper nes or synthesized a	usor being obtained from	DET analyses
Adsorbent	Particles size, mm	Surface area, m^2/g	Pore volume, cm ³ /g
Raw corn cob	0.2 0.4 0.6	24 21 6	0.0031 0.0014 0.0012
Activated corn cob	0.2 0.4 0.6	245.12 210.25 96.34	

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3.2 Parametric Effect on BT Adsorption

3.2.1 Effect of Feed Flow Rate

Figure 3 shows the effect of feed flow rate on the adsorption of benzene and toluene. The change in flow rate can significantly affect the continuous adsorption process in the fluidized column. The adsorption experiments were conducted at a range of flow rates (15-25) l/hr. the results reveled that, the lower flow rate (15 l/hr) has the best performance for both benzene and toluene with removal of 70.13% and 75.8% respectively. However, increasing the flow rate to 20 ml/min cause a reduction in removal of the benzene and toluene and recorded 63.8% and 70.83% respectively. Furthermore, the higher flow rate (25 l/hr) show the lowest removal performance with 55.7% for benzene and 66% for toluene. This behavior can be explained by the fact that at higher rates, The flow takes less time to penetrate the pores of the adsorbent material and lower the mass transfer and inter-particle diffusion. In other word, the higher feed flow rate affected the retention time of BT pollutant in the aqueous phase, causing a reduction of interaction of the adsorbates surface and the adsorbents, thereby resulting in higher effluent concentrations before equilibrium is reached.

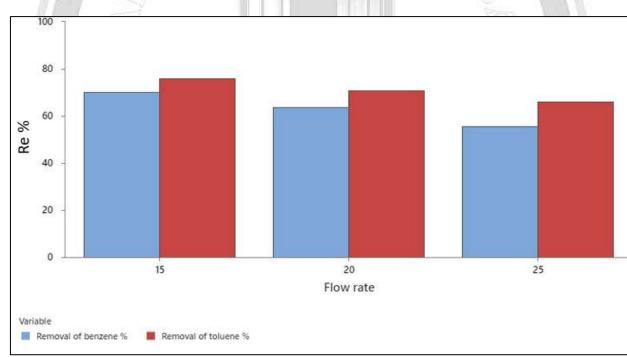


Figure 3: Removal of benzene and toluene with respect to feed flow rate.

3.2.2 Effect of Temperature

Figure 4 shows the effect of temperature on the adsorption of benzene and toluene. The change in temperature can significantly affect the continuous adsorption process in the fluidized column. The adsorption experiments were conducted at a range of temperature (30-40 °C). The results reveled that, the higher temperature (40 °C) has the lowest performance for both benzene and toluene with removal of 60.4667% and 67.4667% respectively. However, the adsorption of benzene and toluene at (35 °C) was increased to 61.4667% and 70.933% respectively. Furthermore, the lower temperature (30 °C) shows the best removal performance with 67.6% for benzene and 74.2333% for toluene.

Although, an increase in temperature enhances the adsorption kinetics, as it provides more thermal energy for the molecules to overcome activation barriers and adsorb onto the surface.

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The experimental results show that, a reduction in the performance upon increasing temperature indicate that the adsorption processes may be exothermic nature. In exothermic processes, heat is released as a byproduct of the adsorption reaction. This means that with increasing temperature, the adsorption process becomes less favorable, and the adsorptive forces weaken. Additionally, at elevated temperatures, the thermal energy can disrupt the attractive forces between the BT molecules and the active sites on the adsorbent surface. The weakening of these adsorptive forces leads to a reduced interaction and lower adsorption capacity.

Furthermore, as hydrophobic compounds both benzene and toluene tend to have lower solubility in the aqueous phase at higher temperatures. The decreased solubility can promote the release (desorption) of BT back into the liquid phase. As a result, the overall adsorption capacity of the adsorbent for BT may be reduced. Also, as BT becomes less soluble, other solutes might have a higher chance of adsorbing onto the active sites of the adsorbent. Such competing interactions can be result from water molecules, where organic adsorbents tend to absorb water as much as absorbing BT and the absorbent will drown eventually.

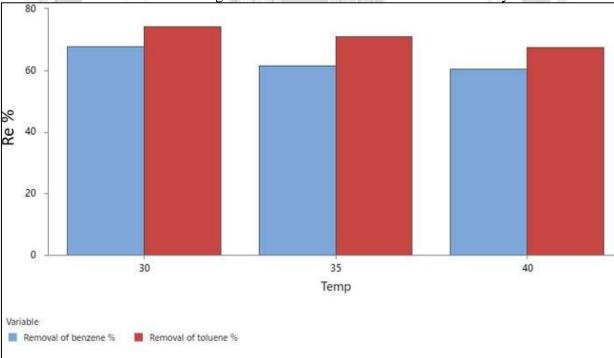


Figure 4: Removal of benzene and toluene with respect to temperature change.

3.2.3 Effect of Bed Depth

Figure 5 shows the effect of bed depth (amount of AC filled in the column) on the adsorption of benzene and toluene. The change in bed depth can significantly affect the continuous adsorption process in the fluidized column. The adsorption experiments were conducted at bed depths of (6, 8, and 10 cm) which are equivalent to (1.37, 1.85, and 2.26 g) of AC.

The results reveled that, the lower bed depth (6 cm) has the lowest performance for both benzene and toluene with removal of 54.13% and 61.633% respectively. However, increasing the bed depth to 8 cm cause an increasing in removal of the benzene and toluene and recorded 63.5% and 71% respectively. Furthermore, the higher bed depth (10 cm) shows the highest removal performance with 72% for benzene and 80% for toluene.

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This behavior can be explained by the fact that, a taller bed increases contact time between the adsorbent and adsorbates, improving adsorption efficiency. therefore, mass transfer can be enhanced by promoting better fluidization. In other word, the deeper bed provides a larger surface area by holding more adsorbent material which translates to a higher adsorption capacity to remove a larger quantity of benzene and toluene before the adsorbent material becomes saturated. A deeper bed will increase the contact time and extending the residence time, allowing more time for benzene and toluene molecules to interact with the adsorbent's active sites. Longer contact time can lead to more comprehensive adsorption. Similar observation was reported by [22].

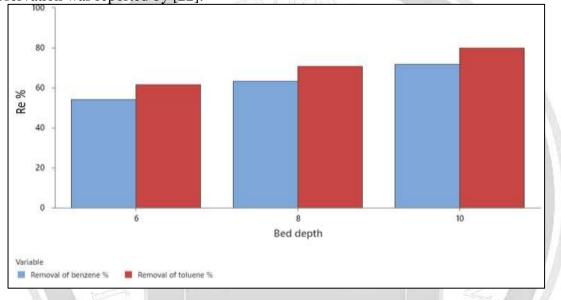


Figure 5: Removal of benzene and toluene with respect to bed depth change.

3.3 Column performance

The breakthrough curves of benzene and toluene were used to determine the column performance. The breakthrough capacity and exhaustion capacity of the adsorbent in the column, as well as the degree of column utilization was determined to understand the impact of the column on the adsorption capacity of the adsorbent. To determine changes to the breakthrough curve (plots of C/Co versus time). Three particle size were used (0.2, 0.4, and 0.6 mm). The experiment was conduct at optimum conditions flow rate 15 l/hr, temperature 30 °C, and bed depth 10 cm.

Figures 6 and 7 show the breakthrough curves obtained from the column experiments for benzene and toluene respectively. The breakthrough point on the curve was selected at the point at which the effluent concentration (Ct) reaches about 10% of the influent concentration (Co). The time at which the breakthrough occurred is called the breakthrough time (tb). The saturation time (ts) was defined as the point when the effluent concentration reaches 90% of Co.

Once can observe the behavior of breakthrough curve shown in figures 6 and 7 and conclude that, both the particles size of (0.4 and 0.6 mm) has affected the time needed to achieve breakthroughs and cause a reduction in saturation time. However, the lowest particles size (0.2 mm) shows the best performance and may extend the saturation time. These behaviors are a result of low surface for both 0.4 and 0.6 mm which shown 210.25 and 96.34 m²/g respectively as indicated by BET analysis. Therefore, both sizes have less active site for sorption as a result of the reduced surface area of the adsorbent. Furthermore, particles size of 0.2 mm depicts an enhanced surface area (245.12 m²/g) available for the interaction of the

adsorbate and the adsorbent. As a result, time required to achieve the total capacity of the column was extended and led to higher adsorption capacity during breakthrough and saturation, increased removal efficiency, and a larger volume of effluent treated at saturation.

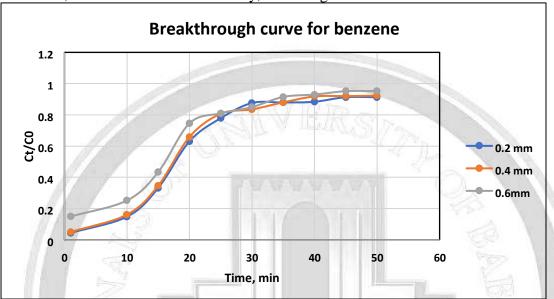


Figure 6: Effect of particle size on breakthrough curve for benzene removal by corn cobs AC adsorbent in continuous fluidized bed column -bed depth: 10 cm, influent concentration: 70 mg/m³; feed flow rate: 15 l/hr; temperature: 30 °C.

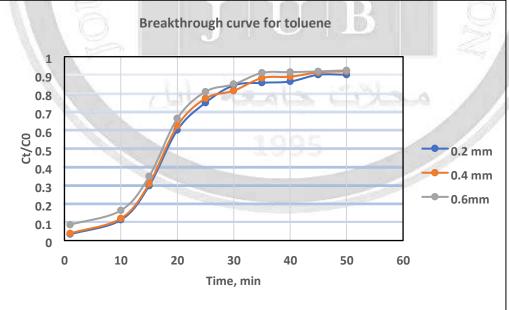


Figure7: Effect of particle size on breakthrough curve for toluene removal by corn cobs AC adsorbent in continuous fluidized bed column -bed depth: 10 cm, influent concentration: 70 mg/m³; feed flow rate: 15 L/hr; temperature: 30 °C.

In Figure 8, the breakthrough curves of benzene and toluene adsorption at their optimum

conditions are presented and depicting the concentration of these compounds in the effluent stream over time during the adsorption process. Notably, the curve reveals that benzene experiences breakthrough earlier than toluene, indicating that benzene molecules appear in

The solubility of benzene and toluene in the liquid phase significantly influences this behavior when present in aqueous phase. Generally, benzene has a higher solubility in the

the effluent stream at an earlier stage of adsorption compared to toluene.

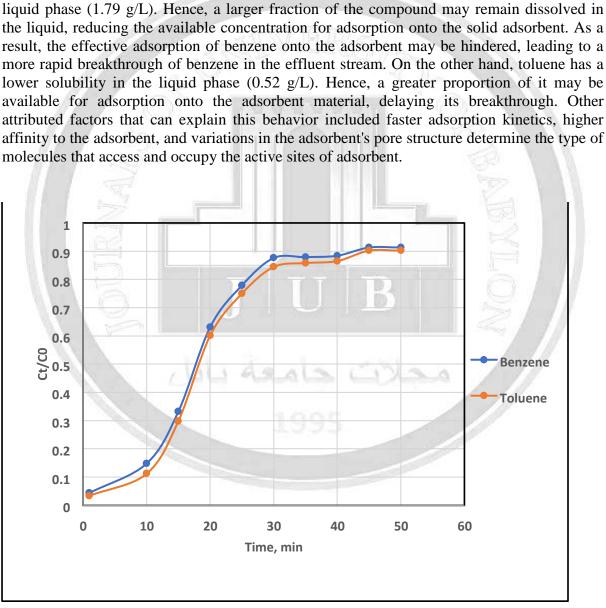


Figure 8: Breakthrough curve for benzene and toluene removal by corn cobs AC adsorbent in continuous fluidized bed column –bed depth: 10 cm, influent concentration: 70 mg/m³;

feed flow rate: 15 l/hr; temperature: 30 °C; particles size: 0.2 mm. Table 5 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.

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C _b (mg/m ³)	Cs (mg/m ³)	tb , min	ts _, min	qb (mg/g)	qs (mg/g)	m in , s (mg)	mads,s (mg)	Re%
10.36	63.91	10	45	0.0699	0.1447	0.7	0.32704	46.72
7.84	63.14	10	45	0.0641	0.15643	0.7875	0.3535	44.894
	10.36	10.36 63.91	10.36 63.91 10	10.36 63.91 10 45	10.36 63.91 10 45 0.0699	10.36 63.91 10 45 0.0699 0.1447	10.36 63.91 10 45 0.0699 0.1447 0.7	10.36 63.91 10 45 0.0699 0.1447 0.7 0.32704

Table 5: Parameters determined from breakthrough curve for 0.2 mm AC particles.

4. Conclusions

In this study, the effectiveness of activated carbon derived from corn cobs was examined for the removal of benzene and toluene from aqueous solutions using a fluidized bed dynamic mode. The study focuses on assessing the impacts of flow rate, bed height, and temperature on the adsorption process, and the following conclusions were drawn:

Firstly, lowering the flow rate and temperature while increasing the bed height had a positive influence on both the adsorption capacity and removal efficiency.

Secondly, particles with sizes of 0.4 mm and 0.6 mm exhibited an earlier breakthrough compared to particles with a size of 0.2 mm due to their larger surface area.

Lastly, analyzing the breakthrough curves for benzene and toluene under optimal conditions revealed that benzene encountered breakthrough earlier than toluene. This discrepancy was attributed to benzene's higher solubility, faster adsorption kinetics, greater affinity to the adsorbent, and differences in the adsorbent's pore structure.

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ARTICLE

إزالة الملوثات العضوية من مياه الصرف الصحي باستخدام عملية الامتزاز عامودية باستخدام الكربون النشط المشتق من قشر الذرة كمادة ممتصة

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الخلاصة

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تركز هذه الدراسة على استخدام الفحم النشط المشتق من كتل النباتات المزروعة من الذرة لإزالة البنزينوالتولوين BT من المياه، وهي ملوثات توجد بشكل شائع نتيجة لأنشطة الإنسان والحوادث مثل تسرب النفط. تستكشف الدراسة تقنيات الامتزاز الفعّالة من حيث التكلفة وتختبر الفحم النشط في عمود حشوي ذوو حركية مستمرة. يتم امتصاص التولوين بشكل أفضل نتيجة لقابليته الأقل للذوبان. تم التعرف على الظروف الأمثل: ارتفاع الحشوة 10 سم، ومعدل التدفق 15 مل/دقيقة، ودرجة الحرارة 30 درجة مئوية. ووفقًا لمنحنى الاختراق، بلغت السعة القصوى للامتزاز 14000 و 156430 (ملغ/جم) مع كفاءات إزالة إجمالية بلغت2.46% للبنزين والتولوين على التوالى. تظهر الدراسة إمكانية هذا الأسلوب لإزالة BT بفعالية، وتقدم رؤى لتنقية المياه وتنظيف البيئة.

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الكلمات الدالة: الامتزاز، قشر الذرة، الامتزاز الحيوي، البنزين، التولوين، معالجة مياه الصرف الصحى.