

Optimizing Column Adsorption for MTBE and BTEX Removal from groundwater using colloidal activated carbon

BY

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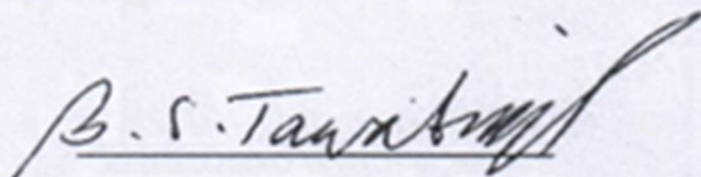
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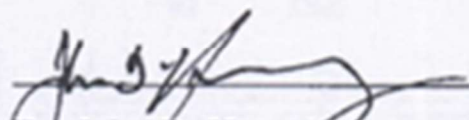
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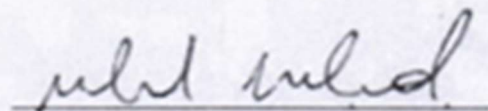


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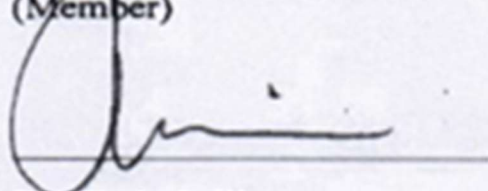


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This thesis work is dedicated to my great grandfather and his great family. It is also dedicated to my father Mr. Mohammad Baqer and to my mother Mrs. Thekayat Ahmad, who were always supporting and motivating me to learn and work hard to help people by my knowledge and expertise, and who always wished to see me in the best positions.

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LIST OF ABBREVIATIONS

CAC	:	Colloidal Activated Carbon
LAC	:	Liquid Activated Carbon
GAC	:	Granular Activated Carbon
AC	:	Activated Carbon
MTBE	:	Methyl tert-butyl ether
BTEX	:	Benzene, Toluene, Ethylbenzene, Xylene
PRB	:	Permeable Reactive Barrier
GC-FID	:	Gas Chromatography- Flame Ionization Detector
GC-MS	:	Gas Chromatography- Mass spectrometry
SEM	:	Scanning Electron Microscopy
EDS	:	Energy Dispersive Spectrometer
FTIR	:	Fourier Transform Infrared Spectroscopy
DI Water	:	De-Ionized Water

ABSTRACT

Full Name : Baqer Mohammad Al-Mousa

Thesis Title : Optimizing Column Adsorption for MTBE And BTEX Removal From
Groundwater Using Colloidal Activated Carbon

Major Field : Environmental Science

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The protection and /or remediation of groundwater is a challenge to water authorities due to the high cost imposed by the various treatment technologies. This study aims to investigate the use of Colloidal Activated Carbon (CAC) material for the removal of organic contaminants particularly Methyl tertiary butyl ether (MTBE), Benzene, Toluene, Ethylbenzene and Xylene (BTEX) from contaminated groundwater using a lab-scale fixed-bed column setup. A full characterization of the CAC was performed using the Scanning electron microscope and Energy-dispersive X-ray spectroscopy (SEM/EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Zeta potential and Brunauer-Emmett-Teller (BET) surface area analyzer. Different dosages of the CAC were loaded into a fixed bed column filled with sandstone and carbonate materials and connected to a pump that transfers contaminated solution to the column at a certain flowrate. Samples were collected at different time intervals after passing through the column, then analyzed using Gas chromatography–mass spectrometry (GC/MS) to determine the MTBE and

BTEX concentrations before and after treatment. Results of the zeta potential analysis showed that the CAC used has a surface that is negatively charged, while the BET analysis revealed a specific surface area of $1160 \text{ m}^2/\text{g}$. In addition, EDS results showed that 99.24% of the CAC composition is carbon and 0.76% is potassium. The size of CAC particles falls between 4.5 and 21 μm . The fixed -bed column experiments results showed that MTBE and BTEX adsorption is mostly affected by CAC dosage, initial contaminant concentrations, and flowrate. Conductivity, bed type, and bed height effects were minor. The optimum treatment conditions that gave maximum removal efficiencies and high adsorption capacities for MTBE were: CAC dosage of 2 g, initial concentrations of 5000 $\mu\text{g/L}$, flow rate of 1 mL/min, using sandstone bed type and bed height of 20 cm at a conductivity of 33850 $\mu\text{S/cm}$. Whereas that of BTEX was found to be at a CAC dosage of 2 g, with initial concentrations of 6000 $\mu\text{g/L}$, flow rate of 2 mL/min, using carbonate bed type and bed height of 20 cm at a conductivity of 16400 $\mu\text{S/cm}$. Furthermore, the experimental data at various conditions was fitted into various models (Adams-Bohart, Thomas and Dose-Response models), and the results showed that Dose-Response model gave the best fit. Based on the laboratory scale results, the used CAC showed that it is feasible to be used as an adsorbent to remediate GW from MTBE and BTEX.

ملخص الرسالة

الاسم الكامل: باقر محمد موسى

عنوان الرسالة: تحسين امتصاص مادة الـ MTBE ومواد الـ BTEX من المياه الجوفية في عمود الامتصاص باستخدام الكربون المنشط السائل.

التخصص: علوم بيئية

تاريخ الدرجة العلمية: ديسمبر 2024

تعتبر حماية و/أو معالجة المياه الجوفية من أبرز التحديات التي تواجه الجهات المعنية بالمياه، وذلك بسبب التكاليف الباهظة التي تفرضها تقنيات المعالجة المختلفة. تهدف هذه الدراسة لاختبار استخدام مادة كربون منشط سائلة (Colloidal Activated Carbon – CAC) لإزالة ملوثات عضوية من المياه الجوفية، تحديدًا مادة الـ ميثيل ثلاثي بيوتيل الإيثر (MTBE) ومواد البنزين والتلوين و إيثيل البنزين و الزايلين أو ما يعرف اختصارًا بالـ BTEX على النطاق المختبري وباستخدام عمود ذو مجال ثابت أو ما يعرف بالـ Fixed-bed column.

تم خلال هذا البحث دراسة الخصائص الفيزيائية والكيميائية لمادة الكربون المنشط السائلة باستخدام المعدات التالية : SEM / EDS ، و XRD ، و FTIR ، و zeta potential و BET. تقوم التجربة المستخدمة في هذا البحث على حقن كميات مختلفة من مادة الكربون المنشط السائلة في العمود، والذي يتم ملؤه إما بالرمل أو مادة الكربونات. العمود متصل بمضخة تنقل إليه المحلول الملوث بمعدل تدفق محدد. يتم خلال التجربة جمع العينات بعد مرورها عبر العمود في فترات زمنية مختلفة، ليتم بعدها تحليلها في جهاز الـ GC/MS وذلك لتحديد تراكيز مواد الـ MTBE والـ BTEX قبل وبعد التجربة. أظهرت نتائج هذا البحث بأن مادة الكربون المنشط السائلة المستخدمة تحوي سطحًا بشحنة سالبة، ومساحة تبلغ $1160 \text{ m}^2/\text{g}$. كما أظهرت نتائج جهاز الـ EDS بأن تركيبة عناصر المادة المستخدمة هو كربون بنسبة تبلغ 99.24%. علاوة على ذلك فإن حجم جزيئات مادة الكربون المنشط السائلة تتراوح ما بين $4.5 - 21 \text{ }\mu\text{m}$. في

الجهة الأخرى، أظهرت نتائج تجارب العمود بأن امتصاص مادتي الـ MTBE و الـ BTEX يتأثر بشكل كبير بكمية مادة الكربون المنشط السائلة و التراكيز الأولية للملوثات و معدل التدفق. فيما كان تأثير الموصلية و نوع المادة التي تملأ العمود و طوله ضئيلاً. الظروف المثلى لعملية امتصاص الـ MTBE على النطاق المختبري والتي أعطت أعلى نسب لكفاءات الامتصاص وقيم مرتفعة لسعة الامتصاص كانت: 2g من مادة الكربون المنشط السائلة، تركيز أولى لـ MTBE يعادل 5000 µg/L ، معدل تدفق يساوي 1 ml/min باستخدام الرمل و طول 20 cm للعمود بموصلية تعادل 33850 µS/cm. في المقابل كانت الظروف المثلى لإزالة الـ BTEX كالتالي: 2g من مادة الكربون المنشط السائلة ، تركيز أولى لـ BTEX يعادل 6000 µg/L ، معدل تدفق يساوي 2 ml/min باستخدام الكربونات و طول 20 cm للعمود بموصلية تعادل 16400 µS/cm. تم كذلك تحديد حركية (kinetics) عملية الامتصاص ضمن الظروف المختلفة عبر ملائمة النتائج مع ثلاثة نماذج رياضية هي :

(Adams-Bohart ، و Thomas ، و Dose-Response) وأظهرت النتائج أن النموذج الذي أعطى الملائمة الأفضل كان نموذج Dose-Response. بناءً على النتائج المستخرجة، فإن مادة الكربون المنشط السائلة المستخدمة تعتبر جيدة للاستخدام كمادة امتصاص لإزالة مادتي الـ MTBE و الـ BTEX من المياه الجوفية الملوثة.

CHAPTER 1: INTRODUCTION

1.1 General Background

Groundwater is one of the most important water resources that covers the agricultural and domestic needs in arid countries like Saudi Arabia (Al Omran et al., 2012; Al harbi, et al., 2021). Saudi Arabia has limited renewable water resources and depends mainly on groundwater in along with the desalination of seawater to meet its increasing local needs (Saud and Abdullah 2009; Al Omran et al., 2016; Alghamdi et al., 2020). Recently, there has been a noticeable focus on water management and reuse in Saudi Arabia, and such focus had made treated water become a new water resource in the kingdom, to meet cooling and irrigation needs (Al Otibi et al., 2020). Despite what was mentioned, the reliance on groundwater to cover most of the needs still dominates within the kingdom and a long period of time will be needed to reduce such reliance and replace it with other resources like treated water.

It is estimated that around 2.5 billion people around the world rely on groundwater, making the pollution of such a water resource very serious problem (Thiruvengkatachari et al., 2008). Groundwater pollution can be caused by some natural geological factors like the presence of radioactive substances and/or some mineral rocks that release contaminants like hydrogen sulfide and uranium (Budania and Dangayach, 2023). There are anthropogenic causes for groundwater pollution as well, which are usually related to industrial activities.

Groundwater pollution in countries like Saudi Arabia can be common due to the abundance of crude oil related activities in the country, which can cause serious environmental and

health impacts. Leakage of gasoline from underground and aboveground storage tanks, and transfer pipelines is one of the typical groundwater pollutions (Reuter, et al., 1998). This is in addition to the accidental discharge of some pollutants like Methyl Tertiary Butyl Ether (MTBE) and Benzene, Toluene, Ethylbenzene, And Xylene (BTEX) which are produced and utilized in large amounts within the kingdom.

MTBE is a gasoline additive that is added to unleaded gasoline to improve oxygenation and reduce the production of carbon monoxide and hydrocarbons that can deteriorate air quality by the formation of smog. MTBE is considered as a genotoxic substance that can cause serious health problems (Zhang et al, 2019). MTBE was banned in some countries; however it is still the second most volatile organic compound that is being detected in shallow groundwater (Levchuk et al., 2014). The United States Environmental Protection Agency (USEPA) has classified MTBE as a carcinogenic substance that can cause health problems to humans even at low concentrations in drinking water (20 - 40 ppb). Other substances like ethanol can play the same role as MTBE when added to gasoline, however MTBE is preferred due to its low cost and simple production (Jacobs et al., 2000; Rick et al., 2001). BTEX are toxic to humans as well and can result in health problems (Mitra and Roy, 2011). BTEX are infused into gasoline to increase the octane rating. MTBE and BTEX have high solubility and mobility in groundwater, with MTBE having higher solubility making it less likely to vaporize or get biodegraded (Alshahrani et al., 2022).

Given the sensitive water resources status of Saudi Arabia, the necessity to remediate available limited polluted water resources can't be overlooked. This acts as a key motivation for researchers to study the removal of common pollutants like BTEX and MTBE in the groundwater resources in Saudi Arabia. Several techniques were investigated

for this purpose, including monitored natural attenuation, bioremediation, air stripping, chemical oxidation, advanced oxidation process, and adsorption (Keller et al., 1999; Jacobs et al., 2000; Georgi and Kopinke, 2005; Fayemiwo et al., 2017; Al Shahrani et al., 2022). Among adsorption techniques, the permeable reactive barrier is a promising approach for the removal of organic contaminants like MTBE and BTEX. Recently novel colloidal activated carbon (CAC) has shown good results in removing organic contaminants (Al Shahrani et al., 2022).

1.2 Research Gap

BTEX and MTBE have high solubility in water. When compared with BTEX, MTBE is less biodegradable, dissolves quicker in groundwater and migrates faster and farther in case of accidental gasoline release. Several remediation technologies such as air stripping, hydrogen peroxide (Fenton)/ultraviolet treatment, adsorption with granular activated carbon or charcoal filter have been used to remove BTEX and MTBE from groundwater, however each technique has its own limitations. A recent study carried out by Alshahrani et al. showed that the use of granular activated carbon as adsorbent is more efficient in removing benzene, toluene and MTBE compared to using a biochar-based liquid activated carbon. The study suggested further research to investigate and enhance the adsorption of colloidal activated carbon (CAC) by studying the effect of different operational conditions. This gives researchers the opportunity to carry out further research that study the CAC adsorption process and enhance the adsorption by the optimization of operational conditions to achieve high removal of BTEX and MTBE from groundwater using CAC.

It is noticed that majority of the research done dealt with the treatment of individual contaminant. In addition, most of the work done used ex-situ treatment by carbonaceous

materials such as GAC and (powdered activated carbon) PAC. Two studies used the Plumestop CAC which uses adsorption and biodegradation mechanisms via providing oxygen in the subsurface waters and thus requires additional oxygenation cost. Up to our knowledge, the use of CAC for the in-situ treatment of GW was not done before in Saudi Arabia, taking into account that usually these types of remediation technologies are site specific.

1.3 Significance of the Study

The national water strategy in Saudi Arabia gives priority to the sustainable use of the limited water sources available within the kingdom. BTEX and MTBE are considered as environmental contaminants, and since groundwater is one of the main drinking water sources in Saudi Arabia; therefore, very low concentrations of BTEX or MTBE can cause water to become unpotable specially with MTBE bad taste and odor. Hence there is a need to explore possible techniques that allow for the effective removal of these contaminants.

Several in-situ and ex-situ techniques were investigated including chemical oxidation, monitored natural remediation, bioremediation, air sparging, and adsorption. The use of permeable reactive barriers (PRBs) in adsorption techniques is promising. Granular activated carbon (GAC) and colloidal activated carbon (CAC) were used to build up PRB systems.

This study focuses on the evaluation of new CAC (S23) and finding the optimum conditions for the removal of BTEX and MTBE from groundwater. The use of S23 CAC in groundwater remediation and unlike the widely used PlumeStop™ Liquid Activated

Carbon™ introduced by REGENESIS Remediation Solutions Co. does not involve the need to enhance bacterial action and thus neglects oxygenation expenses. The potentiality of using this CAC as an adsorbent in the real permeable reactive barrier (PRB) systems will be tested.

1.4 Objectives of the study

The primary objective of this study is to investigate MTBE and BTEX removal using colloidal activated carbon (CAC) in a fixed-bed column setup. The specific objectives include:

- 1) Characterization of the CACs using different techniques such as: SEM/EDS, XRD, FTIR, BET, zeta potential, and laser diffraction.
- 2) Optimizing operational factors, including CAC dosage, initial concentration, water conductivity, bed height, and type, to achieve the best removal of MTBE and BTEX in fixed-bed columns.
- 3) Evaluate the kinetics of breakthrough curves, find the best fit models including Adams-Bohart model, Dose-Response, and Thomas model.

CHAPTER 2: LITERATURE REVIEW

Researchers have used different methods to remove pollutants from contaminated groundwater (Bhandari et al., 2007; Hashim et al., 2011; Jadhav et al., 2015). Majority of these methods use the concept of ‘pump and treat’ in which contaminated groundwater is pumped to the surface where it gets treated (Budania and Dangayach, 2023). However, these techniques are expensive, consume large amount of energy and are of small scale (Budania and Dangayach, 2023). Over the last thirty years, several investigations were done on in-situ contaminated groundwater remediation techniques like bio-thermal treatment and Permeable reactive barriers techniques (Henderson and Demond, 2007).

Techniques that aim to remove MTBE from groundwater are known to be expensive and this is associated with the unique characteristics of MTBE i.e., high mobility, low biodegradability, and high solubility (Kinner, 2001). Techniques that involve adsorption are promising in terms of MTBE removal from groundwater (Sutherland et al., 2004). Permeable Reactive Barriers (PRB) is one of those in-situ promising techniques (Hou et al., 2014). In laboratories, PRBs are simulated using fixed bed columns that help to find out the kinetics for the removal of pollutants which is needed to design the real PRB to be implemented on site (Gavaskar, 1999; Cruz Viggi et al., 2010).

Various materials were used as adsorbents for the PRB technique and their performance in removing different pollutants was tested. Ahamd et al. discussed and presented technical consideration for the use of organic mulch as adsorbent in the design of a PRB. Dong et al. used zero valent iron (ZVI) as adsorbent and studied the effect of manganese dioxide (MnO₂) on the removal of tetracycline (TC), their results showed that addition of MnO₂

has accelerated the removal of TC. Freidman et al. used ammonium exchanged zeolite and granular activated carbon bed to simulate a sequenced PRB that contains nutrient releasing material and an adsorbent to study the removal of petroleum hydrocarbon in low nutrient environments, their results showed that biodegradation of petroleum hydrocarbons and biofilm formation occurred on the zeolite and concluded that bio-reactive barriers can successfully be able to biodegrade and adsorb petroleum hydrocarbons.

Gao et al. used sand-supported ZVI as adsorbent to study the removal of 2,4-dichlorophenol from contaminated groundwater, their results showed that the removal mechanism involved adsorption, desorption and dichlorination and that the latter was the main degradation process that took place. Grajales-Mesa and Malina compared the use of ZVI as an adsorbent with other materials (compost, brown coal, and brown coal-compost mixture) to select the best adsorbent material for the removal of Trichloroethylene (TCE) from contaminated groundwater, their results showed that brown coal is the most effective adsorbent material that can be used to treat groundwater contaminated by TCE.

Liu et al. prepared two new adsorbent materials that are made up of “biochar/straw and calcium peroxide” to study the removal of polycyclic aromatic hydrocarbons (PAHs) from contaminated groundwater, their results showed that the adsorbent that used straw achieved a PAH removal of 100%. Mondal et al. studied the removal of TCE from contaminated groundwater using sawdust and peat as adsorbents, their results showed that adsorbent made up of beat is better than that made up of sawdust when it comes to the use of this adsorbent in PRB applications for the removal of TCE from contaminated groundwater. Han et al. used “iron oxide coated zeolite” (IOCZ) as adsorbent to test the removal of Cu (II) from contaminated water, they found that IOCZ is effective for the removal of Cu (II)

from water and that the adsorption of Cu (II) increases with the increase of bed length, initial concentration and flow rate. Calero et al. applied the fixed bed column experiments to evaluate the use of olive stone to remove Cr (III) from a contaminated water, they found that the saturation time of the olive stone increases with the increase in the bed length and reduction in the flow rate.

Some researchers used activated carbon derived from biomass as an adsorbent in fixed bed experiment to remove paracetamol from contaminated water, the effect of operational variables was analyzed (García et al., 2015). Zhang et al. used ZSM-5 as an adsorbent in fixed bed column experiments to remove MTBE from contaminated water, they found that the highest capacity for adsorption increase with the increase in the length of the bed and with the reduction in flow rate.

Few studies made use of “LAC/COC” as adsorbents to remove contaminants from water. Sara studied the use of Plumestop CAC to remove chlorinated solvents from groundwater in Rhode Island. The result of her study showed that there is a reduction in contaminant concentrations downgradient the injection points of the Plumestop. McGregor used CAC to remove of “Poly- and perfluoroalkyl substances” (PFASs) from contaminated site in Canada. Results of his study showed that all PFASs showed analysis results that are below detection limits in all CAC postinjection samples after 18 months.

Septian et al. prepared CAC from powdered AC -DARCO® and used it to remove phenol from groundwater. The result of their study showed that a removal of ~100% was achieved using the prepared CAC which is greater than that of AC (~90%) and that of the conventional system (~30%). In similar study Lee et al. prepared CAC from GAC and used

it to remove ibuprofen (IBP) from groundwater. Results of the study showed that ~92% removal of IBP was achieved during 240 min, which is six times more than that of the GAC (14.7%).

Hakimabadi et al. used the plumstop CAC to investigate parameters that might have an effect on the adsorption of 7 PFASs on the CAC. Their study results showed that the affinity of PFAS to CAC increased with the increase in solution ionic strength, PFAS adsorption was suppressed by the presence of dissolved organic carbon, and the presence of benzene suppressed the adsorption of one type of PFAS (PFOA). Alshahrani et al. investigated the use of “raw biochar-based liquid activated carbon” (LAC) and “iron-modified biochar-based liquid activated carbon” to remove benzene, toluene (BT) and MTBE from water using batch-scale setup. Their study also involved the use of granular activated carbon (GAC). Results revealed that removal of MTBE (80%) and BT (90%) by GAC was higher than that of the LAC. Results also showed that LAC and iron-modified LAC better removed BT (~ 40%) than MTBE (~ 20%) and that the water chemistry has no impact on the removal efficiency.

CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Materials

Chemicals used in this study include MTBE (p.a.; ≥ 99.5 %GC); benzene (≥ 99.5 %GC); toluene (ACS ≥ 99.5); a xylene mixture (80% xylene, 20% ethylbenzene); and methanol (HPLC, $\geq 99.5\%$).

The highly pure BTEX and MTBE are purchased from Sigma Aldrich company, United States of America.

The deionized (DI) water was obtained using a water purification system. A stock solution mixture was prepared by dissolving MTBE and BTEX in methanol at a concentration of 1000 mg/L, with individual component concentrations of 1000 mg/L for MTBE, 500 mg/L for benzene and toluene, 300 mg/L for the xylenes mixture and 75 mg/L for ethylbenzene. For each experimental run, a spiked solutions mixture was freshly prepared by diluting the stock mixture in deionized (DI) water to obtain the target concentration. The diluted mixture was stirred to ensure complete dissolution of all compounds. The pH of the mixture was maintained at a value of around 6 throughout the experiment.

The CAC used in this study was purchased by Jacobi Carbons Group (jacobi.net), Sweden. The commercial name of the used CAC is AquaSorbTM HYDROSOLTM S23 and it is made from different raw materials like wood, coconut shell and coal that were activated chemically or by steam. It is capable of removing high concentrations of various pollutants like pesticides, hydrocarbons, phenols, etc. It is in homogenous suspension as shown in Figure 1 and its characteristics, provided by the manufacturer are listed in Table 1.

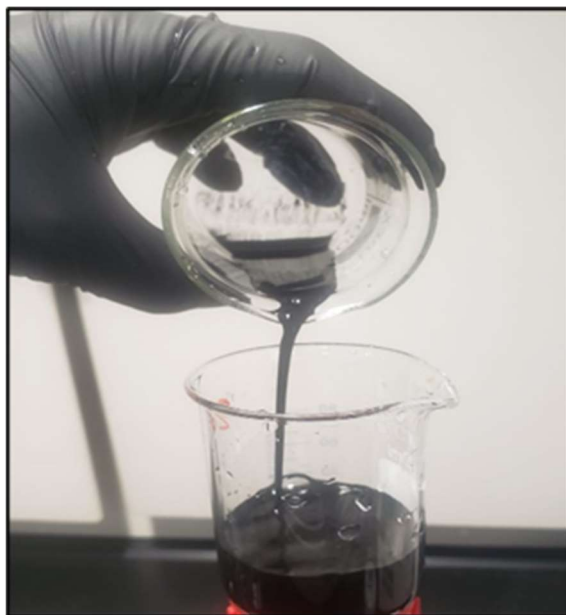


Figure 1. The CAC used in this study (homogenous suspension)

Table 1- Characteristics provided by the manufacturer for the CAC used in this study

Character	HYDROSOL™ S23
Visual inspection	homogeneous suspension
Median diameter of the adsorbing material (Wet)	16.14 μm
Iodine index after dilution at 1/20 and drying	> 900 mg/g
Level of revivable microorganism at 22 and 37°C	105 nb/ml max
Surface area (BET)	1050 m ² /g

The CAC material was characterized using various techniques to identify its physiochemical properties which help to better understand the CAC adsorption behaviors. The CAC was firstly dried in an oven at 110 °C for 24 hours to convert it to solid phase, after which it was crunched to powder, to enable it being analyzed in the SEM, EDS and FTIR.

The surface chemistry and morphology were investigated using scanning electron microscopy (SEM) coupled with an energy dispersive spectrometer EDS (JEOL JCM-7000 BENCHTOP). Figure 2 shows the SEM/EDXS instrument used.

The zeta potential at different pH values (2-12) was measured using Anton Paar Litesizer 500, at 25 °C. A background electrolyte of KNO_3 at a concentration of 10 mM was employed. To prepare solutions for zeta potential measurement, 30 mL of the KNO_3 was placed in 50 mL conical flasks. Subsequently, the pH levels were adjusted to values of 2,4,6,8,10, and 12 using diluted solutions of NaOH and HNO_3 . Following the pH adjustments, 0.1 g of the CAC was added to each flask. To ensure the equilibrium interactions between the CAC and the solution, the mixture was shaken and left overnight. Subsequently, the samples underwent centrifugation, separating any precipitates, and the zeta potential was then measured using the instrument shown in Figure 3.



Figure 2 - SEM/EDS instrument used in the study.



Figure 3- Zeta potential instrument used in the study.

The Fourier Transform Infrared spectrum (FT-IR) was recorded using the KBr pellet method with the Bruker FT-IR spectroscope (INVENIO S, Germany) shown in Figure 4.

The particle size distribution was measured using a wet particle size analyzer by laser diffraction (QUIXEL HELOS SYMPATEC). Figure 5 shows the particle size analyzer used.

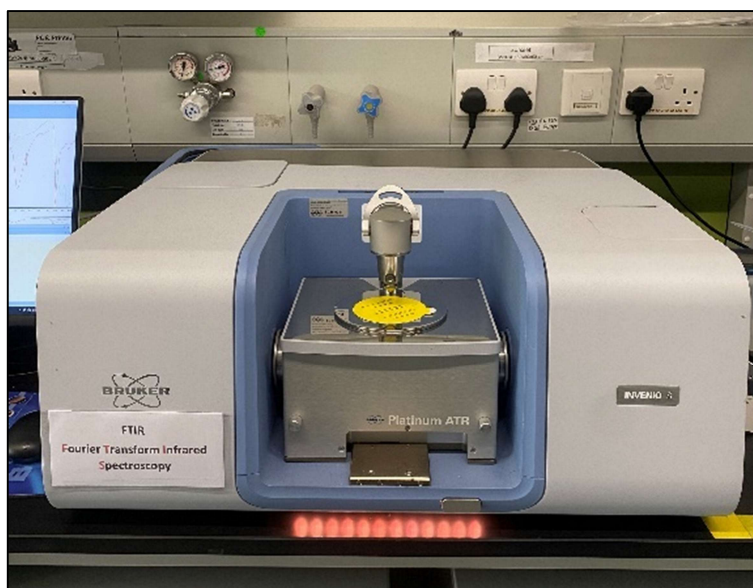


Figure 4 - FTIR instrument used in the study.



Figure 5 - Particle size analyzer used in the study.

The surface area and pore volume of the CAC were determined using the BET instrument (Brunauer–Emmett–Teller; Model: Autosorb iQ- Quantachrome) shown in Figure 6. Nitrogen adsorption-desorption is conducted for this purpose and the measurement is done under liquid nitrogen that is at 77 Kelvin.



Figure 6- Quantachrome Aquasorb iQ BET instrument.

The density and dynamic viscosity of the CAC aqueous solution were measured using a Densitometer for liquids (Anton Paar DMA 4500M).

3.2 Analytical methods

MTBE and BTEX concentrations were measured using a Thermofisher Trace Ultra Gas Chromatography/ ISQ Mass Spectrometry (GC/MS) (Figure 7) following EPA Method 8260. Headspace analyzer was coupled to the GC/MS for automated analysis. One (1) mL of the solution was collected in 5 mL vials at each sampling interval and transferred to the GC/MS for analysis. The GC/MS had a headspace injection unit, which was used to incubate solutions in an agitator for 5 minutes at 90 °C before injecting volatile components directly into the GC column using a headspace syringe heated to 120 °C.



Figure 7- The GC/MS instrument used in the study .

3.3 Fixed-bed column Experiments

Fixed bed column experiments were conducted using acrylic/Teflon columns (1.05 cm diameter, 20 cm length), packed with Ottawa sand H-3825. Additionally, 1 g of graded gravel and a thin layer of glass wool were placed at both ends of the column to maintain uniform flow. The porosity

of packed columns was approximately estimated as 0.57. A predetermined amount of CAC was injected into the bottom of the columns. The MTBE and BTEX solution at different concentrations was prepared by dissolving MTBE and BTEX in methanol at a concentration of 1000 mg/L, with individual component concentrations of 1000 mg/L for MTBE, 500 mg/L for benzene and toluene, 300 mg/L for the xylene mixture and 75 mg/L for ethylbenzene. For each experimental run, a spiked solutions mixture was freshly prepared by diluting the stock mixture in DI water to obtain the target concentration. The diluted mixture was stirred to ensure complete dissolution of all compounds, and then was transferred to containers in which it gets pumped at flow rates of 0.5, 1, or 2mL/min, controlled by a peristaltic pump (LongerPumb BT100-1L). The operational parameters investigated in the current study are shown in Table 2 and 3. The samples were collected at different times to develop time-residuals concentrations profiles and breakthrough curves. The CAC was diluted 8 times to ensure its distribution and mobility inside the packed columns. The samples were collected at different times and the concentrations of MTBE and BTEX were measured using GC-MS, thermos scientific. Control experiments at different conditions were also conducted, where no CAC was added to quantify the adsorption of MTBE and BTEX by the bed material and the losses in the system. All experiments were conducted for continuous flow to develop the breakthrough curves. The fixed-bed column setup is depicted in Figures 8 and 9.

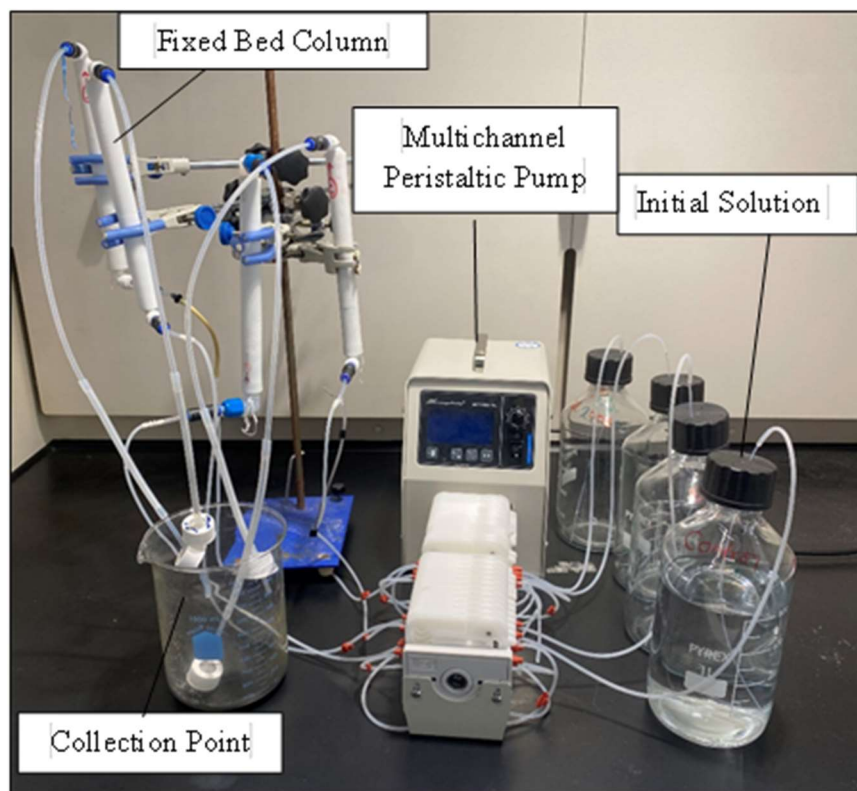


Figure 8- Fixed bed column experiment setup.

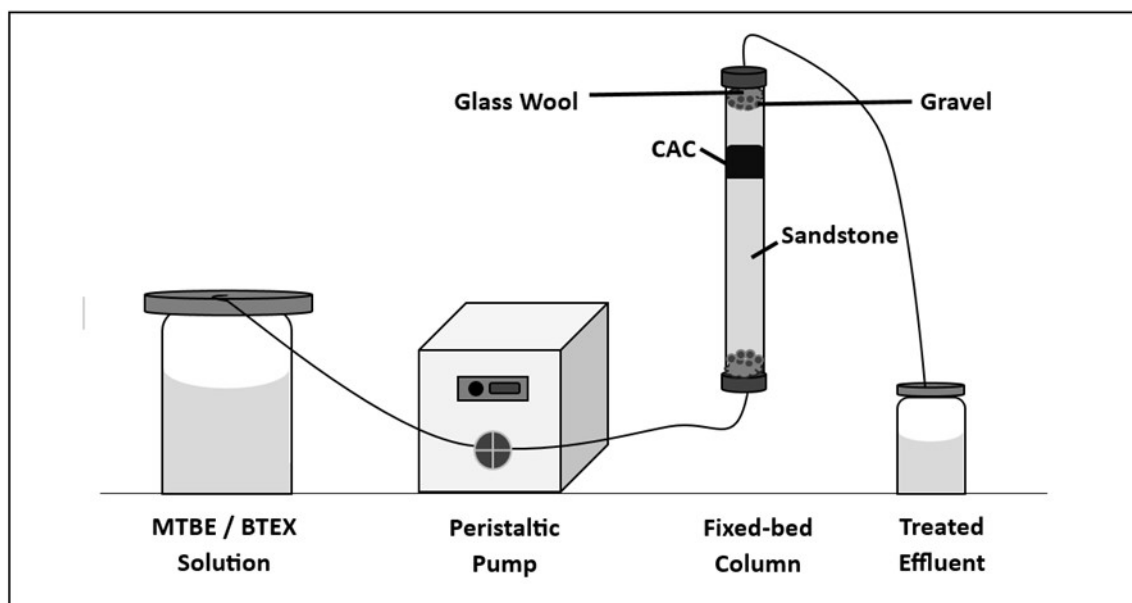


Figure 9- Schematic diagram of the study's fixed-bed column experiments set-up.

It should be noted that at the beginning of the study, one experimental layout was used to investigate optimum conditions for the removal of MTBE and BTEX, however results showed that only MTBE removal could be detected whereas that of BTEX is either totally removed or below detection limit. Thus, another layout for BTEX was designed by raising up initial concentrations and flowrate to 6000 ppb and 2 mL/min respectively as shown in Table 3.

Table 2- Experimental layout of the MTBE removal optimization experiments.

Exp. NO	Investigated parameter	Bed height (cm)	CAC dosage (g)	Initial conc. (µg/L)	Conductivity (µS/cm)	Bed Type	Flowrate (ml/min)
1	Flowrate	20	2	5000	< 5.0	Sandstone	0.5
2		20	2	5000	< 5.0	Sandstone	1
3		20	2	5000	< 5.0	Sandstone	2
4	CAC dosage	20	0.5	5000	< 5.0	Sandstone	1
5		20	1	5000	< 5.0	Sandstone	1
6		20	2	5000	< 5.0	Sandstone	1
7	Initial Concentrations	20	2	10000	< 5.0	Sandstone	1
8		20	2	5000	< 5.0	Sandstone	1
9		20	2	2000	< 5.0	Sandstone	1
10	Conductivity	20	2	5000	<5.0	Sandstone	1
11		20	2	5000	18600	Sandstone	1
12		20	2	5000	33850	Sandstone	1
13	Bed height	10	2	5000	< 5.0	Sandstone	1
14		20	2	5000	< 5.0	Sandstone	1
15	Bed Type	20	2	5000	< 5.0	Sandstone	1
16		20	2	5000	< 5.0	Carbonate	1

Table 3- Experimental layout of the BTEX removal optimization experiments.

Exp. NO	Investigated parameter	Bed height (cm)	CAC dosage (g)	Initial conc. ($\mu\text{g/L}$)	Conductivity ($\mu\text{S/cm}$)	Bed Type	Flowrate (ml/min)
1	Flowrate	20	2	6000	< 5.0	Sandstone	0.5
2		20	2	6000	< 5.0	Sandstone	1
3		20	2	6000	< 5.0	Sandstone	2
4	CAC dosage	20	0.5	6000	< 5.0	Sandstone	2
5		20	1	6000	< 5.0	Sandstone	2
6		20	2	6000	< 5.0	Sandstone	2
7	Initial Concentrations	20	2	20000	< 5.0	Sandstone	2
8		20	2	10000	< 5.0	Sandstone	2
9		20	2	6000	< 5.0	Sandstone	2
10	Conductivity	20	2	6000	< 5.0	Sandstone	2
11		20	2	6000	16400	Sandstone	2
12		20	2	6000	31300	Sandstone	2
13	Bed height	10	2	6000	< 5.0	Sandstone	2
14		20	2	6000	< 5.0	Sandstone	2
15	Bed Type	20	2	6000	< 5.0	Sandstone	2
16		20	2	6000	< 5.0	Carbonate	2
17		20	2	6000	< 5.0	Sandstone& Carbonate	2

3.4 Breakthrough Curve Mathematical Models

Evaluation of columns adsorption performance requires studying different operational factors, including shape of breakthrough curves, saturation time, breakthrough time, and adsorption capacity. This can be performed by plotting C/C_o against time (t) and then applying the non-linear regression methods to fit the experimental data to various models. Several mathematical models have been developed and frequently used to fit the experimental data of fixed-bed column experiments in order to predict the concentration-time profiles and breakthrough curves. These models include Thomas model, Adams-Bohart model, Logit model, Dose-Response model, and Yoon-Nelson model, the corresponding equation of each model are depicted in Table 4. Three of the aforementioned models were fitted to the experimental data of this study to determine the best model describing the breakthrough curves and determine the maximum column capacity. This step is crucial to avoid unnecessary costs in design and operation of full-scale column a raised from oversaturated or underutilized columns.

Table 4- Breakthrough curve mathematical models

Model	Equation	Parameters	Ref.
Adams-Bohart model	$\frac{C}{C_o} = \frac{e^{k_{AB}C_o t}}{e^{\left(\frac{K_{AB}NoZ}{v}\right) - 1 + e^{k_{AB}C_o t}}}$	k_{AB} : rate constant (L/mg/min) No : volumetric adsorption capacity (mg/L)	(Goel et al., 2005)
Thomas model	$\frac{C}{C_o} = \frac{1}{1 + e^{\frac{k_{TH}}{Q}(q_o m - c_o V)}}$	Q_o : maximum adsorption capacity (mg/g), k_{TH} : rate constant (L/mg/min), V effluent volume (L), Q flowrate (l/min)	(Zhang et al., 2019)
Dose-Response model	$\frac{C}{C_o} = 1 - \frac{1}{1 + \left(\frac{C_o V}{q_o m}\right)^a}$	$B = V50\% = \left(\frac{q_o m}{c_o}\right)$, a is the constant, b the concentration when 50% of the maximum response	(Yan et al., 2001)

3.5 Calculation of Adsorption Parameters

The total amount of MTBE and BTEX adsorbed (mg) by the CAC was calculated from the breakthrough curve at different conditions using equation (1):

$$m_{adsorbed} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} (C_o - C_t) \quad (1)$$

where Q is the flow rate (mL/min), Co is the initial concentration, and Ct is the concentration at time t. This is correspondent to the area above the curve of the C/Co Vs. t graph as shown in Figure 10 (green shaded area). The total amount passed through the column m_{total} is calculated using equation (2):

$$m_{total} = \frac{CoQt_{total}}{1000} \quad (2)$$

where Co is the initial concentration (mg/L), Q is the flowrate (mL/min), t is the total flow rate (min).

The total removal efficiency (R %) was calculated using equation (3):

$$R (\%) = \frac{m_{adsorbed}}{m_{total}} * 100 \quad (3)$$

The total amount adsorbed at the equilibrium or maximum adsorption capacity (q_e) was calculated using equation (4):

$$q_e = \frac{m_{adsorbed}}{m} \quad (4)$$

where m is the dosage of CAC (g).

The treated volume was calculated by multiplying the area of the developed breakthrough curves and the flowrate.

Generally, the breakthrough time (t_b) can be calculated by finding the time at which $C/C_o = 0.1$, whereas the saturation time (t_s) can be determined by finding the time at which $C/C_o = 0.85$ as shown in Figure 10.

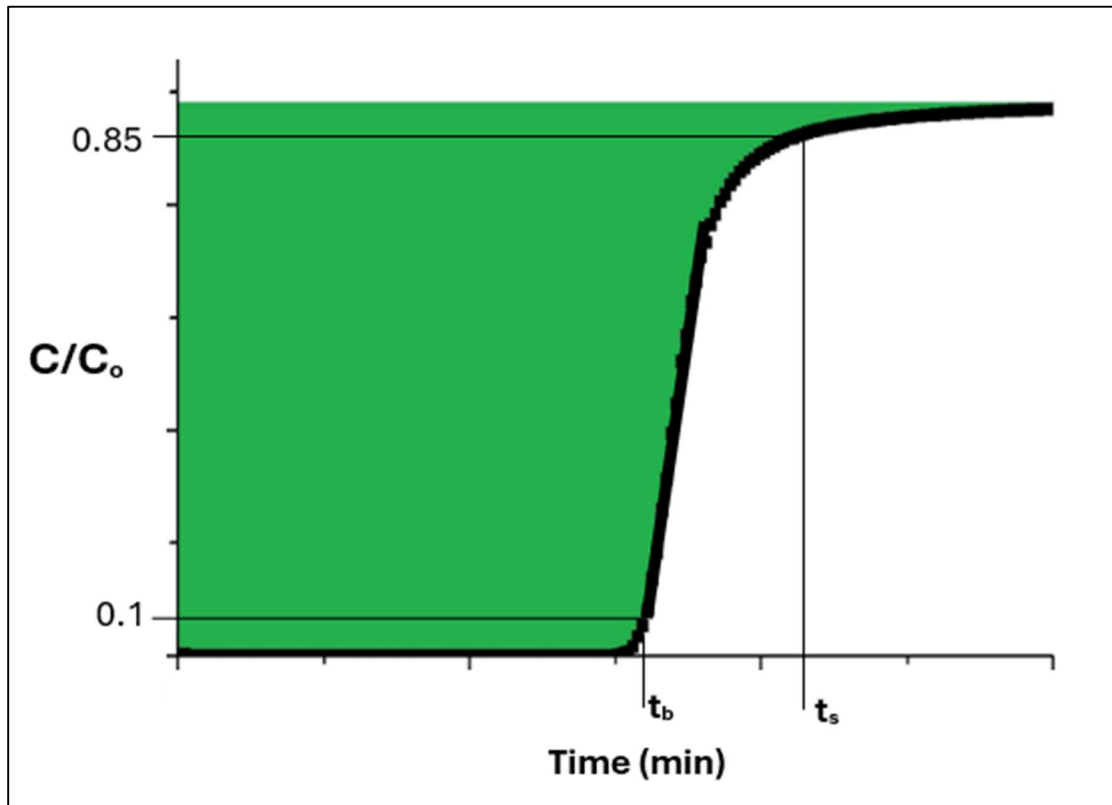


Figure 10- A typical adsorption breakthrough curve.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of CAC

4.1.1 SEM / EDS analysis

SEM/ EDS analysis was done to investigate the morphology and the surface chemistry of the CAC used. CAC surface morphology, porous characteristics and elemental surface composition are shown in Figure 11. Figures 11 (a,b) show very clearly that CAC has a heterogenous morphology with an amorphous porous surface that looks like a sponge. Figures 11(c,d) demonstrate that CAC has a smooth texture. Figure 12 shows that the pore sizes of the CAC vary and that they range between 14-30 μm . These pores are believed to be a result of the carbon activation process during which evaporation of the activating agent occurs leaving behind many cavities (Uçar et. al., 2009). Figure 5e shows that 99.24% of the CAC composition is carbon and only 0.76% is potassium, which implies the important role of the CAC as an adsorbent. The 0.76% of potassium can be traces of the additives used

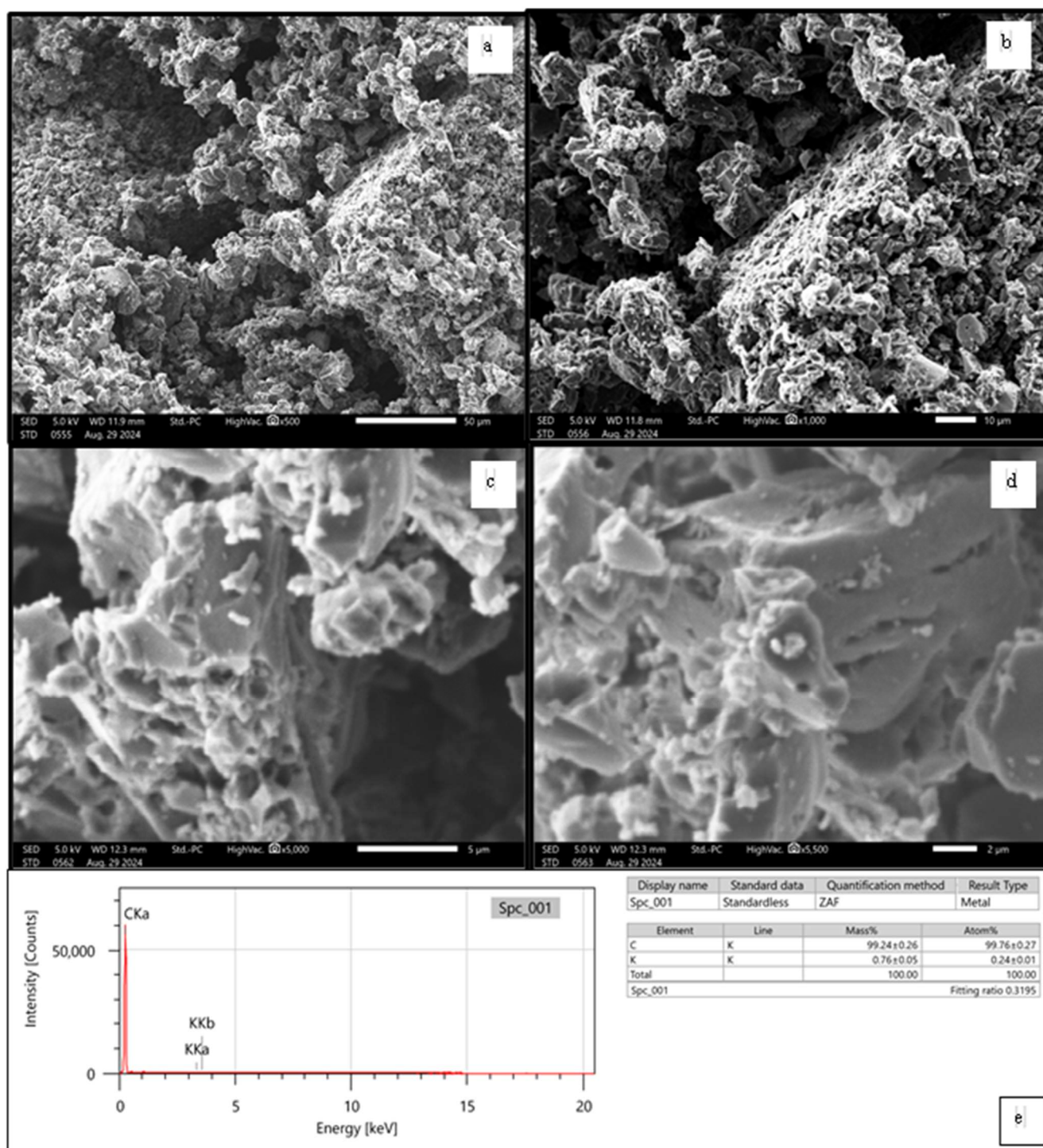


Figure 11- Surface morphology of CAC at different magnifications: (a) x500 (b) x1000 (c) x5000 (d)x5500;(e) EDS spectra /Elemental composition of CAC.

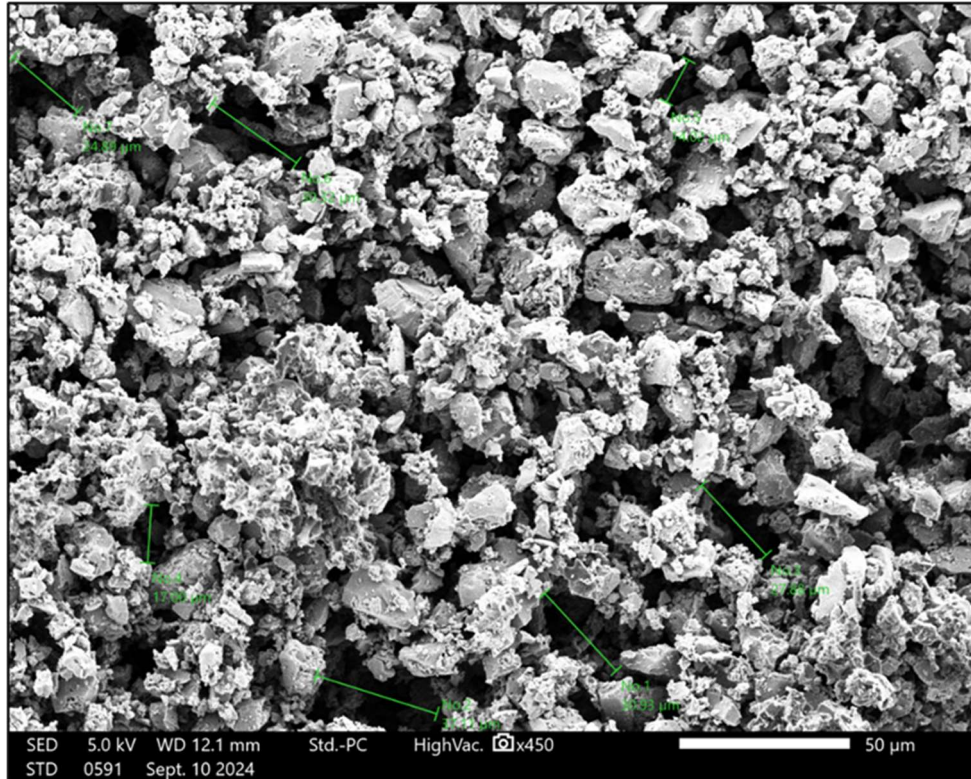


Figure 12 - Pores sizes in microscopic scale.

4.1.2 BET Surface area

BET analysis was done to measure the surface area of the CAC used and its pore volume. Figure 13 show the Nitrogen adsorption – desorption isotherm of the CAC. According to the IUPAC classification, the used CAC has type I isotherm. Type I isotherm is a characteristic of microporous materials i.e. those materials with pore diameter less than 2 nm (Thommes et al., 2015).

Table 5 shows the characteristics of the CAC pore that is based on the nitrogen adsorption-desorption isotherm. When compared to a coconut powdered activated carbon found in the literature (Mirzaee and Sartaj, 2022), it was found that the characteristics of the used CAC are better in terms of adsorption, with a BET surface area equivalent to 1160 m²/g (compared to 920.6 m²/g of the PAC), a total pore volume of 0.5 cc/g (compared to 0.4 cc/g PAC) and a mode pore

width of 3 nm (compared to 3.75 nm). These results indicate that CAC is a better adsorbent due to its large surface area, greater number of pores and smaller pore size.

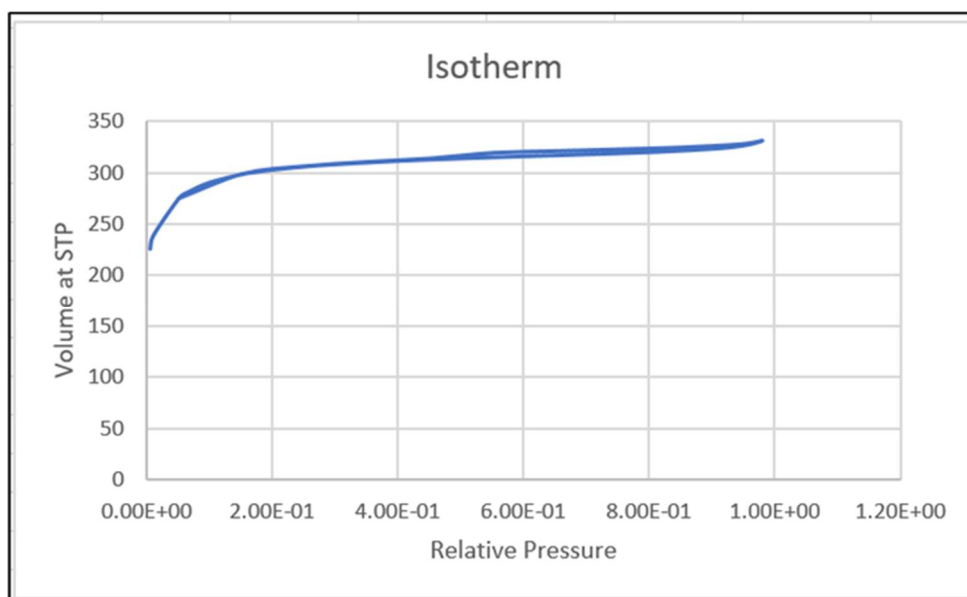


Figure 13- CAC isotherm: Volume Vs. Relative pressure

Table 5- - BET characteristics of the study's CAC and the literature's PAC.

Adsorbent	BET surface area (m ² /g)	Total pore volume (cc/g)	Mode pore width (nm)
CAC	1160	0.507	3
PAC	920.6	0.41	3.75

4.1.3 Zeta Potential Analysis

Zeta potential analysis was carried out to examine the charge present at the surface of the used CAC. The zeta potential of the CAC was plotted against pH as shown in figure 14. The results show that all of the zeta potential values obtained at different pH are negative which is a clear indication that the surface charge of the used CAC is negative. The results also show that the negative charge increases from -10 to -45 as the pH is increased from 2 to 10. Therefore, it can be expected that the CAC will work best in the adsorption of positively charged surfaces contaminant along with the neutral charged surface contaminants but will be least favored with negatively charged surface contaminants.

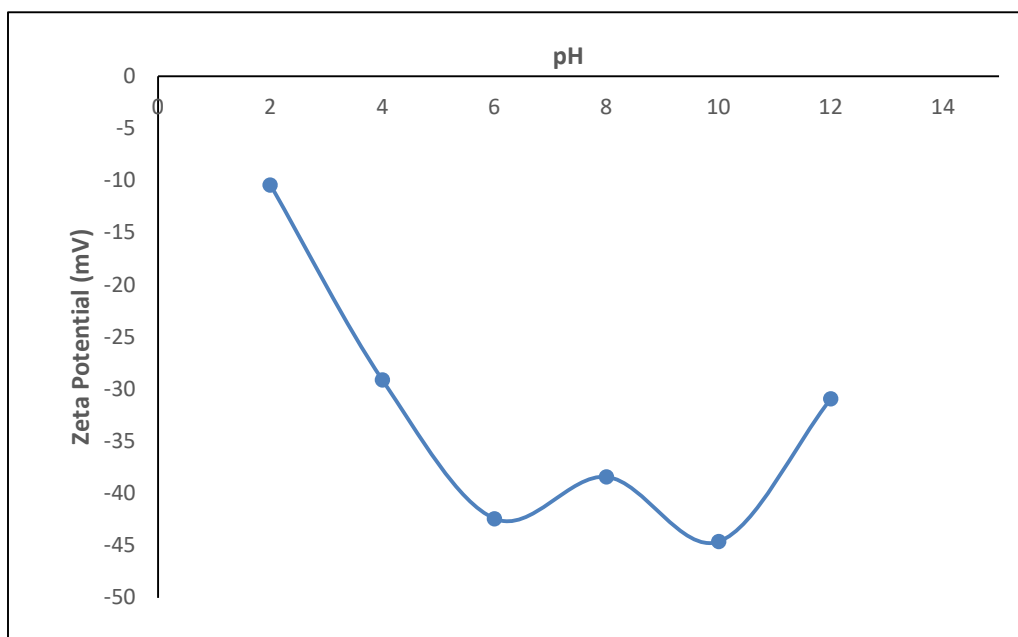


Figure 14- Zeta Potential plot of CAC.

4.1.4 FTIR analysis

FTIR analysis was performed to know the functional groups found in the surface of the used CAC. Figure 15 shows the FTIR spectrum of the S23 CAC. The spectrum exhibits strong peaks at 1875, 2125 and 2260 cm^{-1} which could indicate for the presence of a triple bond, specifically a carbon

triple bond (Mecozzi et al., 2012). The band at 3000 cm^{-1} indicate for a C-H stretching alkene group (Mecozzi et al., 2012).

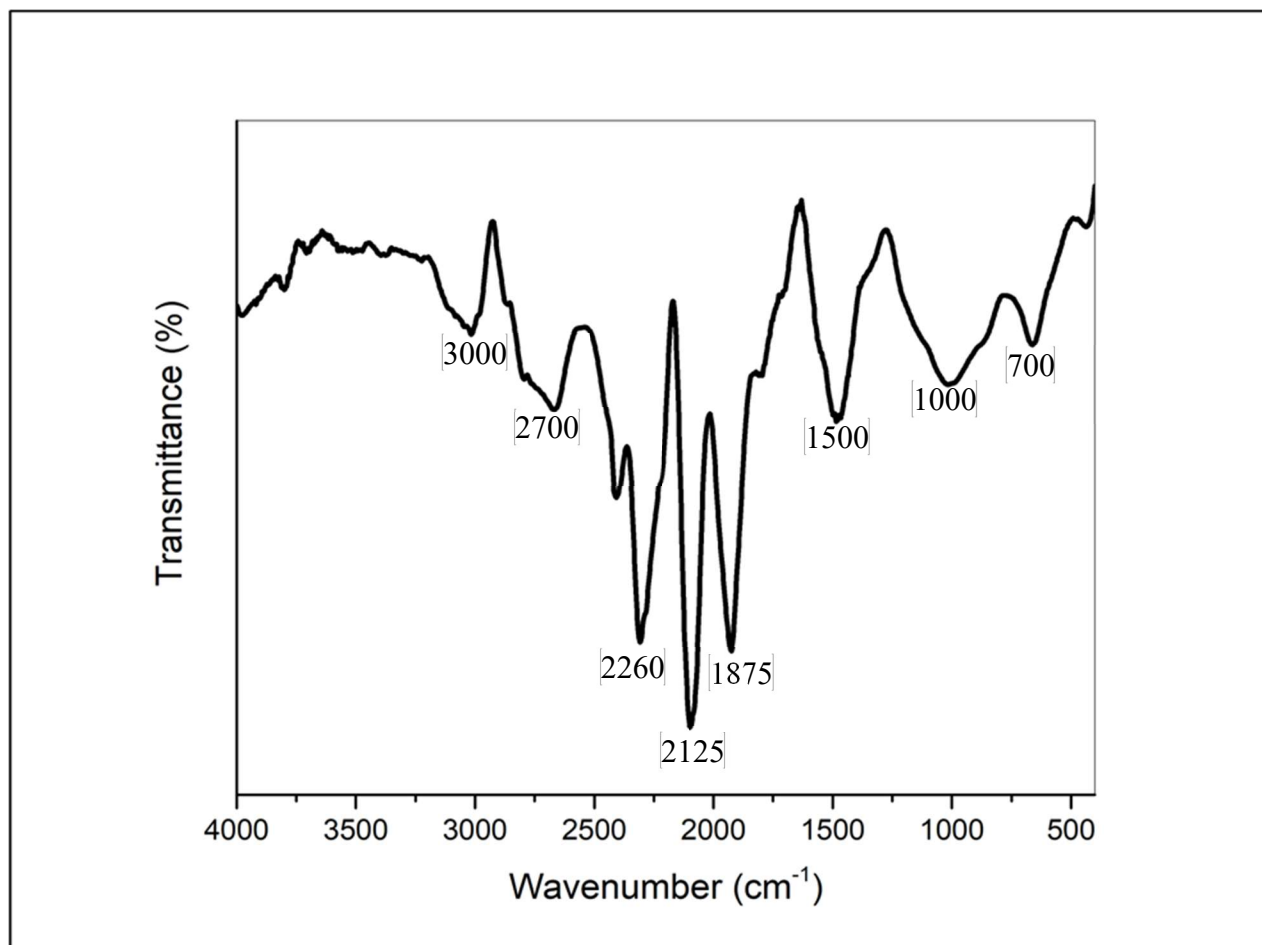


Figure 15- FTIR spectroscopy result of the CAC.

4.1.5 Particle Size Distribution

The laser diffraction analyzer device was used to obtain the particle size distribution of the CAC.

Table 6 below shows the particle size distribution of the CAC.

Results from the laser diffraction analysis show that 10% of the analyzed CAC sample has a particle size smaller than $4.51\text{ }\mu\text{m}$, 50% of the sample is of size smaller than $11.61\text{ }\mu\text{m}$ and 90% of the sample has a size smaller than $20.64\text{ }\mu\text{m}$. This means that the CAC particles size fall between

around 21 and 4.5 μm . This particle size is relatively larger than that found in the literature where researchers obtained particle size ranging between 0.1 -1.1 μm for the commercial plumestop[®] (Sorengard et al., 2019), and 0.8- 1.6 μm for another CAC (Georgi et al., 2015).

Table 6- Particle size distribution of the S23 CAC.

Percentile	Particle size (μm)
d ₁₀	4.51
d ₅₀	11.61
d ₉₀	20.64

4.1.6 Density & Dynamic Viscosity

The densitometer was used to measure the density and the dynamic viscosity of the CAC used. Table 7 shows the density and dynamic viscosity of the CAC used. Both, the original and the diluted CAC were tested. The movement of the CAC through the aquifer is controlled by amount of CAC collision to the sediment grains and the probability of its attachment after collision, thus CAC with density close to that of water will have the fastest movement within the aquifer (Georgi et al., 2015). The lower the viscosity of the CAC the easier will be the in-situ subsurface injection (O'Connor et al., 2018). This emphasizes the need for dilution of the CAC used and this what had been done in the study.

Table 7- Density and Dynamic Viscosity of the S23 CAC.

CAC solution type	Density (g/cm³)	Dynamic Viscosity (mPa.s) at room temperature
Diluted (8 times with DI water)	0.99	1.56
Non-diluted	1.09	27.7

4.2 Effect of Operational Parameters on The Removal of MTBE

4.2.1 Effect of flowrate

The effect of the flowrate on the removal of MTBE was investigated. Three different flowrates (0.5, 1 and 2 mL/min) were used to pump 5000 µg/L of the MTBE solution into three different sandstone bed columns each of 20 cm height, and to which 2 g of CAC was injected. Breakthrough curves of MTBE removal are depicted in Figure 16 and MTBE adsorption parameters are listed in Table 8. As expected, results of the MTBE removal showed that both breakthrough and saturation time decreased with the increase in the flowrate. The breakthrough time decreased from 120 to 45 min when the flowrate was increased from 0.5 to 1 mL/min, and it further decreased to 40 min with the increase in flowrate to 2mL/min. Likewise, saturation time was 300 min at 0.5 mL/min and decreased to 240 at 1 mL/min and reached 100 min when the flowrate was increased to 2 mL/min. This is attributed to the fast saturation that takes place because of the high MTBE masses that will be pumped to the column with the raise in flowrate. The steepness of the breakthrough curves in Figure 16 shows this very clearly, as the flowrate increases the steepness of the curve increases too, which indicates a higher (faster) adsorption rate. These results are in consistent with other studies found in the literature (Ghorai and Pant, 2004; Lopez-Cervantes et al., 2017). In addition, the removal efficiency of the MTBE decreases with the increase in flowrate, and this is

attributed to the fact that MTBE has more time at lower flowrates to contact with the CAC in the column. These results are similar to results of other studies in the literature (Ahmad and Hameed, 2009; Sheng et al., 2018).

The 0.5 ml/min flowrate showed the highest removal efficiency and good mass adsorbed and adsorption capacity values. However, this is not a practical flowrate as it will require the experiment to take very long time to last. Thus the 1 ml/min flowrate is the best (optimum) flowrate in this study since it showed a higher removal efficiency than the 2ml/min flowrate and a comparable value of mass adsorbed and adsorption capacity.

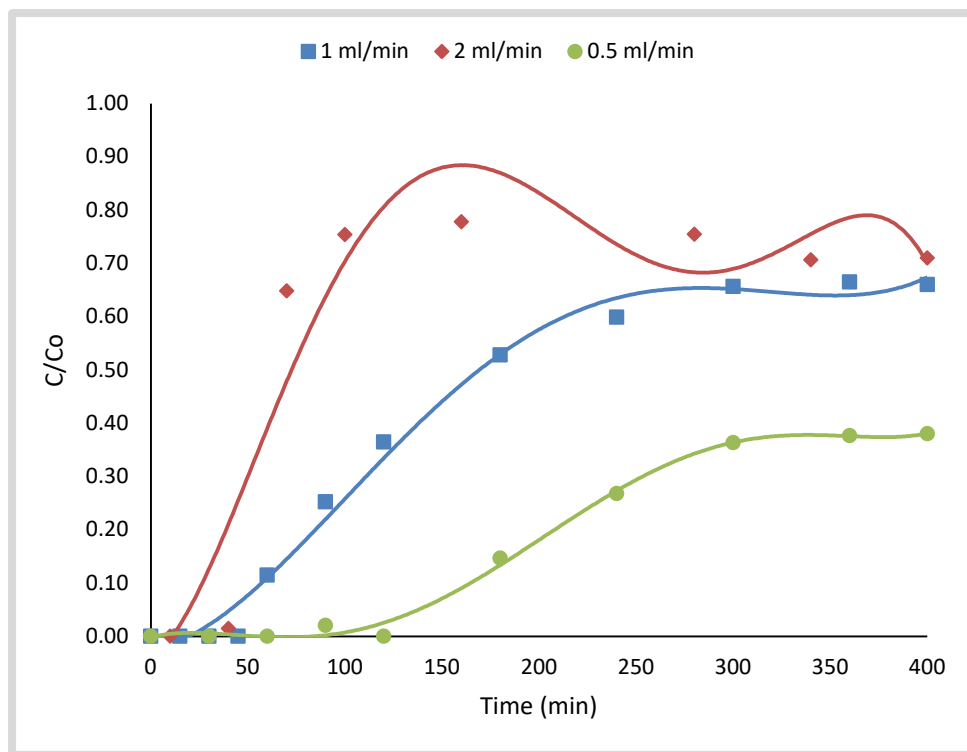


Figure 16- Breakthrough curves of MTBE at different flowrates as a function of time. Conditions: bed type: sandstone, bed height: 20 cm, Co: 5000 µg/L, dosage 2 g

Table 8- MTBE adsorption parameters for the effect of flowrate.

Flowrate (ml/min)	t _b (min)	t _s (min)	m _{adsorbed} (µg)	m _{total} (µg)	Volume treated (mL)	q _e (µg /g)	Removal Efficiency (%)
0.5	120	300	484	1000	97	242	52
1	40	100	492	2000	98	246	75
2	45	240	591	4000	118	296	85

4.2.2 Effect of CAC Dosage

The effect of CAC dosage on MTBE removal was conducted at three dosages, namely 0.5, 1, and 2 g, at flow rate of 1 mL/min, and MTBE initial concentrations of 5000 ppb. Moreover, a control experiment was conducted under the same conditions where no CAC was injected. It was observed that around 50 % of MTBE was lost in the control experiment due to adsorption and/or volatilization. It was also noted that the increase in the CAC dosage increased the removal efficiency. The plot of effluent MTBE concentration versus time are depicted in Figure 17. The column parameters for MTBE removal are presented in Table 9. As expected, the breakthrough and saturation times increased with higher CAC dosages. When the dosage was increased from 0.5 to 1 g, the breakthrough time increased slightly from 15 min to 43 min. A further increase to 2 g led to a more substantial increase in the breakthrough time reaching 100 mins. Similarly, the saturation time showed a consistent increase, from 120 min at 0.5 g to 350 min at 2 g. This improvement in adsorption performance with higher dosage is ascribed to the increase in the available sites for MTB binding. As the number of these sites increases, more MTBE will adsorb to the sites available in the CAC, resulting in an increase in the adsorption rate. The results obtained

are consistent with the results of other studies found in the literature (Mondal et al., 2008; Abas et al., 2013; Padmavathy et al., 2016).

CAC dosage of 2 g shows highest value for adsorbed mass of MTBE and the highest removal efficiency, along with its high adsorption capacity value. Thus, this dosage is the best (optimum) dosage for MTBE removal in this study.

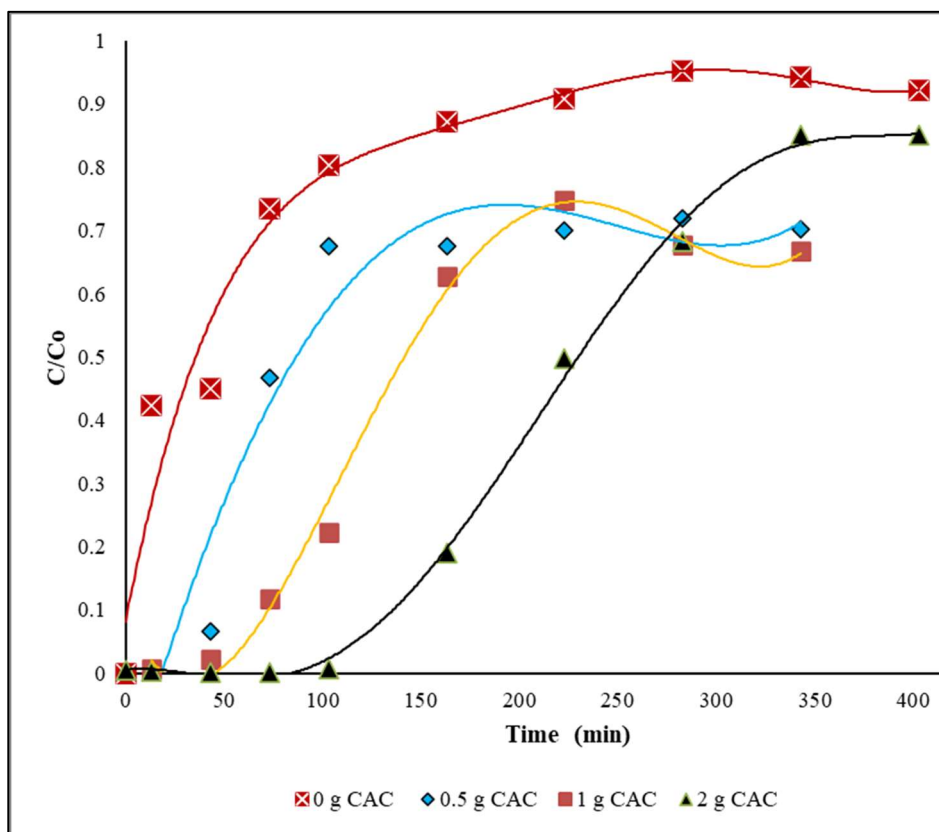


Figure 17- The breakthrough curves for MTBE removal at different dosages with time.

Table 9- MTBE Adsorption parameters for the effect of CAC dosage

CAC dosage (g)	t_b (min)	t_s (min)	m_{adsorbed} (µg)	m_{total} (µg)	Volume treated (mL)	q_e (µg /g)	Removal Efficiency (%)
0.5	15	120	406	2000	81	811	80
1	43	220	585	2000	117	585	71
2	100	350	1470	2000	294	735	26

4.2.3 Effect of Initial Concentrations

The effect of inlet initial concentrations of MTBE on the removal was investigated at three initial concentrations; 10,000, 5,000, and 2,000 µg/L, under constant flow rate flowrate of 1 mL/min, and a dosage of 2 g. The column parameters for MTBE removal listed in Table 10 and the breakthrough curve is depicted in Figure 18. It was observed that the breakthrough and saturation time decreased as the initial concentration increased. The breakthrough time shortened significantly from 210 to 45 min as the initial concentration increased from 2,000 to 1,0000 µg/L. This is ascribed to the build up of a concentration gradient that will increase the driving force needed to overcome the mass transfer resistance between CAC surface and water molecules (Zhu et al., 2008; Foroughi-Dahr et al., 2014; Sadaf et al., 2015). Due to the increase in this driving force a rapid occupation of adsorption sites available on the CAC takes place, leading to shorter breakthrough and saturation time. Results obtained show that total MTBE adsorbed increased from 732 µg to 830 µg as the initial concentrations increased from 2,000 to 10,000 ug/L. These results coincide with the results of similar studies found in literature (Moyo et al., 2017; Saravanan et al., 2018).

The concentration of 2000 ppb shows the highest removal efficiency of MTBE compared to that of the two other concentrations. In addition, the values for adsorption capacity and mass adsorbed at this concentration are high. However, this high removal efficiency value could be attributed to the fact that has been shown by the control experiment at section 4.2.6 which showed that a reasonable amount of the MTBE gets removed by the sandstone bed alone. Thus, this concentration is not high enough to show the action of the CAC adsorbent. As a result, 5000 ppb was chosen as the best (optimum) concentration to achieve maximum MTBE removal in this study, as it has a comparable mass adsorbed and adsorption capacity values and shows higher removal efficiency than that of 10000 ppb.

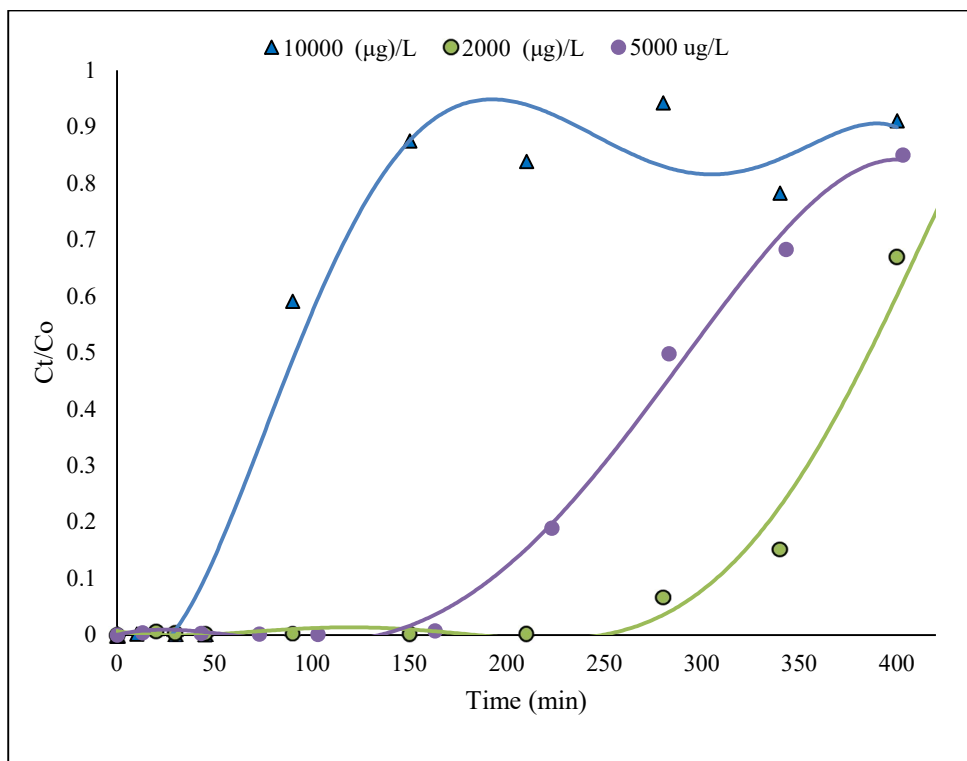


Figure 18- Breakthrough curves for MTBE removal at different initial concentrations.

Table 10- MTBE Adsorption parameters for the effect of Initial concentrations

Initial Concentrations	t_b (min)	t_s (min)	m_{adsorbed} (µg)	m_{total} (µg)	Volume treated (mL)	q_e (µg /g)	Removal Efficiency (%)
10000	45	150	1263	1500	83	631	16
5000	163	400	1630	2000	139	815	19
2000	210	460	732	800	366	366	9

4.2.4 Effect of Conductivity

To study the effect of conductivity on the CAC performance for MTBE adsorption, solutions at concentrations of 5000 µg/L were prepared in a brine matrix. The brine was prepared using three sodium chloride concentrations: 0, 10,600 and 21,200 mg/l resulting in three corresponding conductivities: <5 , 18000, and 33850 µS/cm respectively. The experiments were conducted at a 1 mL/min flow rate and CAC dosage of 2 g. The breakthrough curves for MTBE removal were plotted as depicted in Figure 19 and the adsorption parameters are listed in Table 11. The obtained results indicated an insignificant change in the CAC adsorption for MTBE as conductivity increased from <5 to 18000 µS/cm. However, a further increase in conductivity to 33850 µS/cm showed slight improvement for MTBE removal. The breakthrough time was observed at 70 mins for conductivities of <5 and 18000 µS/cm. While at the conductivity of 33850 µS/cm, the breakthrough time increased to 100 min, indicating an enhancement in MTBE removal at high conductivity. This might be ascribed to the salt-out effect (Endo et. al, 2012). As conductivity increases, the MTBE solubility in water decreases due to the increased interaction between water molecules and salt ions , which enhances the MTBE adsorption onto the CAC surface.

The very high conductivity resulted in higher MTBE removal efficiency and higher values of adsorption capacity and mass adsorbed. Thus the 33850 $\mu\text{S/cm}$ is the best (optimum) conductivity for the removal of MTBE in this study.

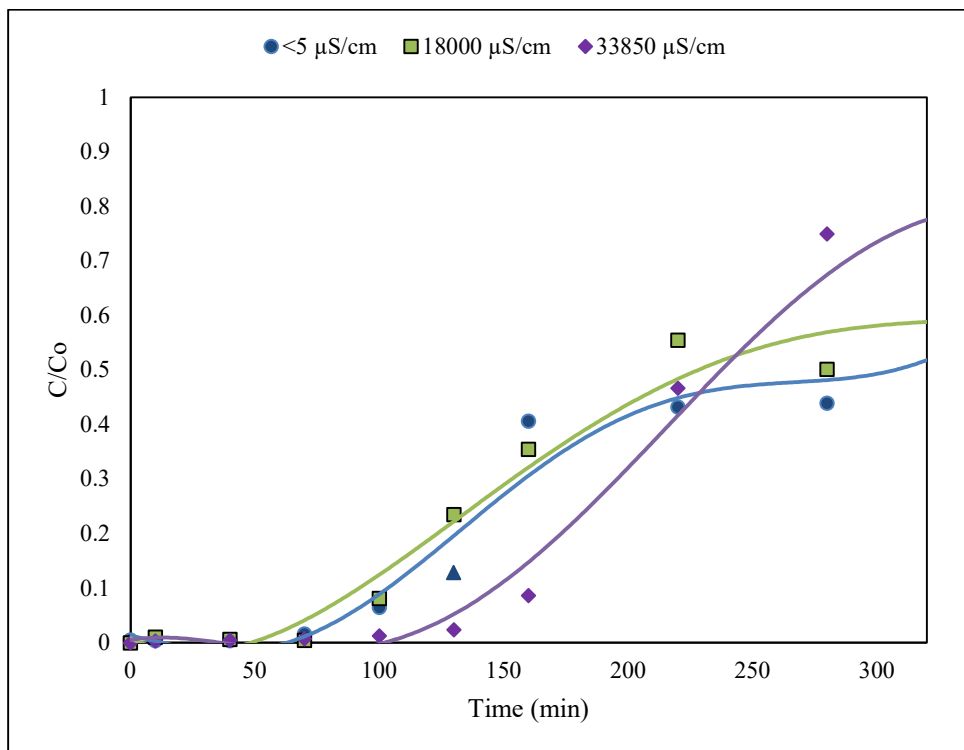


Figure 19- Breakthrough curves of MTBE at different conductivities.

Table 11- MTBE Adsorption parameters for the effect of conductivity.

Conductivity ($\mu\text{S/cm}$)	t_b (min)	t_s (min)	m_{adsorbed} (μg)	m_{total} (μg)	Volume treated (mL)	q_e ($\mu\text{g/g}$)	Removal Efficiency (%)
<5	70	250	910	2000	182	455	55
18000	70	250	735	2000	147	368	63
33850	100	340	1050	2000	210	525	48

4.2.5 Effect of bed height

The effect of bed height on the adsorption performance of the CAC for MTBE was investigated in this study. Two columns were prepared with varying bed heights of 10, and 20 cm packed with sand, and 2 g of CAC was injected into each column. The initial concentrations of the MTBE were 5000, with a flow rate maintained at 1 mL/min. The breakthrough curves for MTBE at various bed heights are presented in Figure 20 and the adsorption parameters are listed in Table 12.

The findings indicated that the bed height has an insignificant effect on the CAC adsorption for MTBE. Breakthrough times were approximately 40 min for both 10 and 20 cm bed heights. The saturation time was consistent at 250 min across both bed heights. The insignificant variation observed in the CAC adsorption at different bed heights may be attributed to the fact that the CAC is injected at the bottom of the column and distributed for a length less than 10 cm in the packed column depending on the dosage of the CAC, and since the dosage at this experiment was the same, then an insignificant effect was observed.

Since no significant effect was observed for the bed height, thus the 20 cm height is the best (optimum) bed height for the removal of MTBE in this study.

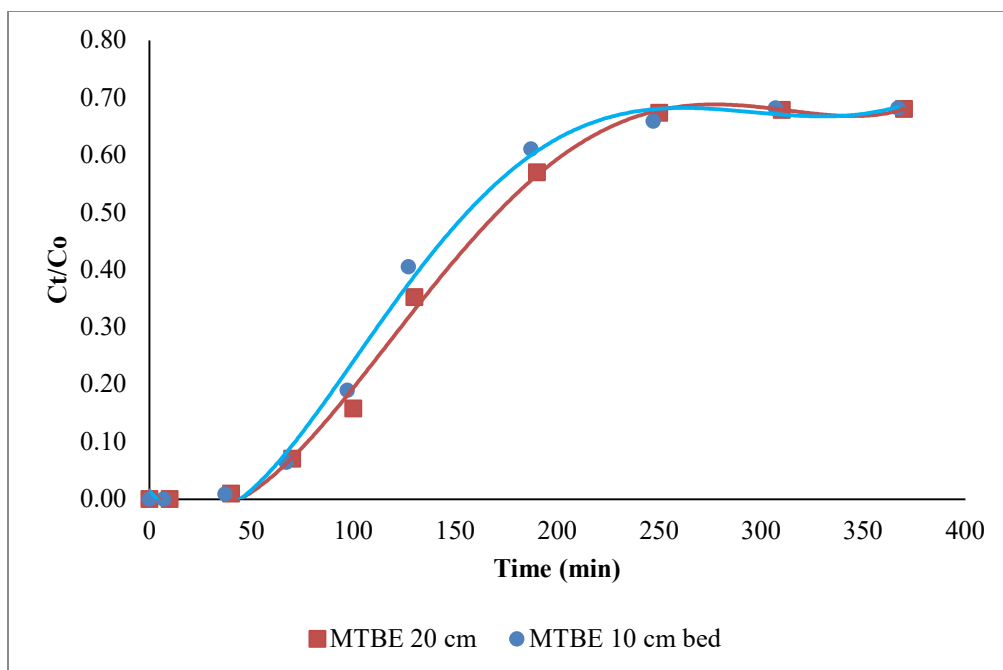


Figure 20- Breakthrough curves of MTBE at different bed heights.

Table 12- MTBE Adsorption parameters for the effect of Bed height.

Bed height (cm)	t_b (min)	t_s (min)	$m_{adsorbed}$ (μg)	m_{total} (μg)	Volume treated (mL)	q_e ($\mu g/g$)	Removal Efficiency (%)
10	40	250	1013	1800	236	501	53
20	40	250	955	1800	227	473	50

4.2.6 Effect of bed type

The effect of the bed type on the removal of MTBE was examined. Two 20 cm long columns were used in which sandstone and carbonate were used as column beds. 2g of CAC was injected in the two columns, at a flowrate of 1mL/min and with MTBE initial concentration of 5000 $\mu\text{g/L}$. The breakthrough curves for the removal of MTBE is depicted in Figures 21 and 22, and adsorption parameters are listed in Table 13. Results obtained showed that the control carbonate bed has longer saturation time (120 min), compared to the control sandstone bed that has a saturation $t_s=45$ min, however both have the same breakthrough time (2 min). The breakthrough time and the saturation time of both beds increased with the injection of CAC. The breakthrough time of sandstone bed increased to 15 min whereas that of carbonate increased to 60 min. The saturation time of sandstone increased from 45 to 120 min, whereas that of carbonate increased from 120 to 180 min. These results indicate that carbonate bed is better in terms of MTBE removal compared to the sandstone bed. This may be attributed to the results provided in literature (Zhou et al., 2020) that proved that carbonate is more porous than sandstone, which means that there are more spaces and active sites available in carbonate bed for MTBE to stick to compared to sandstone, and hence result in a greater saturation and breakthrough time.

The carbonated bed showed higher removal efficiency, adsorption capacity and mass adsorbed values, thus it is the best (optimum) bed type for the removal of MTBE in this study.

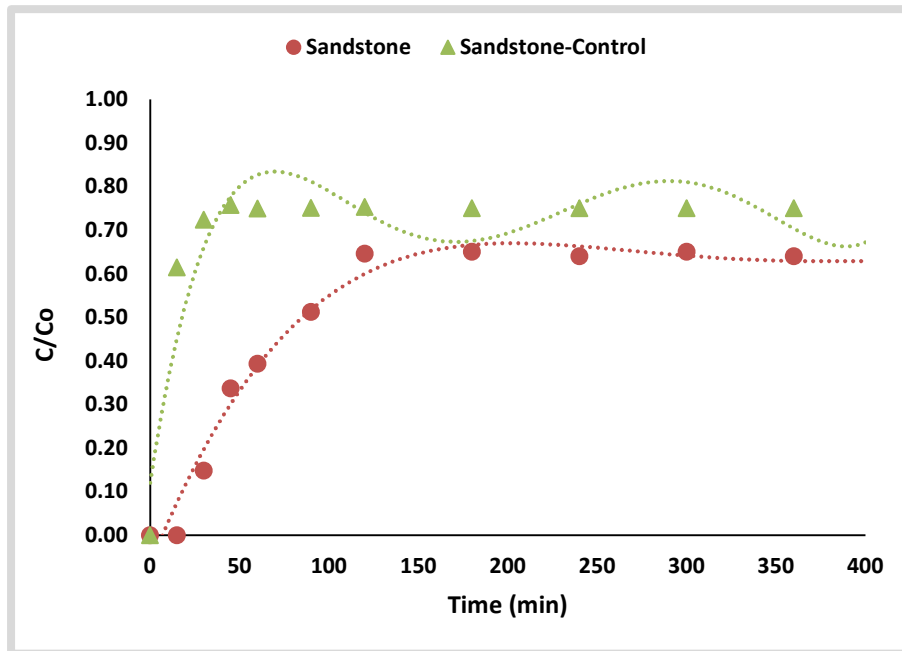


Figure 21 - Breakthrough curves of MTBE with sandstone bed type.

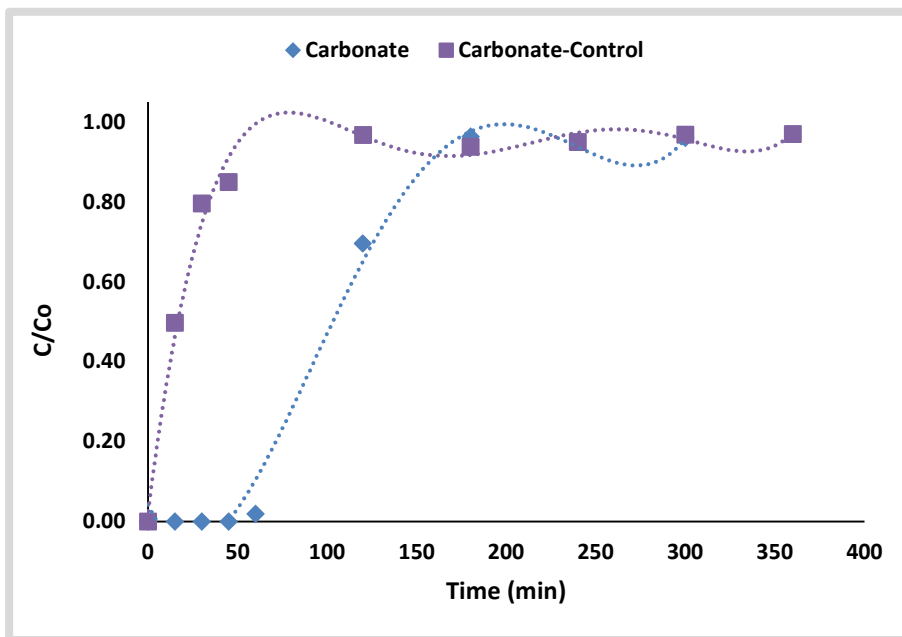


Figure 22 - Breakthrough curves of MTBE with carbonate bed type.

Table 13- MTBE Adsorption parameters for the effect of Bed type.

Bed type	t_b (min)	t_s (min)	m_{adsorbed} (µg)	m_{total} (µg)	Volume treated (mL)	q_e (µg /g)	Removal Efficiency (%)
Carbonate	60	180	557	1800	111	279	69
Sandstone	15	120	1048	1800	210	524	42

4.2.7 Optimum experimental conditions for MTBE removal

Based on the results presented above, optimum conditions for MTBE removal can be determined based on mass adsorbed, adsorption capacity and removal efficiency values. The optimum experimental conditions for MTBE removal in this study is given in the below table.

Table 14- Optimum experimental conditions for the removal of MTBE.

CAC dosage (g)	Initial concentrations (µg/L)	Conductivity (µS/cm)	Bed height (cm)	Bed type	Flowrate(mL/min)
2	5000	33850	20	sandstone	1.0

4.3 Effect of operational conditions on the removal of BTEX

Fixed-bed column parameters and breakthrough curves of BTEX removal couldn't be obtained in the above conducted experiments, since these compounds were either totally removed or detected at very low level. Therefore, another set of experiments was designed by raising the initial concentration of the BTEX solution to 6000 $\mu\text{g/L}$ and flowrate to 2 mL/min. It should be noted that neither Ethylbenzene nor Xylenes could be detected in the new set as shown Figure 23, and this is attributed to the same reasons mentioned before. Toluene also showed very low concentrations in several experiment as shown in Figure 24. As a result, column parameters and breakthrough curves could only be obtained for Benzene and sometimes for Toluene. Hence only Benzene breakthrough curves and column parameters are presented in this section. Toluene column parameters and breakthrough curves can be found in the Appendix (Table A1 and Figures A1-A6).

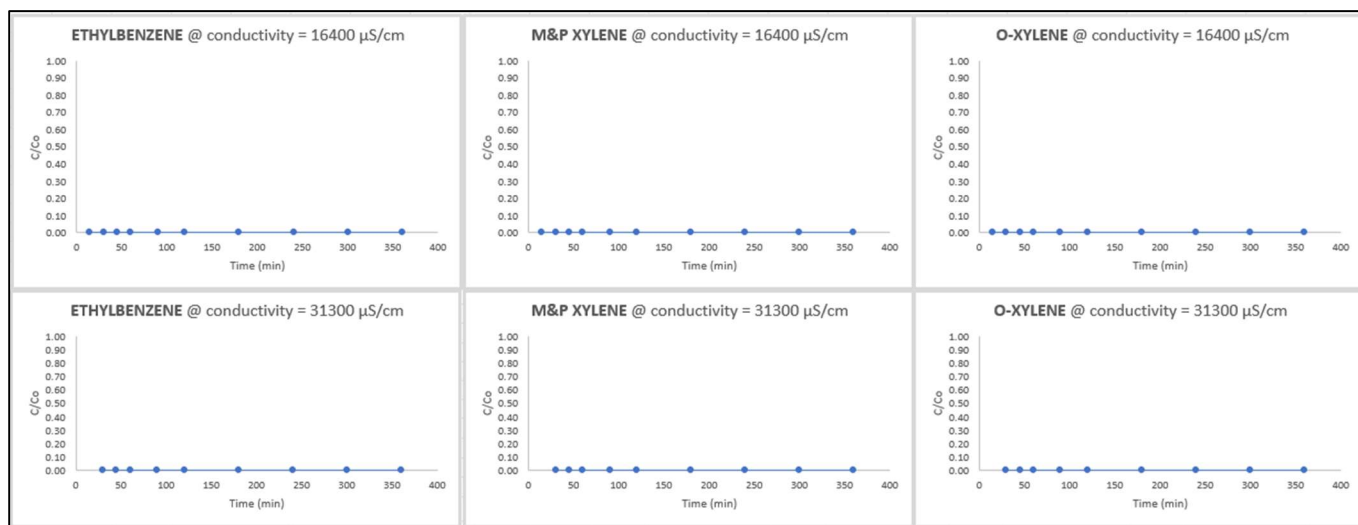


Figure 23 –Undetectability of Ethylbenzene and Xylenes concentrations in the study.

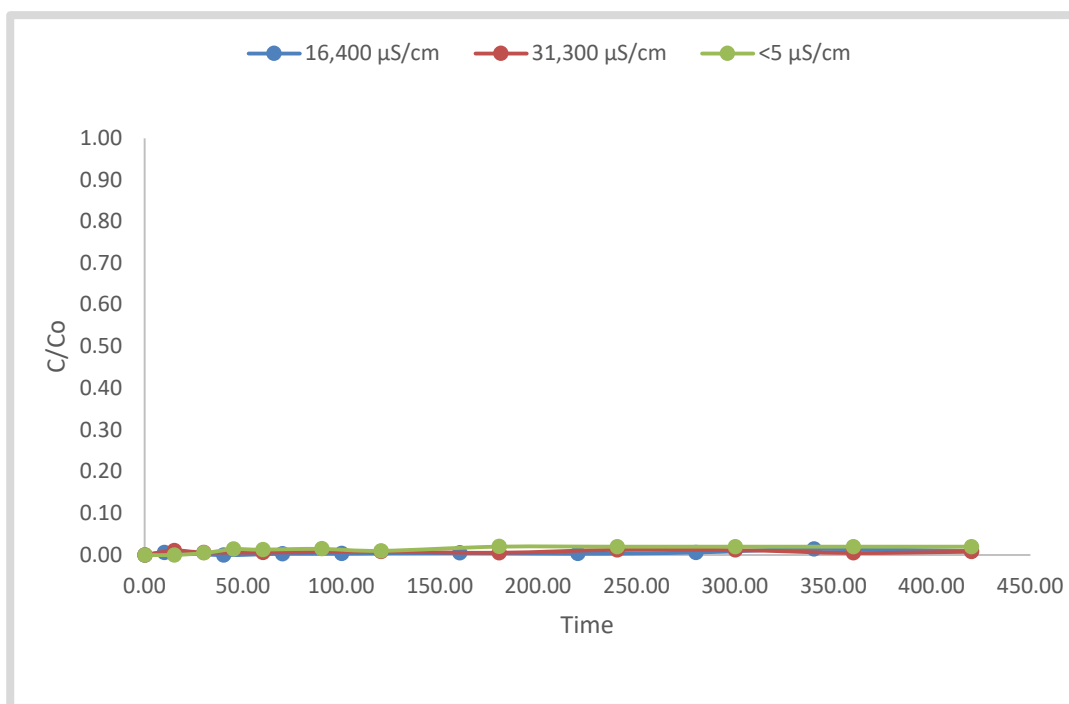


Figure 24- Sample graph for the undetectability of Toluene concentrations in the study.

4.3.1 Effect of flowrate

The effect of the flowrate on the removal of Benzene was investigated. Three different flowrates (0.5, 1 and 2 mL/min) were used to pump 6000 $\mu\text{g/L}$ of the BTEX solution into three different sandstone bed columns each of 20 cm height, and to which 2 g of CAC was injected. Breakthrough curves of Benzene removal are depicted in figure 25 and adsorption parameters are listed in Table 15. As expected, results of the Benzene removal showed that both breakthrough and saturation time decreased with the increase in the flowrate. This is attributed to the fast adsorption of Benzene into the active sites found on CAC surface. The mass of Benzene adsorbing to the CAC surface increases with the increase in flowrate. These results are in consistent with other studies found in the literature (Ghorai and Pant, 2004; Lopez-Cervantes et al., 2017). Experiments with flowrates of 0.5 and 1 mL/min showed very long breakthrough time. It should be noted that no benzene was

detected until the end of the experiment (400 min), which could be an indication of the slow Benzene adsorption occurring at these low flowrates.

Flowrate 0.5ml/min can't be the optimum flowrate for the removal of Benzene in this experiment because it is not a practical flowrate, as it will require the experiment to take very long time to last. On the other hand, the 1 ml/min flowrate when used, the detected BTEX concentrations were extremely low, thus the flowrate of 2 ml/min was the best (optimum) flowrate for Benzene removal, as it gives the highest removal efficiency, mass adsorbed and adsorption capacity.

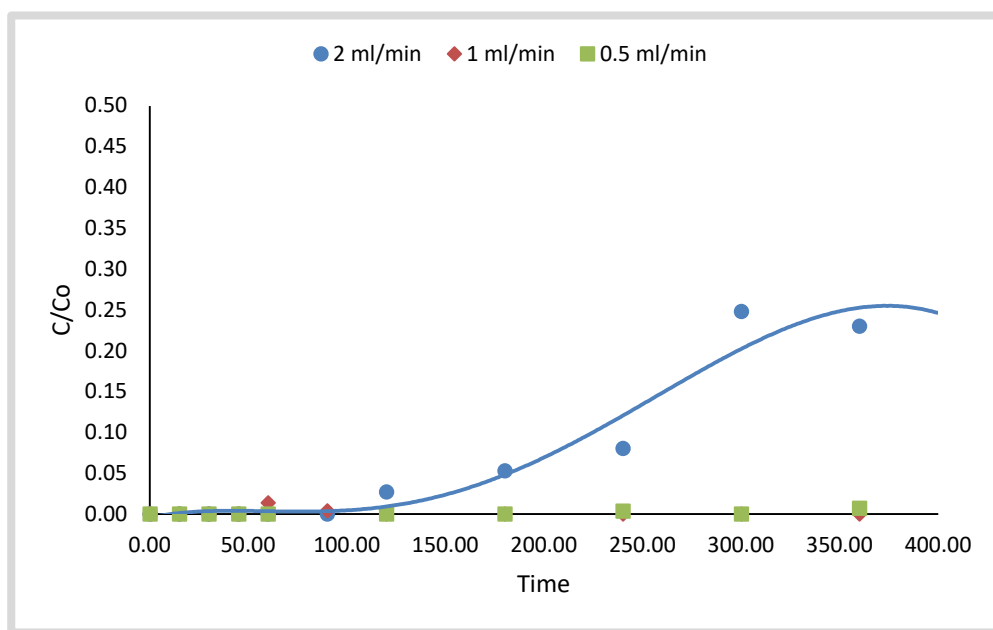


Figure 25- Breakthrough curves of Benzene at different flowrates.

Table 15- Benzene Adsorption parameters for the effect of flowrate.

Flowrate (ml/min)	t_b (min)	t_s (min)	m_{adsorbed} (µg)	m_{total} (µg)	Volume treated (mL)	q_e (µg /g)	Removal Efficiency (%)
0.5	420	NA*	9	1200	1.5	5	99
1	420	NA*	31	2400	5	16	99
2	90	300	472	3600	79	236	87

* No benzene was detected and hence breakthrough curve was not formed.

4.3.2 Effect of CAC Dosage

The effect of CAC dosage on Benzene removal was conducted at three dosages, namely 0.5, 1, and 2 g, at flow rate of 2 mL/min, and BTEX initial concentrations of 6000 ppb. Moreover, a control experiment was conducted under the same conditions where no CAC was injected. It was observed that around 80 % of the detected Benzene was removed in the control experiment due to adsorption and/or volatilization. The plots of effluent Benzene concentration versus time are depicted in Figure 26 and the adsorption parameters are listed in Table 16. As expected, the breakthrough and saturation times increased with higher CAC dosages. When the dosage was increased from 0.5 to 2 g, the breakthrough time of Benzene removal increased from 15 min to 90 min. In terms of the saturation time, an increase, from 300 min at 0.5 g to 360 min at 2 g was noted in Benzene removal. This improvement in adsorption performance and Benzene removal efficiency with the increase in the CAC dosage is ascribed to the increase in the available sites for Benzene binding. As the number of these sites increases, more Benzene will adsorb to the sites available in the CAC, resulting in an increase in the adsorption rate. The results obtained are

consistent with the results of other studies found in the literature (Mondal et al., 2008; Abas et al., 2013; Padmavathy et al., 2016).

The dosage of 2 g showed the highest Benzene removal efficiency and mass adsorbed, in addition to its good adsorption capacity. Thus, it is the best (optimum) CAC dosage for Benzene removal in this study.

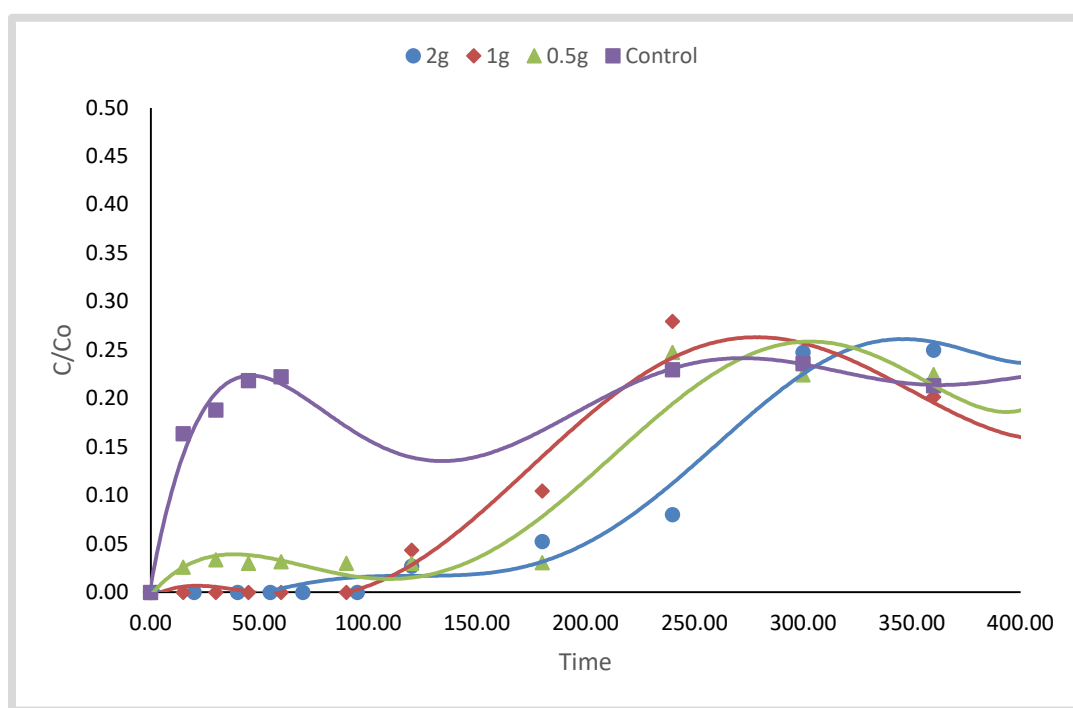


Figure 26- Breakthrough curves of Benzene at different CAC dosages.

Table 16- Benzene Adsorption parameters for the effect of CAC dosage.

CAC dosage (g)	t_b (min)	t_s (min)	$m_{adsorbed}$ (μg)	m_{total} (μg)	Volume treated (mL)	q_e ($\mu\text{g/g}$)	Removal Efficiency (%)
0.5	15	240	660	4800	110	1320	86
1	90	240	708	4800	118	708	85
2	90	300	783	4800	131	392	84

4.3.3 Effect of Initial concentrations

The effect of inlet initial concentrations of BTEX on the removal of Benzene was investigated at three initial concentrations: 20,000, 10,000, and 6,000 $\mu\text{g/L}$, under constant flowrate of 2 mL/min, and a dosage of 2 g. The fixed column parameters and the breakthrough curve were identified for Benzene and listed in Table 17 and depicted Figure 27. As expected, the breakthrough and saturation time decreased as the initial concentration increased. The breakthrough time shortened from 90 to 2 min, and the saturation time decreased from 360 to 240 min as the initial concentration increased from 6,000 to 20,000 $\mu\text{g/L}$. This is ascribed to the buildup of a Benzene concentration gradient that will increase the driving force needed to overcome the mass transfer resistance between CAC surface and water molecules (Zhu et al., 2008; Foroughi-Dahr et al., 2014; Sadaf et al., 2015). Due to the increase in this driving force a rapid occupation of adsorption sites available on the CAC takes place, leading to shorter breakthrough and saturation time. Results obtained show that total Benzene adsorbed increased from 149 μg to 1418 μg as the initial concentrations increased from 6,000 to 20,000 $\mu\text{g/L}$. These results coincide with the results of similar studies found in literature (Moyo et al., 2017; Saravanan et al., 2018).

The concentration 6000 ppb showed a benzene removal efficiency of 94%, in addition to the good adsorption capacity and mass adsorbed values. Thus, it is the best (optimum) initial BTEX concentration for benzene removal in this study.

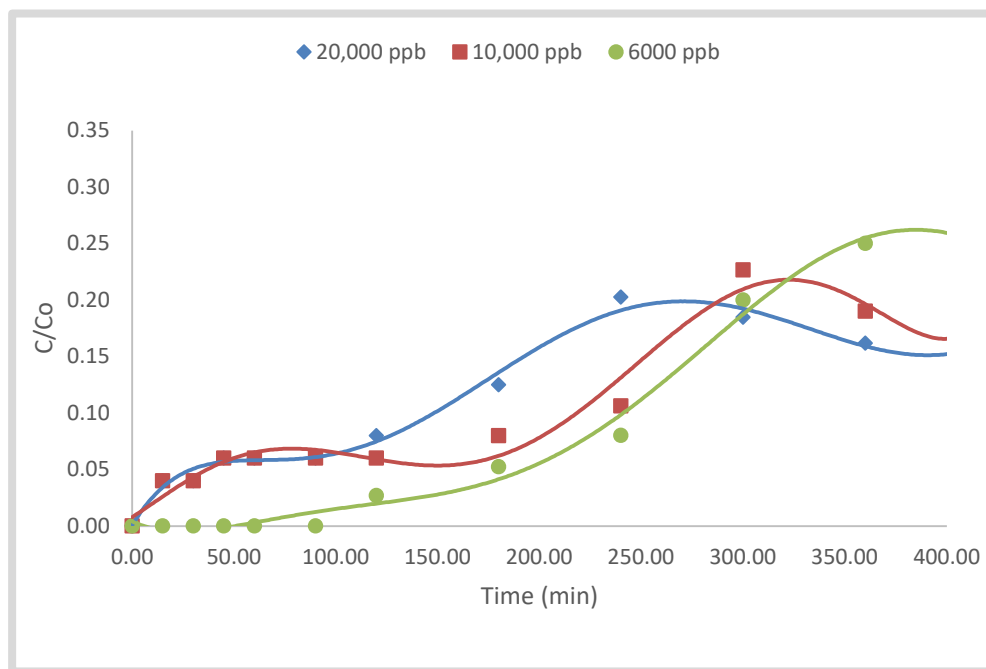


Figure 27- Breakthrough curves of Benzene at different initial concentrations.

Table 17- Benzene Adsorption parameters for the effect of Initial concentrations.

Initial Concentration	t_b (min)	t_s (min)	m_{adsorbed} (μg)	m_{total} (μg)	Volume treated (mL)	q_e ($\mu\text{g/g}$)	Removal Efficiency (%)
20,000	2	240	12920	16000	71	709	91
10,000	2	300	6000	8000	118	592	85
6000	90	360	4080	4800	25	75	97

4.3.4 Effect of Conductivity

To study the effect of conductivity on the CAC performance for Benzene adsorption, solutions at BTEX concentrations of 6000 µg/L were prepared in a brine matrix. The brine was prepared using three sodium chloride concentrations: 0, 10,000 and 20,000 mg/l resulting in three corresponding conductivities: <5, 16400, and 31300 µS/cm respectively. The experiments were conducted at a 2 mL/min flow rate and CAC dosage of 2 g. The breakthrough curves were plotted for Benzene as depicted in Figure 28 and the adsorption parameters are listed in Table 18. The obtained results indicated insignificant change in the CAC adsorption for Benzene as conductivity increased from <5 to 16400 µS/cm which was described by the small increase in the breakthrough time from 90 to 100 minutes. A further increase in conductivity to 31300 µS/cm showed a significant increase in Benzene removal. The breakthrough time increased to 270 min, indicating an enhancement in Benzene removal at high conductivity. This might be ascribed to the salt-out effect (Endo et. al, 2012). As conductivity increases, the Benzene solubility in water decreases due to the increased interaction between water molecules and salt ions which enhances the Benzene adsorption onto the CAC surface.

Conductivity of 16400 µS/cm is the best (optimum) conductivity for the removal of Benzene in this study as it showed the highest Benzene removal efficiency, adsorption capacity and mass adsorbed values.

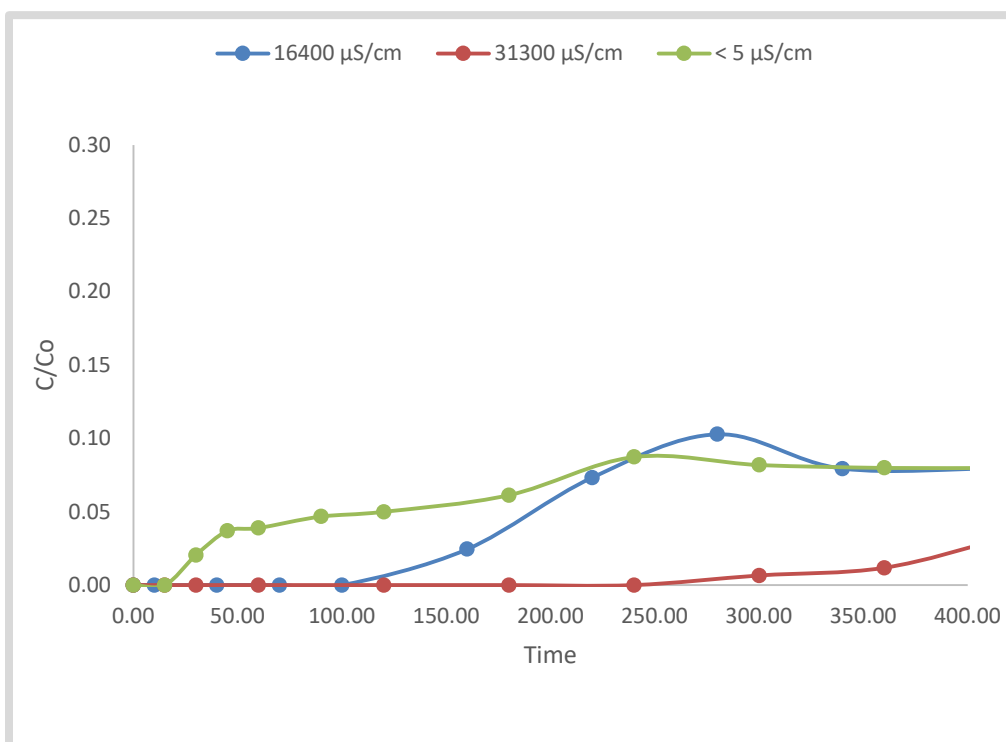


Figure 28- Breakthrough curves of Benzene at different conductivities.

Table 18- Benzene Adsorption parameters for the effect of conductivity.

Conductivity ($\mu\text{S/cm}$)	t_b (min)	t_s (min)	m_{adsorbed} (μg)	m_{total} (μg)	Volume treated (mL)	q_e ($\mu\text{g/g}$)	Removal Efficiency (%)
< 5	90	300	149	4800	25	75	97
16400	100	270	615	4800	103	308	87
31300	270	400	447	4800	86	258	89

4.3.5 Effect of bed height

The effect of bed height on the adsorption performance of the CAC for Benzene was investigated in this study. Two columns were prepared with varying bed heights of 10, and 20 cm packed with sand, and 2 g of CAC was injected into each column. The initial concentration of the BTEX was 6000 mg/L, with a flow rate maintained at 2 mL/min. The breakthrough curves for Benzene at various bed heights are presented in Figure 29 and adsorption parameters are listed in Table 19. The findings for Benzene removal indicated that the bed height has an insignificant effect on the CAC adsorption for BTEX. Breakthrough times were the same (90 min) for both 10 and 20 cm bed heights. The saturation time for Benzene removal was also consistent at 300 min across both bed heights. The insignificant variation observed in the CAC adsorption at different bed heights may be attributed to the fact that the CAC is injected at the bottom of the column and distributed for a length less than 10 cm in the packed column depending on the dosage of the CAC, and since the dosage at this experiment was the same, then an insignificant effect was observed.

Since no significant effect was observed for the bed height, thus the 20 cm height is the best (optimum) bed height for the removal of Benzene in this study.

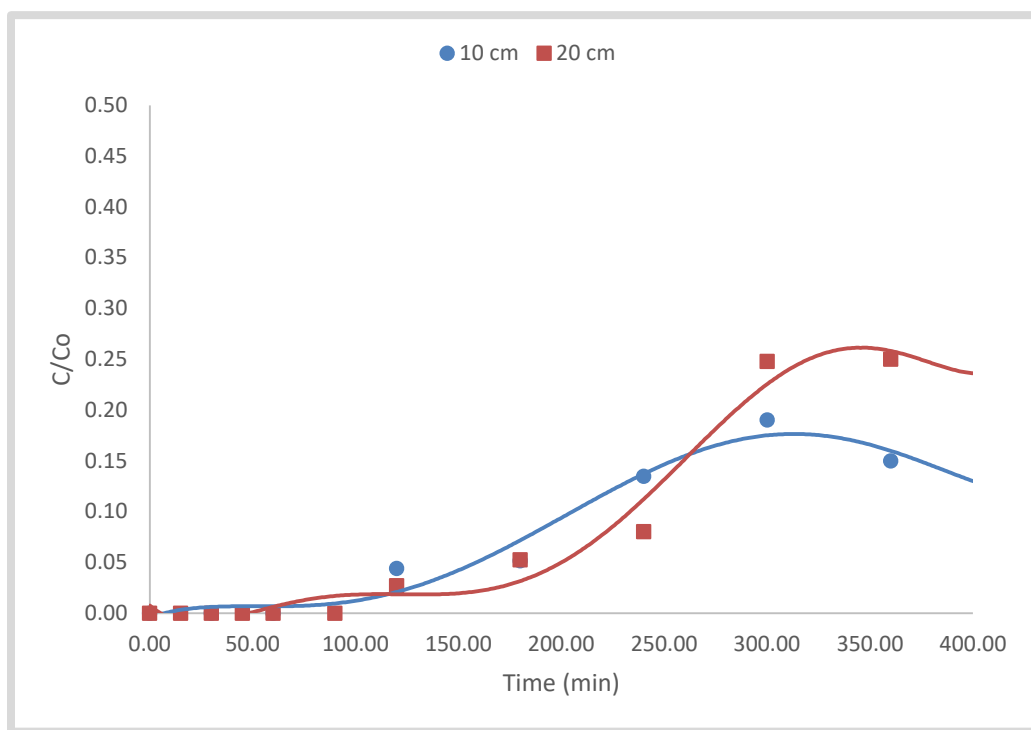


Figure 29- Breakthrough curves of Benzene at different bed heights.

Table 19- Benzene Adsorption parameters for the effect of Bed height.

Bed height (cm)	t_b (min)	t_s (min)	$m_{adsorbed}$ (μg)	m_{total} (μg)	Volume treated (mL)	q_e ($\mu\text{g/g}$)	Removal Efficiency (%)
10	90	300	578	4800	96	289	88
20	90	300	201	4800	34	101	96

4.3.6 Effect of bed type

The effect of the bed type on the removal of BTEX was examined. Two columns were used in which sandstone and carbonate were used as column beds. 2g of CAC was injected in the 20 cm columns, with a constant flowrate of 2 mL/min and an initial concentration of 6000 $\mu\text{g/L}$. The breakthrough curves for the removal of Benzene is depicted in Figures 30 and 31, and adsorption parameters are listed in Table 20. Results obtained from Benzene removal showed that carbonate bed has longer breakthrough time (60 min), compared to that of sandstone (15 min). The saturation time is also longer for the carbonate beds (300 min) compared to that of the sandstone (240 min). These results may be explained by the fact provided in literature (Zhou et al., 2020) which states that carbonate sand is more porous than sandstone, therefore there are more spaces and active sites available in carbonate bed for Benzene to stick to compared to sandstone, and this will consequently result in a greater breakthrough and saturation times.

The carbonated bed showed higher removal efficiency, adsorption capacity and mass adsorbed values, thus it is the best (optimum) bed type for the removal of Benzene in this study.

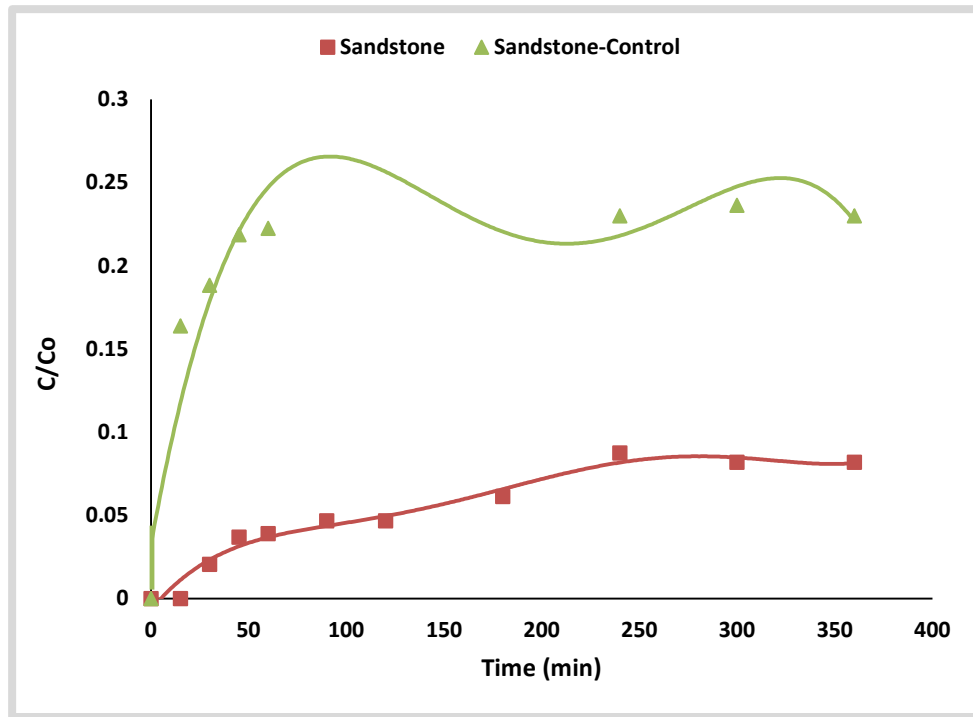


Figure 30- Breakthrough curves of Benzene at sandstone bed type.

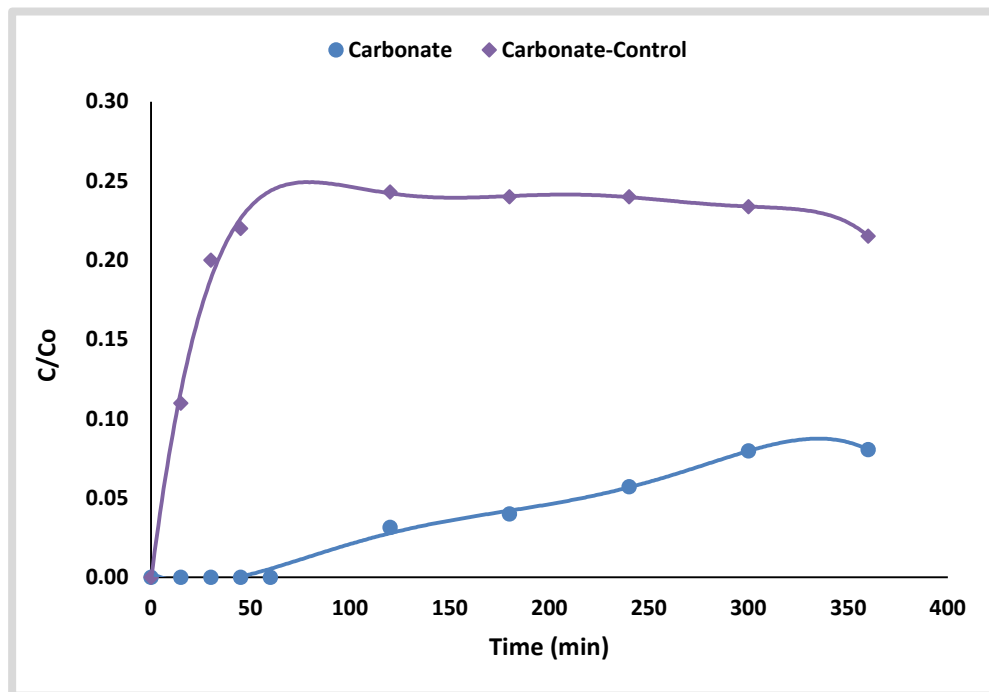


Figure 31- Breakthrough curves of Benzene at carbonate bed type.

Table 20- Benzene Adsorption parameters for the effect of Bed type.

Bed type	t_b (min)	t_s (min)	m_{adsorbed} (μg)	m_{total} (μg)	Volume treated (mL)	q_e (μg /g)	Removal Efficiency (%)
Carbonate	60	300	184	4800	31	92	96
Sandstone	15	240	149	4800	25	75	97

4.3.7 Optimum experimental conditions for Benzene removal

Based on the results presented above, optimum conditions for Benzene removal can be determined based on mass adsorbed, adsorption capacity and removal efficiency values. The optimum experimental conditions for Benzene removal in this study are given in the Table 21 below.

Table 21- Best conditions for BTEX removal

CAC dosage (g)	Initial concentrations (μg/L)	Conductivity (μS/cm)	Bed height (cm)	Bed type	Flowrate(mL/min)
2	6000	16400	20	Carbonate	2

4.4 Modeling of the breakthrough curve

The breakthrough curves for the fixed-bed column experiments under different conditions were developed by plotting concentration-time profile. The experimental data was fitted to three models using OriginPro software. The values of correlation coefficients (R^2) were used to compare different models. The obtained results showed that the experimental data under various conditions is described best by the dose-response model. The fitting results of the Dose-Response model are listed in the Tables 22- 33 below, while the results of other models are listed in the Appendix (Tables A2-A3 and Figures A7-A12). Toluene Dose response model fitting parameters and curves are given in the Appendix (Table A4 and Figures A13-A18).

4.4.1 Models fit for MTBE adsorption

4.4.1.1 Effect of Flowrate

The best fitted curve ($R^2 = 0.969$) was that of flowrate equivalent to 1 ml/min, followed by that of 0.5 ml/min (Table 22 and Figure 31). The adsorption capacity (q_0) values calculated decrease with the increase in flowrate, which is consistent with experimental results obtained previously.

Table 22- Dose-Response model parameters: Effect of flowrate on MTBE removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 (mg/g)
Flowrate (mL/min)	0.5	0.946	1.90	463	1157
	1	0.969	1.50	199	497
	2	0.791	1.21	80.7	202

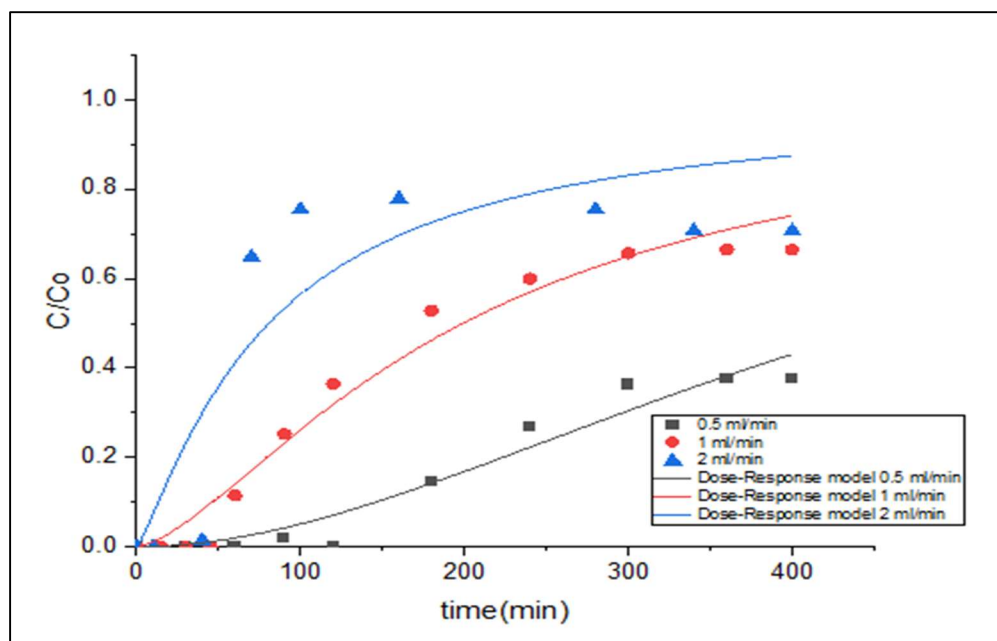


Figure 32- Dose-Response model fit: Effect of flowrate on MTBE removal.

4.4.1.2 Effect of CAC dosages

The best fitted curve ($R^2 = 0.997$) was that of dosage equivalent to 2 g, followed by that of 1g (Table 23 and Figure 32). The adsorption capacity (q_0) values calculated generally increase with the increase in dosage, which is consistent with experimental results obtained previously.

Table 23- Dose-Response model parameters: Effect of Dosage on MTBE removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 (mg/g)
CAC dosages (g)	0.5	0.986	4.85	66.5	665
	1	0.978	4.37	119	595
	2	0.997	5.34	290	725

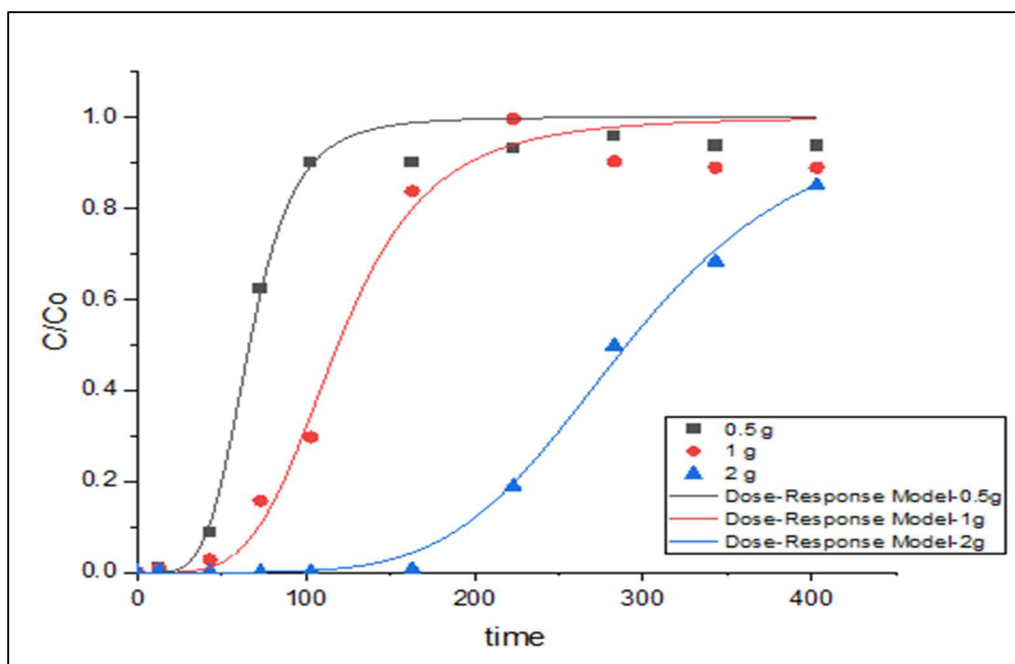


Figure 33 - Dose-Response model fit: Effect of CAC Dosage on MTBE removal.

4.4.1.3 Effect of Initial concentrations

The best fitted curve ($R^2 = 0.992$) was that of initial concentration equivalent to 2000 $\mu\text{g/L}$, followed by that of 5000 $\mu\text{g/L}$ (Table 24 and Figure 33). The adsorption capacity (q_0) values calculated showed that optimum concentration (2000 $\mu\text{g/L}$) has the maximum adsorption capacity value. This is not consistent with the experimental results, however the q_0 value of the 5000 $\mu\text{g/L}$ is very close to that of the 2000 $\mu\text{g/L}$.

Table 24- Dose-Response parameters: Effect of concentration on MTBE removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 (mg/g)
Initial Concentrations ($\mu\text{g/L}$)	10000	0.954	3.16	87.6	219
	5000	0.991	6.93	328	820
	2000	0.992	14.4	381	953

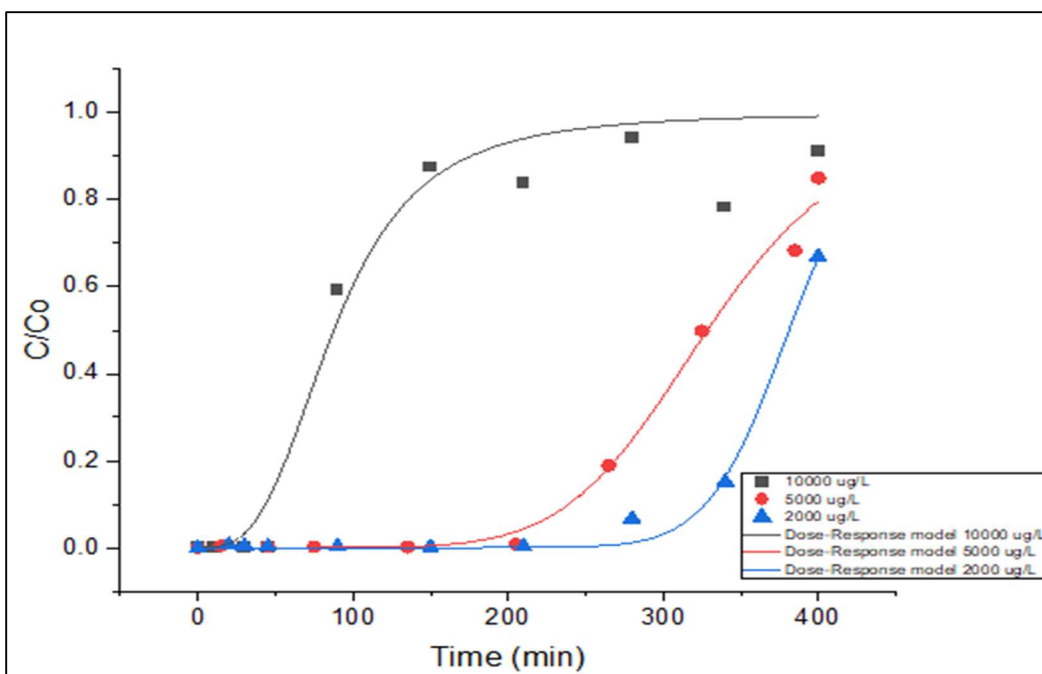


Figure 34- Dose-Response model fit: Effect of initial concentration on MTBE removal.

4.4.1.4 Effect of conductivity

The best fitted curve ($R^2 = 0.951$) was that of conductivity equivalent to 33.85 mS/cm (Table 25 and Figure 34). The adsorption capacity (q_0) values calculated are close to each other, which is consistent with experimental results obtained previously.

Table 25- Dose-Response parameters: Effect of conductivity on MTBE removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 (mg/g)
Conductivity	18600	0.942	3.61	199	498
	33850	0.951	3.33	212	530

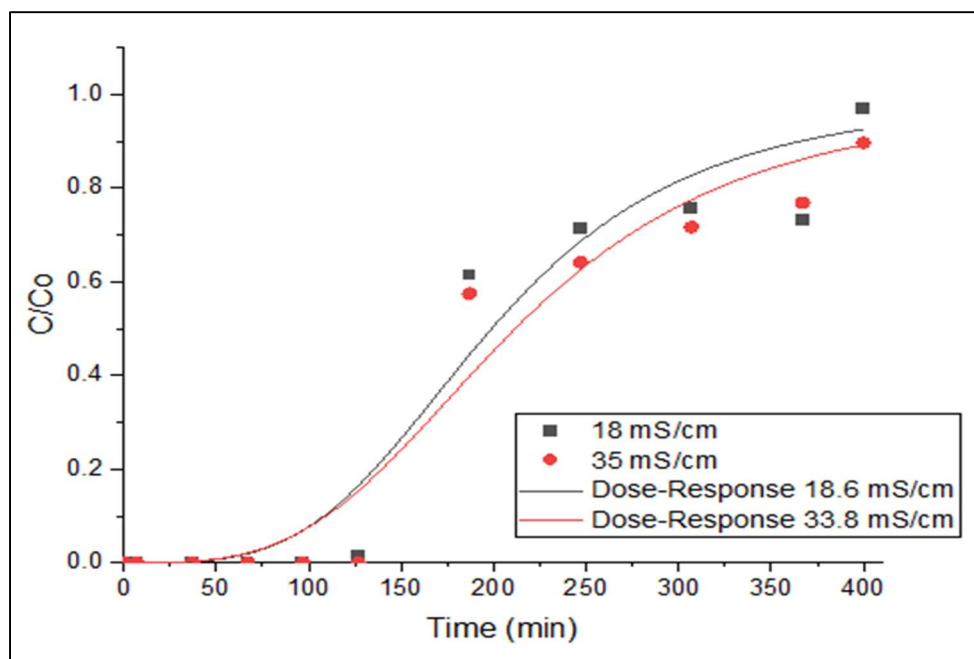


Figure 35- Dose Response model fit: Effect of Effect of conductivity on MTBE removal.

4.4.1.5 Effect of Bed height

The adsorption capacity (q_0) values calculated are close to each other, and this is consistent with experimental results obtained previously. The R^2 values show a very good fitting of the model with R^2 values of 0.998 and 0.997 (Table 26, and Fig. 35).

Table 26- Dose-Response model parameters: Effect of bed height on MTBE removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 (mg/g)
Bed height (cm)	10	0.998	3.88	175	437
	20	0.997	3.93	186	465

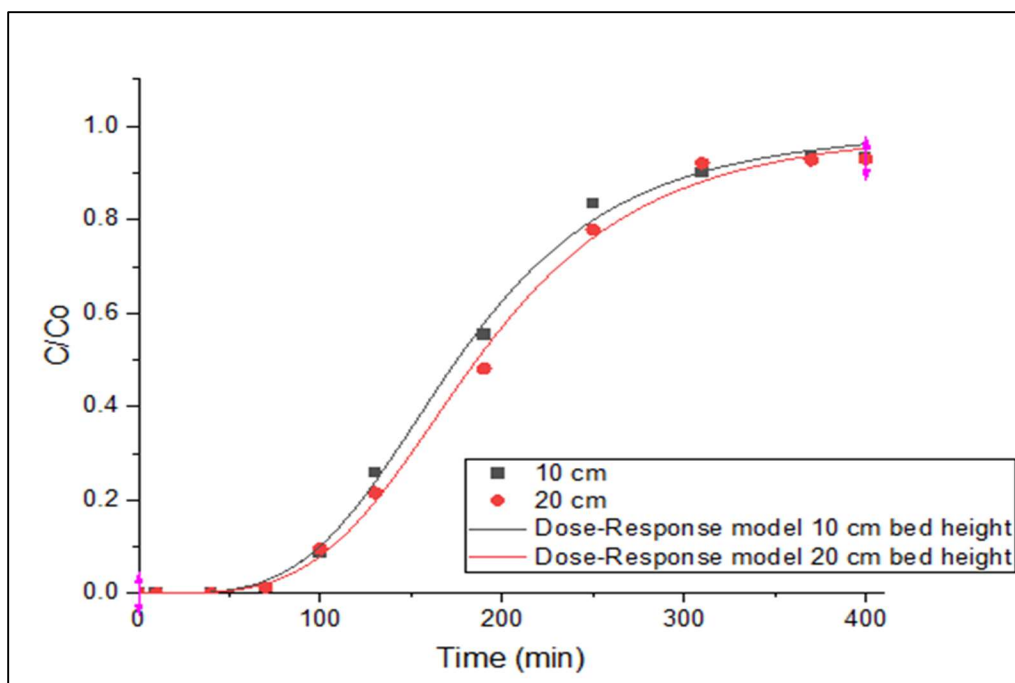


Figure 36- Dose-Response model fit: Effect of bed height on MTBE removal.

4.4.1.6 Effect of Bed type

The best fitted curve ($R^2 = 0.983$) was that of sandstone bed (Table 27 and Fig. 36). The adsorption capacity (q_0) value calculated of the sandstone bed is greater than that of the carbonate bed, which is inconsistent with experimental results obtained previously.

Table 27- Dose-Response model parameters: Effect of bed type on MTBE removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 (mg/g)
Bed type	Sandstone	0.983	0.161	0.150	375
	Carbonate	0.946	0.833	10.9	27.3

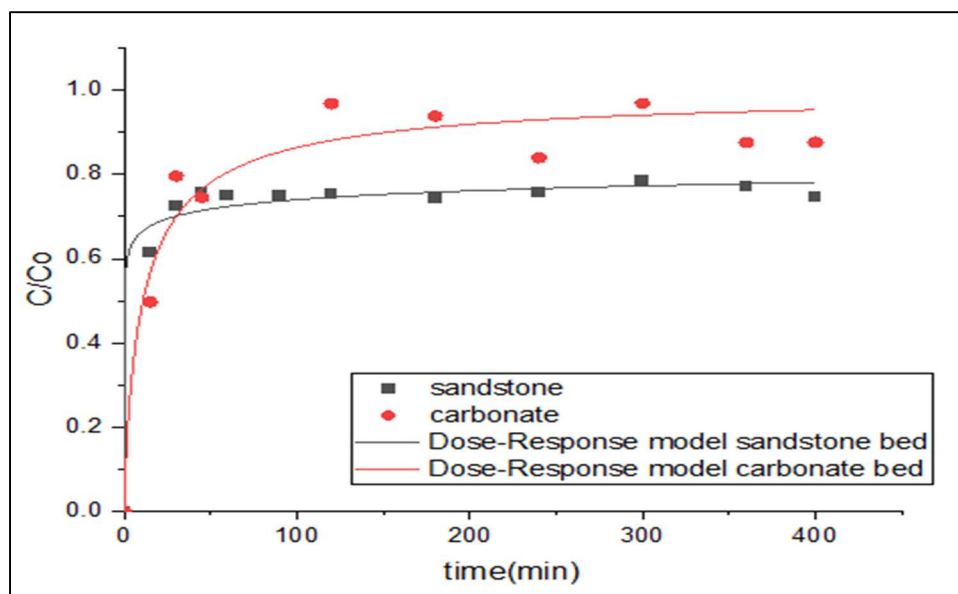


Figure 37- Dose-Response model fit: Effect of bed type on MTBE removal.

4.4.2- Models fit for Benzene adsorption

4.4.2.1 Effect of Flowrate

The best fitted curve ($R^2 = 0.988$) was that of flowrate equivalent to 2 ml/min, followed by that of 0.5 ml/min (see Fig. 37). No breakthrough curve was obtained for flowrate 1 ml/min and hence R^2 value couldn't be calculated. The adsorption capacity (q_0) values calculated in Table 28 increase with the increase in flowrate, which is consistent with experimental results obtained previously.

Table 28- Dose-Response model parameters: Effect of flowrate on Benzene removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 ($\mu\text{g/g}$)
Flow rate (mL/min)	0.5	0.971	4.4×10^{-4}	0.023	69
	1	NA	NA	NA	NA
	2	0.988	0.006	0.162	486

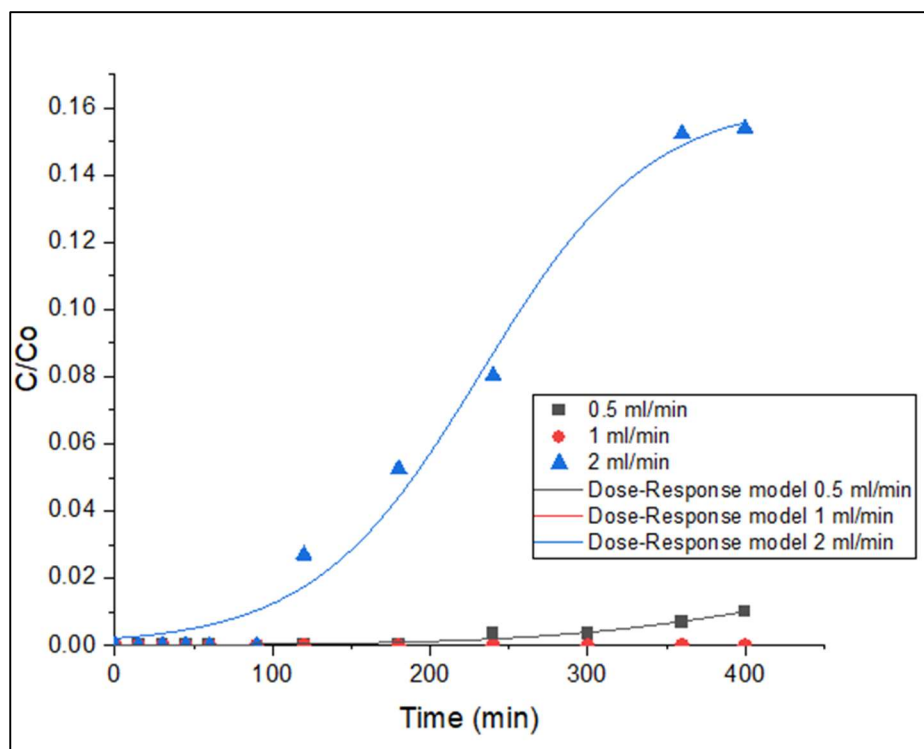


Figure 38- Dose-Response model fit: Effect of flowrate on Benzene removal.

4.4.2.2 Effect of CAC dosages

The best fitted curve ($R^2 = 1$) was that of dosage equivalent to 1 g, followed by that of 2g (Table 29, and Figure 38). The adsorption capacity (q_0) values calculated increase with the increase in dosage, and this inconsistent with experimental results obtained previously.

Table 29 - Dose-Response parameters: Effect of CAC Dosage on Benzene removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 ($\mu\text{g/g}$)
CAC dosages (g)	0.5	1	2.5×10^{-5}	0.225	675
	1	0.992	7.2×10^{-4}	0.237	771
	2	0.999	1.9×10^{-4}	0.253	759

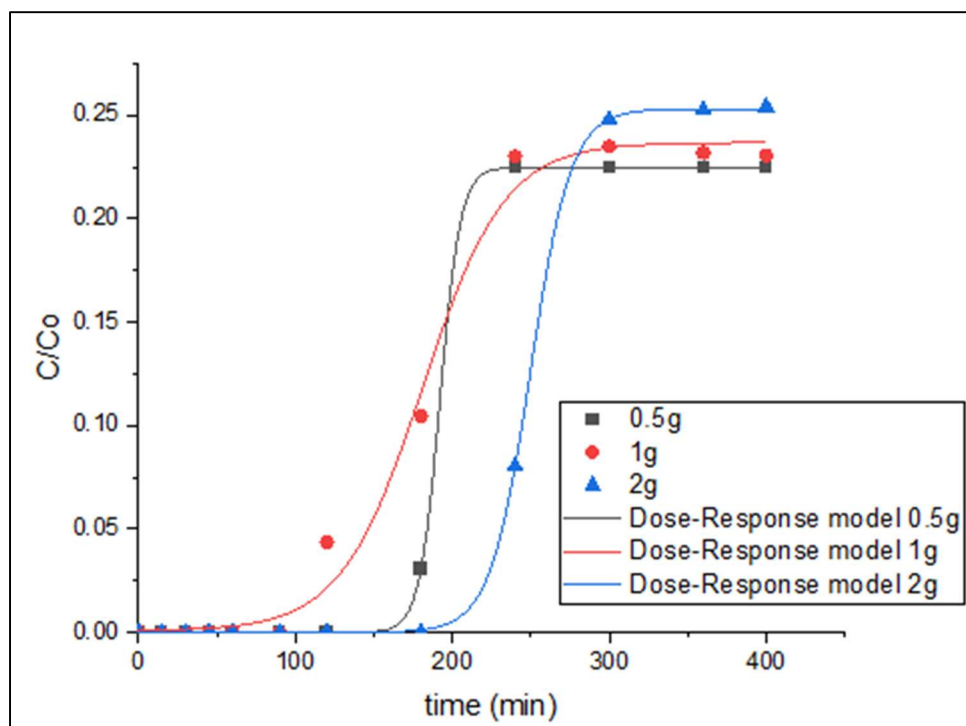


Figure 39- Dose-Response model fit: Effect of CAC Dosage on Benzene removal

4.4.2.3 Effect of Initial concentrations

The best fitted curve ($R^2 = 0.999$) was that of initial concentration equivalent to 20000 $\mu\text{g/L}$, followed by that of 10000 $\mu\text{g/L}$ (Table 30 and Fig. 39). The adsorption capacity (q_0) values obtained increase with the increase in initial concentration values, and this is consistent with experimental results obtained previously.

Table 30 - Dose-Response parameters: Effect of concentration on Benzene removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 ($\mu\text{g/g}$)
Initial Concentrations ($\mu\text{g/L}$)	6000	0.997	0.001	0.083	249
	10000	0.998	0.001	0.230	690
	20000	0.999	8.5×10^{-6}	0.202	606

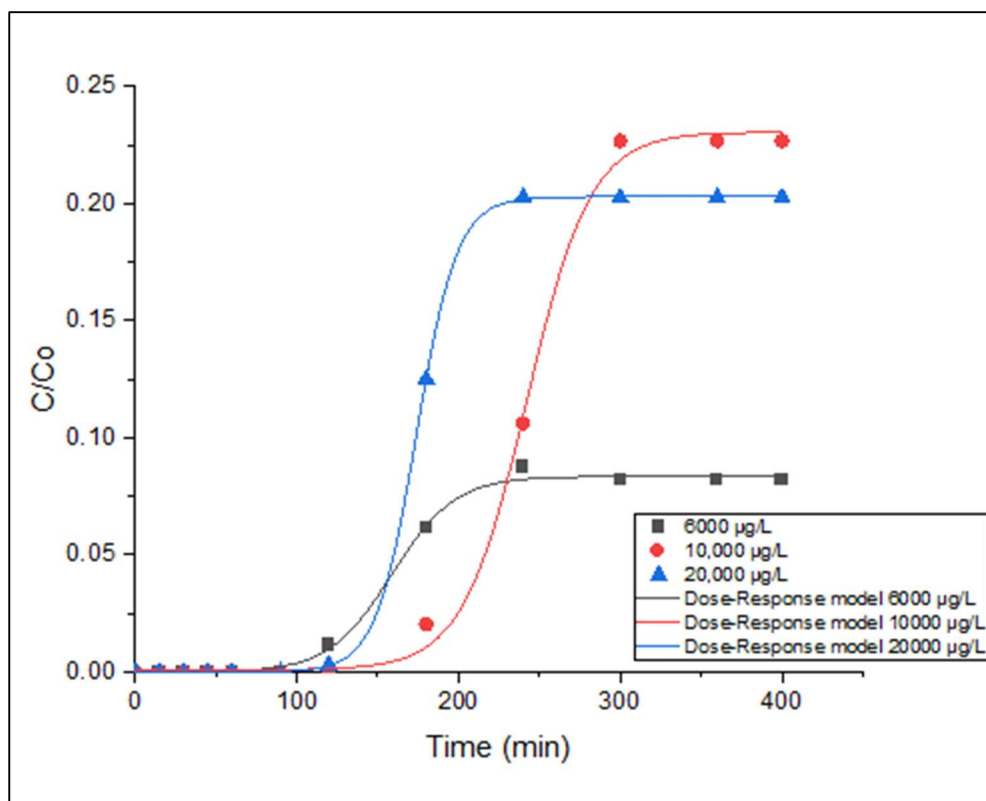


Figure 40- Dose-Response model fit: Effect of initial concentration on Benzene removal.

4.4.2.4 Effect of conductivity

The best fitted curve ($R^2 = 0.999$) was that of conductivity equivalent to 31.3 mS/cm (Table 31 and Fig. 40). The adsorption capacity (q_0) decreased with the increase in conductivity which is in consistent with the experimental results obtained previously.

Table 31- Dose-Response parameters: Effect of conductivity on Benzene removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 ($\mu\text{g/g}$)
Conductivity (mS/cm)	16.4	0.993	0.003	0.195	585
	31.3	0.999	2.8×10^{-4}	0.184	552

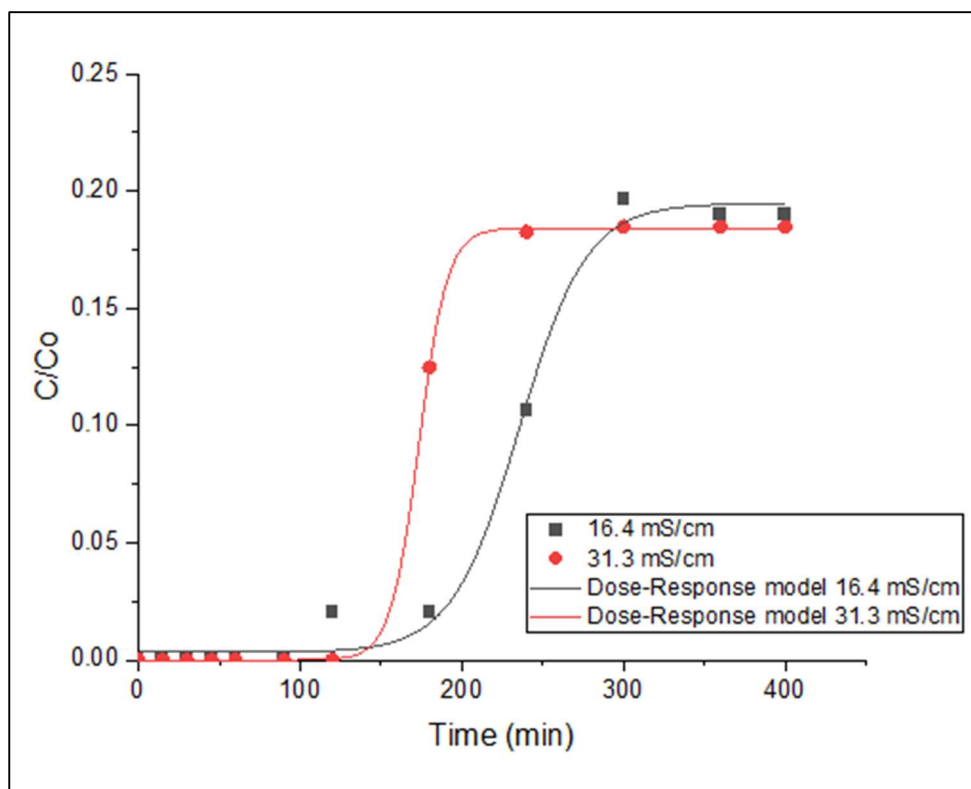


Figure 41- Dose-Response model fit: Effect of conductivity concentrations on Benzene removal.

4.4.2.5 Effect of Bed height

Both curves were best fitted with $R^2 = 0.997$ (Table 32 and Fig. 41). The adsorption capacity (q_0) decreased with the increase in conductivity which is inconsistent with the experimental results obtained previously.

Table 32- Dose-Response parameters: Effect of bed height on Benzene removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 ($\mu\text{g/g}$)
Bed height (cm)	10	0.997	0.003	0.193	579
	20	0.997	0.002	0.185	555

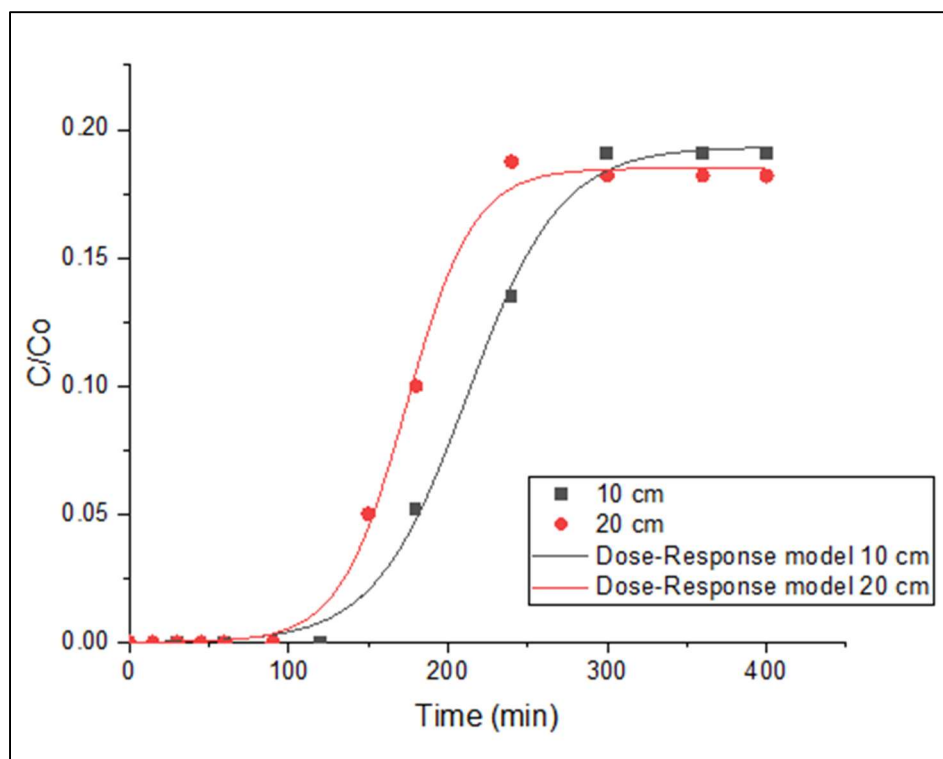


Figure 42- Dose-Response model fit: Effect of bed height on Benzene removal.

4.4.2.6 Effect of Bed type

The best fitted curve ($R^2 = 0.997$) was that of carbonate bed. The adsorption capacity (q_0) values calculated showed that carbonate bed has the maximum adsorption capacity value (Table 33, Fig. 42). These results are in consistent with experimental results obtained previously.

Table 33- Dose-Response parameters: Effect of bed type on Benzene removal.

Investigated parameter	Parameter value	R^2	a	b (L)	q_0 ($\mu\text{g/g}$)
Bed Type	Sandstone	0.992	0.003	0.081	243
	Carbonate	0.997	0.007	0.235	705

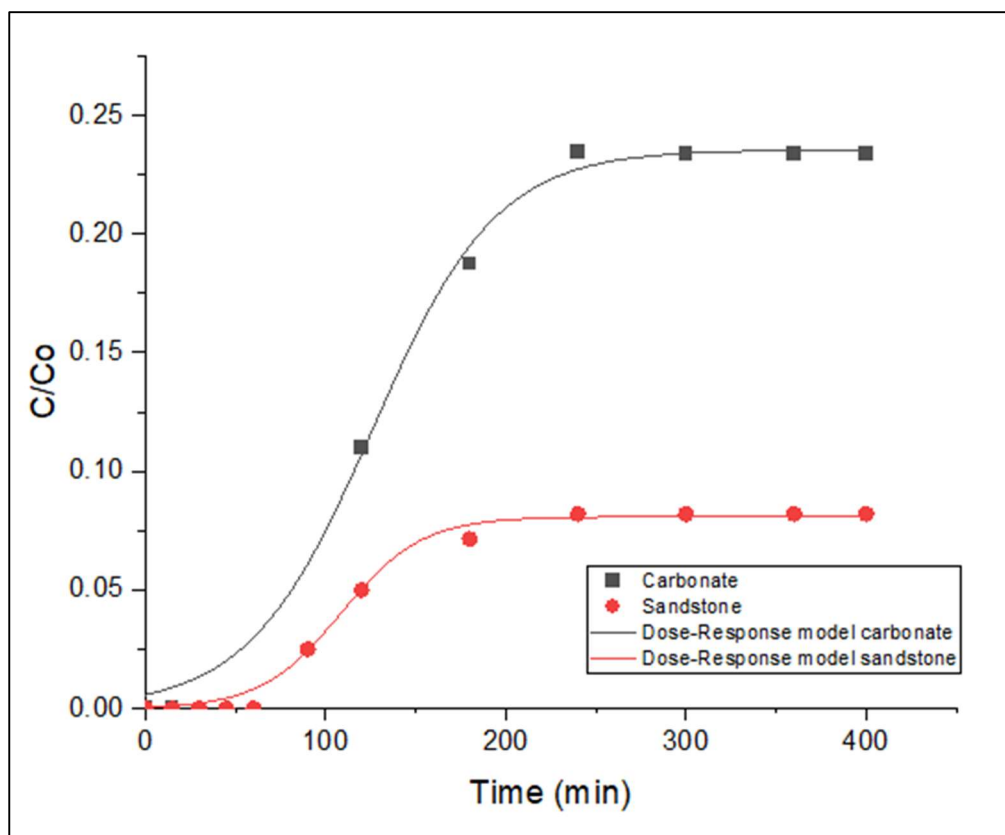


Figure 43- Dose-Response model fit: Effect of bed type on Benzene removal.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A series of fixed bed column experiments were conducted to evaluate the efficiency of novel new CAC as an adsorbent for in-situ remediation of groundwater contaminated with MTBE and BTEX. Characterization of the CAC was done using different techniques like SEM/EDXs, XRD, FTIR and surface area. Results obtained showed that the CAC used in this study has a surface that is negatively charged and of an area $1160 \text{ m}^2/\text{g}$. In addition EDS results showed that 99.24% of the CAC composition is carbon. According to the results obtained from the laser diffraction analyzer the size of CAC particles falls between 21 and $4.5 \text{ }\mu\text{m}$. Various operational factors, including dosage, initial concentrations, conductivity, flowrate, bed type and bed height were evaluated for their impact on adsorption performance. The fixed -bed column experiments results showed that MTBE and BTEX adsorption is mostly affected by CAC dosage, initial contaminant concentrations, and flowrate. Conductivity, bed type, and bed height effects were minor. The optimum treatment conditions that gave maximum removal efficiencies and high adsorption capacities for MTBE were: CAC dosage of 2 g, initial concentrations of $5000 \text{ }\mu\text{g/L}$, flow rate of 1 mL/min, using sandstone bed type and bed height of 20 cm at a conductivity equivalent to $33850 \text{ }\mu\text{S/cm}$. Whereas that of BTEX was found to be at a CAC dosage of 2 g, with initial concentrations of $6000 \text{ }\mu\text{g/L}$, flow rate of 2 mL/min, using carbonate bed type and bed height of 20 cm, at a conductivity equivalent to $16400 \text{ }\mu\text{S/cm}$. Breakthrough curves under different conditions were fitted to three different models which are Adams-Bohart, Thomas, and Dose-Re model with Dose-Response providing the best fit to the experimental data. Notably, the adsorption performance was significantly affected by the dosage and initial concentrations, flowrate, and bed type while bed height and conductivity showed insignificant effect under the investigated conditions.

5.2 Limitations

Several limitations were encountered during the study. Volatility of the contaminants is considered as one of the main limitations as it could directly interfere with the experimental results and hence affect the validity and the reliability of the study. The long-time duration of the laboratory experiments is another limitation, as some experiments required more than 6 hours to reach saturation. Moreover, shortage of extra peristaltic pumps is another limitation. Experiments of different flowrates were conducted in different days due to the availability of single peristaltic pump only, hence the reliability and reproducibility of the results gets affected.

5.3 Recommendations

It is recommended for future similar studies to further study the effect of the CAC molecular configuration on the MTBE and BTEX adsorption. The use of CAC that is made up of natural organic waste will also be recommended. Moreover, the use of a real bed type material and on-line analysis will increase the reliability of future studies.

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APPENDIX

Toluene breakthrough curves and adsorption parameters

Table A-1 Fixed-bed column parameters for Toluene removal under different operational conditions

Parameter/ Experiment	CAC dosage (g)			Initial concentrations ($\mu\text{g/L}$)			conductivity ($\mu\text{S/cm}$)			Bed height (cm)		Bed type		Flowrate(mL/min)		
	0.5	1	2	20,000	10,000	6000	<5	16400	31300	10	20	Carbonate	Sandstone	0.5	1	2
t_b (min)	180	135	180	0	0	180	180	NA*	NA	NA	190	60	180	NA	NA	190
t_s (min)	275	180	300	0	0	300	275	NA	NA	NA	360	240	275	NA	NA	275
m_{adsorbed} (μg)	4788	2867	4920	14280	7094	4245	4245	4256	3996	4987	4962	4216	4242	1249	2490	4923
m_{total} (μg)	5040	5040	5040	14400	7200	4320	4320	4320	4320	5040	5040	4320	4320	1260	2520	5040
Volume treated (mL)	798	477	820	714	709	707	707	709	666	831	827	702	707	208	415	820
q_e (mg/g)	9576	2866	2460	7140	3547	2122	2122	2128	1998	2493	2481	2108	2121	624	1245	2461
Removal efficiency (%)	95	56	97	99	98	98	98	98	92	98	98	98	98	99	98	97

* The concentrations obtained were extremely and no S-shaped curve was formed.

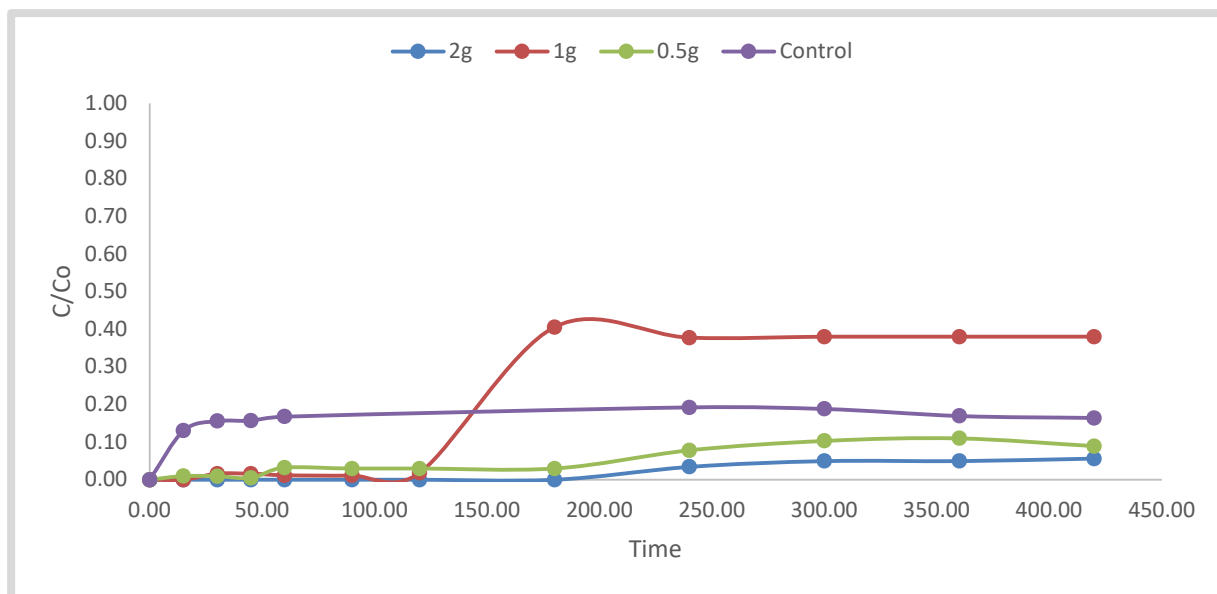


Figure A-1 - Breakthrough curves of Toluene at different CAC dosages.

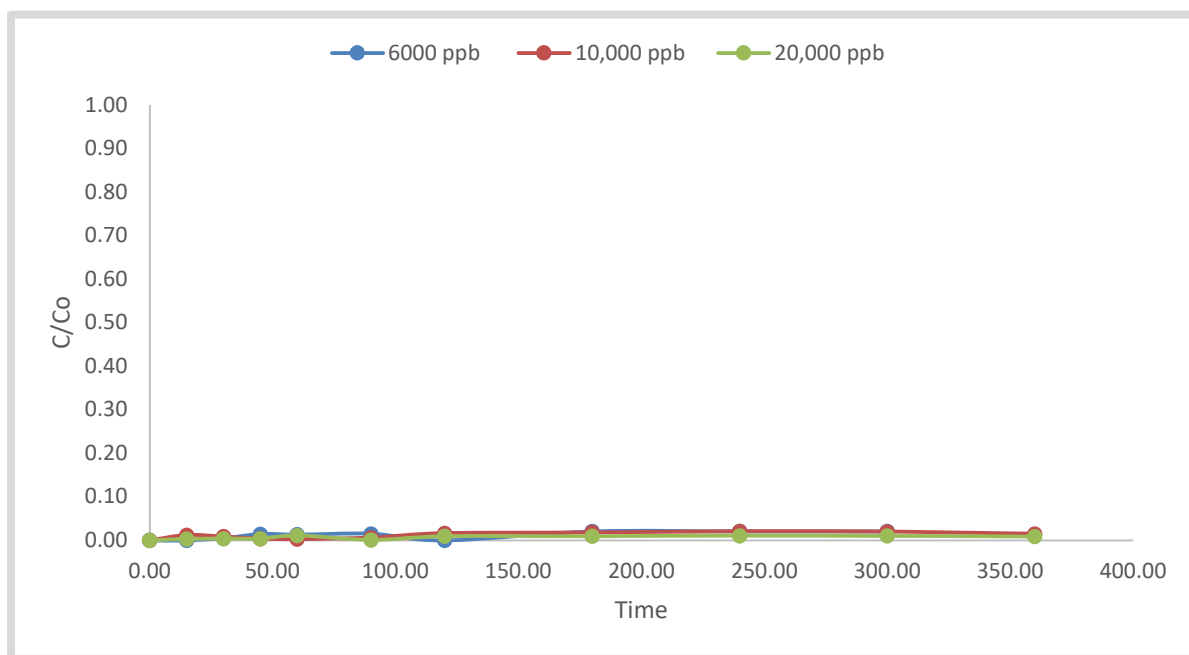


Figure A-2- Breakthrough curves of Toluene at different initial concentrations.

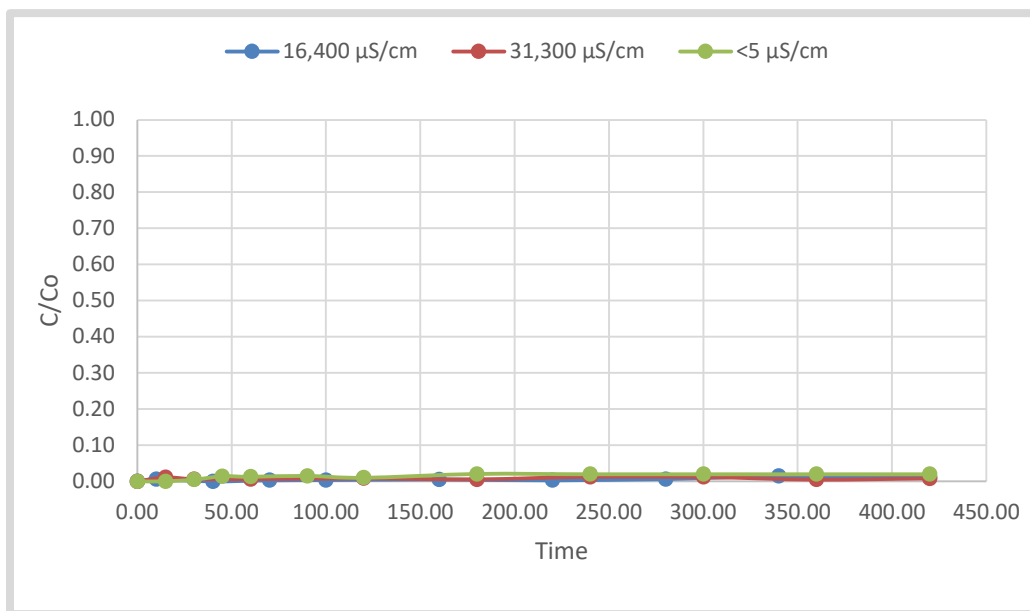


Figure A-3- Breakthrough curves of Toluene at different conductivities.

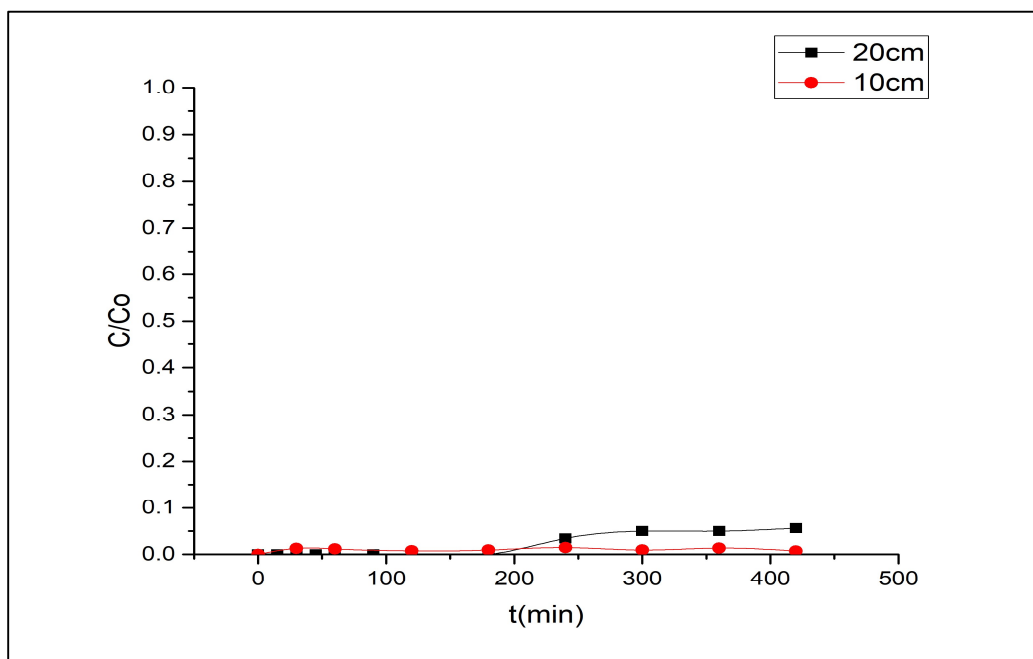


Figure A-4- Breakthrough curves of Toluene at different bed heights.

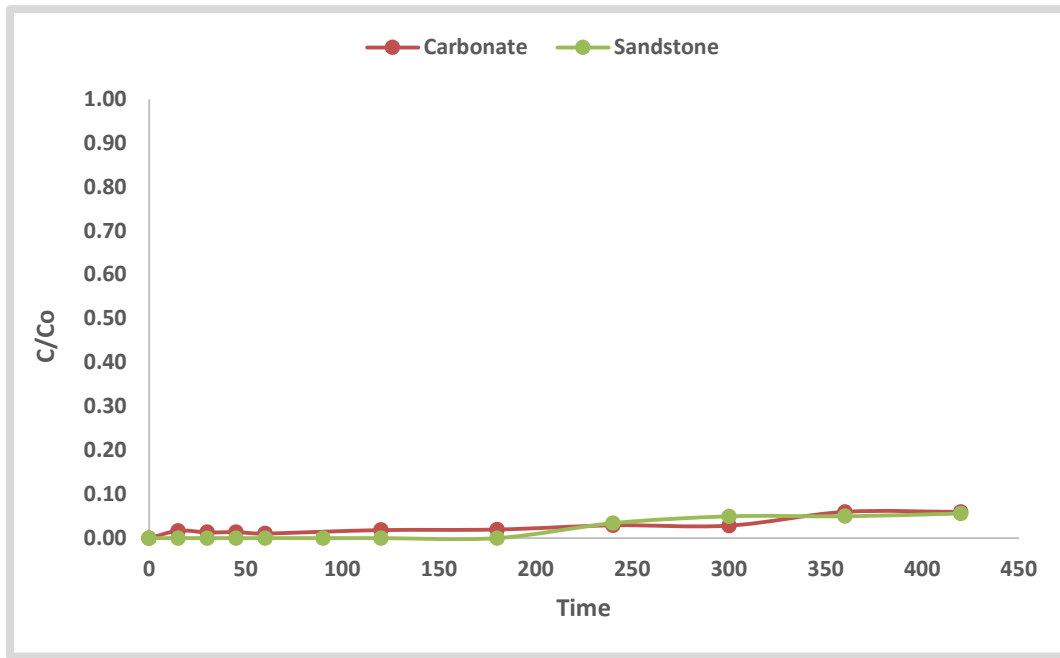


Figure A-5- Breakthrough curves of Toluene at different bed types.

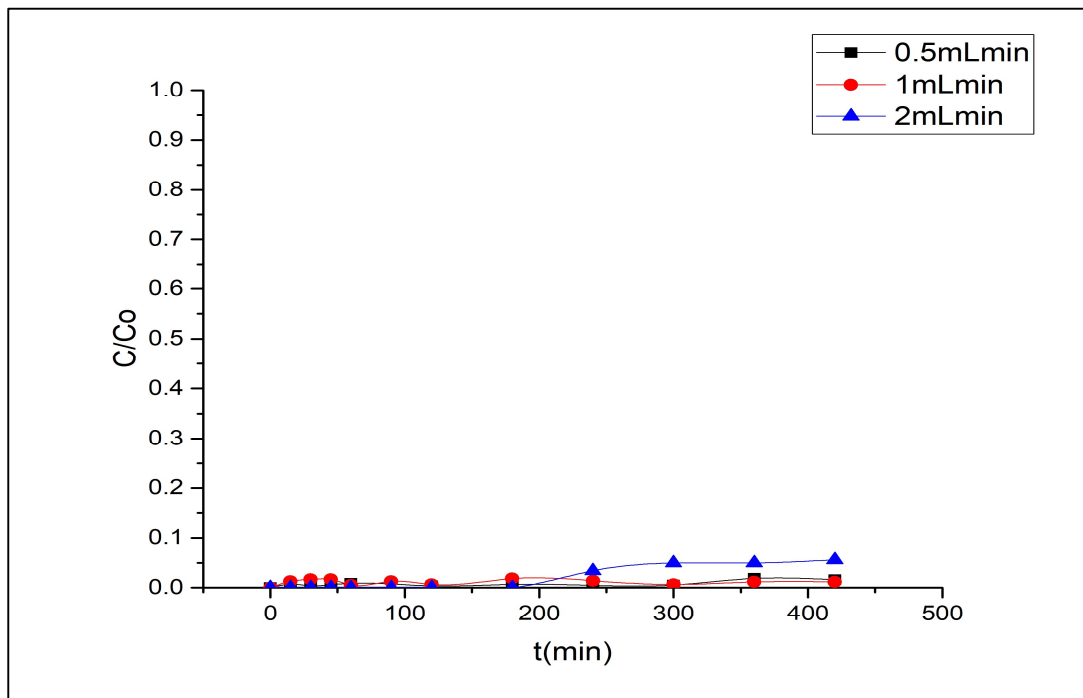


Figure A-6- Breakthrough curves of Toluene at different flowrates.

Adams-Bohart and Thomas Models parameters and fitting

Table A-2 - Adams-Bohart Model parameters for MTBE removal at various conditions

Exp. NO	Investigated parameter	Parameter value	R ²	Adj. R ²	K _{AB} (L/mg/min) (10 ⁻³)	No (mg/L)
1	CAC dosages (g)	0.5	0.76	0.69	0.69± 70.2	0.12
2		1	0.87	0.84	0.79± 30.9	0.16
3		2	0.99	0.99	1.67± 6.8	0.17
4	Concentrations (µg/L)	2000	0.99	0.99	21 ± 24	0.04
5		5000	0.94	0.92	3.29 ± 11031.8	0.26
6		10000	0.94	0.92	0.51 ± 71.5	0.80
7	Conductivity (mS/cm)	0.1	0.94	0.93	0.62 ± 10.2	0.25
8		18	0.88	0.86	0.66± 18.4	0.19
9		35	0.93	0.91	0.01 ± 0.2	14.8
10	Bed height (cm)	10	0.99	0.99	0.73 ± 5.1	0.30
11		20	0.99	0.99	1.54 ± 8.3	0.14
12	Bed Type	Sandstone	0.18	0.002	0.45 ± 2.8E6	0.12E-7
13		Carbonate	0.86	0.81	0.49 ± 39.4	0.19
14		Sandstone & Carbonate	0.83	0.78	1.18 ± 1506	0.18
15	Flow rate (mL/min)	0.5	0.89	0.86	0.47 ± 11.2	0.40
16		2	0.76	0.66	4E-5 ± 0.002	5405
17		1	0.86	0.83	0.64 ± 21.9	0.19

Table A-3- Thomas Model parameters for MTBE removal at various conditions

Exp. NO	Investigated parameter	Parameter value	R ²	Adj. R ²	K _{TH} (L/mg/min) (10 ⁻³)	q _o (mg/g)
1	CAC dosages (g)	0.5	0.76	0.69	0.69	1.18
2		1	0.87	0.84	0.79	1.58
3		2	0.99	0.99	1.67	1.7
4	Concentrations (µg/L)	2000	0.99	0.99	21.0	0.35
5		5000	0.94	0.92	3.29	2.60
6		10000	0.94	0.94	0.51	8.00
7	Conductivity (mS/cm)	0.1	0.94	0.93	0.62	2.47
8		2	0.92	0.91	0.68	2.17
9		18	0.88	0.86	0.66	1.92
10		35	0.93	0.91	0.01	148
11	Bed height (cm)	10	0.99	0.99	0.72	3.00
12		20	0.99	0.99	1.54	1.42
13	Bed Type	Sandstone	0.18	0.002	0.45	0.12E-6
14		Carbonate	0.86	0.81	0.45	1.90
15		Sandstone & Carbonate	0.83	0.78	1.18	0.60
16	Flow rate (mL/min)	0.5	0.89	0.86	0.47	4.00
17		2	0.76	0.66	4E-5	54049
18		1	0.86	0.83	0.64	1.90

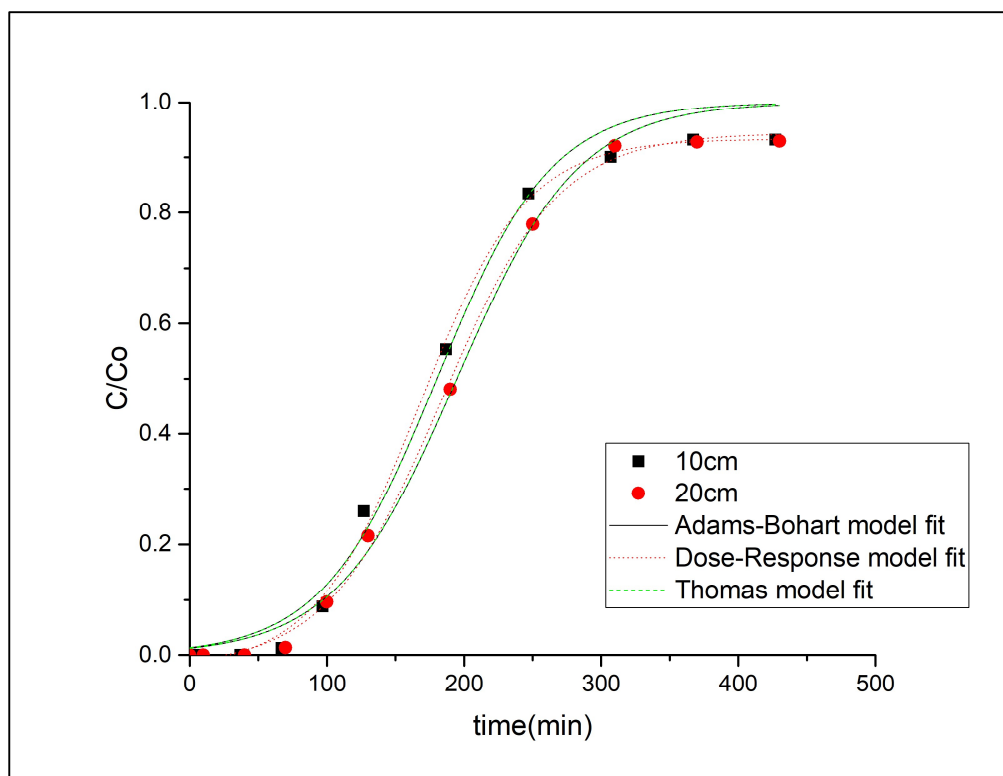


Figure A-7 - Three model fits: Effect of bed height on MTBE removal

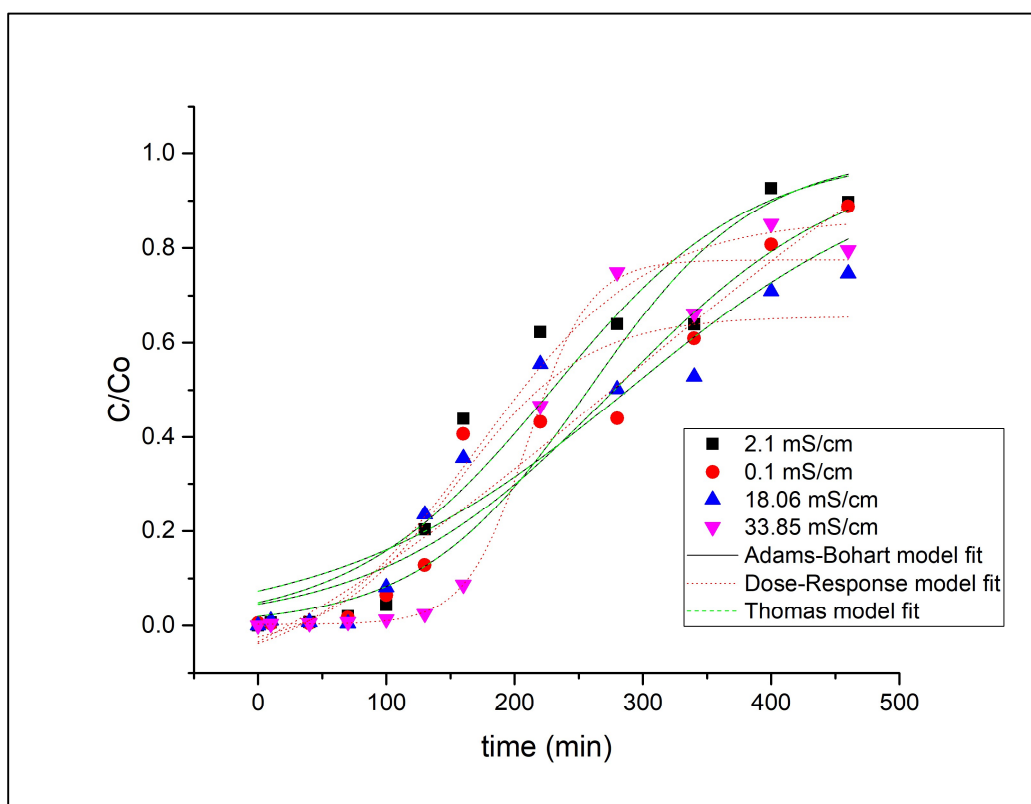


Figure A-8- Three model fits: Effect of conductivity on MTBE removal

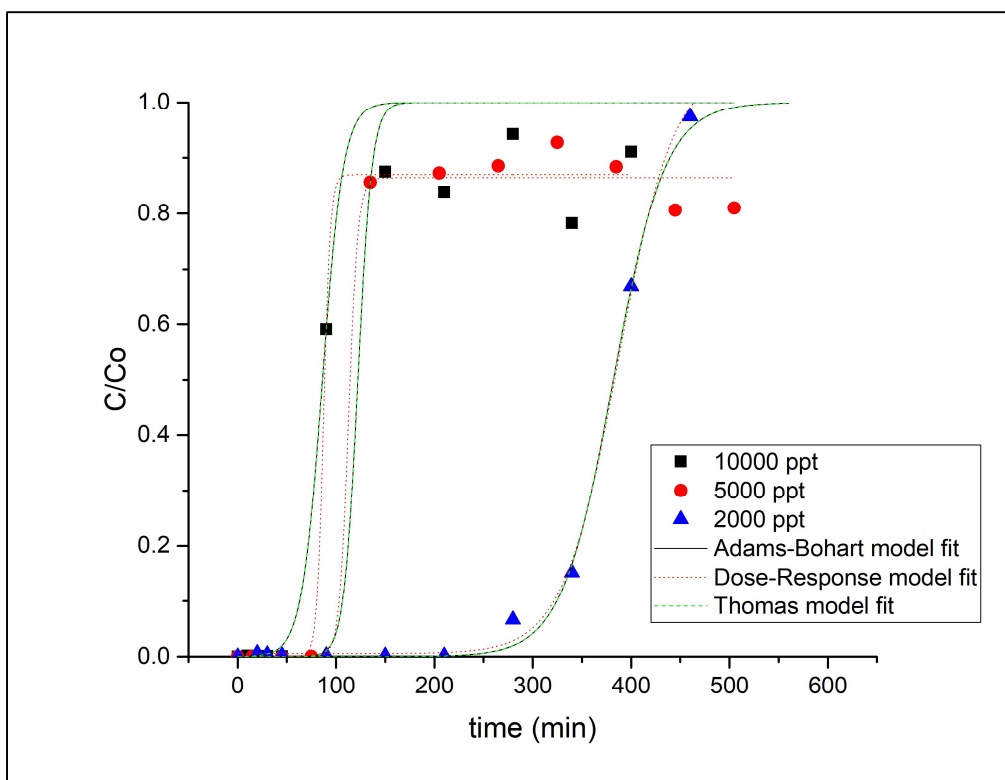


Figure A-9- Three model fits: Effect of initial concentration on MTBE removal

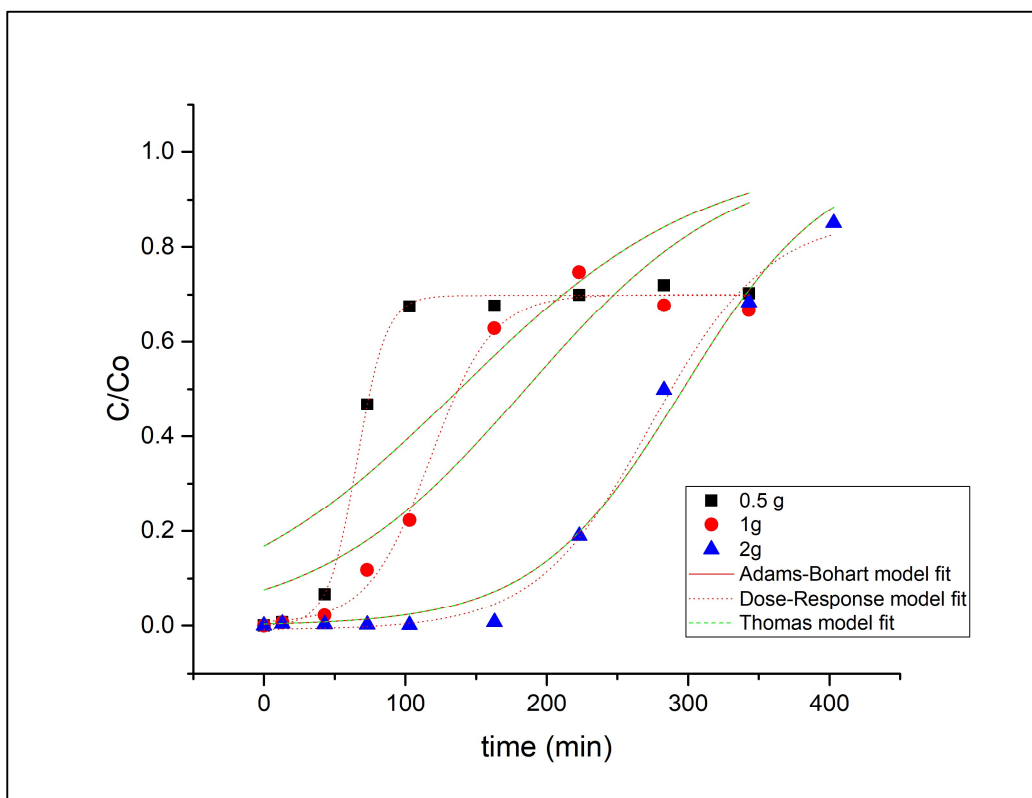


Figure A-10- Three model fits: Effect of CAC dosage on MTBE removal

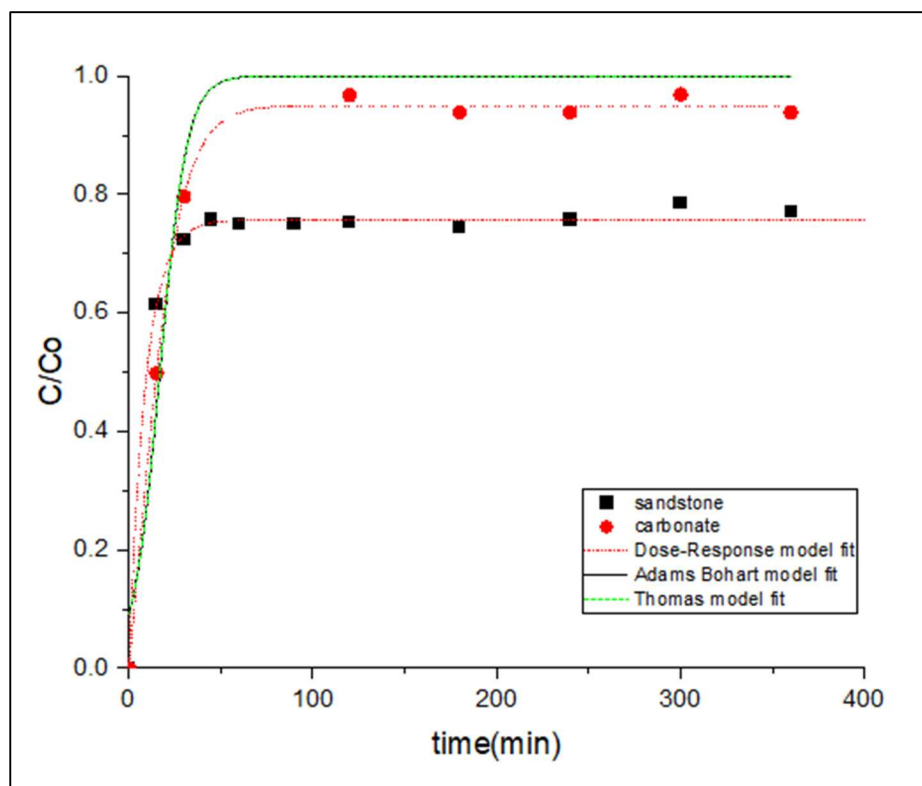


Figure A-11- Three model fits: Effect of bed type on MTBE removal

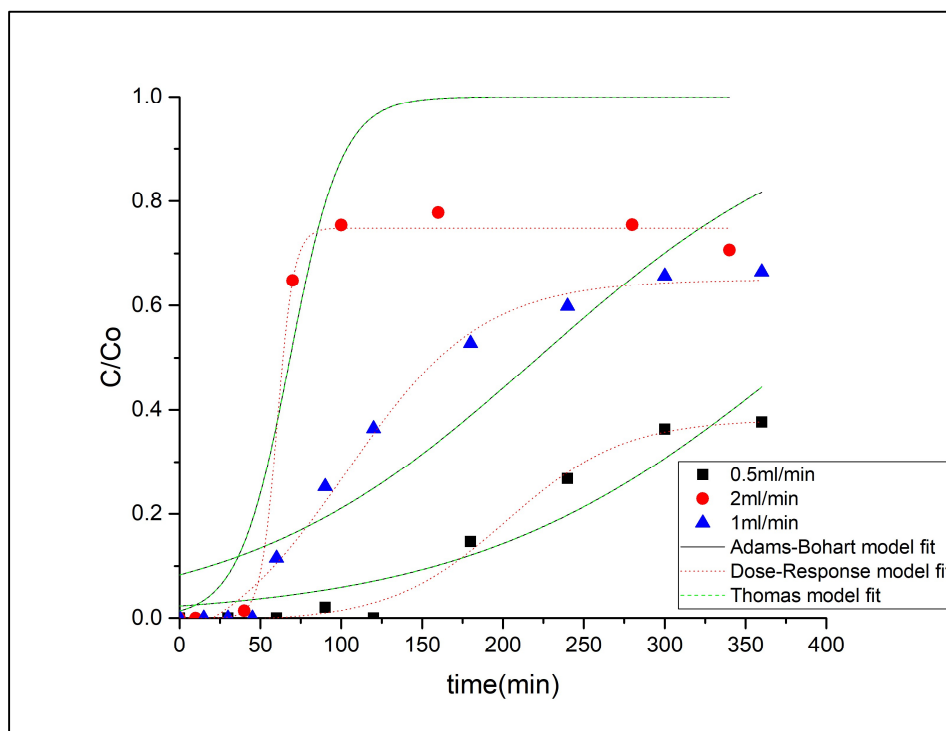


Figure A-12- Three model fits: Effect of flowrate on MTBE removal

Models fit for Toluene adsorption

Table A-4 Dose-Response model parameters for the Toluene adsorption onto CAC under various conditions

Exp. NO	Investigated parameter	Parameter value	R ²	a	b	q ₀ (μg/g)
1	CAC dosages (g)	0.5	0.986	0.002	0.101	1.21
2		1	1	2.1x10 ⁻⁴	0.405	2.43
3		2	0.995	7.1x10 ⁻⁴	0.052	0.156
4	Concentrations (μg/L)	6000	0.952	0.007	0.020	0.06
5		10000	0.946	0.010	0.020	0.06
6		20000	0.969	0.002	0.010	0.03
7	Conductivity (μS/cm)	<5	0.976	0.003	0.020	0.06
8		16400	0.993	8.3x10 ⁻⁴	0.021	0.06
9		31300	0.962	0.004	0.010	0.03
10	Bed height (cm)	10	0.989	0.107	0.014	0.04
11		20	0.976	0.003	0.020	0.06
12	Bed Type	Sandstone	0.988	0.002	0.051	0.15
13		Carbonate	0.993	8.0x10 ⁻⁴	0.028	0.08
14	Flow rate (mL/min)	0.5	0.997	0.001	0.019	0.06
15		1	0.999	3.0x10 ⁻⁵	0.014	0.04
16		2	0.989	0.001	0.051	0.15

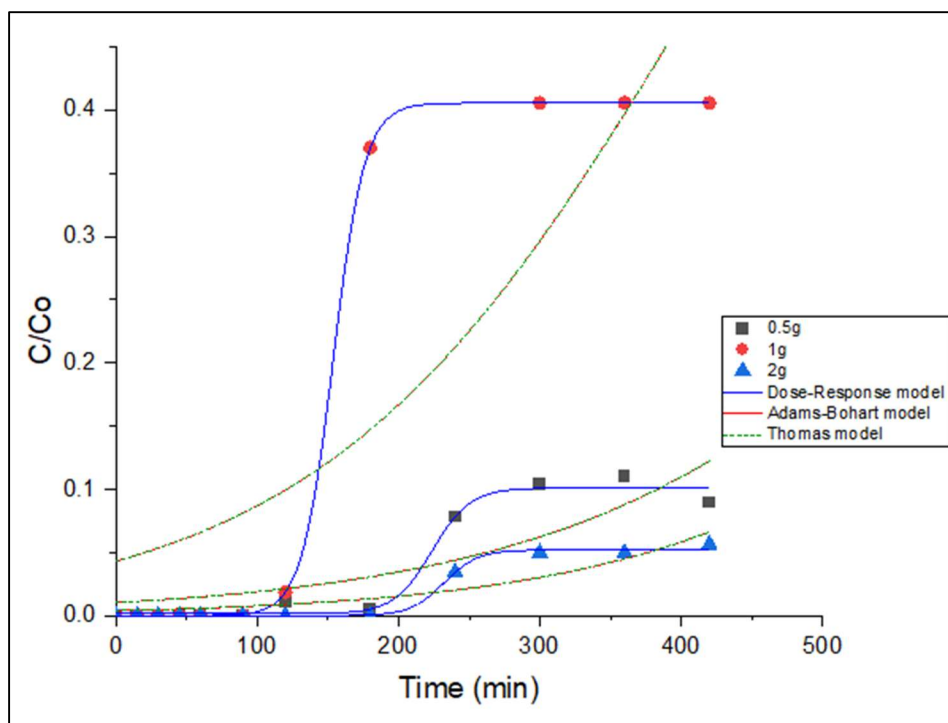


Figure A-13- Three model fits: Effect of CAC dosage on Toluene removal

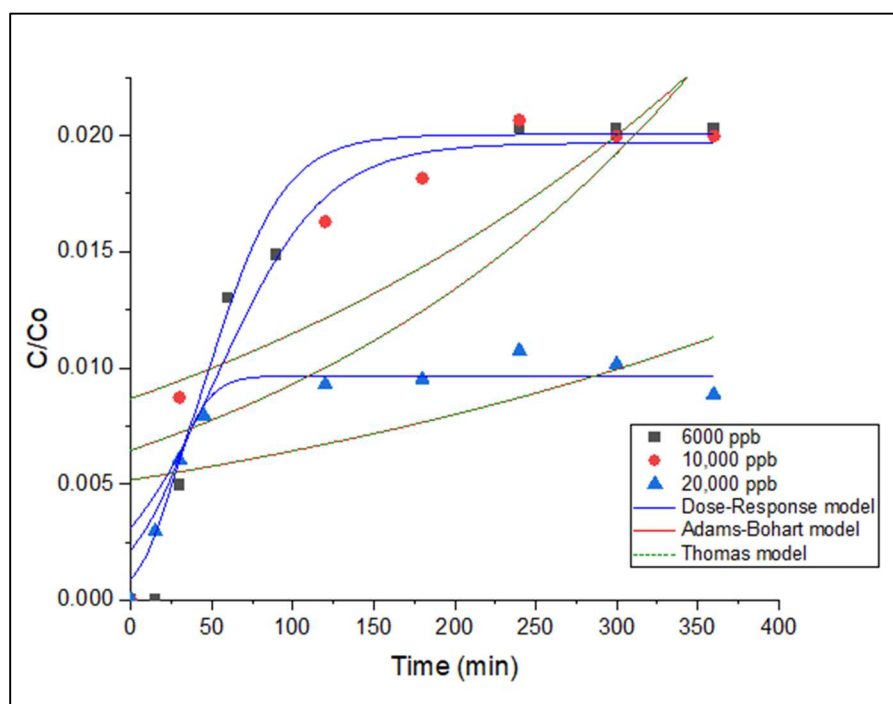


Figure A-14- Three model fits: Effect of initial concentration on Toluene removal.

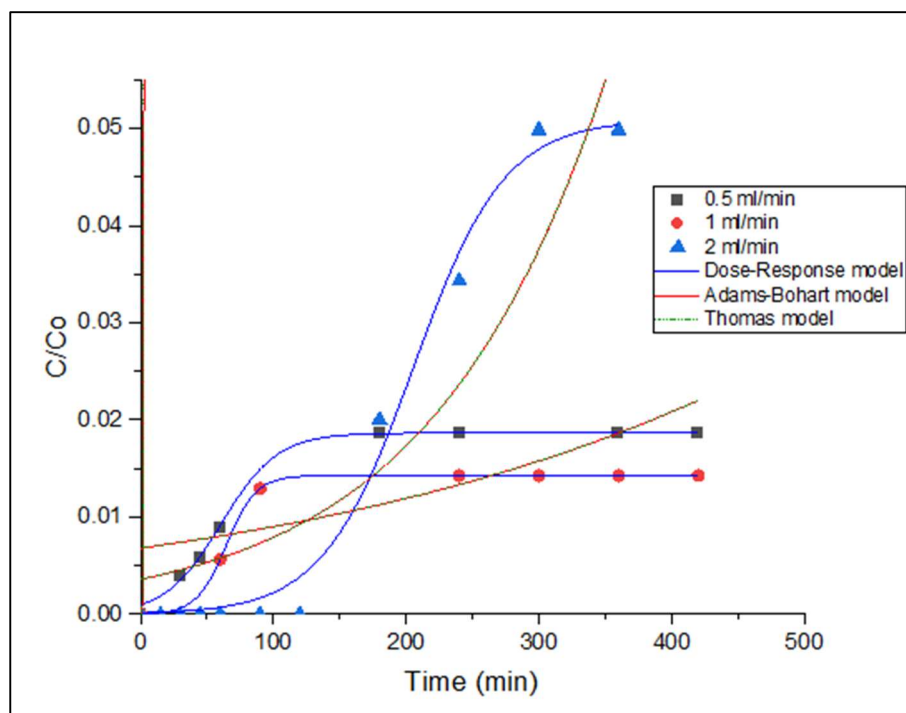


Figure A-15- Three model fits: Effect of flowrate on Toluene removal

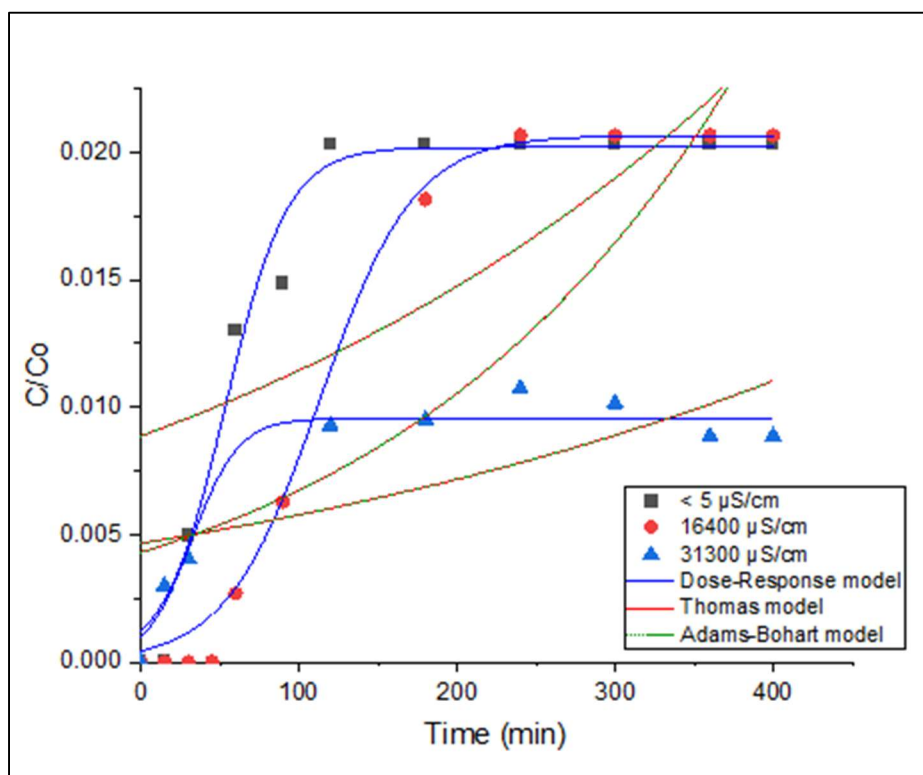


Figure A-16- Three model fits: Effect of conductivity on Toluene removal

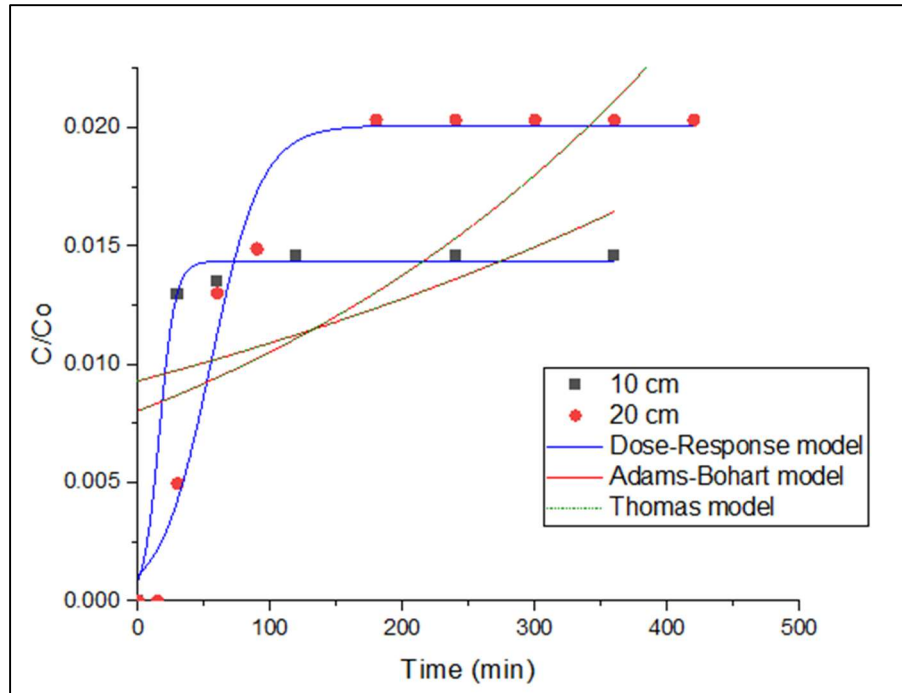


Figure A-17- Three model fits: Effect of bed height on Toluene removal

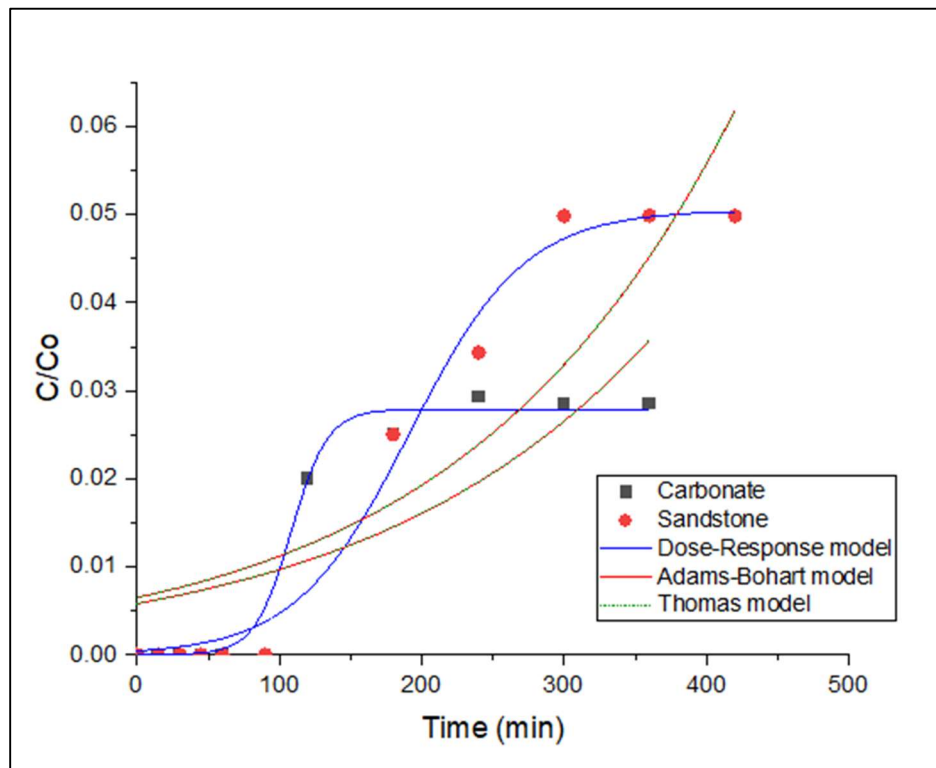


Figure A-18- Three model fits: Effect of CAC bed type on Toluene removal.

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