

## Removal of Acetaminophen (Paracetamol) From Pharmaceutical Waste Water Using Organic Membrane (Coconut Shell)

Anochie, Lydia Onyinye

[anochielydia@gmail.com](mailto:anochielydia@gmail.com)

Department of Chemical Engineering,

Federal University of Technology Owerri (FUTO)

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### Abstract

*This research work was carried out in order to reduce the harmful effects of pharmaceutical waste water on the environment. Acetaminophen 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 chemically activating coconut shell (agro-waste) with NaOH. The adsorbent was poured into three columns with varying heights of 4.0cm, 3.0cm and 0.8cm respectively. 150ml of waste water containing 439.42 $\mu$ g/ml of acetaminophen was passed through each column and after filtration it was found that the concentration of acetaminophen reduced to 148.58 $\mu$ g/ml, 184.42 $\mu$ g/ml and 76.09 $\mu$ g/ml respectively. The adsorption capacity of each column was calculated to be 3833.57 $\mu$ g/g, 4478.92 $\mu$ g/g and 23903.29 $\mu$ g/g for column 1, 2 and 3 respectively. The data obtained was modelled using Langmuir, Freundlich and Temkin adsorption isotherms. The  $R^2$  values were compared and we concluded that 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 which implies that the reaction was endothermic and after converting  $\Delta Q$  to Kcal/mol we found that both chemical and physical adsorption took place as 5.7kcal/mol lies between 1-20.*

**Keywords:** Acetaminophen, Adsorption, Waste Water Treatment, Organic Membrane (Coconut shell)

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### 1.0 Introduction

#### 1.1 Background of Study

Pharmaceutical effluent is simply waste water from pharmaceutical manufacturing companies (PMCs). Pharmaceutical waste water varies from those containing large amounts of toxic chemicals to those containing trace elements depending on the active pharmaceutical ingredients (API) used by the pharmaceutical company and the strictness of the regulatory body.

"The occurrence of APIs in the environment has become an important issue in the last few years. These agents along with their metabolites, which can be even more harmful than their parent compounds, are continuously released into the environment, mainly through disposal of unused or expired drugs or directly from pharmaceutical discharges" (Gros M. et al., 2006).

According to the UN and WHO, "about one-fifth of the world population live in regions with water scarcity, and in most cases, the water scarcity is related to the lack of clean water due to contamination".

Conventional methods used to treat domestic waste water such as use of activated sludge are not efficient in the treatment of industrial waste water as organic colloids and ions cannot be completely removed by this method. Therefore, additional treatment methods like membrane filtration and use of granular activated carbon (GAC) are considered. In some membrane configurations, granular/powdered activated carbon may be used as adsorbents. For this research project, we will be considering sourcing precursor materials for the activated carbon from coconut shell which is a good source of organic polymer (cellulose).

### 1.2 Problem Statement

Recently, the terming of pharmaceutical effluents which includes active pharmaceutical ingredients (APIs), solvents, intermediates and colloids as an "emerging pollutant" has a lot of eyebrows wagging. Sadly, "in developing nations like Nigeria, there is little or no evidence of regulatory disposal of pharmaceutical wastes, and a large number of pharmaceutical manufacturing companies either lack an effluent treatment plant (ETP), or installed ones are non-functional" (Ngwuluka N.C. et al., 2011). We hope to reduce the amount of harmful chemicals released into our water bodies via pharmaceutical effluents by fabricating a membrane that uses activated carbon with coconut shell as its precursor material as its adsorbent.

It is worthy of note that "activated carbons are mostly used in adsorbent process as it is inexpensive, easy to prepare in addition to the possibility of tailoring their structure, physical and chemical properties" (Hisham S., 2011).

### 1.3 Research Objectives

The main objective of this research is to fabricate a membrane that will be used to filter pharmaceutical effluents using coconut shell.

The specific objectives are:

- i) To characterise the fabricated membrane.
- ii) To characterise a sample of pharmaceutical effluent.
- iii) To separate the pharmaceutical effluents using the fabricated membrane
- iv) To characterise the filtrate and compare its constituents by % with that stipulated by regulatory bodies.

### 1.4 Scope of Research

- i) Fabrication of filtration membrane using granular activated carbon from coconut shell.
- ii) Characterisation of membrane.
- iii) Filtration of pharmaceutical effluent (waste water) using fabricated membrane.
- iv) Characterisation of filtrate.

### 1.5 Justification of Research

It is estimated that "90% of the available water resources will be expended in 15 years and by 2025, nearly 60% of the world population will have scarcity of water if the rate of consumption continues at its present level" (Saritha Vara et al., 2020).

Inadequate supply of potable water is one of the problems facing countries with increased industrial activities. Even with the presence of water bodies, the water may not be suitable for human consumption or even support aquatic life as it usually contains trace or large amounts of toxic constituents of API and personal care products depending on its proximity to industrial areas.

This research is carried out in order to find an adequate and cost-effective means to reclaim useable water from pharmaceutical effluents, thus, making potable water more readily available. The membrane to be fabricated in the course of this research using coconut shell (agro waste) may be employed by pharmaceutical companies to treat their effluents before discharging it into water bodies. It can also be used by individuals for domestic use as it does not require much technical know-how.

## 2.0 Material and Methods

### 2.1 Equipment Used

- |                                        |                                          |
|----------------------------------------|------------------------------------------|
| i. N4S UV-Visible spectrophotometer    | ix. Dissolved oxygen meter-JPB-607A      |
| ii. PH meter                           | x. Industrial Blender-Silver Crest 3800w |
| iii. Conductivity meter                | xi. Measuring cylinder                   |
| iv. Thermometer                        | xii. Beakers                             |
| v. Analytical weighing balance         | xiii. Conical flasks                     |
| vi. Scanning electron microscope (SEM) | xiv. Retort stands with clamps           |
| vii. Infrared (IR) spectrometer        | xv. Burets                               |
| viii. Muffle Furnace-SX-5-12,          | xvi. Pipettes                            |

### Reagents

- |                                                        |                                                        |
|--------------------------------------------------------|--------------------------------------------------------|
| i. 4-Acetamidophenol (LOBA CHEMIE PVT. LTD)            | vi. Potassium hypochlorite solution (KClO)             |
| ii. Sodium nitrite solution ( $\text{NaNO}_3$ ) (0.5%) | vii. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )      |
| iii. Hydrochloric acid solution (HCl) (0.5 mol/l)      | viii. Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) (98%) |
| iv. 2,4 dinitrophenyl hydrazine solution (DNPH) (2%)   | ix. Sodium carbonate ( $\text{NaCO}_3$ )               |
| v. Sodium hydroxide solution (NaOH) (2M)               | x. Petroluem ether                                     |
|                                                        | xi. Ethanol                                            |
|                                                        | xii. Selenium catalyst                                 |
|                                                        | xiii. Phenolphthalein indicator                        |
|                                                        | xiv. Deionized water                                   |

### 2.2 Methods

#### Preparation of Samples

The coconut shells were washed with deionized water to remove suspended particles and then sun dried for seven days.

The dried material was then broken into smaller pieces using a mallet and further grinded into fine powder using an industrial blender.

The coconut shell powder was then dried in the oven at  $60^\circ\text{C}$  until constant weight was attained.

The powder was removed from the oven and allowed to cool at ambient temperature and then weighed.

#### Chemical activation of adsorbent (coconut shell powder)

10% NaOH was used to impregnate the sample with an impregnation ratio of 1:10

This was done in a conical flask and it was corked properly in order to improve reflux and aid digestion.

The mixture was autoclaved at  $121^\circ\text{C}$  and 15psi for 1hr in order to remove hemicellulose and lignin.

Allow to cool down, wash with water and sieve with a cheese filter cloth.

### **Bleaching**

This was achieved using hydrogen peroxide ( $H_2O_2$ ) and potassium hypochlorite ( $KClO$ ).

Pour the chemically activated coconut shell powder into a conical flask, then add 300ml of  $H_2O_2$  and 20 ml of  $KClO$ .

Heat the mixture for 45 mins.

Allow to cool down, wash with deionized water until colour stops coming off and then filter using a cheese filter cloth.

Dry in an oven at  $60^\circ C$

### **Column design (Phase Inversion Technique)**

22g of the adsorbent powder was mixed with appropriate portion of Acetone, Magnesium perchlorate and water.

The mixture was poured into three 20cm long hollow tubes with 5cm diameter and a mesh on one end.

Each column had varying mass of adsorbents; 11.38g, 8.54g and 2.28g for column 1, 2 and 3 respectively.

The columns were placed in an oven and dried at  $60^\circ C$ .

### **Preparation of acetaminophen standard solution**

Weigh 0.251 g of 4-Acetamidophenol (Acetaminophen).

Dissolve this in 15 ml of ethanol.

Then, transfer this solution into a 250 ml standard flask, and fill up to the mark with distilled water. This gives an acetaminophen solution with concentration of  $1000 \mu g/ml$ .

Prepare a working solution by diluting 150 ml of  $1000 \mu g/ml$  paracetamol solution with 20 ml of 4 mol/l of hydrochloric acid in 250 ml round bottomed flask.

Reflux for 1 hour, keep aside to cool the solution, then neutralize with 20% of sodium carbonate solution and then dilute with distilled water to the 250 ml mark.

Measure 16.6 ml of the above solution and dilute with distilled water in a 100 mL volumetric flask to prepare  $100 \mu g/ml$  acetaminophen solution.

Transfer an aliquot of the solution containing Acetaminophen ( $100 \mu g/ml$ ) into a string of 10 ml calibrated flasks.

Add 1 ml of 0.5% solution of  $NaNO_3$  and 0.5 ml of 0.5 mol/l solution of  $HCl$  and then mix the solution thoroughly and keep aside for accomplishment of diazotization reaction.

Then, add 1 ml of 2% 2, 4-dinitrophenyl hydrazine and 1.5 mL of 2 mol/l  $NaOH$  solutions and then dilute to 10 ml using distilled water, and mix thoroughly.

The absorbance of the colored azo dye formed was measured at 429 nm or 430 nm beside the reagent blank using a spectrophotometer.

## **2.3 Proximate Analysis**

### **Determination of Moisture Content**

#### **Oven -Dry Method**

Wash the beakers thoroughly and dry in the oven at  $110^\circ c$ . Put inside the desiccator to cool and weigh each beaker.

Put the adsorbent powder into the weighed beaker and take the weight of dish plus weight of

sample.

Dry in the oven at 60°C for 2 hours and at 105°C for the next 4 hours or until weight is constant.

Cool the sample in the desiccators and take the dry weight of sample plus dish.

Calculate the moisture content as described in the equation below.

### Calculation of Moisture

$$\% \text{ Moisture} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad \dots\dots\dots (\text{equation 1.0})$$

Where;

$W_1$  = Initial weight of empty crucible

$W_2$  = Weight of crucible + sample before drying.

$W_3$  = Final weight of crucible + sample after drying.

### Total Solid (Dry Matter)

% Total solid (dry matter) = 100 - % moisture.

### Determination of Ash Content

Weigh accurately 2-5g finely ground, dry sample (for high moisture food or liquid samples, evaporate to dryness or small volume on water bath or in oven at 100°C), into a tared silica or porcelain crucible. Char sample on a heater or Bunsen flame inside fume cupboard, to drive off most of the smoke. Transfer sample into a pre-heated muffle furnace at 550°C. Leave at this temperature for 2 hours or until a white or light grey ash results when the residue is black in colour, moisten with a small amount of water dissolve salts, dry in an oven and repeat the ashing process.

Cool in desiccators and reweigh

### Calculation:

$$\begin{aligned} \% \text{ Ash (dry basis)} &= \frac{\text{Weight of ash}}{\text{Weight of original food}} \times 100 \quad \dots\dots\dots (\text{equation 2.0}) \\ &= \frac{W_3 - W_1}{W_2 - W_1} \times 100 \end{aligned}$$

Where;

$W_1$  = Initial weight of empty crucible

$W_2$  = Weight of crucible + food sample before drying and/or ashing.

$W_3$  = Final weight of crucible + ash.

### Determination of Fiber Content

Defat about 2g of material with petroleum ether.

Boil under Reflux for 30 minutes with 200mL of a solution containing 1.25g of  $\text{H}_2\text{SO}_4$  per 100mL of solution.

Filter the solution through linen or several layers of cheese cloth on a fluted funnel.

Wash with boiling water until the used water is no longer acidic.

Transfer the residue to a beaker and boil for 30 minutes with 200mL of a solution containing 1.25g carbonate free NaOH per 100mL.

Filter the final residue through a thin but close pad of washed and ignited asbestos in a Gooch crucible.

Dry in an electric oven and weigh.

Incinerate, cool and weight.

The loss in weight after incineration x 100 is the percentage of crude fibre.

#### **Determination of Crude Fiber Content (%)**

- Weigh 2g of thoroughly mix food sample ( $W_o$ ) and transfer into a porous crucible.
- Then place the Crucible into a Dosi-fiber unit and keep the valve in “OFF” position.
- After that, add 150mL of preheated  $H_2SO_4$  solution (0.1281) and some drops of foam-suppress to each column.
- Open the cooling circuit and turned on the heating elements (power at 90%). When it starts boiling, reduce the power at 30% and leave it for 30minutes.
- Open the valves for drainage of acid and raise with distilled water thrice to completely ensure the removal of acid from sample.
- Dry the sample and cool in a desiccators and weigh ( $W_1$ ).
- Keep the sample crucibles in muffle furnace at  $550^\circ C$  for 3-4 hours. Cool the samples in desiccators and weigh again ( $W_2$ ).
- Calculate the fibre content.

#### **Calculation;**

$$\% \text{ Crude fibre} = \frac{W_1 - W_2}{W_o} \times 100 \quad \dots\dots\dots (\text{equation 3.0})$$

#### **Determination of Crude Protein**

##### **Reagents:**

0.1MHCl (standard)

Concentrated sulphuric acid

Sodium hydroxide solution 40% w/w

Digestion mixture: potassium sulphate ( $K_2SO_4$ ) and copper sulphate ( $CuSO_4$ )

Boric acid: Dissolve 40g of boric acid in sufficient distilled water and made the volume up to 1000ml

Indicator: Methyl red.

##### **Procedure:**

1.0g of dried sample is weighed and put into a digestion flask.

15ml of concentrated  $H_2SO_4$  and 8g of digestion mixture i.e.  $H_2SO_4$ :  $CUSO_4$  (8:1) is also added into the flask.

Swirl the flask in order to mix the contents thoroughly under a running tap.

The content in the flask is then place a heater to start digestion till the mixture become clear (blue-green in colour).

The digest is then cool and transfer to 100ml volumetric flask and made up to mark with distilled water.

Distillate 10ml of the digest in a markan still distillation apparatus added with 10ml of 0.50M NaOH through the same way and distillate for 10mins.

Ammonia ( $NH_3$ ) is collected using 20ml of 4% boric acid solution as  $NH_4OH$  in a conical flask with few drops of modified methyl red indicator.

Titrate the distillate against standard 0.1M HCl solution till the appearance of pink colour.

A blank is also run through all steps as above. Percent crude protein content of the sample is calculated using the following formula:

$$\% \text{Crude protein} = 6.25 \times \% \text{N} (*\text{correction factor}) \dots\dots\dots (\text{equation 4.0})$$

$$\% \text{N} = \frac{(S - B) \times N \times 0.014 \times 100}{\text{Weight of the sample} \times V}$$

Where;

S = sample titration reading

B = Blank titration reading

N = Normal of HCl

D = Dilution of sample after digestion

V = Volume taken for distillation

0.014 = milli equivalent weight of Nitrogen

### Determination of Crude Fat/Lipid

Crude fat content is determined by ether extract method using Soxhlet apparatus.

5g of moisture free sample is wrapped in filter paper, and placed in fat free thimble and then introduce into the extractor tube.

Weigh the clean and dried receiving flask and fill with petroleum ether and fit into the Soxhlet apparatus.

Turn on water and heater to start extraction.

After 4 – 6 siphoning allow ether to evaporate and disconnect the flask before the last siphoning.

Transfer the flask into a water bath to evaporated ether, then place the flask in oven at 105°C for 2 hours and cool in a desiccator.

Weigh the flask and content.

$$\% \text{Crude fat} = \frac{\text{weight of ether sample} \times 100}{\text{Weight of sample}} \dots\dots\dots (\text{equation 5.0})$$

### Determination of Total Carbohydrates (By Difference)

By this, the total carbohydrate content of sample is the percentage remaining after the moisture, ash, lipid, fibre and protein contents have been removed.

Mathematically, it is given as;

%Total Carbohydrate

$$= 100\% - \% (\text{Protein} + \text{Lipids} + \text{Fibre} + \text{Ash Content} + \text{Moisture Content})$$

### Determination Energy Value

The percentage calories in selected food samples can be calculated by multiplying the percentage of crude protein and carbohydrates with 4 and crude fat with 9. The values would be converted to calories per 100g of the sample.

$$\begin{aligned} \text{Energy Value (KJ/100g)} &= 186(\% \text{protein} \times 4) + (\% \text{lipid} \times 9) + (\% \text{carbohydrate} \times 4) \\ &= 186(4.07 \times 4) + (0.32 \times 9) + (58.87 \times 4) \end{aligned}$$

**Determination of Volatile Matter** 1.0 g of each sample was heated at a temperature of 500°C for 10 minutes. The volatile matter was calculated using the equation where volatile weight is the difference in weight before and after heating of the samples.

$$\text{Volatile \%} = \frac{\text{Weight of Volatile Components}}{\text{Oven dry weight}} \times 100 \dots\dots\dots (\text{equation 6.0})$$

### **Fourier Transform Infrared (FTIR) Analysis**

The Fourier transform Infrared (FTIR) 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 the examination of the spectra.

For sample analysis, 0.5 g of adsorbent (coconut shell powder) was mixed with about the same amount of potassium bromide (KBr).

The mixture was crushed in a mortar to obtain a homogeneous powder which was then introduced into a mould to obtain very fine plates. The plates were then introduced into the spectrophotometer for analysis.

The wave number was found to vary between 4000 and 350  $\text{cm}^{-1}$ .

### **Determination of Chemical Oxygen Demand (COD)**

Add 50 ml of sample in a 500 ml refluxing flask, add 1g  $\text{HgSO}_4$ , few glass beads, and 5 ml sulphuric acid reagent, mix, cool.

Also add 25 ml of 0.0417M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and mix.

Connect the flask to the condenser and turn on cooling water, add additional 70 ml of sulphuric acid reagent through open end of condenser, with swirling and mixing.

Reflux for 2 hours; cool, wash down condenser with distilled water to double the volume of contents, cool. Add 2 drops of Ferroin indicator and titrate with ferrous ammonium sulphate (FAS) until a colour change from bluish green to reddish brown. Also reflux and titrate a distilled water blank with reagents.

### **Determination of Dissolved Oxygen (DO)**

Pour 300 ml of the sample into BOD bottles (they are amber bottles and this is to prevent photosynthetic production of oxygen) and drain any liquid in the flared lip of bottle.

Add 1 mL of  $\text{MnSO}_4$  followed by 1 ml alkali-iodide-azide reagent using a pipette.

Stopper carefully to exclude air bubbles.

Mix by inverting the bottle a few times.

Allow the brown manganese hydroxide floc (white floc/cloud-like particles indicates presence of Dissolved Oxygen) to settle approximately to half the bottle volume.

Add 1.0 mL conc.  $\text{H}_2\text{SO}_4$  and re-stopper.

Mix by inverting several times until dissolution is complete.

Titrate 201ml with Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) until the blue colour disappears.

### **Determination of Biological Oxygen Demand (BOD)**

The biochemical oxygen demand (BOD) test is based on mainly bio-assay procedure which measures the dissolved oxygen (DO) consumed by micro-organisms while assimilating and oxidizing the organic matter under aerobic conditions. The standard test condition includes incubating the sample in dark air tight bottles, at a specified temperature for five (5) days.

$$\text{BOD}_{5, 27^\circ\text{C}} (\text{mg/l}) = (\text{DO}-\text{DT})/\text{P}$$

**Where:**

DO = DO of diluted sample initially (mg/l)

DT = DO of diluted sample after 5 days incubation at 27°C (mg/l)

P = decimal volumetric fraction of sample used

### Measuring Electrical Conductivity (EC)

This is done using a conductivity meter and is measured in  $\mu\text{S}/\text{cm}$ .

Place the probe of the conductivity meter in the sample

Note the conductivity and specify the measuring unit

Wipe the probe with a clean cloth or rinse using deionized water and repeat for other samples.

### Determination of Total Dissolved Solids (TDS)

Total dissolved solids ( $\text{mg}/\text{l}$ ) = conductivity ( $\mu\text{S}/\text{cm}$ )  $\times$  0.65

### Measuring Color

This is measured using a spectrophotometer and its unit is PCU.

Use distilled water as a blank to standardize the test.

Pour the sample into the spectrophotometer's 10 mm absorption cells.

Note the colour.

Empty and rinse the adsorption cell with clean water.

Repeat the above steps for other samples.

### Measuring PH

This is measured using a PH meter with values ranging from 0 to 14.

Place the probe of the PH meter in the sample.

Note the PH.

Wipe the probe with a clean cloth or rinse using deionized water and repeat for other samples.

## 3.0 Results and Discussion

Table 3.1: Proximate analysis of organic membrane (coconut shell)

| PARAMETERS            | VALUES |
|-----------------------|--------|
| Ash Content, %        | 2.72   |
| Moisture Content, %   | 5.72   |
| Fibre Content, %      | 47.28  |
| Lipid Content, %      | 0.03   |
| Protein Content, %    | 0.69   |
| Carbohydrate, %       | 43.56  |
| Energy Value, KJ/100g | 742.05 |
| Volatile Solid, %     | 38.68  |
| Total Solid, mg/l     | 94.28  |

Table 3.2: Characterization of Waste Water Containing Acetaminophen

| PARAMETERS                     | VALUES        |
|--------------------------------|---------------|
| pH                             | 5.8           |
| Conductivity, $\mu\text{S/cm}$ | 25.20 - 29.70 |
| Colour, PCU                    | 327.00        |
| Dissolved Oxygen, mg/l         | 2.50          |
| Biological Oxygen Demand, mg/l | 2.40          |
| Chemical Oxygen Demand, mg/l   | -             |
| Total solid, mg/l              | 2,232.00      |

Table 3.3: Absorbance of different concentrations of Acetaminophen

| Concentration, $\mu\text{g/ml}$ | Absorbance |
|---------------------------------|------------|
| 0                               | 0          |
| 5                               | 0.026      |
| 10                              | 0.03       |
| 15                              | 0.036      |
| 20                              | 0.046      |
| 25                              | 0.048      |
| 30                              | 0.052      |
| 35                              | 0.056      |
| 40                              | 0.062      |
| 45                              | 0.066      |

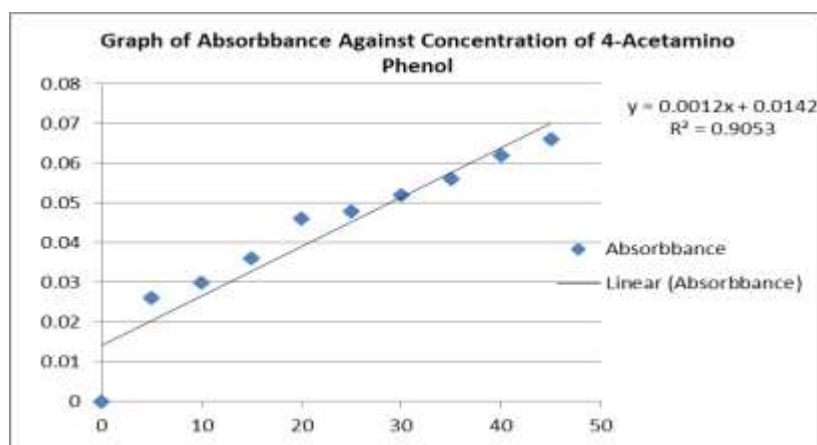


Figure 3.1: Graph of absorbance against concentration of Acetaminophen

Table 3.4: Height of column and time taken for filtration  
Volume of Waste Water Used =150ml

| Membrane      | Sample Column | Height (Cm) | Mass of adsorbent (g) | Total Time (s) | Total Time (min) | Total Volume Extracted (ml) | Total Volume Retained (ml) |
|---------------|---------------|-------------|-----------------------|----------------|------------------|-----------------------------|----------------------------|
| Coconut Shell | 1             | 4.00        | 11.38                 | 980.00         | 7.25             | 130.00                      | 20.00                      |
| Coconut Shell | 2             | 3.00        | 8.54                  | 524.00         | 8.73             | 130.00                      | 20.00                      |
| Coconut Shell | 3             | 0.80        | 2.28                  | 435.00         | 16.33            | 143.00                      | 7.00                       |

Table 3.5: Concentration of Acetaminophen in treated and untreated waste water

| Coconut shell membrane | Run 1      |                       | Run 2      |                       | Average    |                       |
|------------------------|------------|-----------------------|------------|-----------------------|------------|-----------------------|
| Column                 | Absorbance | Concentration (µg/ml) | Absorbance | Concentration (µg/ml) | Absorbance | Concentration (µg/ml) |
| 1                      | 0.1880     | 144.83                | 0.1970     | 152.33                | 0.1925     | 148.58                |
| 2                      | 0.2355     | 184.42                | 0.2355     | 184.42                | 0.2355     | 184.42                |
| 3                      | 0.1050     | 75.67                 | 0.1060     | 76.50                 | 0.1055     | 76.09                 |
| Untreated waste water  | 0.5490     | 445.67                | 0.5340     | 433.17                | 0.5415     | 439.42                |

Table 3.6: Characterization of filtrates from columns of varying heights

| Parameters          | Column 1 | Column 2 | Column 3 | Column 1 (2) | Column 2 (2) | Column 3 (2) |
|---------------------|----------|----------|----------|--------------|--------------|--------------|
| Ph                  | 6.40     | 6.10     | 6.60     | 6.70         | 6.80         | 6.30         |
| Conductivity, µs/cm | 6270.00  | 5470.00  | 1975.00  | 1403.00      | 518.00       | 1755.00      |
| Colour, PCU         | 4460.00  | 2690.00  | 1070.00  | 2240.00      | 560.00       | 2580.00      |

Table 3.7: Chemical Analysis of Membrane Filtrate

| Parameters                    | Column 1 |       | Column 2 |        | Column 3 |        |
|-------------------------------|----------|-------|----------|--------|----------|--------|
|                               | Run 1    | Run 2 | Run 1    | Run 2  | Run 1    | Run 2  |
| Dissolved Oxygen mg/l         | 4.20     | 4.30  | 4.00     | 4.30   | 6.40     | 6.60   |
| Biological Oxygen Demand mg/l | 340.00   | 82.00 | 155.00   | 150.00 | 305.00   | 128.00 |

|                                       |           |          |          |           |           |          |
|---------------------------------------|-----------|----------|----------|-----------|-----------|----------|
| Chemical Oxygen Demand mg/l           | 5,600.00  | 3,760.00 | 600.00   | 400.00    | 1,600.00  | 5,440.00 |
| Total Solid, mg/l                     | 29,500.00 | 5,700.00 | 2,750.00 | 31,500.00 | 20,250.00 | 7,200.00 |
| Total Suspended Solid, mg/l           | 25.42     | 2,144.50 | 1466.25  | 30,588.05 | 19,913.30 | 6.059.25 |
| Conductivity, $\mu\text{S}/\text{cm}$ | 6,270.00  | 5,470.00 | 1,975.00 | 1,403.00  | 518.00    | 1,755.00 |
| Total Dissolved Solid, mg/l           | 4,075.50  | 3,555.50 | 1,283.75 | 911.95    | 336.70    | 1,140.75 |

Table 3.8: Adsorption capacity of each filtration column

| Column | Mass of adsorbent (g) | Run 1                                                          |                                                |                        | Run 2                                                          |                                                |                        |
|--------|-----------------------|----------------------------------------------------------------|------------------------------------------------|------------------------|----------------------------------------------------------------|------------------------------------------------|------------------------|
|        |                       | Conc. of Acetaminophen in filtrate ( $\mu\text{g}/\text{ml}$ ) | Adsorption capacity ( $\mu\text{g}/\text{g}$ ) | Removal efficiency (%) | Conc. of Acetaminophen in filtrate ( $\mu\text{g}/\text{ml}$ ) | Adsorption capacity ( $\mu\text{g}/\text{g}$ ) | Removal efficiency (%) |
| 1      | 11.38                 | 144.83                                                         | 3883.00                                        | 67.04                  | 152.33                                                         | 3784.14                                        | 65.33                  |
| 2      | 8.54                  | 184.42                                                         | 4478.92                                        | 58.03                  | 184.42                                                         | 4478.92                                        | 58.03                  |
| 3      | 2.28                  | 75.67                                                          | 23930.92                                       | 82.78                  | 76.50                                                          | 23876.32                                       | 82.59                  |

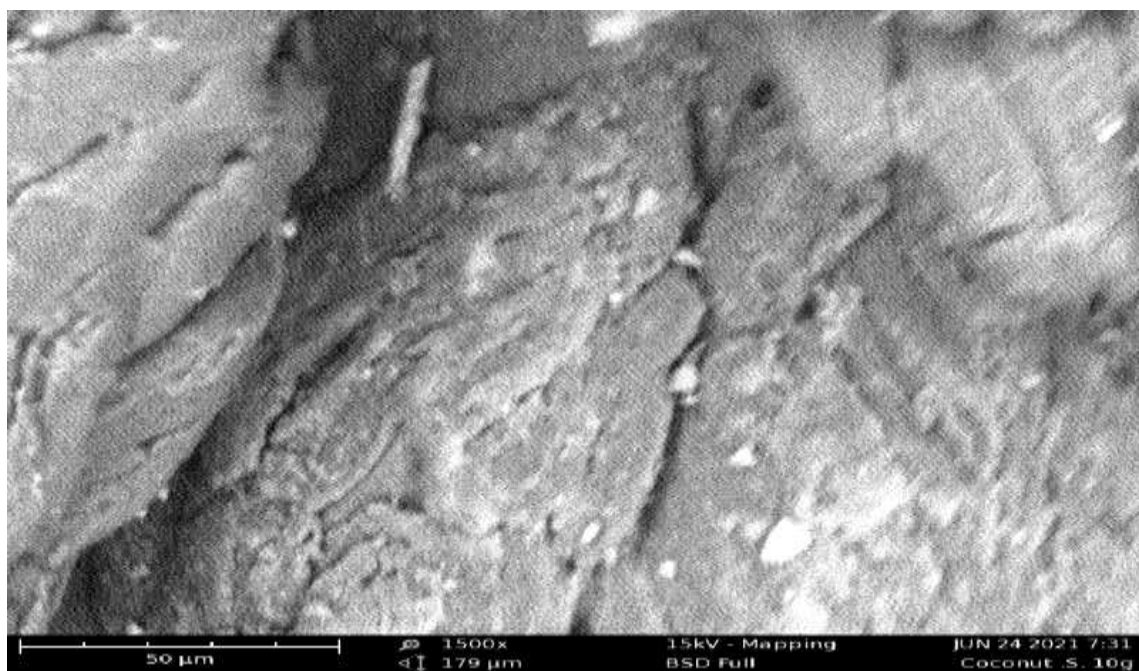


Figure 3.2: SEM image of coconut shell membrane before filtration

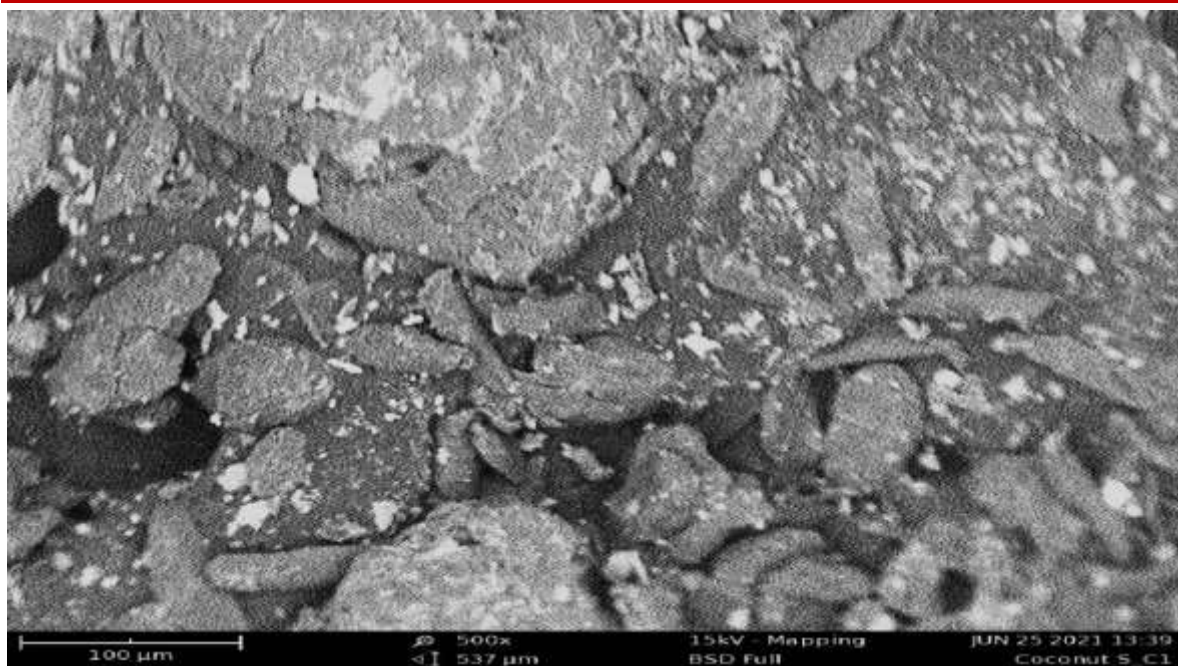


Figure 3.3: SEM image of coconut shell membrane (column 1) after filtration

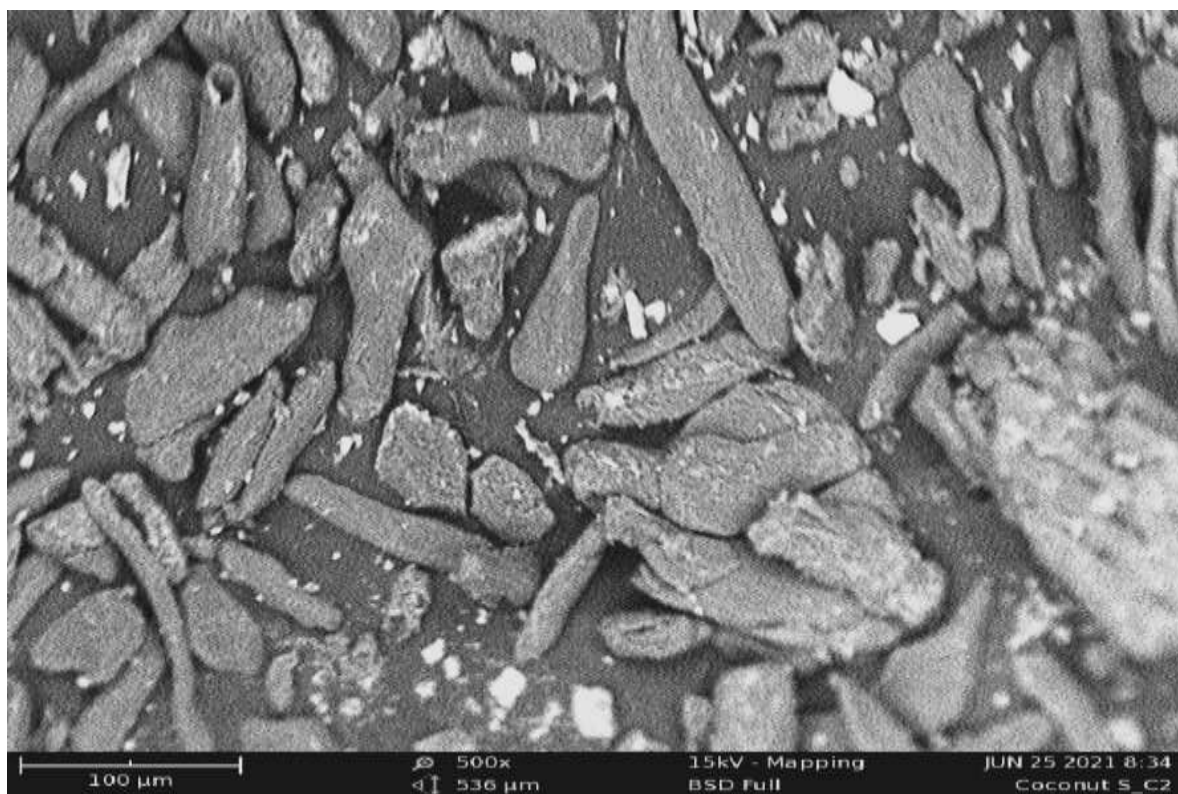


Figure 3.4: SEM image of coconut shell membrane (column 2) after filtration



Figure 3.5: SEM image of coconut shell membrane (column 3) after filtration

Table 3.9: 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 |
| Langmiur - 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  |

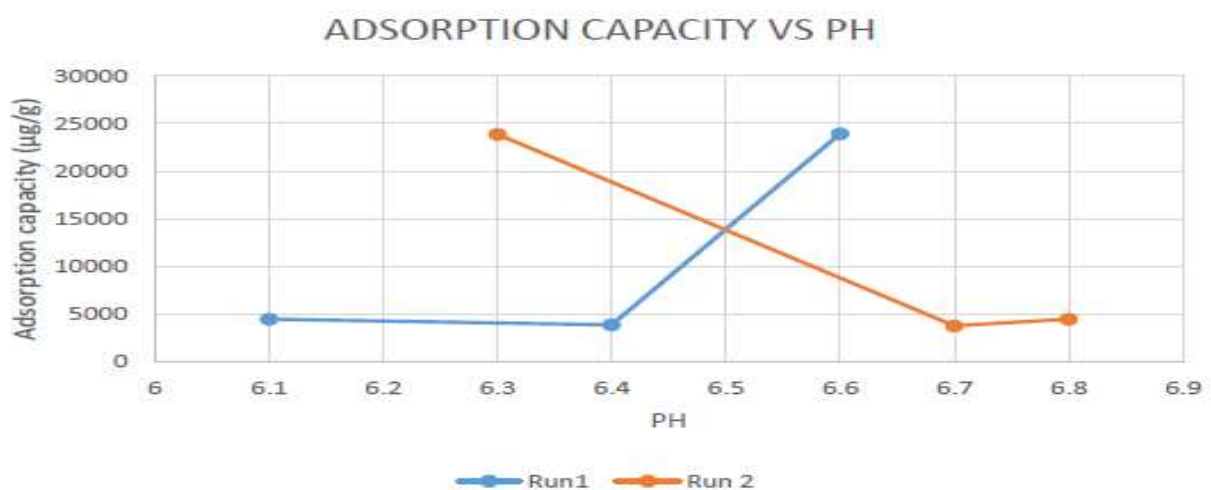


Figure 3.6: Graph of Adsorption capacity against pH

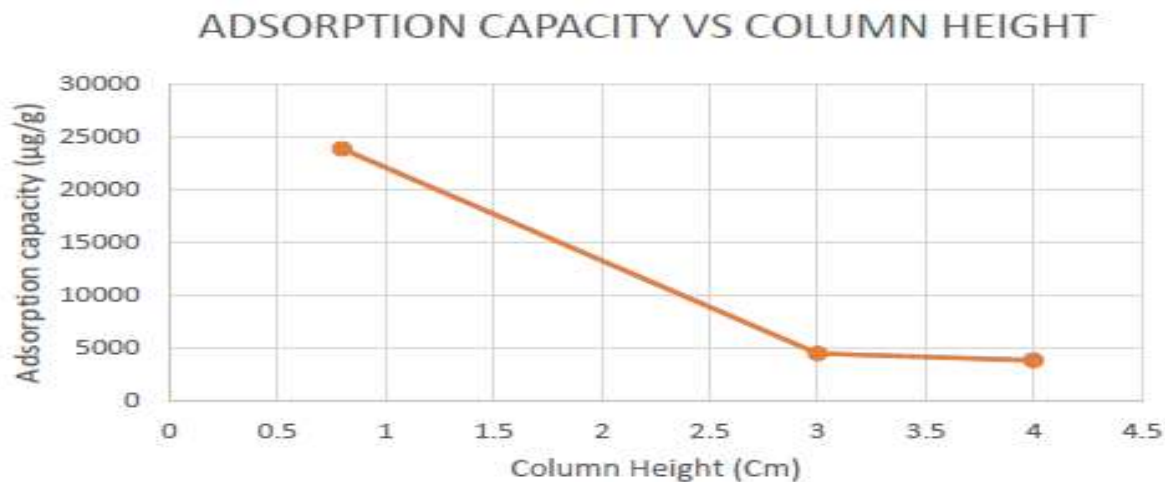


Figure 3.7: Graph of adsorption capacity against column height



Figure 3.8: Graph of Adsorption capacity against time taken for filtration

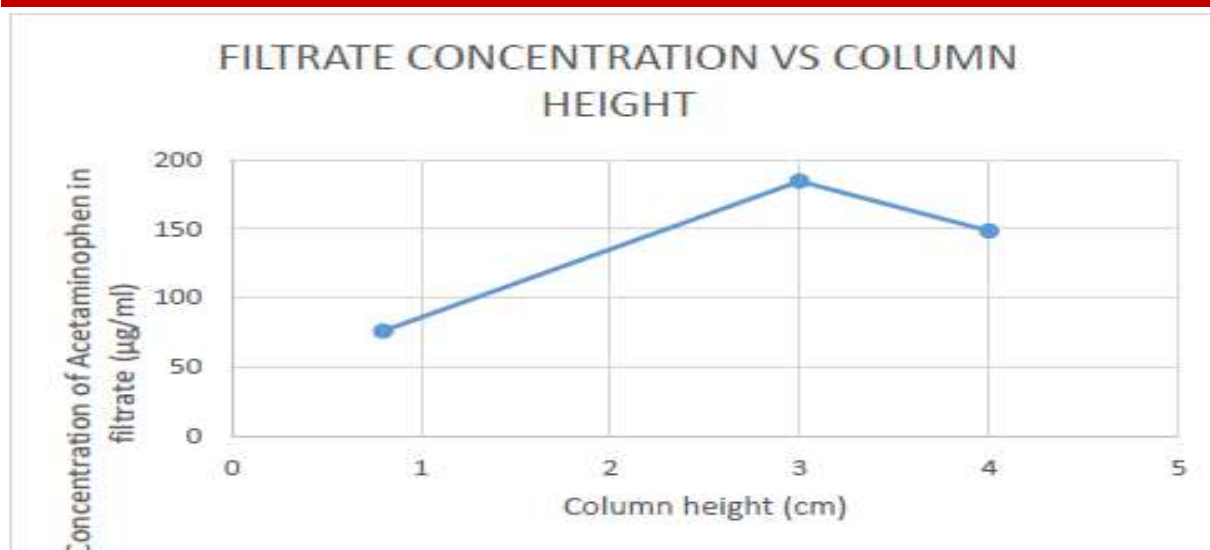


Figure 3.9: Graph of concentration of Acetaminophen against height of column

Table 3.10: Adsorption Isotherm Parameters

| LANGMUIR-1  |        | LANGMUIR-2  |          | FREUNDLICH  |         | TEMKIN   |          |
|-------------|--------|-------------|----------|-------------|---------|----------|----------|
| Ce/q        | Ce     | 1/q         | 1/Ce     | Log q       | Log Ce  | Q        | ln Ce    |
| 0.003183244 | 76.09  | 0.000041835 | 0.013142 | 4.37845768  | 1.88132 | 23903.29 | 4.331917 |
| 0.038757607 | 148.58 | 0.000260853 | 0.00673  | 3.583603398 | 2.17196 | 3833.57  | 5.001124 |
| 0.041175105 | 184.42 | 0.000223268 | 0.005422 | 3.651173305 | 2.26580 | 4478.92  | 5.217216 |

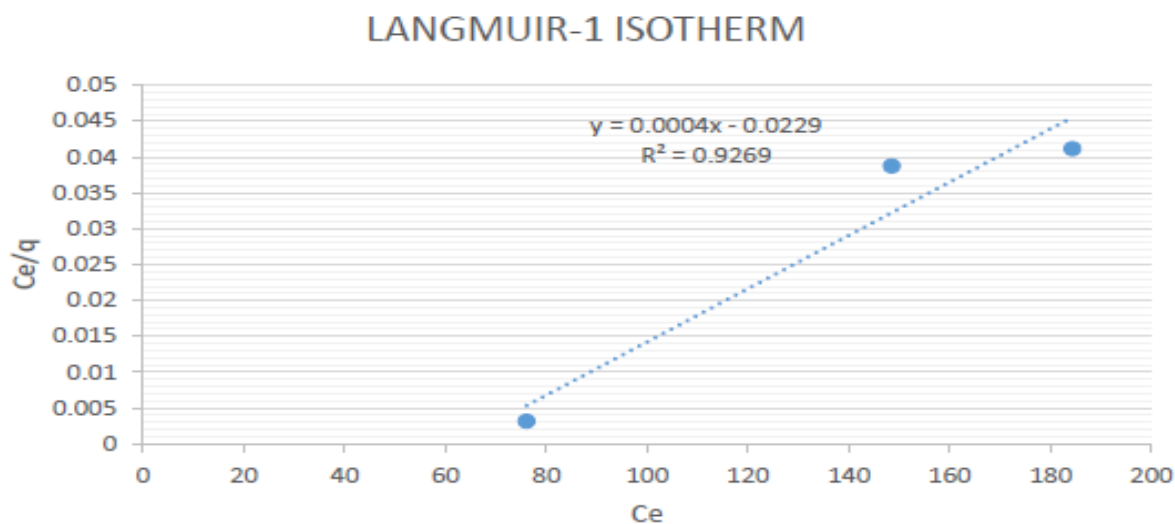


Figure 3.10: Langmuir-1 adsorption isotherm graph

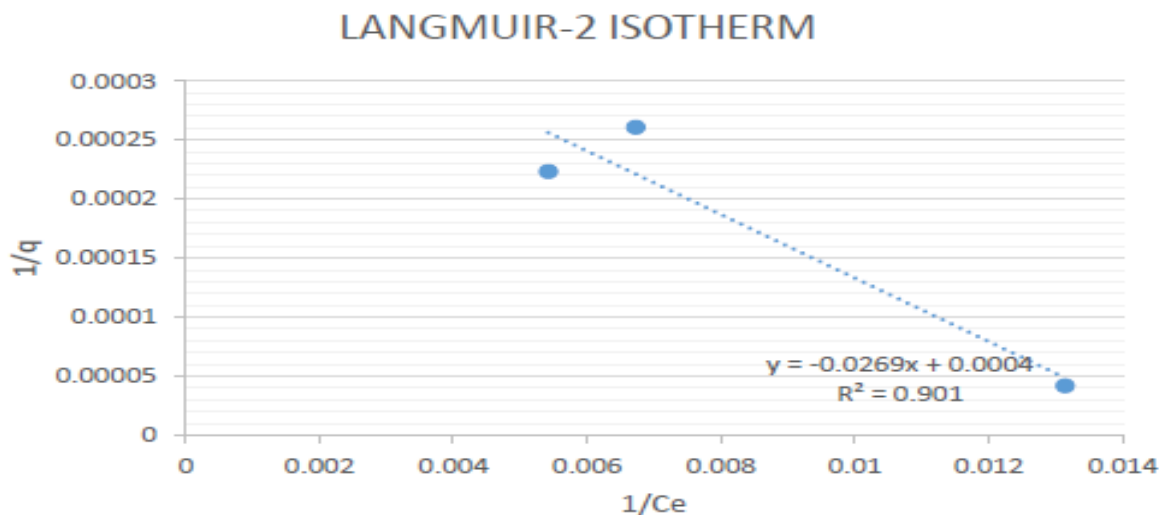


Figure 3.11: Langmuir-2 adsorption isotherm graph

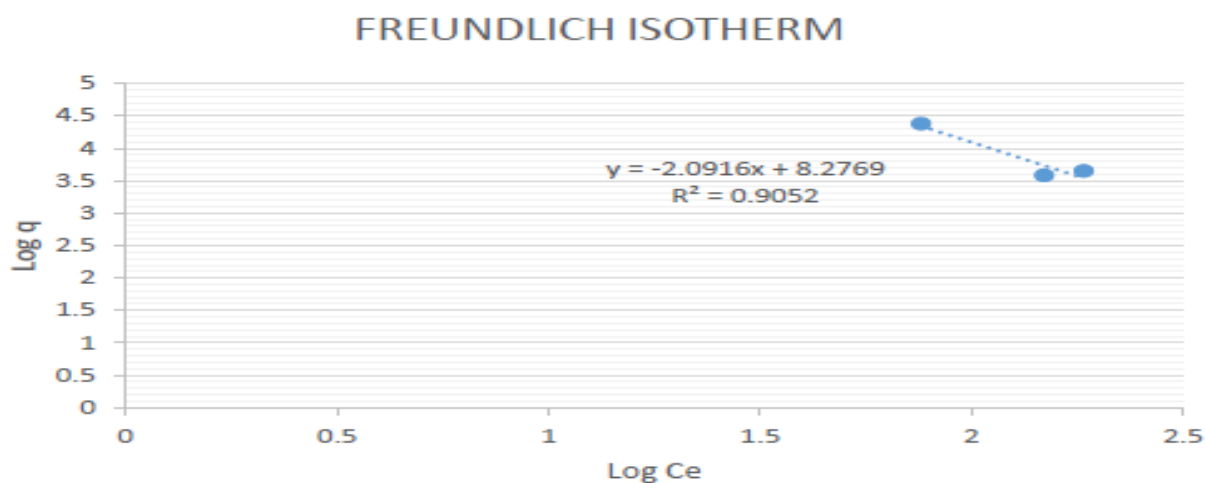


Figure 3.12: Freundlich adsorption isotherm graph

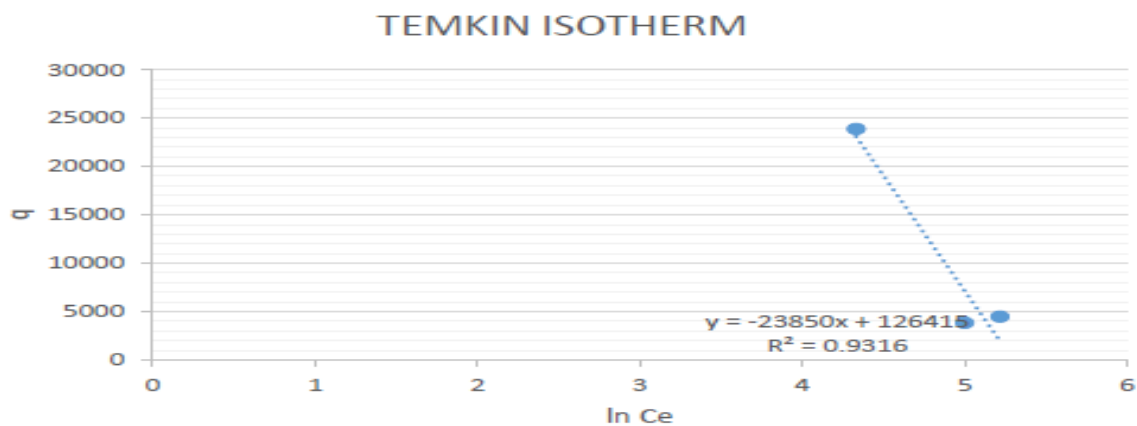


Figure 3.13: Temkin adsorption isotherm graph

### 3.2 Discussion

#### Effect of PH on adsorption capacity

From figure 3.6, it can be seen that at a pH of 6.1, adsorption capacity was 3883 $\mu\text{g/g}$  which was quite low but it peaked between 6.3 and 6.7 with values ranging between 23876.32  $\mu\text{g/g}$  and 23930.92  $\mu\text{g/g}$ . This shows that the optimal pH for filtration is between 6.3 and 6.7.

#### Effect of column height on adsorption capacity

From figure 3.7, When the column height was 0.8 cm, adsorption capacity was found to be 22903.29 $\mu\text{g/g}$ . As the column height (adsorbent mass) was increased to 3cm, the adsorption capacity reduced to 4478.92 $\mu\text{g/g}$ . this implies that the adsorption capacity is inversely proportional to the adsorbent dose, and this could be due the fact that higher adsorbent dose provides more active adsorption sites which results in the adsorption sites remaining unsaturated during the adsorption reaction (Li et al., 2013).

#### Effect of contact time on adsorption capacity

From figure 3.8, It can be seen that adsorption capacity increases with increase in contact time. When the time was 16.33 mins, adsorption capacity was found to be 23903.29 $\mu\text{g}$  of acetaminophen /g of coconut shell powder. In contrast, adsorption capacity was found to be 3833.57  $\mu\text{g/g}$  when contact time was 7.25 mins.

#### Effect of column height on concentration of Acetaminophen in filtrate

From figure 3.9, It can be seen that the least column height gives the smallest concentration of acetaminophen with 83% removal efficiency. This confirms that the height of column is inversely proportional to adsorption capacity.

#### Implication of $R^2$ value

The Langmuir, Freundlich and Temkin isotherm constants evaluated from the isotherms with the correlation coefficients are listed in Table 3.9. 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 both the Langmuir 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,  $q = B \ln K + B \ln C_e$

$B = \Delta Q = -\Delta H$ ,

where:

$\Delta Q$  is a variation of adsorption energy.

If  $\Delta Q$  is positive (which means that the slope is positive when we plot the linearized Temkin equation) the  $\Delta H$  is negative and the adsorption is exothermic. However, if  $\Delta Q$  is negative (which means that the slope is negative when we plot the linearized Temkin equation) the  $\Delta H$  is positive and the adsorption is endothermic.

As shown in the appendix, B was calculated using the slope of the Temkin adsorption isotherm graph (Figure 3.13)

7 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 from and 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.

#### **4.0 Conclusion and Recommendation**

##### **4.1 Conclusion**

Organic membrane made by chemically activating coconut shell powder using NaOH was able to reduce the concentration of Acetaminophen in waste water. This shows that there was adsorption of the pollutant (Acetaminophen).

The adsorption capacity is inversely proportional to the adsorbent dose, and this could be due the fact that higher adsorbent dose provides more active adsorption sites which results in most of the adsorption sites remaining unsaturated during the adsorption reaction.

The adsorption mechanism followed Temkin adsorption isotherm.

##### **4.2 Recommendation**

More than three columns should be prepared for filtration in order to increase data points.

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