

Kinetic Studies of Emerging Contaminants Removal from Wastewater using Organo Modified Activated Carbon

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Abstract:- In these studies, an efficient organo-modified activated carbon adsorbent from sugarcane bagasse with high adsorption capacity was prepared and used for the removal of emerging contaminants from wastewater gotten from the Kaduna Polytechnic female hostel. The produced adsorbent was characterized to determine the functional groups, surface area, crystal structures, FTIR, BET, and XRD analyses. The BET surface areas of the direct modified activated carbon and the acid-pretreated activated carbon for adsorption were found to be 572 m²/g and 356 m²/g, respectively. The effect of adsorption parameters, which include contact time, adsorbent dosage, and temperature, on uptake behavior was all examined. Langmuir and Freundlich isotherm models were fitted to the adsorption data. The adsorption of triclosan, diclofenac, bisphenol A, and methyl paraben followed pseudo-second-order kinetics and fit well to the Freundlich isotherms indicating chemisorption. The wastewater compositions were found to contain major ECs identified as diclofenac, triclosan, methylparaben, and bisphenol A, which account for 76.206% of the ECs that are detrimental to human health and the environment. The effect of adsorbent dosage shows that all ECs removed rise rapidly from 0.5–1.0 g adsorbent dosage and then slowly to reach a maximum of 100% Triclosan, 99.86% Diclofenac, 92.91% BPA, and 69.26% Methyl-Paraben removal as adsorbent dosage increases to 2g. On the other hand, as the adsorbent dosage increases to 3g, the removal rate of all ECs is observed to

drop slightly and then attain maximum removal as the dosage rises to 4g. Also, the adsorbent characterization shows that the morphology of the acid-pretreated organo-modified AC adsorbents has better pore development with a higher amorphous structure that enhances uptake of contaminants into the adsorbents. Directly modified AC adsorbents show the highest methyl-paraben removal with an increase in adsorbent dosage when compared to other adsorbents.

Keywords:- Emerging Contaminants, Organo Modified Adsorbents, Activated Carbon, Adsorption Efficiency, Wastewater.

I. INTRODUCTION

Environmental pollution, particularly water pollution, has become a prime concern for nations around the world, as water is increasingly being contaminated by several activities including, industrial pollution, washing of fertilizer into the water bodies, open defecation, oil spillage, which has led to increase in the depletion of water quality [1]. Domestic and industrial wastewater usually contains different contaminants such as organic, inorganic toxic substances and heavy metals and this causes negative effects on the environment. In recent times, domestic wastewater has been found to contain organic contaminants of emerging concern derived from human and household products and infrastructure, which are widely scattered over the environmental, while wastewater from the

industries covers a variety of poisonous substances that is produced because of industrial activities [2,3]. Some of these contaminants have resulted in negative impacts on animals found in aquatic environments and adversely affecting public health [4,5].

For instance, the environment is seriously threatened by the release of poisonous materials such as heavy metals, greenhouse gases, oil spillage, non-biodegradable materials, farm pesticides, the usage of inorganic fertilizers, other hazardous products into the environment [6,7,3]. Emerging contaminants (ECs) which are regarded as micro-pollutants, which are a diverse group of anthropogenic substances that are frequently found in water but recently being recognized as major water pollutants [8,3]. Though, several studies on environmental pollution by hydrocarbon and several arrays of heavy metals in wastewater have been reported, however very little or no studies have been conducted on the treatment of ECs and suitable remedial technique. The total removal and elimination of a variety of contaminants of emerging environmental concern from different biological and environmental wastes has proven to be impossible using traditional treatment procedures. Water pollution removal is a critical procedure that is becoming increasingly crucial because of the expansion of industrial activity and emerging contaminants from domestic wastewater across the globe [9]. This necessitates the need for treatment of wastewater contaminated by industrial pollutants and ECs.

Several materials including activated carbon from agricultural waste, industrial waste, and clay materials as well as hybrid diatomite/carbon composites have been used as adsorbent for wastewater treatment [10,13,6,14,1,15,7,3]

Because of its high effectiveness, ease of use, and economic viability, methods, such as adsorption, are particularly regarded as a straightforward and suitable strategy for pollutants removal in polluted wastewater [16,3]. Membrane purification procedures and biological methods are among other technologies that have been utilized in the cleansing of toxic constituents from wastewater. These techniques are majorly utilized in very important and unique circumstances in the treatment of wastewater because they are super expensive and not easy to maintain because it's economically undesirable. Capturing ECs from wastewater by employing natural material was a relatively new green method for the treatment of ECs in contaminated wastewater. Biomass materials means of adsorption has been demonstrated to be a highly effective method for treating poisonous wastewater, with a lot of benefits including affordability, abundance, simplicity of use, and so efficient with positive yield [1]. Therefore, production and preparations of adsorbent from biomass materials are easy and cheap which can be easily found across the globe and is efficient in the elimination of various contaminants from water and wastewater.

II. METHODOLOGY

➤ *Activated Carbon Preparation*

Sugarcane bagasse was collected, contaminants removed by washing with distilled water, and dried. The dried sugarcane bagasse was burned in an oven to burn off volatile matter before carbonization in a furnace at a temperature of about 500 °C in a vacuum. The result generated pure, mesoporous activated carbon, following the research trends developed by [17]. Followed by manually crushing of the dried carbonized sugarcane bagasse. Crushing made larger particles smaller which open the surface area, and this enhances the chemical activation of the raw biomass material to be more effective. The crushed carbonized material was sieved to produce particles around 600 µm. The Chemical activation of the carbonized sugarcane bagasse was done by using 200 ml of 25 v/v phosphoric acid which was then dissolved in 200g of carbonized sugarcane bagasse followed by effective mixing in a beaker. Slurries of the carbonized sugarcane bagasse containing the acid activating agent were carefully mixed at a steady temperature of 85°C for 4 hours on a magnetic stirrer with heater so that there would be a complete reaction between the mixtures. Immediately after the chemical activation, the sample mixture was subjected to pyrolysis for two hours at a temperature of 350°C. The resulting activated carbon was further subjected to another round of grinding which produces fine powder after drying, and the produced activated carbon samples were then exposed to light and humidity for around 4 hours to promote the growth of the active carbon pore structure and the procedures aid the pyrolysis with consistent carbonization reactions. The produced activated carbon was then rinsed with 1.2 M HCl and distilled water to remove extra activating agents and leftover inorganic materials and this made the sugarcane bagasse activated carbon acid-free [18]. Then the produced sugarcane bagasse activated carbon was dried at ambient temperature and stored in sample bottle awaiting modification using organic compound.

➤ *Organo- Modified Activated Carbon*

The organo modified activated carbon was produced using the cation exchange reaction method according to the procedure that was stated by [19]. The activated carbon was dispersed in a specific volume of distilled water (4% w/w) followed by gentle shaking on a magnetic stirrer for 30 minutes and left for a day for the mixture to settle. Then Cetyltrimethylammonium bromide (CTMABr) was added to the activated carbon suspension followed by vigorously agitation for 20 minutes before being allowed to settle for 24 hours. After being filtered out, the organo-modified activated carbon was dried at 60 ± 5 °C until a constant weight was achieved. The resulting organo modified activated carbon was grinded and sieved to a thickness of about 200 microns followed by characterization and adsorption process investigation.

➤ Adsorbent Characterization

The produced modified activated carbon was characterized using FTIR, XRD and BET analyzers which was used to determine the functional groups using the Shimadzu FTIR- 8400S analyzer, determination of the crystal structure using XPERT-PRO X-ray diffractometer and determination of surface area, volume and pores pore size were performed using Micromeritis Tristar 3000 surface area analyzer device.

➤ Wastewater Sampling And Collection

The main considerations for the wastewater sampling strategy in this study are diagnostic evaluation and target pollutants in the wastewater stream. The sampling locations selected in this study for the wastewater collection are the Kaduna Polytechnic female hostel wastewater source and drainages, where the wastewater from different sources was well mixed, as the representative collection site. The Grab sampling method, which involves either taking a single discrete sample or a series of samples spaced no more than 15 minutes apart, was used. To provide a representative sample of the wastewater conditions at the time of sample collection, the wastewater was collected using the grab sampling technique at roughly 9 a.m. 5-liter samples of wastewater were taken from the sampling location.

➤ Wastewater Characterization

The wastewater used in this study was characterized to determine the constituents and ECs present in the wastewater. The wastewater collected was characterized to determine the qualitative and quantitative ECs present in the wastewater using an HPLC-UV spectrometry analyzer. All the compounds were identified using the NIST library. The NIST library was used to identify all the chemicals. Operating conditions for the mass spectrometer included a range of 40 to 1000 m/z, an interface temperature of 240°C, and an ion source temperature of 200°C. Also, a UV spectrophotometer was used to determine the concentration of the various identified ECs from GCMS analysis.

➤ Batch Adsorption Study

The Adsorption procedure was carried out using the batch process to obtain equilibrium data. 1g of adsorbent (organo modified activated carbon) was contacted with 20 mL of the pretreated wastewater in an adsorption column with a known initial concentration at a pH of 6–7. The adsorption experiment was carried out at ambient temperature. At the established equilibrium time, the distilled water and the adsorbent were separated using filtration process. Followed by UV- visible sample analysis to ascertain the concentration of unadsorbed ECs in the filtrate using a UV-visible spectrophotometer.

The equilibrium adsorption capacities (q_e) of the organo modified adsorbent samples was calculated using equation 1.

$$q_e = \frac{(C_o - C_f) \times V}{M} \quad 1$$

Where, q_e = the adsorption capacity of ECs in aqueous solution (mg/g),

C_o and C_e = initial and equilibrium ECs concentrations in the solution (mg/L), respectively. V is the aqueous solution volume (ml) and M is the mass of adsorbent (g).

The ECs adsorption efficiency, which is the ratio of difference between initial and equilibrium concentration divided by initial concentration expressed in percentage would be determined using equation 2.

$$\text{Removal Efficiency} = \frac{C_o - C_f}{C_o} \times 100 \quad 2$$

Where, C_o = Initial concentration and C_f = final concentration after of the current designations.

III. RESULT AND DISCUSSION

A. Characterization of Wastewater

The wastewater used in this study was characterized to determine its constituent and ECs present in the wastewater. The wastewater collected was characterized using HPLC-UV spectrometry instrument to analyze several ECs present in the wastewater and quantity of each ECs in the wastewater. Table I presents the identified ECs in the wastewater from the HPLC chromatogram shown in Figure.

Table 1 shows the major identified ECs from the analyzed wastewater. Triclosan accounted for 24.955% of the in the wastewater followed by Diclofenac, Bisphenol A and Methylparaben which account for 21.772%, 16.805% and 12.674% of the identified ECs respectively. Also 6.464% Syringoside, 1.778% Adenine and 1.428% Calycosin-7-O- β -D-Glucopyranoside were identified from the HPLC analysis of the wastewater. The obtained result shows that Diclofenac, Triclosan, Methyl paraben and Bisphenol A are the major ECs in the wastewater which account for 76.206% of the total contaminants in the water. The high concentration of Triclosan detected from the analysis could be attributed to rise in the used of personal care products mostly by the female gender which are rinse and washed off into drainage and then to surface water. This corroborated by [20,7] assertions that major source of Triclosan in wastewater from personal care products such as musk fragrances and antimicrobials.

Also, Table 1 shows that Diclofenac has the highest concentration in wastewater which is an anti-inflammatory drug which could result in the compromised health of stream biofilms organisms on exposure [21,3]. Similarly, Methylparaben (16.805%) and Bisphenol A (12.674%) reported to be of major ECs of concern and have gained much attention in recent years because of their demonstrated ability to cause endocrine disruption [22,8,7,3]. Hence, the major ECs identified using HPLC from wastewater are mainly Diclofenac, Triclosan, Methylparaben and Bisphenol A which portends demonstrated ability to be detrimental to human health and environments. To this end, the adsorption and kinetics studies will focus on the first four ECs (Diclofenac, Triclosan, Methylparaben and Bisphenol A) with the highest concentration which account for 76.206% of the ECs in the wastewater.

Table 1 Identified Component Analysis in Wastewater

Max. Wavelength (nm)	Retention Time (min)	Area (%)	Identified ECs
276	7.3073	24.955	Diclofenac
352	14.3372	21.772	Triclosan
254	1.46	16.805	Methylparaben
229.5	11.2566	12.674	Bisphenol A
267	12.5779	6.464	Syringoside
260	3.581	1.778	Adenine
258	19.632	1.428	Calycosin-7-O- β -D-Glucopyranoside

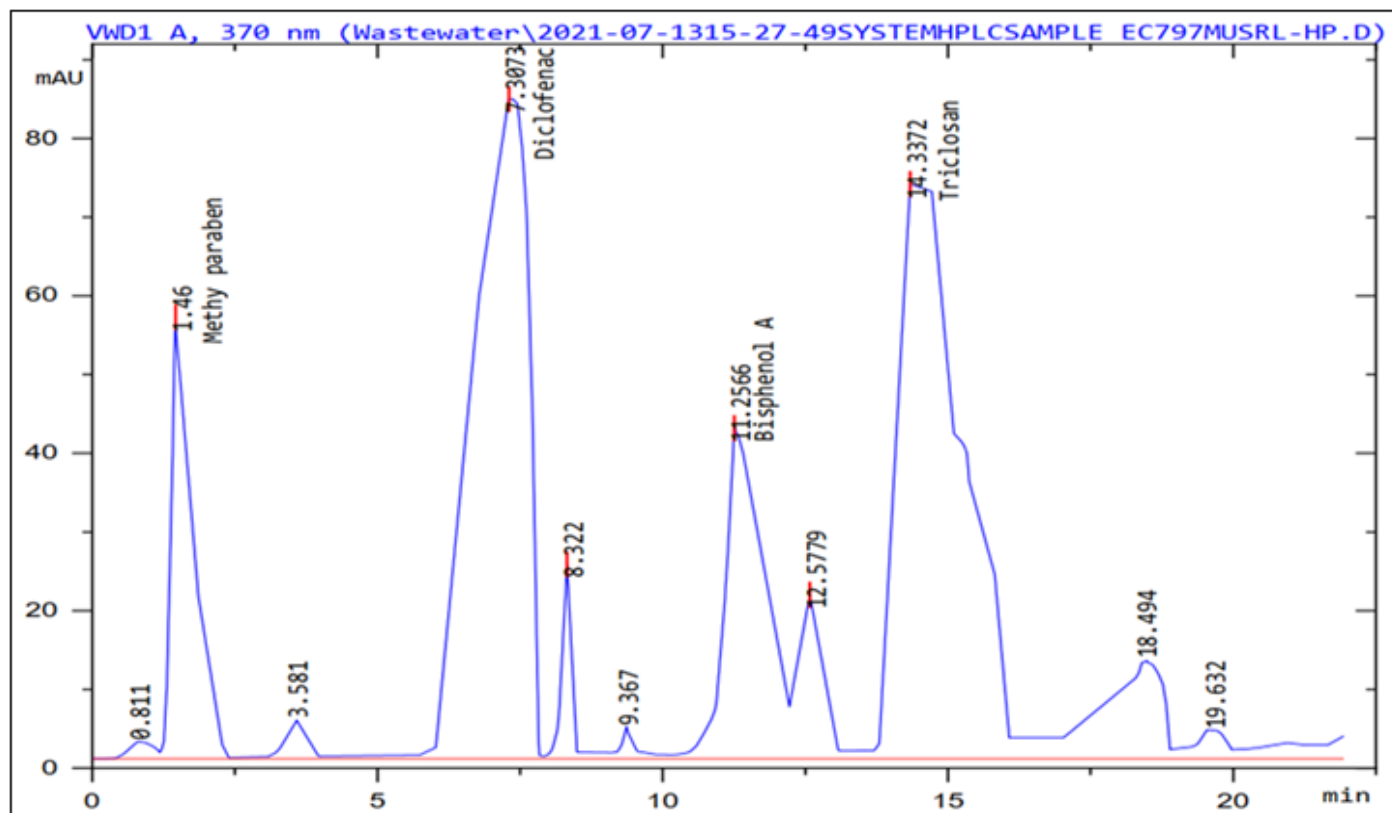


Fig 1 HPLC Finger Print Analysis of Waste Water

B. Adsorbents Characterization

➤ X-Ray Diffraction Analysis

Crystal structure for the produced organo-modified AC adsorbent was analyzed before and after adsorption. The produced organo-modified activated carbon (AC) from sugarcane bagasse was also characterized using XRD analysis to identify the crystal structure before adsorption and effect of adsorption of ECs on the crystal structure after adsorption. Figure 2 shows the XRD pattern of modified activated carbon (DMAC) adsorbent before adsorption. It was observed that the diffraction peak at 2θ angle of 26.27° and 44.82° were the typical diffraction peak of graphite carbon and corresponds to a diffraction plane of (002) and (100) respectively, assigned to graphite crystallographic plane [23]. The peak at 2θ angle of 26.27° and 44.82° , signifies increase in regularity of crystalline structure while the crystallographic composition shows 96.7% graphite,

2.2% cristobalite and 1.1% urea, which will result in a better layer alignment and enhance adsorption efficiency.

Likewise, the produced organo-modified AC after usage for ECs adsorption from wastewater, was also characterized using XRD analysis to identify the crystal structure and effect of adsorption of ECs on the crystal structure after adsorption. Figure 3 shows the XRD pattern of acid pretreated modified activated carbon (APMB) adsorbent after adsorption. Similar diffraction peaks at 2θ angle of 26.27° and 44.82° , typical diffraction peak of graphite carbon and corresponds to a diffraction plane of (002) and (100) respectively were observed for graphite crystallographic planes [23]. However, the crystallographic composition shows 89% graphite, 2% cristobalite, 0.2% urea and 10% garnet which differs from that obtained before adsorption. Indicating a change in the crystallographic structure of the APMAC adsorbent after adsorptions of ECs.

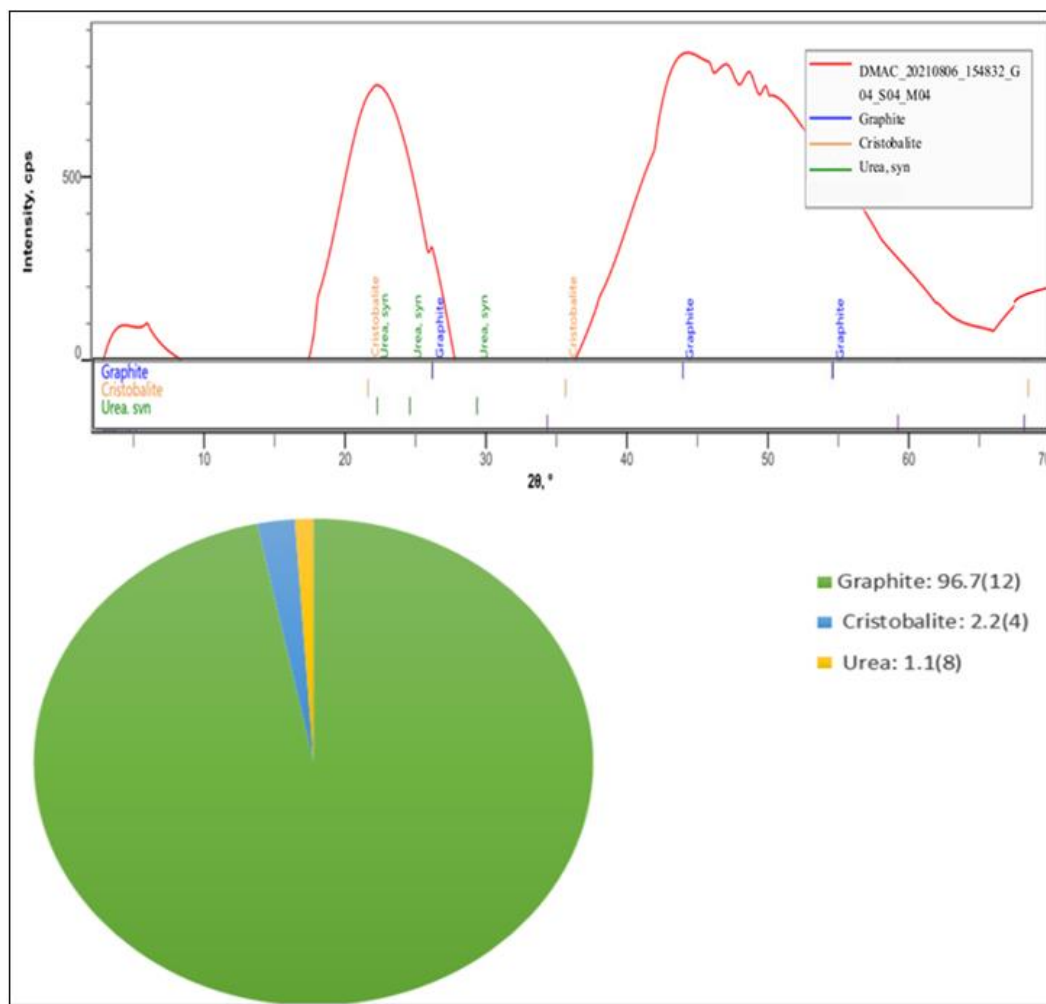


Fig 2 XRD Pattern of Modified Activated Carbon (DMAC) Adsorbent before Adsorption

Comparatively, further analysis of the organo-modified AC adsorbent before and after usage displayed the degree and level of crystallinity of the DMAC adsorbent (before adsorption) is low (8.63% with corresponding high amorphous graphite phase (91.37%), which portends high adsorptive capacity of DMAC [24,25]. The 8.63% crystallinity and 91.37% amorphous graphite phase obtained for the produced adsorbent corroborate with the 8.5% crystallinity and 91.5% amorphous reported for kenaf core fiber activated carbon by [26]. The low crystallinity and high amorphous structure are confirming the high ECs removal by the produced oxalic acid pretreated organo-modified AC adsorbent. Hence, the crystal structure of the produced DMAC adsorbent shows high adsorption capacity of the AC adsorbents. Modification of AC with quaternary salt (Cetyltrimethylammonium bromide, CTMABr), enhances the adsorption capacity of the produced adsorbents with low crystallinity and high amorphous phase.

➤ Fourier Transforms Infra-Red Analysis

The FTIR, which is a measure of the organic and inorganic functional group present in a material was also determined.

Figure 4(b) shows the FTIR spectrum of the produced acid pretreated sugarcane bagasse AC after usage (APMAC)

for adsorption of ECs from the wastewater. The band at 775.3 cm^{-1} is assigned to a strong C–H bend and medium C=C bending of alkene functional group which is like that identified from DMAC sample (before adsorption). Conversely, there was a shift in the band from 1047.4 cm^{-1} to 1036.2 cm^{-1} which was because of strong C–O stretch of anhydride functional group as well as medium C–N stretching amine attributed to the presence of quaternary salt used for modification [27]. Equally, the characteristic band at 1682.9 cm^{-1} observed from Figure 4(b) is assigned to strong C=O stretching conjugated of ketone and C=O stretching of secondary amide. Additionally, the band at 1882.9 cm^{-1} shifted to 1830.1 cm^{-1} which was also assigned to weak C–H bending of aromatic compound while 2102.2 cm^{-1} is assigned to strong N=C=N stretching carbodiimide attributed to the presence of alkylammonium in the produced AC adsorbent. The shift in the band from 1047.4 cm^{-1} to 1036.2 cm^{-1} and 1882.9 cm^{-1} to 1830.1 cm^{-1} is attributed to adsorption on ECs from the wastewater by the adsorbent after usage. Similarly, the characteristic band at 3436.6 cm^{-1} is assigned to a strong broad O–H stretching alcohol functional group. It can be suggested from the spectrum that after ECs adsorption (Figure 4b) the variation in FTIR spectrum is attributed to adsorption of foreign organic compound from wastewater.

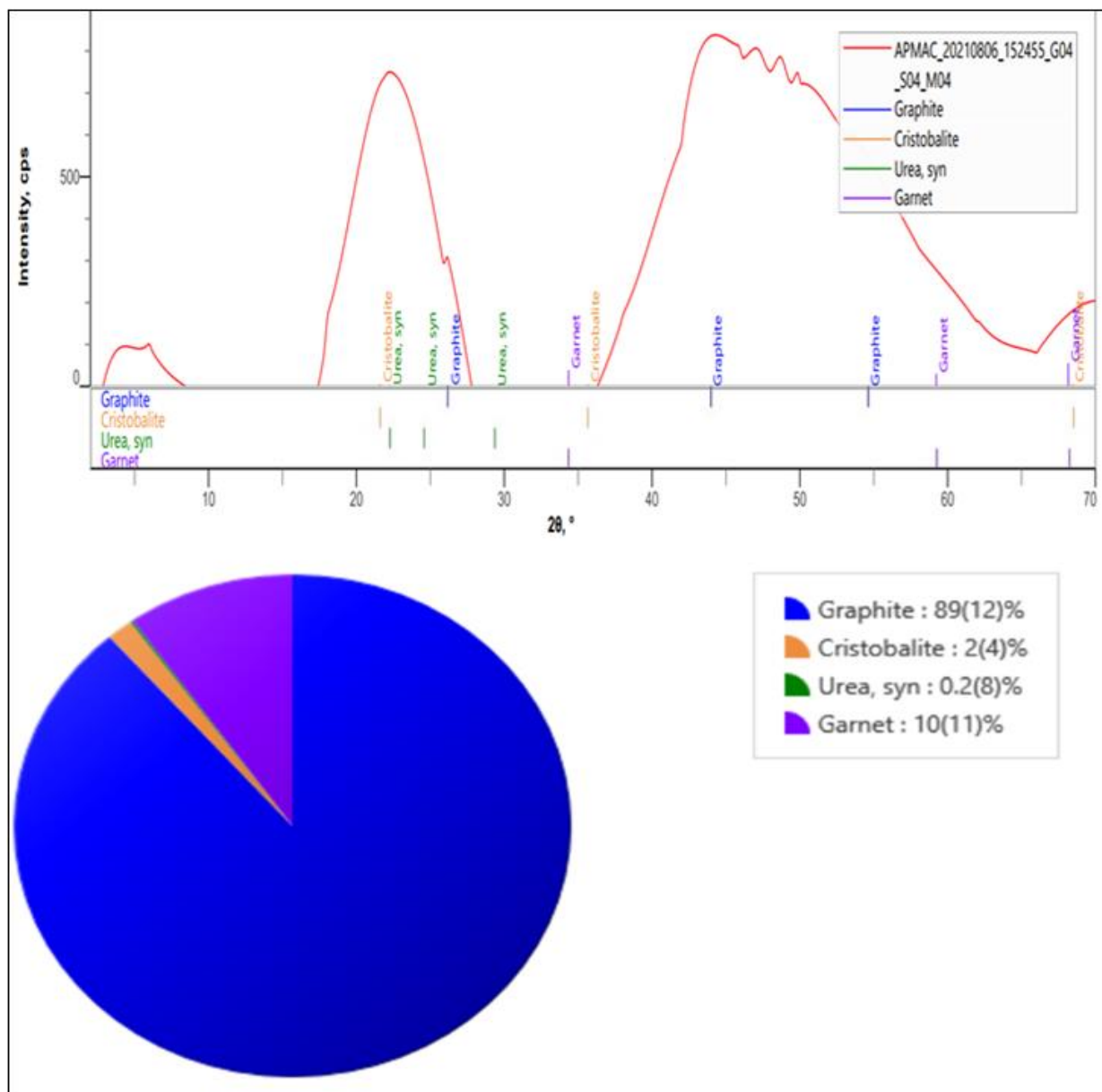


Fig 3 XRD Pattern of Acid Pretreated Modified Activated Carbon (APMAC) Adsorbent after Adsorption

➤ Brunauer–Emmett–Teller Analysis

The micro porosity of the adsorbents generated both prior to and after their application in wastewater treatment plays a very important role in the determination of the efficacy of the manufactured adsorbent. To achieve this objective, it is crucial to consider the surface area, pore volume, and pore size of both oxalic acid pretreatment activated carbon (APMAC) and DMAC, both before and after usage. These factors help in the determination of the effectiveness of the adsorbent for pollutants removal. The BET approach was employed to assess the overall surface area and volume of pores using Quantachrome equipment.

The cumulative adsorption surface area and volume of the meso and macropores were evaluated using the BJH, DH, and DFT methods. The t-method was employed to investigate the exterior surface area, the DR method was utilized to examine the micropore area of the generated adsorbents. As per the (IUPAC), porosity can be subdivided into three distinct classifications based on the size of the pores. These classifications include micropores, consists of a width of less than 2 nm, mesopores, which have a width ranging from 2 to 50 nm, and macropores, which have a width beyond 50 nm [28]. The BET surface area analysis of the adsorbent is presented in Table 2.

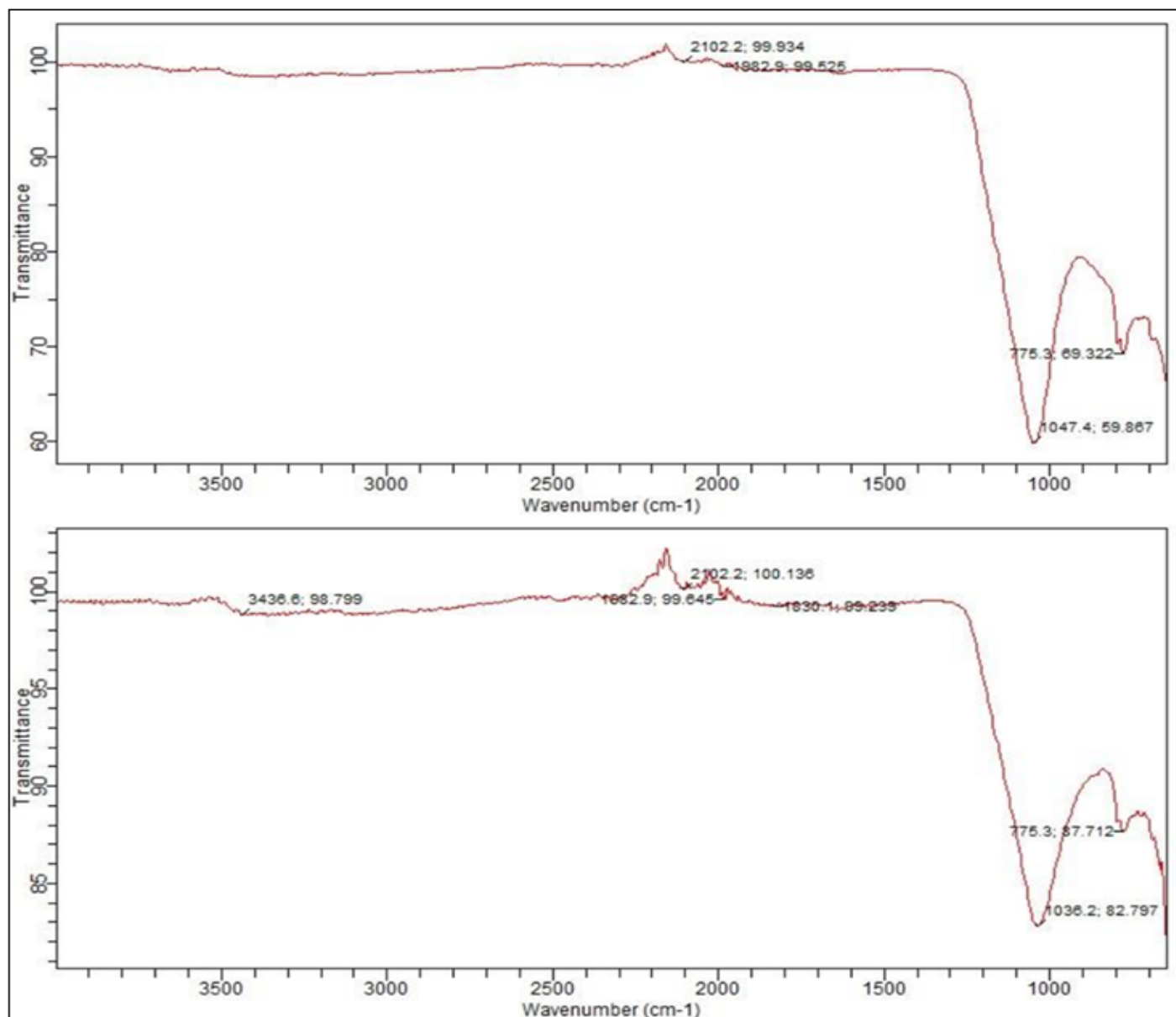


Fig 4 FTIR analysis of acid pretreated AC adsorbent (a) before (DMAC) and (b) after (APMAC) adsorption

Table 2 presents the surface area, pore volume and pore size of the produced oxalic acid pretreated organo-modified adsorbent before and after usage for adsorption of ECs from wastewater. The surface areas for the produced DMAC adsorbent were found to be higher than that of the produced APMAC adsorbents for all methods. This further corroborates the finding from the XRD analysis which shows produced DMAC adsorbent to have higher amorphous content compared to APMAC adsorbent before usage for ECs adsorption. The higher specific surface area of the produced DMAC adsorbent portends high adsorption capacity more than that of APMAC adsorbents. However, after the produced AC adsorbents have been used for ECs adsorption from wastewater, the specific surface area of the adsorbents was found to be reduced, indicating that foreign materials (ECs) have been adsorbed into the pores of the adsorbents.

Equally, the pore volume of the adsorbents is another important parameter. According to the data presented in Table II, the micropore volume of the adsorbents serves to validate the adsorption surface area. The pore volume of the DMAC adsorbent produced is more than that of the APMAC adsorbent produced. This finding provides additional evidence that the DMAC adsorbent has a greater adsorption capability in comparison to the APMAC adsorbent. The observed phenomenon can be ascribed to the significant enhancement in adsorbent porosity achieved through acid pretreatment of the adsorbent precursor prior to its modification with alkylammonium salt.

The determination of pore size in adsorbents is an important metric that provides valuable information regarding the adsorption capacity of said adsorbents. According to the data presented in Table II, the pore diameters of the direct modified activated carbon (DMAC) adsorbent are largely comparable to those of the acid pretreated organo-modified

Table 2 BET Surface Area Analysis

Surface Area	DMAC	APMAC
	Before (m ² /g)	After (m ² /g)
Single Point BET	218.80	195.80
Multi Point BET	572.00	356.00
Langmuir Surface Area	7823.00	6830.00
BJH Method Cumulative Adsorption Surface Area	487.40	368.40
DH Method Cumulative Adsorption surface Area	412.80	391.20
t-Method External Surface Area	538.60	356.00
DR Method Micropore Area	529.90	357.30
DFT Cumulative Surface Area	134.60	75.49
Pore Volume	cm ³ /g	cm ³ /g
BJH Method Cumulative Adsorption Pore Volume	0.1820	0.1815
DH Method Cumulative Adsorption Pore Volume	0.2652	0.1855
DR Method Micropore Volume	0.1700	0.1270
HK Method Micropore Volume	0.0666	0.0501
SF Method Micropore Volume	0.0098	0.0083
DFT Method Cumulative Pore Volume	0.1982	0.0913
Pore Size	nm	nm
BJH Method Cumulative Adsorption Pore Diameter (Mode Dv(d))	2.422	2.105
DH Method Cumulative Adsorption Pore Diameter (Mode Dv(d))	2.488	2.426
DR Method Micropore Pore Width	6.538	6.503
DA Method Pore Diameter (Mode)	3.420	3.000
HK Method Pore Diameter (Mode)	2.084	1.847
SF Method Pore Diameter (Mode)	3.892	3.479
DFT Pore Diameter (Mode)	2.747	2.647

APMAC activated carbon adsorbent. The DMAC and APMAC adsorbents predominantly exhibit pore sizes within the mesoporous range as classified by the International Union of Pure and Applied Chemistry (IUPAC), which spans from 2 to 50 nm. Additionally, a portion of these adsorbents possess micropores with sizes less than 2.0 nm, as reported by [29,28]. According to [28], the presence of micropores inside the interlayer spacing suggests the development of mesopores and a significant adsorption capacity in the resulting adsorbent. The observations demonstrate that the application of DMAC and APMAC adsorbents leads to an improved surface structure. Additionally, it suggests that the process of adsorption primarily occurs within the mesopores, which play a crucial role in facilitating the transportation of fluids to and from the micropores.

Hence, it can be concluded that DMAC and APMAC adsorbents possess higher adsorption capacity for ECs removal from wastewater. Also, the adsorbent characterization shows that the morphology of the produced DMAC and APMAC adsorbents has better pore development with higher amorphous structure that enhances uptake of contaminate into the adsorbents.

C. Adsorption Studies

➤ Effect of Contact Time

Figure 5 presents the effect of contact time (0 – 60 min) on the adsorption of the identified ECs from wastewater using oxalic acid pretreated organo-modified AC (Figure 5a) and direct organo-modified AC (Figure 5b). Figure 5a shows an almost linear and rapid uptake of Triclosan, Diclofenac, BPA and Methyl-paraben to over 83% removal for each ECs

in first 30 min of adsorption time while extending the time beyond 30 min to 60 min only result in percentage removal rise to 86.49% for Triclosan, 94.44% for Diclofenac, 87.94% for BPA and 77.73% for Methyl-paraben. The sharp rise in ECs removal in the first 30 min is attributed to the availability of sufficient adsorption sites which gradually gets saturated as more and more ECs are being adsorbed, thus, the adsorption rate became much slower beyond 30 min adsorption time [30,31].

Similarly, Figure 5b shows a fluctuating rise in removal of Triclosan, Diclofenac, BPA, and Methyl-paraben from wastewater as contact time rise from 0 to 50 min to attain a maximum removal rate of 82.33%, 75%, 78.01% and 81.56% respectively using direct modified AC adsorbent. Extending contact time beyond 50 min to 60 min only results in a slight rise in percentage removal to 83.37% for Triclosan, 77.78% for Diclofenac, 77.30% for BPA and 81.28% for Methyl-paraben. The slow rise from 50 min to 60 min is attributed to the direct modified AC adsorbent getting saturated by the adsorbate (Talaat et al., 2011). It was however, observed that direct modified AC adsorbent gives a higher removal of 81.56% Methyl-paraben compared to 77.32% Methyl-paraben removal with acid pretreated modified AC adsorbent. This infers that acid pretreatment has a negative impact on Methyl-paraben removal by organo-modified AC. Comparatively, acid pretreated modified bentonite adsorbent shows highest removal rate for Triclosan, Diclofenac and BPA compared to both AC adsorbent while direct modified AC adsorbent shows highest Methyl-paraben removal compared to all other 3 adsorbents as time rises.

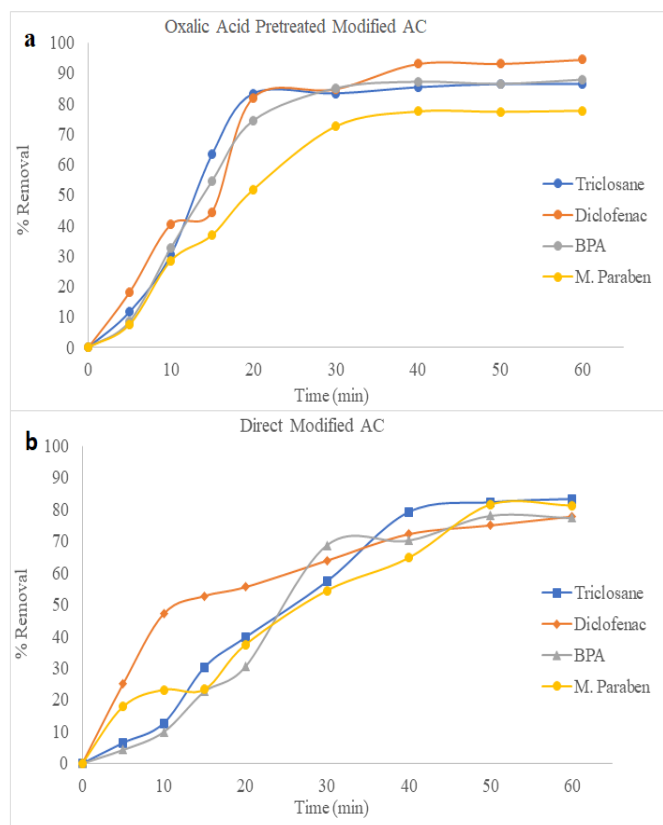


Fig 5 Effect of Contact Time on ECs Removal (a) Oxalic Acid Pretreated and (b) Direct Organo-Modified AC Adsorbent

➤ *Effect of Adsorbent Dosage*

Organo-modified AC adsorbents were also used to evaluate the effect of variation in adsorbent dosage on ECs removal. Figure 6 presents the effect of variation in adsorbent dosage from 0.5 – 4 g on the percentage removal of the identified ECs from wastewater using oxalic acid pretreated organo-modified AC (Figure 6a) and direct organo-modified AC (Figure 6b). Figure 6a shows a linear and rapid uptake of ECs as adsorbent dosage rises from 0.5 – 1.5 g adsorbent dosage and then slowly to reach 98.96% Triclosan, 90.28% Diclofenac, 94.68% BPA and 61.48% Methyl-Paraben removal as adsorbent dosage increases to 2.5g oxalic acid pretreated modified AC. A further increase in oxalic acid pretreated modified AC adsorbent dosage to 4.0g resulted in a slight increase in the removal of Triclosan, Diclofenac, BPA, and Methyl-Paraben to reach a maximum of 100%, 100%, 94.68% and 61.75% respectively.

In the same way, the use of direct organo-modified AC adsorbent presented in Figure 6b shows a linear and rapid uptake of ECs as adsorbent dosage rises from 0.5 – 1.5 g adsorbent dosage and then rises slowly to reach 88.57% Triclosan, 86.11% Diclofenac, 90.78% BPA and 70.22% Methyl-Paraben removal as direct organo-modified AC adsorbent dosage increases to 2.0g. Conversely, a slow rise in the removal of Triclosan, Diclofenac, BPA, and Methyl-Paraben to reach a maximum of 89.61%, 86.11%, 90.78% and 70.49% removal respectively as adsorbent dosage rises to 4.0g. The rapid rise in percentage removal of Triclosan, Diclofenac, BPA and Methyl-Paraben for both AC adsorbent

as adsorbent dosage increases to 2 – 2.5g is attributed to the high number of adsorption sites available per unit mass of adsorbents [32,33,19,11,12,19]. However, continuous increase in adsorbent dosage beyond 2.5 g of produced AC adsorbents do have significant rise in the percentage removal of ECs which is attributed to possible aggregation of the AC adsorbent in the wastewater [32,19]. On the contrary, the effect of adsorbent dosage shows that direct modified AC adsorbent shows higher affinity for Methyl-Paraben removal compared to the other AC, direct modified AC adsorbent shows highest Methyl-paraben removal with rise in adsorbent dosage when compared to the other adsorbent.

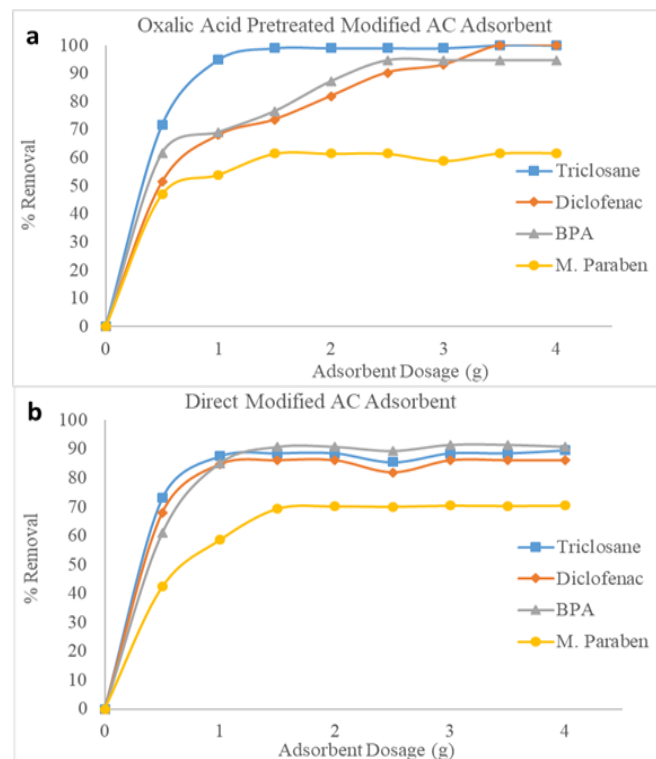


Fig 6 Effect of Adsorbent Dosage on ECs Removal (a) Oxalic Acid Pretreated and (b) Direct Organo-Modified AC Adsorbent

➤ *Effect of Adsorption Temperature*

Figure 7 presents the effect of temperature on the adsorption of the identified ECs from wastewater using oxalic acid pretreated organo-modified AC (Figure 7a) and direct organo-modified AC (Figure 7b) adsorbent. Figure 7 (a) and (b) also similar trend of maximum percentage removal of Triclosan,

Diclofenac, BPA, and Methyl-Paraben at 35 °C and percentage removal of the ECs decline as temperature rises to 35 °C. This also implies that the adsorption of ECs into both AC adsorbent decreases with an increase in temperature beyond 35 °C. This indicates that, at higher temperature, the molecule of the ECs gets lighter and could move freely and fast out of the pores of the adsorbent thereby resulting in increased rate of desorption of the ECs back into the bulk solution [34]. The decrease in the rate of adsorption by both AC adsorbents with increasing temperature signifies low energy requirement for ECs adsorption onto oxalic acid

pretreated organo-modified AC and direct organo-modified AC adsorbents.

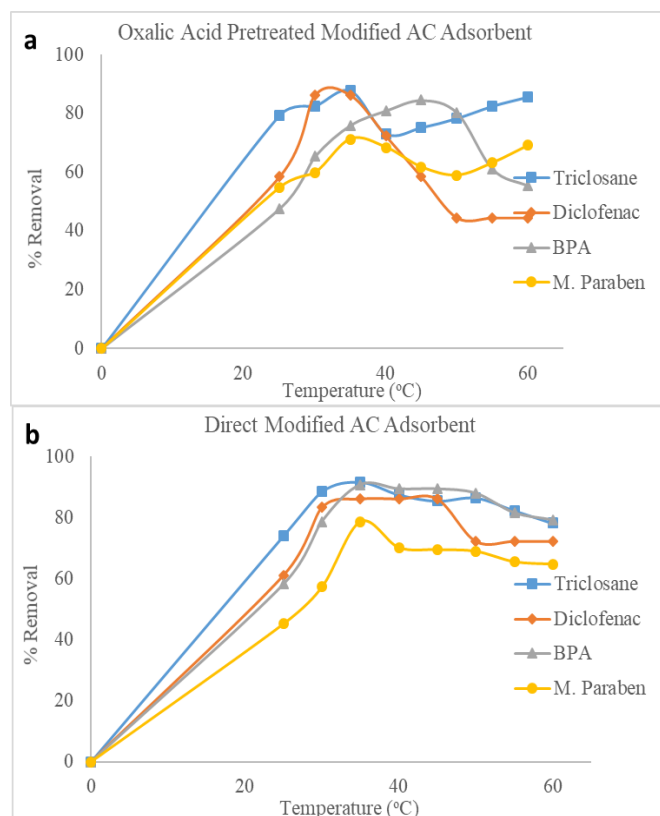


Fig 7 Effect of Temperature on ECs Removal (a) Oxalic Acid Pretreated and (b) Direct Organo-Modified AC Adsorbent

➤ *Adsorption Isotherm*

The adsorption isotherm of the produced adsorbents was investigated to describe the equilibrium of the adsorption materials at the surface of adsorbent and, particularly at the surface boundary at constant temperature. The isotherm model considered in this study are Langmuir and Freundlich isotherm models which are discussed subsequently.

The adsorption data acquired from the organo-modified activated carbon (AC) adsorbents that were created were analyzed using the Langmuir and Freundlich isotherm models. Table III illustrates that the equilibrium of the adsorption materials on the surface of adsorbents, including organo-modified activated carbons (ACs), is most accurately described by the Freundlich isotherm. This is evident from the correlation coefficients (R² values) ranging from 0.9691 to 0.9984, which indicate a strong fit to the experimental data. In contrast, the Langmuir isotherm yields lower correlation coefficients, ranging from 0.3899 to 0.6122. The strong agreement between the experimental data and the Freundlich isotherm suggests that adsorption process occur on the surfaces that are heterogeneous and contain active sites. These active sites have varying energies, which can be attributed to multilayer adsorption and the establishment of equilibrium [11,12,34].

Additionally, the parameter n serves as an indicator of the adsorption intensity and surface heterogeneity. It also provides insights into the distribution of energy and heterogeneity across the adsorbate sites [35]. According to the data presented in Table III, the value of n was determined to range from 1.1626 to 4.2954 for all adsorbents. The values of n generated in this study were greater than 1, suggesting that all the organo modified ACs adsorbents exhibit favorable adsorption characteristics for Triclosan, Diclofenac, BPA, and Methyl Paraben under the experimental conditions employed. Moreover, this finding further supports the notion that adsorption is the primary process occurring in this context. Additionally, the Freundlich adsorption capacity (k_f) was determined to range from 0.4634 to 1.3049 L/mg, with the maximum value of 1.3049 L/mg observed for the adsorption of triclosan using direct modified activated carbon (DMAC) adsorbent (refer to Table III). Therefore, the Freundlich isotherm shows the most accurate description of the equilibrium of adsorption materials at the surface of both organo-modified ACs adsorbent.

Table 3 Adsorption Isotherm Studies

Parameters	Langmuir Isotherm				Freundlich Isotherms		
	q _{max}	b	R _L	R ²	k _f	n	R ²
Direct Modified AC							
Triclosan	0.0423	-0.2695	-0.2043	0.5088	1.3049	1.6600	0.9748
Diclofenac	0.0617	-0.5280	-0.0948	0.5924	0.6883	2.5160	0.9904
BPA	0.0191	-0.3148	-0.1699	0.4125	0.9859	1.3879	0.9691
M. Paraben	0.0384	-0.7038	-0.0695	0.6122	0.5576	2.2721	0.9918
Acid Pretreated Modified AC							
Triclosan	0.0738	-0.3763	-0.1383	0.5495	1.0759	2.4654	0.9946
Diclofenac	0.0711	-1.8935	-0.0247	0.4162	0.5035	4.2954	0.9900
BPA	0.0421	-0.6287	-0.0784	0.3899	0.7173	2.3953	0.9834
M. Paraben	0.0220	-0.5219	-0.0960	0.4035	0.7141	1.7128	0.9889

➤ *Adsorption Kinetics*

Investigation of the adsorption kinetics of the generated adsorbent aimed to characterize the adsorption capacity of emerging contaminants (ECs) over time under a constant pressure condition. The kinetic models examined in this

paper encompass the pseudo-first order and pseudo-second-order kinetics, which will be further described.

The adsorption kinetics data obtained from the various organo-modified activated carbon (AC) adsorbents were analyzed using the pseudo-first order and pseudo-second-

order kinetics models to investigate the adsorption mechanism. Table IV presents the adsorption behavior of Triclosan, Diclofenac, BPA, and Methyl Paraben on various adsorbents. The results indicate that the adsorption of these compounds generally follows the pseudo-second-order kinetic model, as evidenced by correlation coefficients (R^2 values) ranging from 0.86601 to 0.99847. However, there are exceptions to this trend, such as adsorption of Triclosan, BPA, and Methyl Paraben on directly modified AC. In these cases, the adsorption process is better described by the pseudo-first-order kinetic model, with correlation coefficients (R^2 values) ranging from 0.87891 to 0.96588. The pseudo-second-order kinetic model provides the most accurate description of the adsorption kinetics of all ECs (Triclosan, Diclofenac, BPA, and Methyl Paraben) in acid pretreatment modified AC.

The adsorption of Methyl Paraben in all adsorbents was seen to have the highest kinetic rate constant in the pseudo-first-order kinetic model, with values ranging from 0.00037 to 0.00054 min⁻¹. In comparison, the pseudo-second-order kinetic model yielded a lower rate constant range of 0.0000029 to 0.0000071 g/mg min. Moreover, the adsorption rate constant of Triclosan in all adsorbents was determined to range from 0.00051 to 0.00071 min⁻¹ for the pseudo-first-order kinetic model, and from 0.000014 to 0.00074 g/mg min

for the pseudo-second-order kinetic model. In a similar vein, the adsorption rate constant of Diclofenac was determined to range from 0.00034 to 0.00075 min⁻¹ for the pseudo-first-order kinetic model, and from 0.0000015 to 0.0061125 g/mg min for the pseudo-second-order kinetic model across all adsorbents. Similarly, the adsorption rate constant of bisphenol A (BPA) in all adsorbents was determined to be in the range of 0.00054 – 0.00071 min⁻¹ for the pseudo-first-order kinetic model, and 4.9 x 10⁻⁷ – 0.00343 g/mg min for the pseudo-second-order kinetic model. The rate constants measured in this investigation for both first and second-order rate constants can be ascribed to the tendency of the adsorbate species (Triclosan, Diclofenac, BPA, and Methyl Paraben) to undergo migration from the solid phase to the bulk phase [34].

The equilibrium of adsorption materials, including Triclosan, Diclofenac, BPA, and Methyl Paraben, on organo-modified activated carbons (ACs) adsorbents was best described by the Freundlich isotherm. Additionally, the kinetics study indicated that the adsorption of Triclosan, Diclofenac, BPA, and Methyl Paraben on both adsorbents followed the pseudo-second-order kinetic model. However, there were exceptions observed for Triclosan, BPA, and Methyl Paraben adsorption on direct modified AC, which favored the pseudo-first-order kinetic model.

Table 4 Adsorption Kinetic Studies

Parameters	First order			Second Order		
	k_1	q_e	R^2	k_2	q_e	R^2
Direct Modified AC						
Triclosan	0.00067	20.32052	0.92588	0.000044	125.26748	0.91661
Diclofenac	0.00034	11.03270	0.84220	0.0061125	18.81925	0.99218
BPA	0.00064	13.08808	0.87891	0.000010	423.18546	0.80586
M. Paraben	0.00054	9.09466	0.96588	0.0000031	743.40828	0.85316
Acid Pretreated Modified AC						
Triclosan	0.00051	20.19788	0.60366	0.000014	378.97035	0.96642
Diclofenac	0.00054	11.04179	0.74647	0.0043181	20.19216	0.96785
BPA	0.00054	13.01666	0.69204	4.8548E-07	1971.67065	0.90156
M. Paraben	0.00051	9.08019	0.80867	0.0000029	1003.98825	0.99382

➤ Intra-Particle Diffusion

The utilization of the intra-particle diffusion model was extended to assess the adsorption kinetics of the adsorbents. The intra-particle diffusion model offers valuable insights into the underlying mechanics of the adsorption process. According to this model, multiple mechanisms are implicated in the adsorption process. The process of intra-particle diffusion can be delineated into three fundamental steps: superficial external adsorption, intra-particle diffusion as the rate-determining phase, and the subsequent attainment of equilibrium, which occurs rapidly [37,11,12,38]. Therefore, if the plot of the experimental data demonstrates a multilinear relationship, it indicates that the adsorption process is influenced by two or more processes. Figure 8 depicts the intraparticle diffusion model employed in the analysis of the adsorption process of emerging contaminants (ECs) onto DMAC.

According to the data presented in Table V, it can be observed that the rate of diffusion is at its peak during the early phase of surface sorption. However, as the process progresses into succeeding stages characterized by intra-particle diffusion and equilibrium adsorption, the rate of diffusion decreases. According to the data shown in Table V, it can be observed that the level of ECs absorbed into DMAC follows the order of $k_{id1} > k_{id2} > k_{id3}$. This observation suggests that the sorption rate is higher initially, perhaps because there are an ample number of adsorption sites available. However, as the adsorption duration increases, the rate of intra-particle diffusion decreases in later stages. The observed high adsorption capacity at the beginning of the adsorption process can be attributed to the presence of micro and meso pores, suggesting that intra-particle diffusion occurs in these pores. This phenomenon contributes to the exceptionally rapid rate of adsorption [39,38].

Figure 9 illustrates the intraparticle diffusion model employed in the adsorption of triclosan, diclofenac, BPA, and M. Paraben onto direct modified activated carbon (DMAC). The results indicate a three-stage multilinear plot for the adsorption process of triclosan and diclofenac, whereas the adsorption process of BPA and M. Paraben exhibits a two-stage multilinear plot. The first region is associated with surface sorption, the second region is associated with intra-particle diffusion, and the third region is associated with equilibrium adsorption [40,41]. Similarly, the R2 values of the intraparticle diffusion model for the adsorption of triclosan, diclofenac, BPA, and M. Paraben onto the DMAC adsorbent are 0.9402, 0.9331, 0.9903, and 0.9865 (Table V), respectively. These values indicate a strong fit between the adsorption process and the intraparticle diffusion model.

Table V illustrates that the rate of diffusion exhibits a higher velocity during the early phase of surface sorption. However, this rate gradually diminishes in succeeding stages, particularly in the region where intra-particle diffusion and equilibrium adsorption play a significant role. This trend is evident from the comparison of the diffusion rates of kid 1, kid 2, and kid 3 (as presented in Table 5) for all ECs absorbed into DMAC. This phenomenon indicates a more rapid uptake of sorbate molecules during the early stages of sorption, accompanied by a decrease in the rate of intra-particle diffusion as the adsorption period increases. This observation provides support for the significant adsorption capacity seen during the initial phase of the adsorption process [39,38]. The adsorption rate of triclosan and

diclofenac onto DMAC is influenced by surface adsorption, intra-particle diffusion, and equilibrium adsorption. On the other hand, the adsorption of BPA and M Paraben is influenced by surface adsorption and intra-particle diffusion.

Figure 4.17 illustrates the intraparticle diffusion model employed in the adsorption process of triclosan, diclofenac, BPA, and M. Paraben onto oxalic acid pretreated modified activated carbon (PMAC). The data suggests a three-stage multilinear plot for the adsorption process of diclofenac and BPA, whereas triclosan and M. Paraben exhibit two-stage multilinear plots. Similarly, the R2 values of the intraparticle diffusion model for the adsorption of triclosan, diclofenac, BPA, and M. Paraben onto the direct MB adsorbent are 0.9457, 0.9069, 0.9497, and 0.9870, respectively (Table V). These values indicate a strong fit between the adsorption process and the intraparticle diffusion model. The adsorption rate of diclofenac and BPA onto the oxalic acid PMAC adsorbent is influenced by surface adsorption, intra-particle diffusion, and equilibrium adsorption. On the other hand, the adsorption of triclosan and M Paraben is influenced by surface adsorption and intra-particle diffusion.

In general, the intraparticle diffusion model indicates that the adsorption rate of emerging contaminants (ECs) onto various adsorbents is influenced by surface adsorption, intra-particle diffusion, and equilibrium adsorption. Alternatively, the rate may be influenced solely by surface adsorption and intra-particle diffusion.

Table 5 Intra-Particle Diffusion Model Parameters for Adsorption of ECs from Wastewater

Parameters	Parameters			
	Triclosan	Diclofenac	BPA	M. Paraben
Direct Modified AC				
$k_{id\ 1}, \text{mg/g. min}^{1/2}$	4.3809	1.6463	1.8711	2.2434
$k_{id\ 2}, \text{mg/g. min}^{1/2}$	2.6626	1.0778	1.5354	1.4031
$k_{id\ 3}, \text{mg/g. min}^{1/2}$	1.3587	0.5020	-	-
C_i	-3.2289	1.0750	-1.1111	-2.2799
$k_{id}, \text{mg/g. min}^{1/2}$	2.8553	1.0472	1.6212	1.9685
R^2	0.9402	0.9331	0.9903	0.9865
Acid Pretreated Modified AC				
$k_{id\ 1}, \text{mg/g. min}^{1/2}$	3.5406	2.7143	2.8591	1.9132
$k_{id\ 2}, \text{mg/g. min}^{1/2}$	1.1320	1.1159	1.4556	0.8499
$k_{id\ 3}, \text{mg/g. min}^{1/2}$	-	0.4946	0.8177	-
C_i	-0.4219	-0.1668	-1.2549	-0.1708
$k_{id}, \text{mg/g. min}^{1/2}$	2.5264	1.4976	1.8588	1.7106
R^2	0.9457	0.9069	0.9497	0.9870

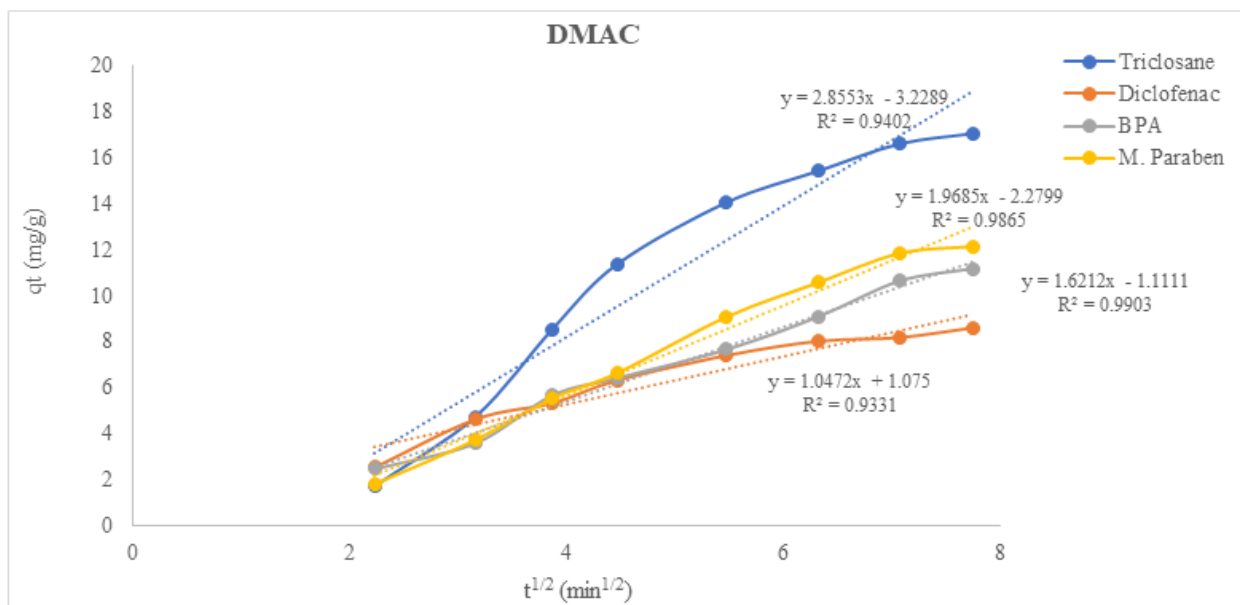


Fig 8 Intraparticle Diffusion Model for the Adsorption of ECs into DMAC

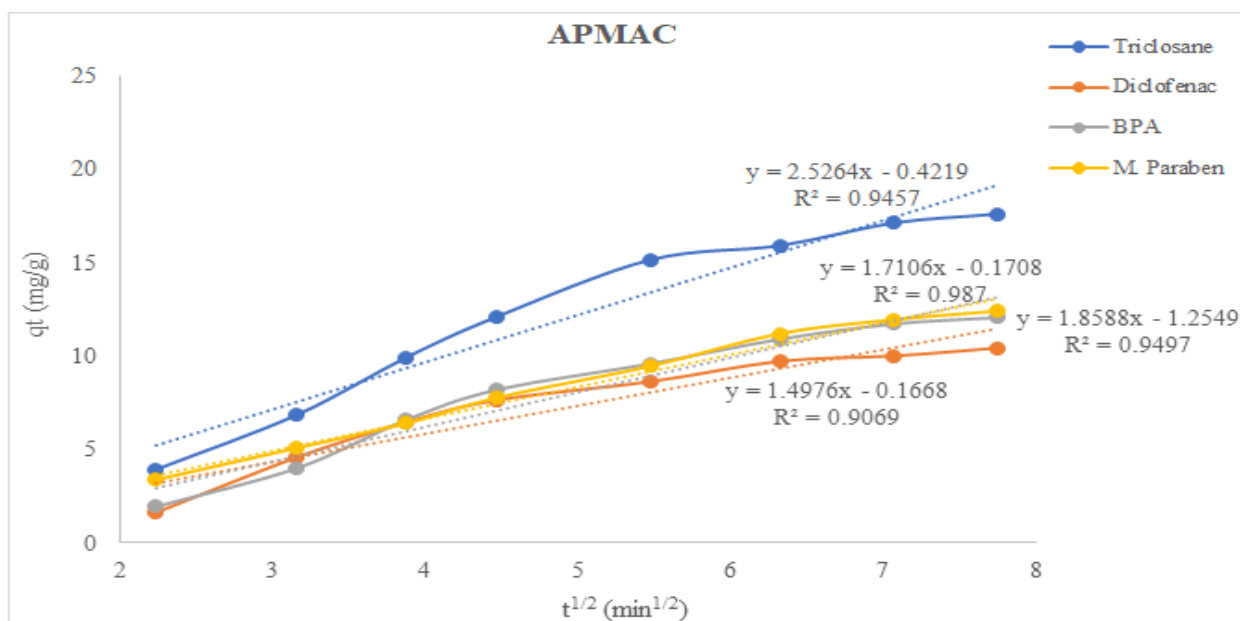


Fig 9 Intraparticle Diffusion Model for the Adsorption of ECs into Oxalic Acid PMAC

➤ *Activation Energy*

The investigation of the activation energy of the adsorption process was conducted to evaluate the interactions between the adsorbate and the adsorbent chemically. This assessment utilized the Arrhenius equation. The determination of the activation energy (E_a) is of utmost importance in the field of adsorption research, as it provides valuable insights into the underlying mechanisms of adsorption. The activation energy

(E_a) values for physical adsorption typically fall within the range of 5 - 40 kJ/mol. On the other hand, chemisorption, which involves the creation of strong bonding, necessitates an energy range of 40 – 800 kJ/mol [42,11,12,13,43]. Table VI presents the activation energy values pertaining to the adsorption process of triclosan, diclofenac, BPA, and M. Paraben onto the four adsorbents.

Table 6 Adsorption Activation Energy

Parameters	E_a (kJ/mol)	k_o (g/mg.min)
	Direct Modified AC	
Triclosan	10.374	0.202
Diclofenac	11.473	44.573
BPA	16.171	0.452
M. Paraben	14.807	0.066

Acid Pretreated Modified AC		
Triclosan	8.519	0.036
Diclofenac	18.333	406.257
BPA	17.161	0.031
M. Paraben	23.168	1.246

From Table VI, the E_a energy for the adsorption of all ECs (triclosan, diclofenac, BPA, and M. Paraben). 10.30 – 16.20 kJ/mol for direct MAC and 8.50 – 23.20 kJ/mol for oxalic acid PMAC adsorbents. This indicates that the adsorption mechanism of triclosan, diclofenac, BPA and M. Paraben into direct MAC and oxalic acid PMAC adsorbent falls in the range of 5 – 40 kJ/mol for physio-sorption [42., 11,12,13,43].

The E_a value less than 40 kJ/mol for all the adsorbents suggest that there is no chemical interaction in adsorption process for all adsorbents and that lesser energy of activation is required for the adsorption of all ECs into the adsorbents which implies that equilibrium will be reach in lesser adsorption time. Hence, the adsorption mechanism of triclosan, diclofenac, BPA and M. Paraben into direct MAC and oxalic acid PMAC adsorbents is physio-sorption and diffusion-controlled.

IV. CONCLUSION

Organo-modified AC adsorbents were successfully produced from sugarcane bagasse using thermal carbonization at 500 oC and the chemical activation method with phosphoric acid solution, with two separate samples of AC adsorbents produced (HCl acid-pretreated AC and untreated AC). The produced acid-pretreated organo-modified AC adsorbent possesses a higher adsorption capacity for ECs removal from wastewater. Also, the adsorbent characterization shows that the morphology of the acid-pretreated organo-modified AC adsorbent has better pore development with a higher amorphous structure that enhances uptake of contaminants into the adsorbents.

The direct modified AC adsorbent shows the highest methyl-paraben removal compared to the other adsorbent as time increases. From the adsorption isotherm and kinetics study of Triclosan, diclofenac, BPA, and methyl paraben from contaminated water, it shows that the ECs were removed by the developed adsorbents. The Freundlich isotherm best described the equilibrium of the adsorption materials at the surface of both organo-modified AC adsorbents, while the kinetics study shows that triclosan, diclofenac, BPA, and methyl Paraben adsorption in all adsorbents favors a pseudo-second-order kinetic model. Triclosan, BPA, and methyl paraben adsorption in direct modified AC favors a pseudo-first-order kinetic model.

The intraparticle diffusion model shows that the rate of adsorption of ECs into all the adsorbents was influenced by surface adsorption, intra-particle diffusion, and equilibrium adsorption, or by surface adsorption and intra-particle diffusion alone. Finally, the adsorption mechanisms of triclosan, diclofenac, BPA, and M. paraben into direct MAC

and oxalic acid PMAC adsorbents are physio-sorption and diffusion-controlled.

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