International Journal of
Science and Engineering Investigations vol. 11, issue 127, August 2022
Received on August 15, 2022 ISSN: 2251-8843

Removal of Acetaminophen (Paracetamol) from Pharmaceutical Waste Water Using Organic Membrane Got from Coconut Shell

M. O. Anusi[1], N. Igboko[2], C. N. Njoku[3], G. U. Ogbuehi[4], D. C. Onwumelu[5]
[1,2,3,4,5]Chemical Engineering Department, Federal University of Technology, Owerri, Imo State, Nigeria
([1]modestus.anusi@futo.edu.ng, [2]ndubuisi.igboko@futo.edu.ng, [3]chigoziri.njoku@futo.edu.ng, [4]uchechukwu543@gmail.com, [5]davidsononwumelu@gmail.com)

Abstract-This research work was carried out to develop a membrane to reduce the harmful effects of pharmaceutical waste water on the environment. Acetaminophen (ACT), commonly known as paracetamol, was targeted because of its high production rate and use in Nigeria. The treatment of the waste water containing Acetaminophen was done using organic membrane made by the phase inversion technique (PIT) using coconut shell (agro-waste) chemically activated with NaOH. Varying membrane doses, 11.38 g, 8.54 g, and 2.28 g, were put into three columns, C_1, C_2, and C_3, with same height (20 cm). 150mL (V_0) of wastewater containing 439.42µg/mL of Acetaminophen was passed through each column and after filtration it was found that the concentration of Acetaminophen reduced to 148.58µg/mL, 184.42µg/mL and 76.09µg/mL respectively. The adsorption capacity of each column was calculated to be 3833.57µg/g, 4478.92µg/g and 23903.29µg/g for columns C_1, C_2 and C_3 respectively showing an inverse relationship between adsorptive capacities and membrane dosage needed for acetaminophen removal. Similarly, the removal efficiencies of the three columns, C_1, C_2, and C_3, were calculated to be 67.04%, 58.03%, and 82.78% respectively. The data obtained was modeled using Langmuir-1, Langmuir-2, Freundlich and Temkin adsorption isotherms. The Temkin isotherm best fitted the data as it had the highest R^2 value of 0.93. The heat of adsorption reaction was evaluated from the Temkin isotherm as 23850 J/mol, implying that the reaction was endothermic. After converting J/mol to Kcal/mol, it was discovered that both chemical and physical adsorption took place as 5.7 Kcal/mol lies between 1-20.

Keywords- *Acetaminophen, Adsorption, Wastewater Treatment, Organic Membrane, Coconut Shell*

I. INTRODUCTION

Pharmaceutical manufacturing companies (PMCs) release lots of wastewater into the environment. These wastewaters vary in composition. Some contain large amounts of toxic chemicals while others have only trace elements. Their composition generally depends on the active pharmaceutical ingredients (API), the manufacturing process(es), machines and equipment used as well as the local regulatory body. Over the years, there has been an increase in the rate at which these APIs and other forms of pharmaceutical wastes such as colloids, intermediates, and solvents get into the environment (particularly water bodies). This has raised lots of concerns. APIs, alongside their metabolites, may pose more threat to the environment than their parent compounds [6]. Although majority of these discharges come from industries, a good percentage also arise from the hospitals and unused, used and expired drugs [5]. Slightly metabolized or non-metabolized can also be passed out through excreta which also poses significant threats to the environment [17]. To save the environment, many countries make regulations to guide against indiscriminate disposal of manufacturing plant effluents. The essence of regulation is to ensure there is little or no contact between these effluents and natural bodies. Sadly, this isn’t the reality in many developing countries around the world. Many companies in these countries lack an effective effluent treatment plant (ETP). If they have, it’s mostly dilapidated or non-functional [12].

In Nigeria, acetaminophen (ACT), commonly known as paracetamol, is a commonly used drug. It is used for common fever, body pains, high body temperature and slight headaches. The market for it is large in the country because of its cheap price and availability hence its high rate of production in the country. It’s not in doubt that acetaminophen (ACT) contributes a larger chunk of pharmaceutical wastewater in the country.

Acetaminophen (ACT) is an organic compound with the name N-(4-hydroxyphenyl) ethanamide [4]. Acetaminophen (ACT) belongs to the analgesics and antipyretics sub-class of pharmaceutical product [7]. There are other classes of pharmaceutical products [13]. Despite having mild effects, an overdose of acetaminophen has its side effects. Fulminating hepatic necrosis, a situation that results from acetaminophen overdose, is responsible for about 450 deaths in the United States annually [4]. It has also been discovered that acetaminophen (ACT) causes water pollution when it finds its way to water bodies in metabolized or non-metabolized forms [17]. There is therefore need to remove as much of acetaminophen (ACT) as possible to reduce its effects on the environment.

Acetaminophen (ACT) wastewater shares similar characteristics with other pharmaceutical liquid effluents which includes high concentration of organic matter (suspended particles and colloids), microbial toxicity, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and low biodegradability [14]. Being an unwanted byproduct, it contains several particles, dirts and contaminants which pose harm to the living organisms and the environment in general [6]. Acetaminophen wastewater is complex and has been classified as a pollutant. Acetaminophen (ACT) as an organic compound, takes quite some time to degrade in water and so separating it out before releasing it to water bodies is necessary [5]. This is imperative because acetaminophen, just like some other drugs such as ketoprofen, ibuprofen, and indomethacin, have a long solid retention time in water. It's presence in water bodies threatens the availability of clean and potable water especially in developing countries.

The recent clamor for water preservation as well as protection of natural water bodies has made it necessary for a search for an effective separation technique for the removal of acetaminophen (ACT) from wastewater before its release into the environment. An estimate of 90% of the world's available water resource will be used up in 14 years and nearly 60% of the earth's population will be hit by water scarcity by 2025 [14]. The UN and WHO reports that about a fifth of the world population live in regions where potable water is scarce. There isn't a doubt that communities in developing countries such as Nigeria make up the greater proportion of this statistic. Even where water bodies are present, they may not be suitable for drinking or other purposes as a result of release of these effluents into them. Aquatic life is also threatened by these APIs and other effluents chief of which is acetaminophen (ACT) wastewater. They can cause a reduction in the amount of oxygen that enters the water body thus endangering the lives of aquatic animals.

Over the years, several researches have been carried out to determine the best method to remove acetaminophen (ACT) and other contaminants of pharmaceutical wastewaters deemed dangerous to humans and the environment. Adsorption still remains the most preferred alternative. Activated sludge has been used and is still in use in many wastewater treatment plants (WWTPs). Some WWTPs use activated carbon got from activated sludge for treatment as activated carbons appeared to have more desirable properties compared to activated sludge. Due to their Van der Waal's forces of attraction, activated carbons have lesser selectivity when it comes to adsorption [2]. Also, activated carbons have very low bonding strength which accounts for their low heat of adsorption and regeneration. Researchers have come to agree that the current activated sludge used in waste water treatment isn't effective when it comes to pharmaceutical wastewater as organic colloids and ions cannot be completely removed by this method and also because of more sludge production in the process. Similarly, more quantity of these adsorbents is needed when larger quantities of wastewater are involved. Hence the need for a separation technique that wouldn't only remove acetaminophen (ACT) and other contaminants from wastewaters, but would also be cost effective and highly efficient. Activated carbon prepared from exhausted olive-waste cake was used in removing ibuprofen [1]. It was also discovered that increase in temperature had little or no effect on the adsorption process. Similarly, the adsorptive capacities of activated carbons from Coal (B), Wood (NS), Plastic Waste (PP), Cork Powder Waste (CC), and Peach Stones (CP) in the removal of acetaminophen (ACT) from water was studied [3]. The concentration of acetaminophen (ACT) was 120mg/L in a 15mL solution and 10mg of each activated carbon sample was used. The activated carbon sample obtained from wood performed better than others. The effectiveness of activated carbon from sisal waste in removing acetaminophen (ACT) from water was studied and discovered it could remove the contaminant in the wastewater to a certain degree [11].

Membranes turned out to be better alternatives. Membranes are cheaper, more efficient (even in smaller quantities), and have high biodegradability making them eco-friendly. They also use up little chemicals, require far less energy and involves fewer equipment [5]. In additional to these, membranes are generally known to produce lesser sludge compared to other adsorbents used in wastewater treatment. Membrane technology has been used extensively in water filtration and treatment over the years and is generally considered an advanced separation technology [8]. Membranes are selective barriers that separate materials with different physical and chemical properties [15]. They are divided into porous membranes (used for materials with larger molecules) and dense membranes (used for materials with smaller molecules). Membrane filtration has become a leading technology due to its effectiveness in removing small organics [16]. However, it isn't without its issues chief of which is membrane fouling. This is the clogging of the membrane pores with molecules of the material to be filtered. This reduces the filtration time as well as quality of the filtrate. There is need for extensive research in order find a membrane that wouldn't only separate materials with high efficiency, but would also resist fouling as much as possible [10].

This research was carried out to find an adequate and cost-effective means to reclaim useable water from acetaminophen wastewater by the use of organic membrane fabricated from coconut shell (generally considered an agro-waste). It also seeks to understand how the amount (mass) of membranes affects acetaminophen (ACT) removal from wastewaters in order to confirm the efficiency of membranes in minute quantities. Furthermore, the spatial arrangement of the membrane would be investigated before and after the filtration.

II. MATERIALS AND METHODS

A. Wastewater collection and standard sample preparation

1) Acetaminophen wastewater collection

The acetaminophen wastewater used in this research work was obtained from Nalis Pharmaceutical Industry, Naze, Owerri, Nigeria. The wastewater was collected using pre-cleaned 2.5 L amber glass bottles. About 10 mL of 1% (v/v) formaldehyde was added immediately on site to prevent degradation. During transit from WWTP to the laboratory, the sample was placed in an ice box. In the lab, the sample was placed in dark condition at 4^0C for 2 days before analyses.

2) Acetaminophen standard solution preparation

A stock acetaminophen solution was prepared in the laboratory for analyses. To prepare a standard solution of concentration 1,000 µg/mL, 0.251 g of 4-Acetamidophenol was weighed and dissolved in 15 mL of ethanol. This solution was then transferred into a 250 mL standard flask, and filled up to the 250 mL mark with distilled water.

The working solution was prepared by diluting 150 mL of 1000 µg/mL acetaminophen (paracetamol) solution with 20 mL of 4 M of hydrochloric (HCl) acid in a 250 mL round bottomed flask. It was further refluxed for 1 hour, kept aside to cool for some time and neutralized with 20% of sodium carbonate solution. This was subsequently followed by diluting the resultant solution by filling the conical flask with distilled water up to the 250 mL mark. 16.6 mL of the above solution was measured out and further diluted with distilled water in a 100 mL volumetric flask to prepare a 100 µg/mL acetaminophen solution. At this point, the required aliquots were drawn out for preparation of the calibration curve.

Aliquots of 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, 30 mL, 35 mL, 40 mL, and 45 mL were drawn out of the new solution containing acetaminophen (100µg/mL) using a standard pipette and transferred into a string of 100 mL calibrated flasks. For each solution, 1 mL of 0.5% solution of $NaNO_3$ and 0.5 mL of 0.5 M solution of HCl added and the mixture stirred. They were then kept for some time to enable completion of the diazotization reaction. Then 1 mL of 2% 2, 4-dinitrophenyl hydrazine and 1.5 mL of 2 M NaOH solution were added to them and they were subsequently diluted to 100 mL mark using distilled water. The solution was stirred thoroughly in preparation for analysis in the spectrophotometer. The absorbance of the colored azo dye formed was then measured at 430 nm. A blank reagent was also spectrophotometry test.

B. Organic membrane fabrication

The coconut shells were obtained from the Eke-ukwu local market in Owerri. They were washed with deionized water to remove suspended particles and sun dried for seven days. The dried shells were broken into smaller pieces using a mallet and further grinded into fine powder using an industrial blender. This was followed by drying the powder in the oven at 60^0C until constant weight was attained. The powder was then allowed to cool at ambient temperature and weighed.

The adsorbent, the crushed and dried coconut shell, was chemically activated by impregnating the sample using 10% NaOH at an impregnation ratio of 1:10. This was done in a conical flask after which it was corked properly to improve reflux and aid digestion. The mixture was autoclaved at 121^0C and 15psi for 1hr to remove hemicellulose and lignin. It was then allowed to cool before washing with water followed by sieving with a cheese filter cloth.

The sieved activated adsorbent was further bleached by pouring it into a conical flask and adding 300mL of H_2O_2 and 20 mL of KClO with a little stirring. The mixture was heated for 45 minutes and allowed to cool to room temperature. After cooling, the adsorbent was washed with deionized water until it stopped giving off color. It was then filtered with cheese filter cloth and oven-dried at 60^0C.

The coconut shell membrane was prepared using Phase Inversion Technique (PIT) as described by Datta et al. (2012). 22g of the dried activated adsorbent was mixed with 66.7g of acetone, 10g of water, and 1.2g of magnesium perchlorate. After shaking, the mixture was filtered to remove excess acetone. The filtered mixture was then placed on a glass plate and rolled over with a glass rod to ensure a uniformly-cast membrane layer. The plate was kept in the refrigerator for 10 minutes to cool at 0^0C. The activated coconut shell membrane was collected carefully to prevent it from damaging.

The above procedure was carried out again to obtain two more activated membrane samples for analyses.

C. Filtration columns design

Three columns were used in this research work. The three 20 cm columns, Columns C_1, C_2, and C_3, were fitted with a mesh on one end and fitted with 11.38g, 8.54g and 2.28g of the coconut shell membrane respectively. They were then placed in an oven to dry at 60^0C for 1 hour. After drying, the three columns were mounted on retort stands and held with clamps in readiness for filtration.

D. Morphological characterization of the membrane

Morphological analyses were carried out on the membrane to determine its structure and molecular orientation. Scanning Electronic Microscope (SEM) was used to analyze 10g of dried membrane mounted on the aluminum stub of the SEM machine using a carbon tab. The magnification was tuned until a clear image appeared.

Fourier transform Infrared (FT-IR) analysis of the samples was carried out by FTIR equipment of mark SPECTRUM ONE FTIR incorporated with software (Perkin Elmer Instruments version 3.02.01) for examining the spectra. 0.5 g of the membrane was studied in the machine.

Morphological characterization of the membranes was done after filtration of the acetaminophen wastewater.

E. Analytical methodology

Proximate analysis of activated coconut shell membrane was carried out. They include; Percentage moisture Content, Percentage Dry Matter (Total solids), Percentage Ash Content, Percentage Fiber Content and Percentage Volatile Matter.

Physio-Chemical Analyses of Acetaminophen (ACT) wastewater before treatment was carried out. They include; pH, Conductivity, Colour, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total dissolved solids (TDS).

F. Membrane filtration of acetaminophen wastewater samples

The three filtration columns C_1, C_2, and C_3, were fitted with the activated coconut shell membranes of masses 11.38g, 8.54g and 2.28g respectively and clamped tightly on three retort stands. 150 mL, V_0, of the acetaminophen wastewater with calibration concentration, $Conc_0$, was passed through the three columns with the time taken for complete filtration to happen measured as T, using a stop watch.

The volume of the filtrates got from the three columns was measured as V_1, V_2, and V_3 while the retained volume remaining in the columns, V_1', V_2', and V_3' was obtained by subtracting the volume of the filtrates from V_0 (150 mL).

G. Analyses and characterization of the filtrates

The filtrates from the three columns were subjected to physio-chemical analyses in order to characterize them. Firstly, the filtrate volumes were recorded. They were then subjected to spectrophotometry analysis to determine their absorbance (Ab_1, Ab_2, and Ab_3), from where their concentrations were determined as ($Conc_1$, $Conc_2$, and $Conc_3$) using the same method as in the case of the wastewater.

The analyses ran on the filtrates are pH, conductivity, color (PCU), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS). These were obtained through the same methods used in the case of the acetaminophen wastewater sample.

H. Analyses of the coconut shell membranes after filtration

1) Determination of adsorptive capacity of the membranes

To obtain the adsorptive capacity of the membranes at the end of each run, the final concentration at the end of filtration, $Conc_t$, was subtracted from the initial concentration of the acetaminophen wastewater (calibration concentration), $Conc_0$. The difference is multiplied by the initial volume of the wastewater, V_0 (150 mL) and the product divided by the mass the mass of adsorbent used for each run, m.

2) Determination of percentage removal efficiency of the membranes

To obtain the percentage removal efficiency of the membranes at the end of each run, the final concentration at the end of filtration, $Conc_t$, was subtracted from the initial concentration of the acetaminophen wastewater (calibration concentration), $Conc_0$. The difference is then divided by initial concentration of the acetaminophen wastewater, $Conc_0$ and the obtained value multiplied by 100.

I. Linear fitting of the adsorption isotherms

The method used in fitting the experimental results into adsorption isotherms followed the procedure described by Bingel et al. (2020). Since the experiment was carried out at room temperature and at the same pressure, it's expected they would have little or no effects on the filtration process neither would they affect the products.

The obtained data was fitted into the Langmuir – 1, Langmuir – 2, Freundlich and Temkin isotherms. The model with the highest R^2 was to be selected as the best fit and best represents the data.

III. RESULTS AND DISCUSSIONS

The obtained results from the proximate analyses and characterization of the activated coconut shell membrane are presented below:

TABLE I. RESULTS FROM PROXIMATE ANALYSES OF THE COCONUT SHELL MEMBRANE

Parameters	Values
Moisture content (%)	5.72
Total solid (mg/l)	94.28
Ash content (%)	2.72
Fibre content (%)	47.28
Volatile solid (%)	38.68

The results obtained from the analyses of the acetaminophen wastewater are presented below.

TABLE II. ANALYTICAL CHARACTERIZATION OF THE ACETAMINOPHEN WASTEWATER

Parameters	Values
pH	5.8
Conductivity (µs/cm)	25.20 - 29.70
Colour, PCU	327.00
Dissolved Oxygen (mg/l)	2.50
Biological Oxygen Demand (mg/l)	2.40
Total solid (mg/l)	2,232.00

The acetaminophen wastewater obtained from Nalis Pharmaceuticals was compared with a standard solution prepared in the laboratory and both were found to have almost the same quality in terms of composition and concentration.

A calibration curve, also known as standard curve, was prepared as shown in figure 1. This was used to ascertain the concentration of the wastewater by taking the absorbance at various concentrations from 5 to 45µg/ml. This method is the commonly acceptable method of determining concentrations of unknown substance by measuring the absorbance. It derives its legitimacy from the Beer-Lamberts law which shows a linear relationship between concentration and absorbance. In this work, the curve gave an equation, $Y = 0.0012x + 0.0142$ and a R^2 value of 0.9053 which shows a very good fit because R^2 tends closely to 1. The calibration concentration obtained for the acetaminophen wastewater was 439.42 µg/ml and has an absorbance of 0.5490. These data was used for further analysis of the filtrate.

During filtration, various amounts of membrane were used as can be seen in table III. Column C1 had 11.38 g, Column C2 had 8.54 g while Column C3 had 2.28 g of membrane in it. The amounts of the coconut shell membrane used undoubtedly affected the whole filtration process and the results.

Volume of acetaminophen wastewater, V_0 = 150 mL

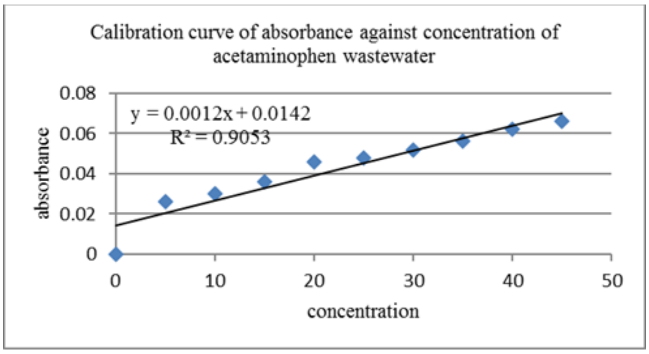

Figure 1. Calibration curve of the acetaminophen wastewater

TABLE III. FILTRATION DATA FOR THE WASTEWATE

Filtration Column	Mass of membrane (g)	Total Time for filtration (sec)	Total Volume Extracted, V, (ml)	Total Volume Retained, V', (ml)
C_1	11.38	980.00	130.00	20.00
C_2	8.54	524.00	130.00	20.00
C_3	2.28	435.00	143.00	7.00

A. Effect of membrane dosage on filtrate concentration

From fig.2, it can be seen that the acetaminophen concentration in the filtrate was lesser than in the raw feed (wastewater). The initial concentration of acetaminophen in the wastewater was 439.42 µg/ml and it reduced to 144.83 µg/ml, 184.42 µg/ml, 75.67 µg/ml when filtered through Columns C_1, C_2 and C_3 respectively. This shows the acetaminophen contaminant had been removed from the wastewater in some measures by the membranes. The acetaminophen in the filtrates reduced by 67.04% in Column C_1, 58.03% in Column C_2, and 82.78% in Column C_3.

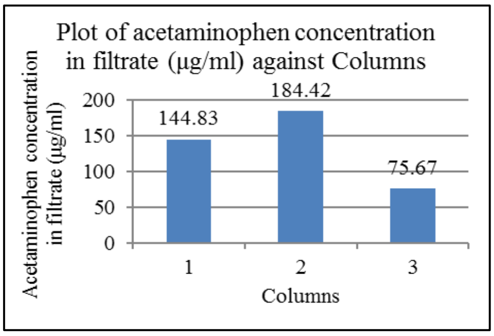

Figure 2. Plot of acetaminophen concentration in filtrate against Columns

This is an irregular relationship but Column C_3, with the lesser membrane dose, performed better than the two other Columns, C_1 and C_2 thereby suggesting an inverse relationship between reduction in contaminant concentration and membrane dose. This is in line with the discovery made by Li et al. (2013). They discovered that higher adsorbent doses have more active sites which could remain "undisturbed" in the course of an adsorption reaction while almost all active sites in lesser dose of membranes go into the reaction.

B. Effect of membrane dosage on filtrate pH

The pH is a measure of the level of acidity or alkalinity of a solution. The acetaminophen wastewater had a pH of 5.8 which proves it is acidic in nature and may contaminate water bodies if released in that state. As shown in fig.3, the pH of the filtrates increased after filtration. Column C_1 produced a filtrate with pH of 6.4, Column C_2's filtrate had a pH of 6.1, while the filtrate obtained from Column C_3 had a pH of 6.6. They all tend to 7, the universally preferred neutral point. This shows the membranes removed some measure of acidity from the wastewater. The relationship though irregular, showed the membrane in Column C_3, being the one with the lowest dose, to be more effective in correcting the pH of wastewaters.

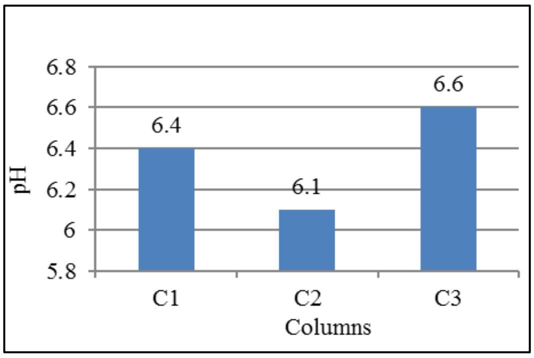

Figure 3. Plot of pH against Columns

C. Effect of membrane dosage on the conductivity of the filtrates

Fig. 4 shows a plot of conductivity of the filtrate µS/cm from each Column. Conductivity is indirectly a measure of the amount of salt in a solution. Normal conductivity for water bodies is between 200 – 1000 µs/cm. The conductivity of the wastewater 25.20 - 29.70 µs/cm while the conductivity of the filtrates obtained increased. The conductivity of the filtrate from Column C_1 is 6270 µs/cm, that of Column C_2 is 5470 µs/cm, while that of Column C_3 is 1975 µs/cm. The increase in the conductivity was as a result of some inorganic soluble salts like nitrates, fluorides, chlorides, and phosphates. Also, the chemicals used in the Phase Inversion Technique (PIT) for membrane formation added to this. An inverse relationship can be seen in the plot. The higher the membrane dose, the lower the conductivity. The conductivity of the filtrate from Column C_3 had the lowest conductivity which isn't far from the generally acceptable range for water bodies.

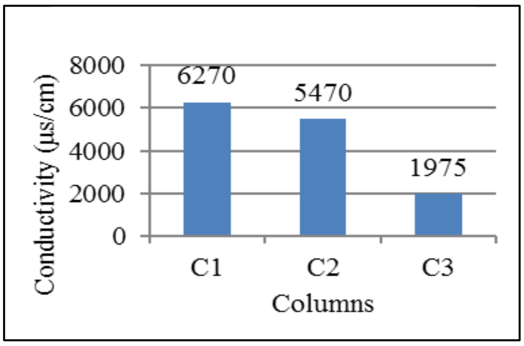

Figure 4. Plot of Conductivity (µs/cm) against Columns

D. Effect of membrane dosage on the colour (PCU) of the filtrates

The plot in fig. 5 shows the relationship between the colour values of the filtrates obtained from the three columns.

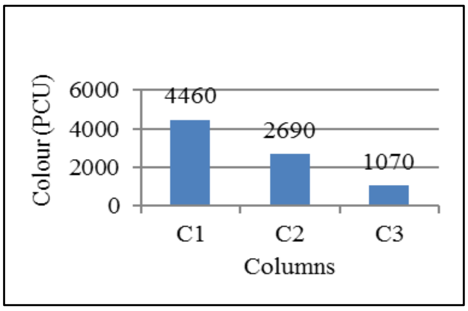

Figure 5. Plot of Colour (PCU) against ColumnsEffect of membrane dosage on the total dissolved solid (TDS) levels in the filtrates

The colour value measured in PCU (platinum cobalt unit) is necessary because it is an indirect measure of the level of contaminants in a solution. Contaminants like metals, non-metals as well as dissolved and insoluble salts can change the colour of a solution. The colour value of the wastewater was 327.00 PCU. After filtration, Column C_1 produced a filtrate with colour value of 4460 PCU, the filtrate from Column C_2 had a colour value of 2690 PCU, while Column C_3 produced a filtrate with colour value of 1070. It can be noticed that the colour value increased and is very high when compared with the colour value of the wastewater. This is due to the presence of inorganic salts in the filtrate especially those in the membrane as a result of the Phase Inversion Technique (PIT).

E. Effect of membrane dosage on the dissolved oxygen (DO) levels in the filtrates

As shown fig. 6 the dissolved oxygen (DO) for the filtrates from the three columns varied one from another. Column C1 has a dissolved oxygen level of 4.20 mg/L, the value dropped to 4.00 mg/L for the filtrate obtained from Column C_2, while the filtrate obtained from Column C_3 had the highest dissolved oxygen level of 6.40 mg/L. These are higher than the dissolved oxygen level of the wastewater which was 2.50 mg/L.

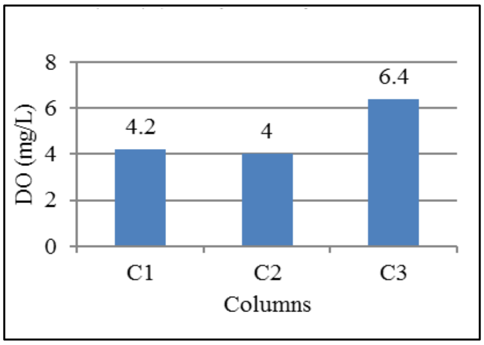

Figure 6. Plot of Dissolved Oxygen (mg/L) against Columns

This is a positive trend since dissolved oxygen is the amount of free oxygen in a liquid. Low dissolved oxygen levels are detrimental to aquatic life as it can lead to the death of animals and plants. The general standard for dissolved oxygen levels in water is 4 mg/L and since the filtrate has levels that are the same and exceed this, it can be said that coconut shell membrane is a perfect adsorbent for wastewater treatment. The filtrate from Column C_3 had more oxygen levels showing that lesser dose of membrane is effective in increasing dissolved oxygen levels.

F. Effect of membrane dosage on the biological oxygen demand (BOD) levels in the filtrates

Fig. 7 shows the biochemical oxygen demand (BOD) levels in the filtrates obtained from the three Columns. Biochemical oxygen demand (BOD) is the amount of oxygen needed by the micro-organisms in a solution. It is the difference in dissolved oxygen (DO) levels over a five-day period in an incubated environment. The BOD level in the wastewater was 2.40 mg/L. The filtrates had higher level of BOD levels. The filtrates from Column C_1 had a BOD level of 340 mg/L, the one from Column C_2 had a level of 155 mg/L while the one from Column C_3 had 305 mg/L. These increments can be ascribed to the inclusion of more chemicals in the filtrate as a result of contact with the membranes. The membranes still retain an amount of acetone and other chemicals which were used in the membrane preparation process. They may react with the free oxygen in the filtrate thereby limiting the amount of dissolved oxygen and increasing the BOD. Since minimal BOD is desired, Column C_3 can be said to perform better than the others in the filtration process.

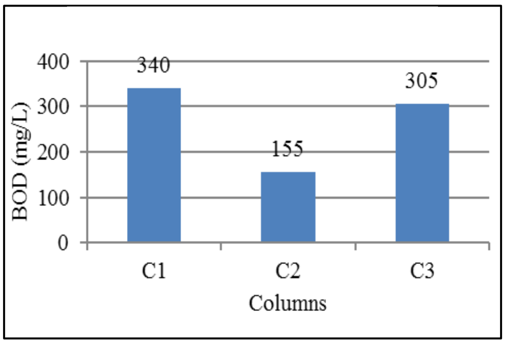

Figure 7. Plot of Biological Oxygen Demand (mg/L) against Columns

G. Effect of membrane dosage on the chemical oxygen demand (COD) levels in the filtrates

The different chemical oxygen demand (COD) levels of the filtrate from the three Columns can be seen in fig. 8. From the plot, we could see an irregular relationship between the COD levels and the amount of membrane used in wastewater filtration. Column C_1 produced a filtrate with COD of 5600 mg/L while Columns C_2 and C_3 produced filtrates with 600 mg/L and 1600 mg/L respectively. COD depends largely on the concentration of organic material in a solution. It also depends on the availability and amount of inorganic compounds that can be oxidized.

Thus, water with low COD is desired with 250 mg/L being the most preferable level. It can be seen that the membrane dose in Column C_2 performed better as the COD level of the filtrate wasn't too far from this mark when compared to others.

H. Effect of membrane dosage on the total dissolved solid (TDS) levels in the filtrates

The relationship between total dissolved solids (TDS) and amount of adsorbent used is established in fig. 9. From the plot, it can be deduced that the TDS in the filtrate followed a regular pattern. As the membrane dosage increases, the TDS decreases correspondingly. Total dissolved solids (TDS) refer to the soluble organic matter and inorganic salts present in the water sample and as can be seen from the plot, the Column C3 with lesser membrane dosage had lesser TDS than others. The inverse relationship that exists between the TDS values and the amount of membrane used depend largely on the ability of the membrane's active sites. This further supports the findings of Li et al. (2013) that some active sites (especially in higher doses of adsorbent) might not be involved in adsorption.

I. Relationship between membrane dosage and adsorptive capacity, Q

Fig.10 shows the adsorptive capacities (µg/g) of the three membranes doses. These values depend on the initial concentration and volume of the wastewater, the concentration of the filtrates as well as the membrane dosage used (g). The adsorptive capacities followed a regular pattern in which it increased as the amount of membrane used decreased as shown in the plot. This further confirms the inverse relationship between adsorptive capacities and membrane dosage. It supports the fact that membranes can be very effective in wastewater treatment even in small quantities thus laying credence to the cost-effective nature of membranes and membrane technology.

J. Relationship between membrane dosage and Removal Efficiency (%)

For removal efficiency, the trend wasn't regular. However, Column C_3 with the least membrane dosage had more efficiency than both C_1 and C_2. The membrane in Column C_3 had a removal efficiency of 82.78%, while the ones in Column C_1 and Column C_2 had efficiencies of 67.04% and 58.03% respectively as can be seen in fig. 11. This further confirms that coconut shell membranes perform better in smaller quantities and further shows that membranes are efficient in low quantities and support claims that membranes are cheap to manufacture, cost-effective to operate and highly efficient in small quantities.

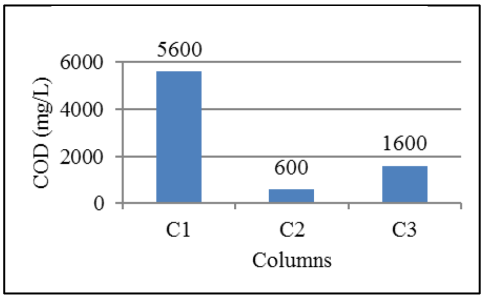

Figure 8. Plot of Chemical Oxygen demand (mg/L) against Columns

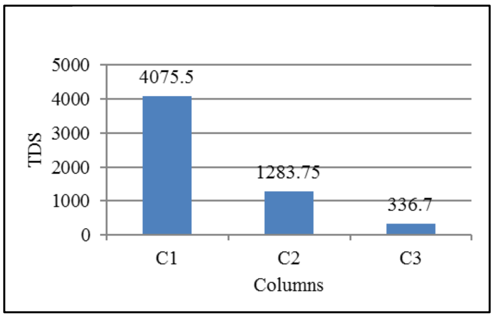

Figure 9. Plot of Total Dissolved Solid against Columns

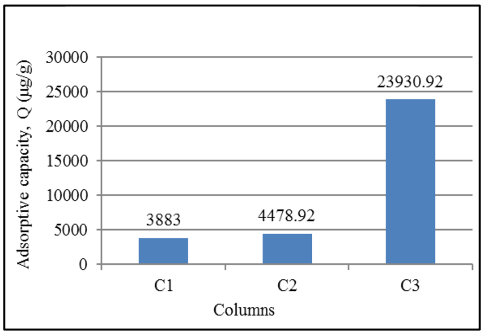

Figure 10. Plot of adsorptive capacity, Q (µg/g) against Columns

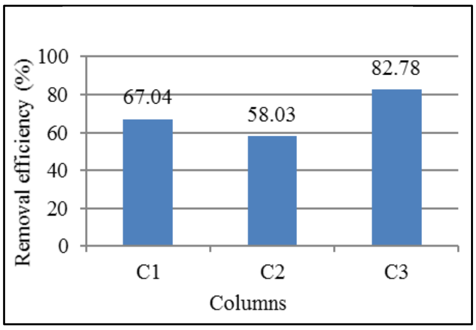

Figure 11. Plot of removal efficiency (%) against Columns

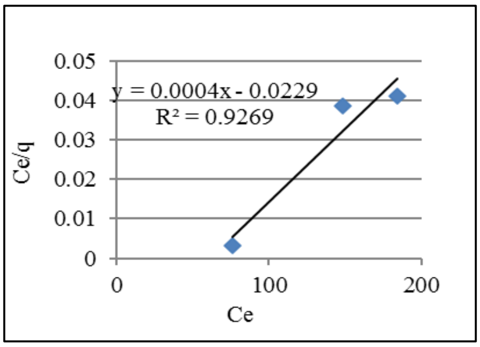

Figure 12. Plot for Langmuir-1 isotherm

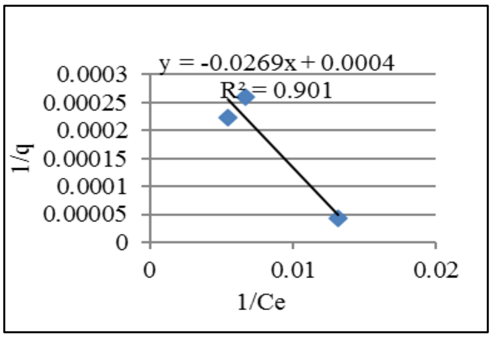

Figure 13. Plot for Langmuir-2 isotherm

K. *Adsorption Isotherms and linear fittings*

The experimental results were fitted in the Langmuir-1, Langmuir-2, Freundlich, and Temkin isotherms as can be seen in fig. 12, 13, 14, and 15 respectively. The regression equations, R^2 and K values obtained are presented in table 5. All of the R^2 values exceed 0.9 suggesting that the three models closely fitted the experimental results.

However, the negative values of K for the Langmuir-1, Langmuir-2, and Freundlich model demonstrated that the Temkin isotherm fitted better. Also, the Temkin model gives the highest R^2 value of 0.9316.

From the Temkin adsorption isotherm,

$$q = BlnK + BlnCe \quad (1)$$

$$B = \Delta Q = -\Delta H \quad (2)$$

Where, ΔQ is a variation of adsorption energy.

If ΔQ is positive (which means that the slope is positive when we plot the linearized Temkin equation) the ΔH is negative and the adsorption is exothermic. However, if ΔQ is negative (which means that the slope is negative when we plot the linearized Temkin equation) the ΔH is positive and the adsorption is endothermic.

The value of *B* was calculated using the slope of the Temkin adsorption isotherm graph (Fig. 15) to be 23850 J/mol. This implies that the adsorption was endothermic.

Also, from the Temkin isotherm, we can tell what type of adsorption took place. The heat of sorption value (*B* in J/mol) is converted to kcal/mol. If heat of sorption value is less than 1.0 kcal/mol, then physical adsorption is occurred. If the heat of sorption value is 20-50 kcal/mol, then chemical adsorption occurred. However, if heat of sorption value is in-between (1 - 20 kcal/mol), then both physical and chemical adsorptions were involved in the adsorption. 23850 J/mol is equivalent to 5.7 Kcal/mol. This shows that both chemical and physical adsorption occurred.

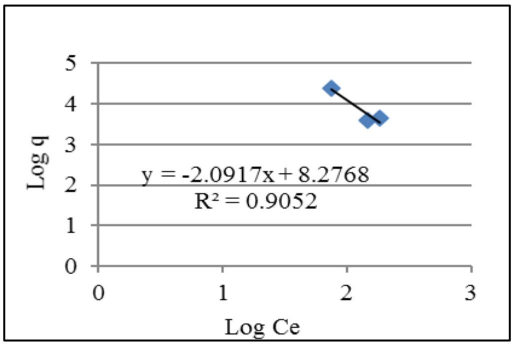

Figure 14. Plot for Freundlich isotherm

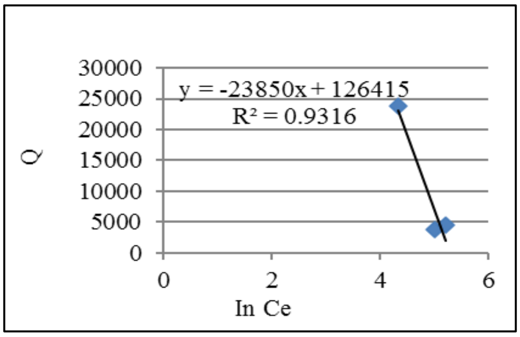

Figure 15. Plot for Temkin isotherm

TABLE IV. ADSORPTION ISOTHERMS PARAMETERS

LANGMUIR-1		LANGMUIR-2	
Ce/q	Ce	1/q	1/Ce
0.003183244	76.09	0.000041835	0.013142
0.038757607	148.58	0.000260853	0.00673
0.041175105	184.42	0.000223268	0.005422

FREUNDLICH		TEMKIN	
Log q	Log Ce	Q	ln Ce
4.37845768	1.88132	23903.29	4.331917
3.583603398	2.17196	3833.57	5.001124
3.651173305	2.26580	4478.92	5.217216

TABLE V. REGRESSION EQUATION AND R^2 VALUES IN RELATION TO CONCENTRATION OF ACETAMINOPHEN REMAINING IN THE FILTRATE

Adsorption isotherm	Regression equation	R^2	K
Langmiur-1	y=0.0004x-0.0229	0.9269	-0.01746
Langmuir-2	y=-0.0269x+0.0004	0.901	-0.01486
Freundlich	y=-2.0916x+8.2769	0.9052	-
Temkin	y=-23580x+126415	0.9316	0.00499

L. Discussion on internal structure of the membrane

The internal structure of the membranes was studied using Scanning electron microscope before and after the filtration process. The SEM analysis for the unused coconut shell membrane was done at a magnification of 1500x and at an accelerating voltage of 15 kV. The image showed a mat-like structure as seen in fig. 16. This structure is perfect for adsorption and has good number of pores with diameter around 50µm. The SEM images of the membranes used in Columns C_1, C_2, and C_3 are presented in fig. 17, 18, and 19. These surfaces have a rough and irregular surface which undoubtedly is due to flocculation that results from the filtration process. A greater part of the acetaminophen (ACT) contaminants have been deposited on the surface as flocs. As seen in the images, more flocs were deposited on the surface of the membrane from Column C_1 while lesser flocs are seen at the surface of the membrane from C_3. The membrane from Column C_2 had more density of flocs on the surface. This explains why the membrane from Column C_3 has the highest removal efficiency (%).

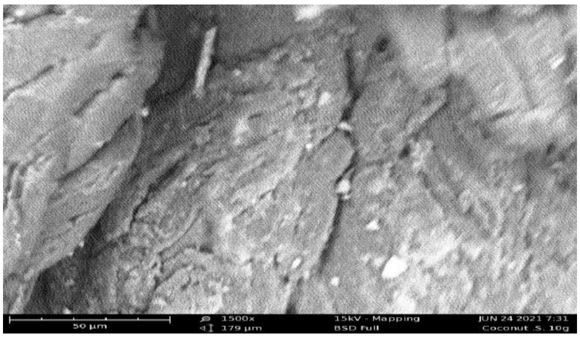

Figure 16. SEM image of the activated coconut shell membrane before filtration

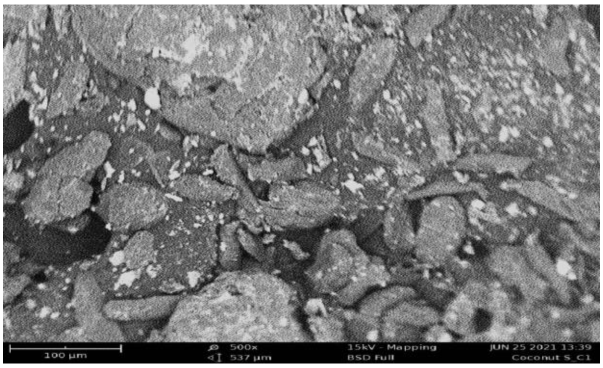

Figure 17. After-filtration SEM image of the membrane used in Column, C_1

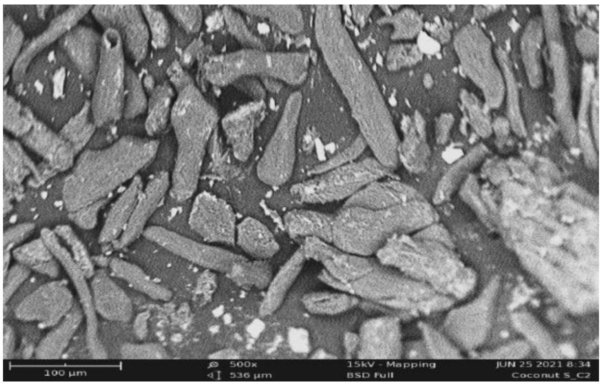

Figure 18. After-filtration SEM image of the membrane used in Column, C_2

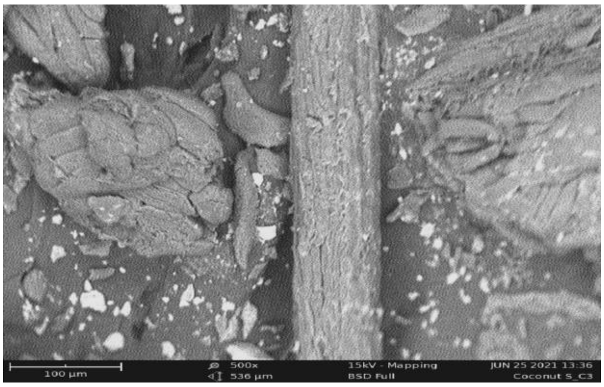

Figure 19. After-filtration SEM image of the membrane used in Column, C_3

For the FT-IR analyses, the wave number was found to vary between 4000 and 350 cm^{-1}. For the freshly-prepared (unused) membrane, the transmittance was between 85 – 100 as seen in fig.20. After filtration, the membranes from Columns C_1, C_2, and C_3 were again analyzed. The transmittance of the membrane from the three Columns was still within the same range but differ in the peaks of transmittance. The differences in these peaks are due to the flocs formed during the filtration process.

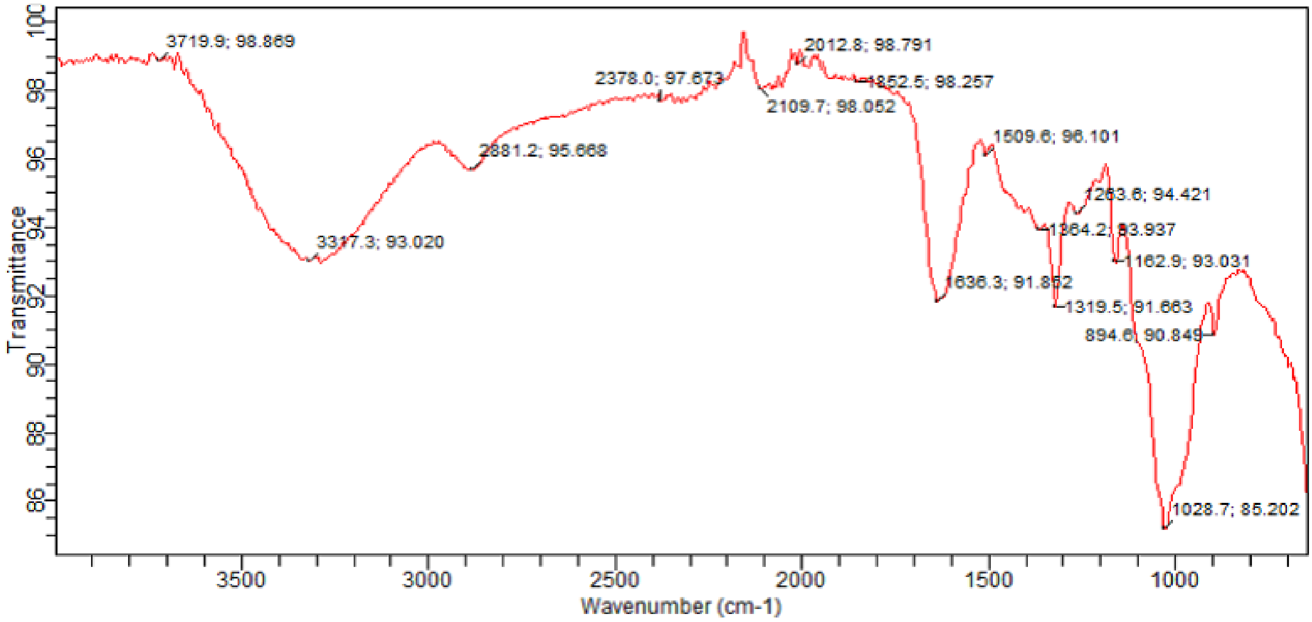

Figure 20. FT-IR curve for the coconut shell membrane

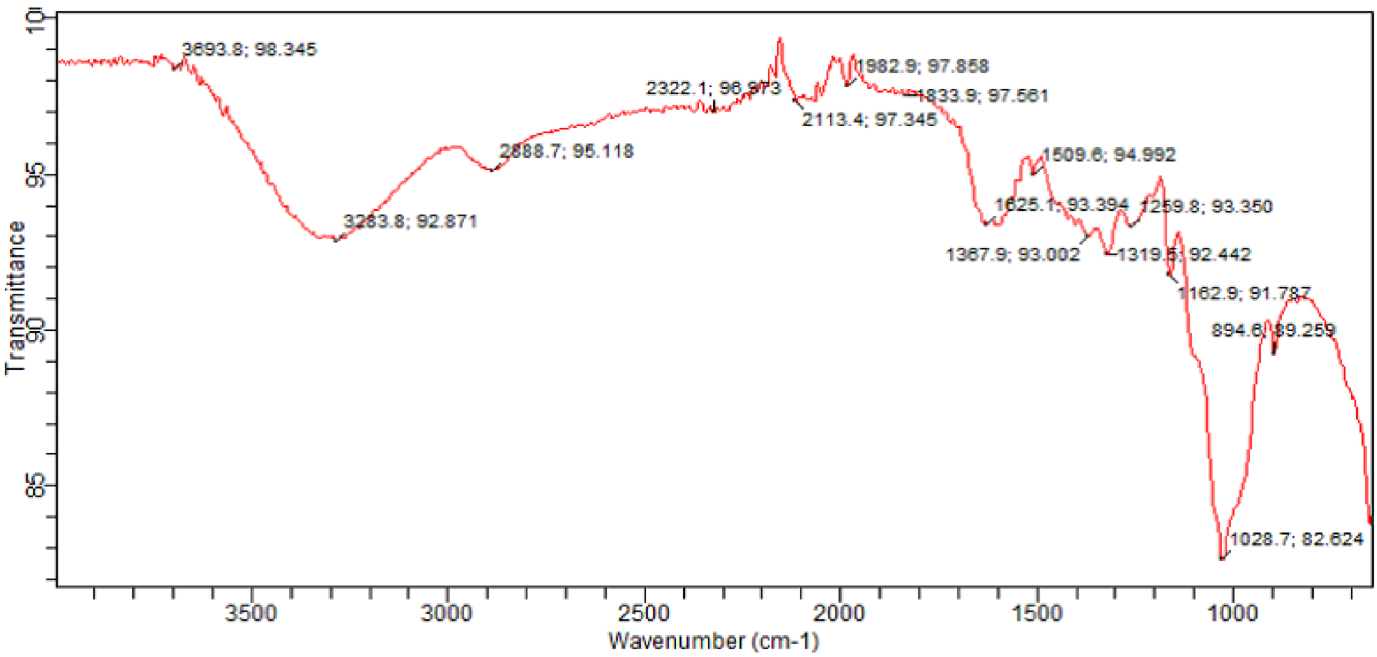

Figure 21. After-filtration FI-TR analysis of the membrane used in Column, C_1

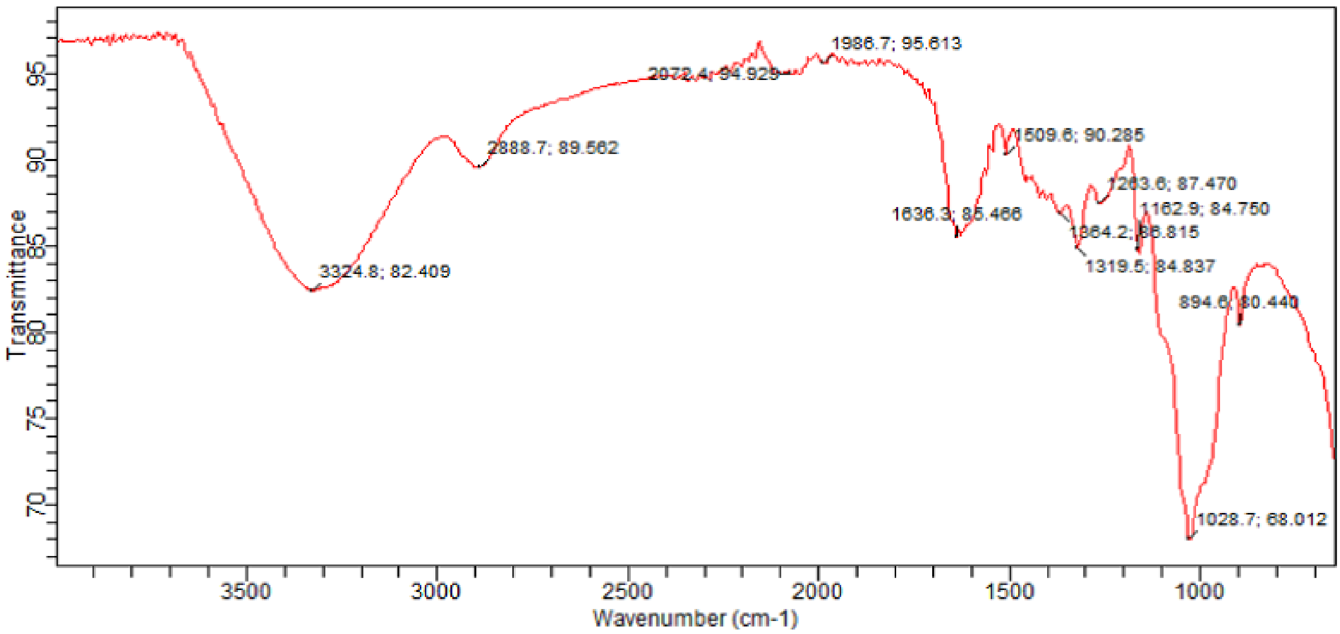

Figure 22. After-filtration FI-TR analysis of the membrane used in Column, C_2

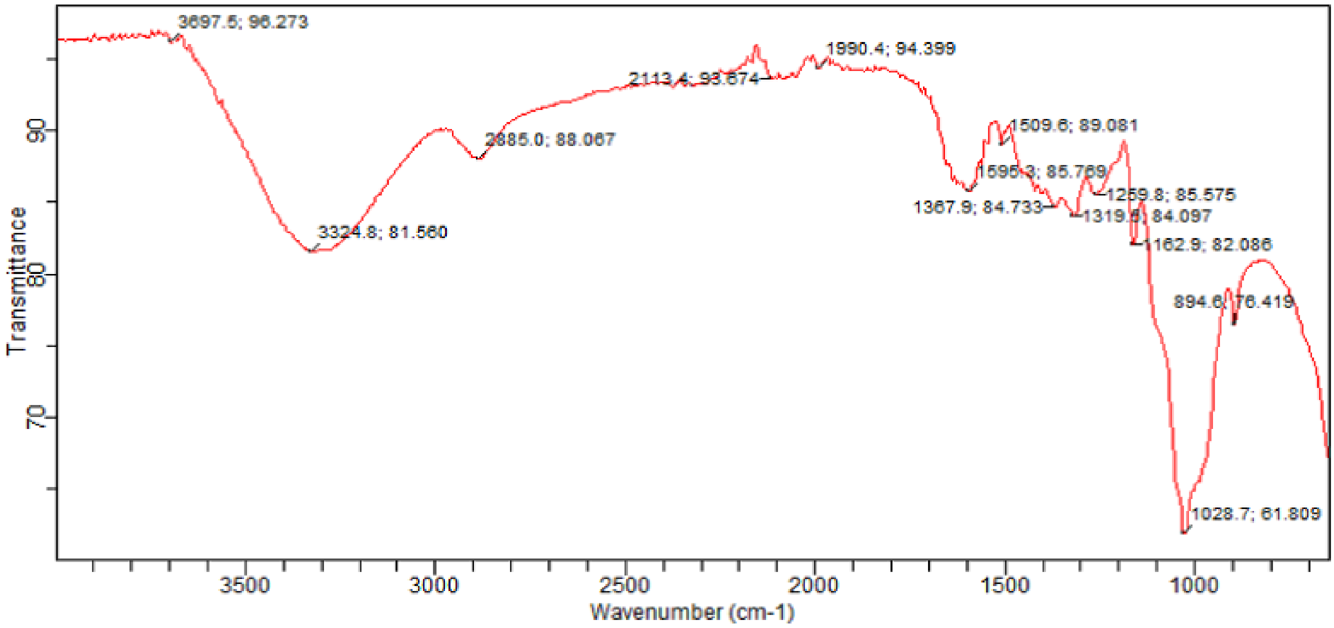

Figure 23. After-filtration FI-TR analysis of the membrane used in Column, C_3

IV. CONCLUSION

The use of organic membrane fabricated from coconut shell proved to be an adequate and cost-effective means to reclaim useable water from acetaminophen wastewater. The Least membrane dosage proved to have the best efficiency and best adsorption capacity. In this research work, Column 3 which had the least membrane dosage had 82.78% removal efficiency and 23,930 µg/g adsorption capacity.

This research work also shows the existence of an inverse relationship between adsorption capacity and the membrane dosage needed. Similarly, the removal efficiency is inversely proportional to the membrane dose, and this could be due the fact that higher membrane dose provides more active adsorption sites which results in most of the adsorption sites remaining unsaturated during the adsorption reaction. This further supports the claim that membranes are very effective in small doses.

In as much as the removal of acetaminophen was the main target of this research work, other parameters such as Dissolved Oxygen, Biological Oxygen Demand, Chemical Oxygen Demand, pH, Colour, Conductivity and Total dissolved solid were affected by the membranes. It could be said that the membranes improved these parameters to favor the quality of the filtrate.

The adsorption mechanism followed Temkin adsorption isotherm and the adsorption reaction is endothermic.

REFERENCES

[1] Baccar, R., Sarrà, M., Bouzid, J., Feki, M., & Blánquez, P. (2012). Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product. Chemical Engineering Journal. 211–212, 310 317.

[2] Bingel, L.W., Chen, A., Agrawal, M., & Sholl D. (2020). Experimental Verified Alcohol Adsorption Isotherms in nanoporous Materials from Literature Meta-Analysis. Journal of chemical and engineering data, 60(10): 4970 – 4979. https://doi.org/10.1021/acs.jced.0c00598

[3] Cabrita, I., Ruiz, B., Mestre, A.S., Fonseca, I.M., Carvalho, & A.P., Ania, C.O. (2010). Removal of an analgesic using activated carbons prepared from urban and industrial residues. Chemical Engineering Journal, 163. 249–255.

[4] Divya, K., Narayana, B., & Sapnakumari, M. (2013). Sensitive Spectrophotometric Determinations of Paracetamol and Priotriptyline HCl Using 3-Chloro-7-hydroxy-4-methyl-2H-chromen-2-one. International Scholarly Research Notices. Volume 2013, ID 935819. https://doi.org/10.1155/2013/935819

[5] Ebele, A.J., Abdallah, M.A-E, & Harrad, S. (2017). Pharmaceutical and personal care products (PCPPs) in the freshwater aquatic environment. Emerging Contaminants 3(1), 1-16. https://doi.org/10.1016/j.emcon.2016.12.004

[6] Gros M, Petrovic M., & Barceló D. (2006). Multi-residue analytical methods using LC-tandem MS for the determination of pharmaceuticals in environmental and wastewater samples: a review. Anal Bioanal Chem, 386(4):941–952.

[7] Hinz, B., & Brune K. (2007). Antipyretic analgesics: nonsteroidal antiflammatory drugs, selective COX-2 inhibitors, paracetamol and pyrazolinones. Handbook of experimental pharmacology, 1(177), 65-93. https://doi.org/10.1007/978-3-540-33823-9_3

[8] Li, C., Li, J., Cao, T., Cai, P., Wang, N., & An, Q. (2021). Impact of crosslinking on organic solvent nanofiltration performance in polydimethylsiloxane composite membrane: Probed by in-situ low-field nuclear magnetic resonance spectroscopy. Journal of Membrane Science 633 (2021) 119382. https://doi.org/10.1016/j.memsci.2021.119382

[9] Li, T., Liu, Y., Peng, Q., Hua, X., Liao, T., & Wanga, H. (2013). Removal of Lead (II) from Aqueous Solution with Ethylenediamine-Modified Yeast Biomass Coated with Magnetic Chitosan Microparticles: Kinetic and Equilibrium Modeling. Chemical Engineering Journal. 214, 189–197.

[10] Ma, Y., Velioglu, S., Yin, Z., Wang, R., & Chew, J.W. (2021). Molecular dynamics investigation of membrane fouling in organic solvents. Journal of Membrane Science 632 (2021) 119329. https://doi.org/10.1016/j.memsci.2021.119329

[11] Mestre, A.S., Bexiga, A.A., Proença, M., Andrade, M., Pinto, M.L., Matos, I., Fonseca, I.M., & Carvalho, A.P. (2011). Activated carbons from sisal waste by chemical activation with K2CO3: kinetics of paracetamol and ibuprofen removal from aqueous solution. Bioresources Technology Journal. 102, 8253–8260.

[12] Ngwuluka N.C., Ochekpe N.A., & Odumosu P.O (2011). An Assessment of Pharmaceutical Waste Management in Some Nigerian Pharmaceutical Industries. African Journal of Biotechnology, 10,11259–11264. https://doi.org/10.5897/AJB10.1194

[13] Struzeski, E.J. (1980). Status of wastes handling and waste treatment across the pharmaceutical industry and 1977 effluent limitations. Proceedings of the 35th Industrial Waste Conference, Purdue University, West Lafayette, IN, 1980, 1095–1108.

[14] Vara, S.; Madhavi Konni, M.; & Karnena, M.K. (2020). Membrane Technology for Treatment of Pharmaceutical Wastewaters: A Novel Approach. Handbook of Research on Resource Management for Pollution and Waste Treatment, 502-530.

[15] Wang, S., Zhang, Y., Han, Y., Fan, Y., & Hou, X. (2021). Design of Porous Membranes by Liquid Gating Technology. Accounts of Materials Research Journal. https://doi.org/10.1021/accountsmr.1c00024

[16] Yang, J., Shen, Z., He, J., & Li, Y. (2021). Efficient separation of small organic contaminants in water using functionalized nanoporous graphene membranes: Insights from molecular dynamics simulations. Journal of Membrane Science 630 (2021) 119331. https://doi.org/10.1016/j.memsci.2021.119331

[17] Zur, J., Pinski, A., Marchlewicz, A., Hupert-Kourek, K., Wojcieszynska, D., & Guzik, U. (2018). Organic micropollutants paracetamol and ibuprofen – toxicity, biodegradation, and genetic background of their utilization by bacteria. Environmental Science Pollution Resources International, 25(22): 21498-21524. https://doi.org/10.1007/s11356-018-2517-x

How to Cite this Article:

Anusi, M. O., Igboko, N., Njoku, C. N., Ogbuehi, G. U. & Onwumelu, D. C. (2022). Removal of Acetaminophen (Paracetamol) from Pharmaceutical Waste Water Using Organic Membrane Got from Coconut Shell. International Journal of Science and Engineering Investigations (IJSEI), 11(127), 8-19. http://www.ijsei.com/papers/ijsei-1112722-02.pdf