Investigating the effect of activated carbon derived from pineapple waste on removing volatile organic compound

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Abstract

This study aims to investigate the efficiency of activated carbon derived from pineapple waste on removing the volatile organic compound Xylene, as well as to compare the efficiency of activated carbon derived from different parts of pineapple waste, namely the peel and crown. This research project uses pineapple (*Ananas comosus)* as the base for the activated carbon, acting as a low-cost adsorbent and solving its waste problem. Specifically, the activated carbon derived from the crown and peel were oven dried, then chemically activated via impregnation with phosphoric acid. Their efficiency on xylene adsorption was investigated by obtaining iodine numbers. The activated carbon derived from the crown adsorbed 91.1% of xylene while activated carbon derived from the peel adsorbed 85.4% of xylene. Langmuir and Freundlich equations were tested for modelling the adsorption isotherms at equilibrium, and it was concluded that the Freundlich model fitted the experimental data more adequately. Overall, the results showed that both types of activated carbon were efficient in its adsorption of xylene. However, activated carbon derived from pineapple crown is more effective than pineapple peel. The finding of this investigation offers a low cost, eco-friendly solution to removing xylene and concurrently creates an avenue to reduce waste created by pineapples parts.

1. Introduction

1.1 Literature Review

Xylene is one of the most common Volatile Organic Compounds (VOCs) present in indoor air. Technical grade xylene is a combination of the three isomers: *ortho, para and meta*, in which among the isomers, the *meta*-form is the most predominant. Xylene is one of the top 30 chemicals produced in the United States and is used extensively as a solvent in the rubber, printing and leather industries. It is also used as a thinner for paints and varnishes. In the field of histopathology, xylene is used as a clearing agent that gives translucency to the tissues. (Rajan & Malathi, 2014)

Exposure to xylene can occur via inhalation, ingestion, eye or skin contact (Kandyala, Raghavendra & Rajasekharan, 2010). It is primarily metabolized in the liver by oxidation of a methyl group and conjugation with glycine to yield methyl hippuric acid, which is excreted in the urine (Niaz, Bahadar, Maqbool & Abdollahi, 2015). The main effect of inhaling xylene vapor is the depression of the central nervous system, causing headache, nausea and vomiting, which will become more noticeable and serious as exposure increases. This is due to xylene disturbing the action of proteins essential for normal neuronal function (Kandyala, Raghavendra & Rajasekharan, 2010). At very high levels of exposure, xylene can affect the musculoskeletal system, injure the liver and kidney or even result in pulmonary edema, a potentially life-threatening condition in which the lungs fill with fluid. Hence, given the detrimental effects of xylene on humans, there is a need for an effective method to remove xylene.

Activated carbon is proposed as a candidate for effective removal of xylene due to its high adsorption capacity which is attributed to its large internal surface area, porosity, and high degree of surface reactivity (Lu, Pan & Zhu, 2015). Also, it has different surface functional groups (Kyzas & Mitropoulos, 2018) and involves low energy costs, even offering the possibility of product recovery (Hsu & Tsair, 2007).

However, VOC adsorption using commercial activated carbon is economically infeasible due to its lower adsorption capacity than organically-derived activated carbon(Kurniawan & Babel, 2003) and usually involves a high cost of production. An alternative is to use an abundant and low cost activated carbon source, such as pineapple waste to produce it.

Furthermore, pineapple is grown in many countries worldwide, on land totaling about 2.1 million acres. After harvesting, a large amount of pineapple waste remains causing various problems for farmers (Kengkhetkit & Amornsakchai, 2014). This is mainly due to the elimination of components unsuitable for human consumption and other factors such as rough handling of fruits that can cause up to 55% of product waste, contributing significantly to the problem of food waste. To add on, recent studies have also shown the potential of pineapple waste for the adsorption of VOCs. Results from (Mopoung & Amornsakchai, 2016) concluded that pineapple fiber is a suitable material for the preparation of adsorption filters. Also, (Selvanathan & Subki, 2015) showed that activated carbon from acid treated pineapple crown was an effective adsorbent for adsorption of certain dyes. Hence, activated carbon derived from pineapple waste to remove xylene is highly possible.

Hence, this study aims to investigate the efficiency of xylene adsorption using activated carbon derived from 2 different parts of pineapple waste, namely the crown and peel.

1.2 Hypotheses

1. Activated carbon derived from pineapple waste can efficiently adsorb xylene.
2. Activated carbon derived from the crown is more efficient at adsorbing xylene compared to pineapple peel.

1.3 Objectives

1. To produce activated carbon derived from 2 different parts of pineapple waste, namely crown and peel.
2. To investigate and compare the efficiency of xylene adsorption by activated carbon derived from 2 different parts of pineapple waste namely crown and peel.
3. Potentially obtain a low cost activated carbon able to remove xylene and concomitantly enhance the value of an abundant biomass and solve its waste problem.

2. Materials and Methodology

2.1 Materials

Sarawak pineapples were purchased from a supermarket and xylene solution was obtained from Sigma-Aldrich

2.2 Synthesis of activated carbon

2.2.1 Preparation of adsorbent

The 6 Sarawak pineapples were purchased from a supermarket and separated into pineapple crown and peel. The three samples were thoroughly washed with deionized water, and cut into smaller pieces with an average length of 2 cm. After that, it was oven dried at 105°C until constant mass. The dried pineapple crown and peel was then ground and sieved using 300μm siever to increase the surface area for reaction with activating agent in chemical activation process.

Fig 1a - pineapple crown **Fig 1b - pineapple peel**

2.2.2 Acid activation

Oven dried pineapple crown and peel were impregnated with 140ml of 1 mol dm^{-3} phosphoric acid (H_3PO_4) and left to stand for a day in the fume hood for activation. The excess H_3PO_4 is drained away and AC is then placed in an oven set at 100 °C and dried to constant mass.

2.2.3 Carbonization

Dried pineapple crown and peel was carbonized in ashing furnace at 350°C for two hours. Carbonized biomass was then taken out and washed with distilled water until the pH reaches 7 to ensure pH of carbon is kept constant. Then it is dried at 105°C in an oven and later removed to cool at room temperature. Activated carbon was then weighed and stored in 2 vials labelled as crown and peel respectively for further studies.

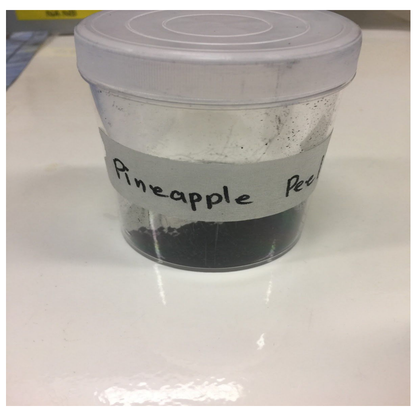


Fig 2a - pineapple crown AC **Fig 2b - pineapple peel AC**

Iodine Number (Designation: D4607 – 94 (Reapproved 2006))

2.3 Iodine number test

The iodine number was used to quantitatively compare the porosity and adsorption capacity of activated carbon derived from the 2 types of pineapple waste.

First, 0.48g of activated carbon from each sample was mixed with 1ml of 5% w/w hydrochloric acid, then stirred with a magnetic stirrer and boiled on a hot plate for 30 seconds. The flasks were removed from the hot plate and cooled to room temperature. After cooling, 10 ml of 0.05 mol dm^3 of iodine in aqueous potassium iodide solution was then added to the mixture and it was shaken vigorously for 30 seconds. Filtration was performed on the mixture to obtain the filtrate for both samples. A burette was first rinsed with sodium thiosulfate solution before being used to titrate 9ml of filtrate with 0.100 N sodium thiosulfate solution until the solution was a pale yellow. 2 mL of the starch indicator solution was added and the titration was continued with sodium thiosulfate until one drop produced a colorless solution. These steps were repeated 5 times.

The mean volume of sodium thiosulfate solution used was recorded and then used in the following formula to determine the iodine number of activated carbon
Mass (mg) of iodine absorbed by per gram of activated carbon=

(A-(DF)x(BxS))÷M (See Appendix A)

Carbon dosage to be used was estimated as follows:

M = [A-(DF)(C)(126.93)(50)]/E (See Appendix A)

2.4 Surface Morphology of activated carbon using SEM

Activated carbon from the 2 types of pineapple waste were also sent to the Scanning Electron microscope to study the surface morphology of the activated carbon.

2.5 Test of adsorption of xylene (mixture of isomers) using UV - vis spectrophotometry

Firstly, serial dilution was carried out to obtain six different concentrations of xylene - 0.0156, 0.0313, 0.0625, 0.125, 0.25 and 0.5 (ppm). Then, these concentrations of xylene were scanned using a UV-Vis spectrophotometer set at 220nm, which was used to calculate the absorbance readings of the different concentrations of xylene. A calibration curve of absorbance readings against known concentrations of xylene was then plotted.

Next, the following set-ups were prepared:

- 1g of activated carbon derived from pineapple crown was added to 1ml of 98.5% xylene and 100ml of methanol as a blank.
- 1g of activated carbon derived from pineapple peel was added to 1 ml of 98.5% xylene, and 100 ml of methanol as a blank.
- Control set-up that consisted of only 1g of activated carbon derived from pineapple crown and 100ml of methanol
- Control set-up that consisted of only 1g of activated carbon derived from pineapple peel and 100ml of methanol

The four Pyrex glass bottles were shaken on an orbital shaker for 3 hours and the mixture was filtered to obtain the filtrate.
Absorbance by the final concentration of xylene after adsorption by pineapple crown and peel activated carbon was determined using UV - Vis spectrophotometer with wavelength of 220nm. The absorbance readings for the two types of pineapple activated carbon was compared to the calibration curve to obtain the final concentration of xylene for the two types of activated carbon.

Percentage of xylene removed by pineapple peel and crown activated carbon was then found out using the following formula.

Percentage of Xylene removed/% =

(Initial concentration - final concentration)/Initial concentration X 100%

The percentage of xylene removed would be used to compare the efficiency of xylene adsorption by activated carbon derived from the 2 types of pineapple waste.

3. Results and discussion

3.1 Iodine Number

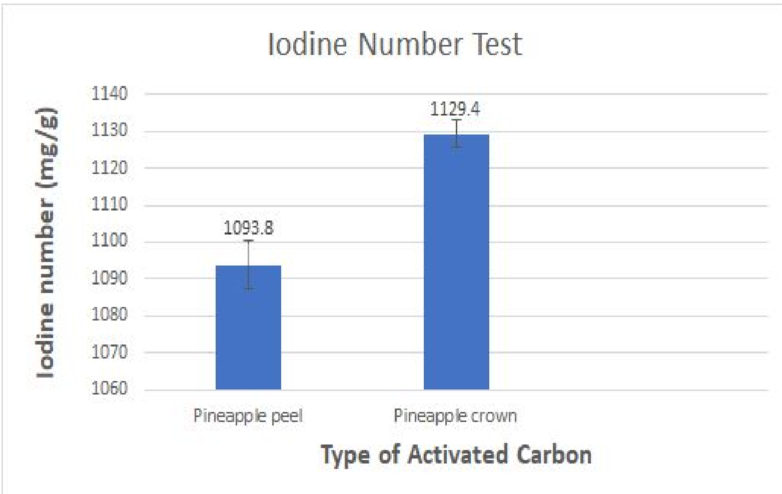


Fig 3 - Iodine number results

The iodine number test was used to quantitatively compare the porosity and adsorption capacity of activated carbon derived from pineapple crown and peel (Ekpete, Marcus & Osi, 2017) as well as to confirm that this activated carbon was comparable to commercial ones.

As seen in Fig 1, the iodine number of activated carbon from pineapple peel was calculated to be **1093.8mg/g** and iodine number of activated carbon from pineapple crown was calculated to be **1129.4mg/g**. A Mann-Whitney U test was conducted for the volume of sodium thiosulfate solution used in the five replicates and the p value was found to be 0.0079. Hence, the result is statistically significant at $p < 0.05$. It can be concluded that the iodine number of pineapple crown activated carbon is significantly higher than the iodine number of pineapple peel. The higher iodine number of activated carbon has been attributed to the presence of large micropore structure and large surface area due to enlargement of their pore structure. Thus, this shows that pineapple crown activated carbon has a higher porosity than pineapple peel activated carbon.
Furthermore, (Mopoung, Moonsri, Palas & Khumpai, 2015) reported that pharmaceutical grade activated carbon has an iodine number with a typical range of 500 – 1200 mg/g, which is equivalent to the surface area of carbon between 900 m^2/g and 1100 m^2/g. This suggests that activated carbon derived from both pineapple peel and crown are comparable to commercial activated carbon.

3.2 Surface Morphology of activated carbon using SEM

Pineapple crown

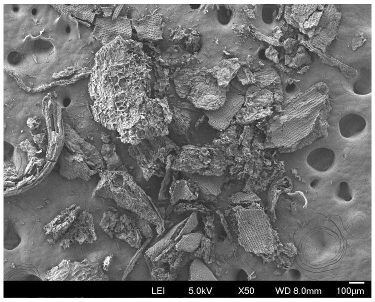


Fig 4a

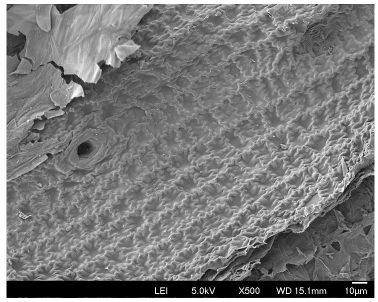


Fig 4b

Pineapple peel

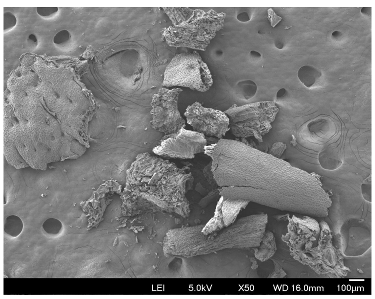


Fig 5a

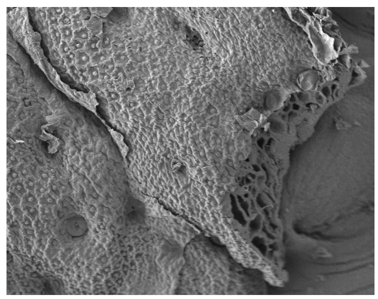


Fig 5b

From the SEM images, presence of well-developed micropores with uniform distribution on the surface is observed for both activated carbon, linking to a high degree of surface reactivity. There are also ridges and protrusions on the surfaces, which increases the surface area of activated carbon. The SEM images also show that the surface is pitted and fragmented which may be due to the carbonization with H_3PO_4 acid and activation process (Baseri , Palanisamy & Sivakumar, 2014). This increases the surface area of the activated carbon which can hold more adsorbate. Lastly, in Fig 4a of pineapple crown and Fig 5b of pineapple peel, it can be observed that on the fragments of carbon, there is a honeycomb structure which provides high mechanical strength and a higher surface area in contact with xylene.

From the SEM images, the morphology of the activated carbon obtained from both pineapple peel and crown suggests that the products should have relatively high adsorption capacities. This will contribute to a large quantity of xylene molecules adhering to the surfaces of the activated carbon.

3.3 UV-Vis spectrophotometry to find out xylene adsorption

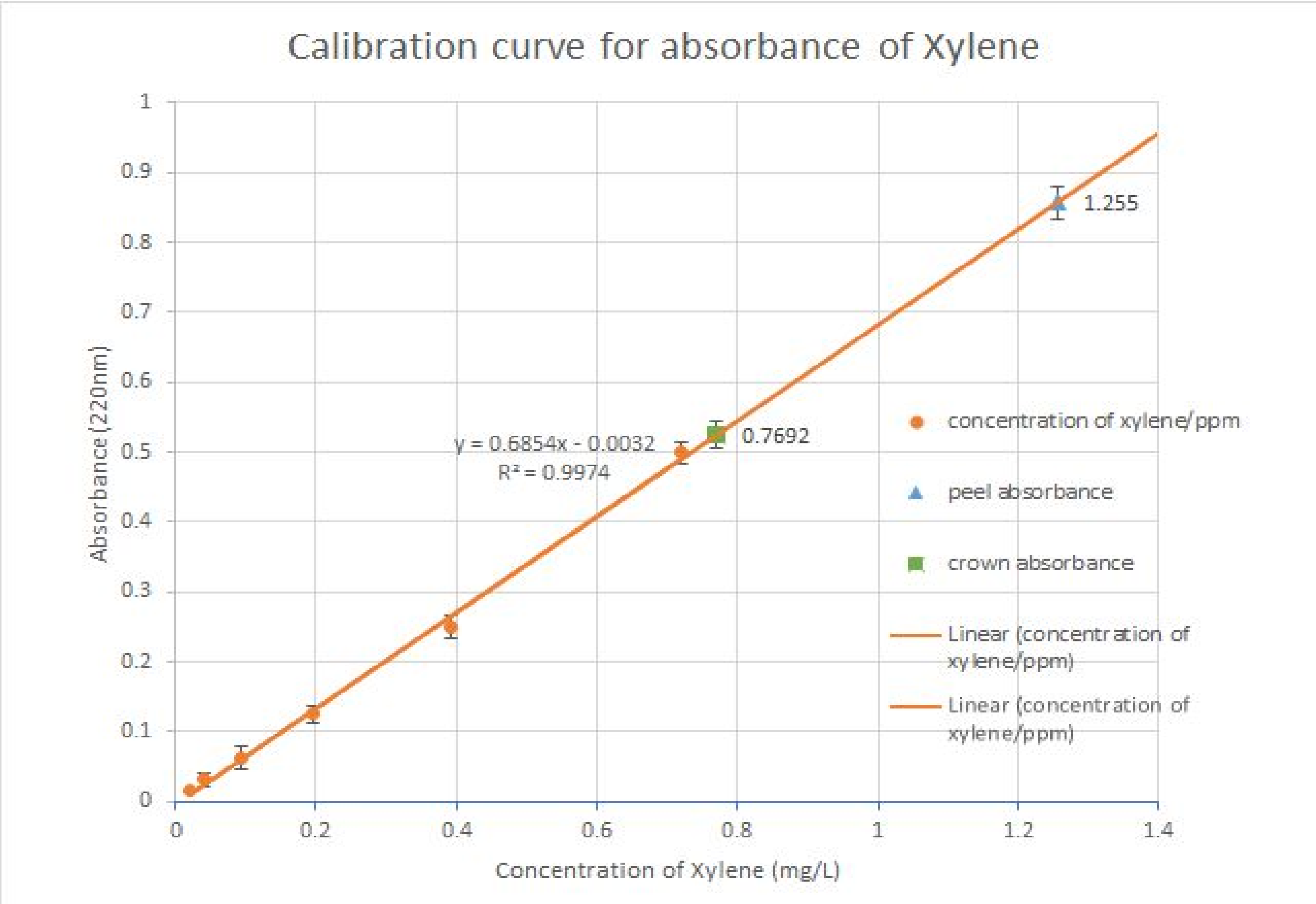


Fig 6 - Calibration curve for absorbance of xylene

After the calibration curve was plotted, 5 samples of the filtrate (mixture of methanol and xylene after adsorption) for each activated carbon was scanned using the UV - Vis spectrophotometer to find its absorbance reading. The mean absorbance readings for both activated carbon were then compared with the calibration curve to obtain the final concentration of xylene left (as shown in Fig 4), which can be used to find out the percentage of xylene removed by each activated carbon

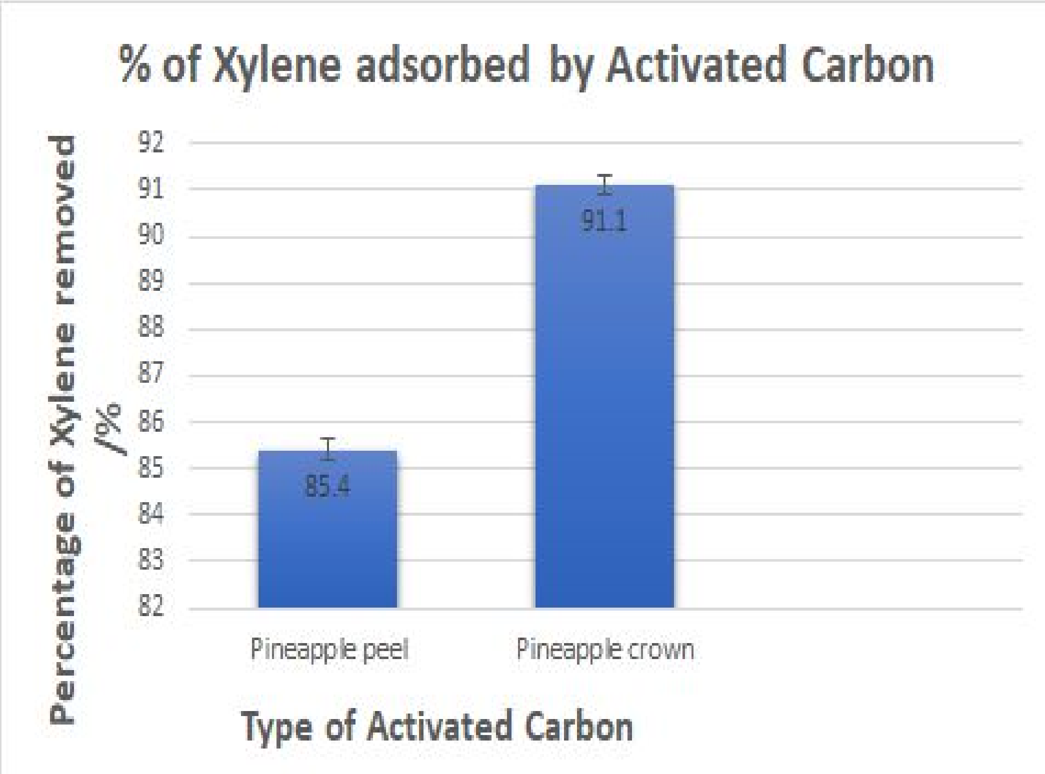


Fig 7 - Percentage of xylene adsorbed by activated carbon

85.4% of xylene was removed by pineapple peel activated carbon.

91.1% of xylene was removed by pineapple crown activated carbon.

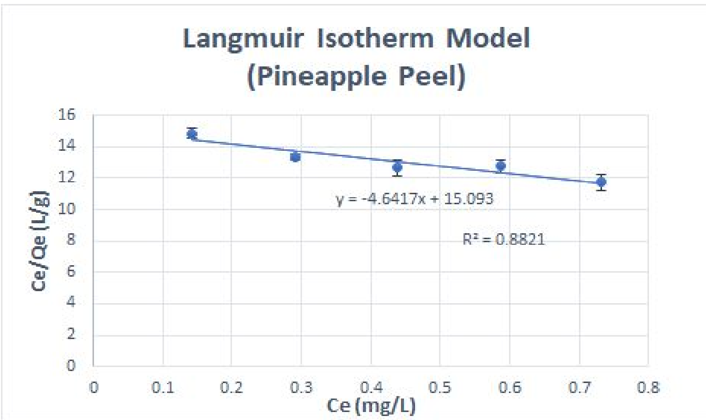
A Mann-Whitney U test was conducted for the five absorbance readings from each activated carbon. The p value was found to be 0.01208, thus the result is statistically significant at $p < 0.05$. The null hypothesis is rejected and the alternate hypothesis is accepted. Hence, it can be concluded that the adsorption of xylene by pineapple crown activated carbon is more efficient than that of pineapple peel.

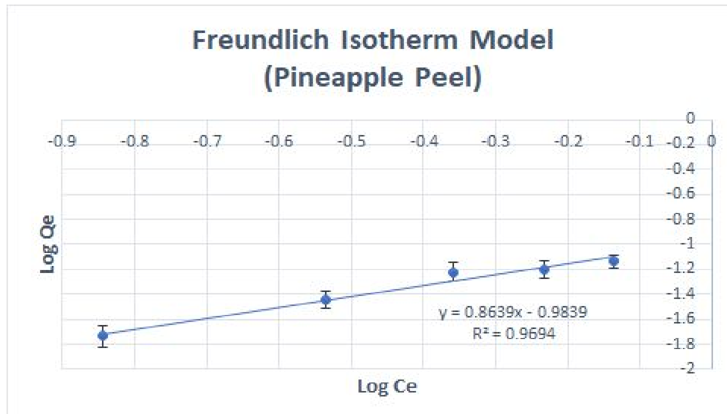
Pineapple crown and peel composed of cellulose, hemicelluloses and lignin. Large number of hydroxyl and carbonyl groups are present in cellulose, hemicelluloses and lignin that gives the adsorptive property to the pineapple waste (Selvanathan, Sulaiman & Subki, 2015). Xylene molecules can dissociate and adsorb on the binding sites of pineapple waste activated carbon which are the hydroxyl and carbonyl groups.

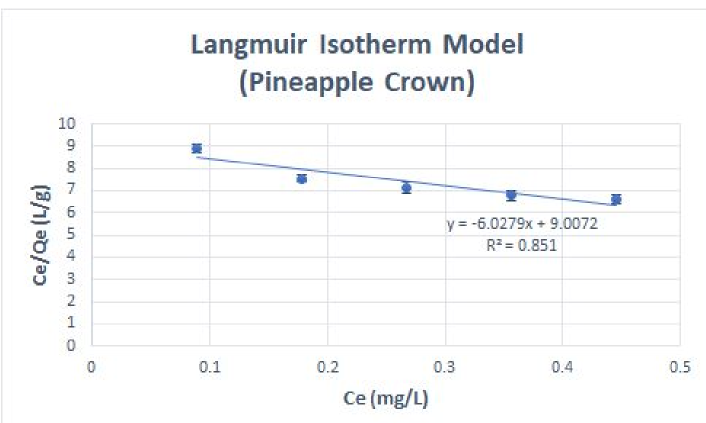
Pineapple crown contains a higher percentage of cellulose and hemicelluloses than pineapple peel (Selvanathan, Sulaiman & Subki, 2015). Thus, the number of active sites for binding are also higher which could have caused the increased adsorption of xylene for pineapple crown. Pineapple peel may also comprise of more sugar and water that degrades during drying process as it is in contact with pineapple flesh. The presence of the higher sugar and water content replaces the cellulose and hemicelluloses which eventually reduces the number of active sites and thus efficiency of pineapple peel to adsorb xylene. Hence, due to the higher cellulose, hemicelluloses and lignin content in pineapple crown which increases the number of binding sites due to carbonyl and hydroxyl groups, pineapple crown activated carbon is a better adsorbent of xylene than pineapple peel activated carbon.

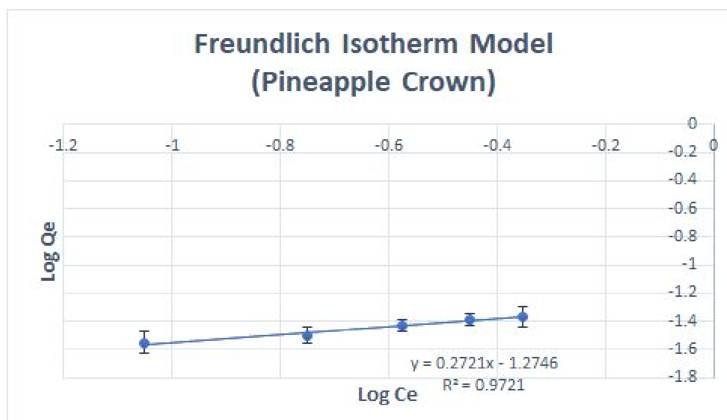
3.4 Langmuir and Freundlich Isotherms

To further study the adsorption capacity of both activated carbon, the graphs of Langmuir and Freundlich isotherms were plotted for both activated carbon on its adsorption of xylene.









The Langmuir isotherm assumes that the adsorption only involves the formation of a monolayer adsorbate on the outer surface of the adsorbent, which contains a finite number of identical sites where the solute molecules can be adsorbed. The model assumes uniform energies of adsorption onto the surface and that a maximum limiting uptake exists (Olalekan, Olatunya, & Oluwasogo, 2012).

The linear equation for Langmuir is expressed as follows:

$(C_e / q_e) = (1 / Q_o) + (C_e / Q_o)$ (See Appendix B)

The Freundlich isotherm assumes that adsorption occurs on a heterogeneous surface through a multilayer adsorption mechanism, and that the adsorbed amount increases with the concentration (Fierro, Torne-Fernandez, Montane & Celzard, 2008).

The linear equation for Freundlich is expressed as follows:

$\log q_e = \log K_f + (1 / n) \log C_e$ (See Appendix B)

From the Langmuir and Freundlich isotherms, it can be seen that both the pineapple peel and crown activated carbon have a higher R^2 value and are better fits when fitted into the Freundlich isotherm, thus it can be inferred that both activated carbon have a multilayer adsorption on xylene and that adsorption occurs on a heterogenous surface of the activated carbon.
Furthermore, the value of $1/n$ was determined for the Freundlich equations of both activated carbon. The values of 1/n can determine the intensity of adsorption by activated carbon (Wu, 2017). If the value of $1/n$ lies between 0.1 and 0.5, it indicates excellent adsorption capability of the adsorbent. If value of 1/n is between 0.5 and 1, it indicates a normal adsorption. If n = 1 then the partition between the two phases are independent of the concentration.
From the Freundlich graphs of the adsorption of xylene, the 1/n value of pineapple peel is 0.8639 and the 1/n value of pineapple crown is 0.2721. Hence, it can be concluded that the activated carbon obtained from pineapple crown is an excellent adsorbent of xylene while activated carbon obtained from pineapple peel fared slightly worse in terms of the intensity of adsorption.

4. Conclusion

Activated carbon from pineapple peel and pineapple crown were successfully prepared and the iodine number of both activated carbon were found. Activated carbon from pineapple crown had a higher iodine number than pineapple peel which signifies that activated carbon from pineapple crown had a significantly higher porosity than pineapple peel. Nonetheless, activated carbon derived from pineapple crown and peel were found to be comparable to commercial ones. SEM images of both activated carbon also showed morphologies consistent with surfaces with large surface areas such as well-developed micropores, ridges, protrusions and fragments on the surfaces, as well as a honeycomb structure which provides high mechanical strength. For the test of adsorption of xylene, activated carbon from pineapple crown was found to have a significantly higher xylene removal percentage than pineapple peel at 91.1% to 85.4% respectively. The adsorption of xylene by the 2 activated carbon were also fitted into the graphs of Langmuir and Freundlich equations, and Freundlich was found to be a better fit for both activated carbon, implying that both pineapple peel and crown activated carbon have a multilayer adsorption on xylene. The 1/n values from the Freundlich graphs also indicates that pineapple crown activated carbon had a better adsorption capability than pineapple peel. These results show that both pineapple waste activated carbon can adsorb xylene, although activated carbon derived from pineapple crown was shown to be a more effective adsorbent of xylene than pineapple peel. Hence activated carbon from pineapple crown shows potential to be used in xylene removal and at the same time enhance the value of an abundant biomass, solving the pineapple waste problem.

5. Future work

As a further extension to the project, the effect of mass of adsorbent, pH of adsorbent, type of activating agent or time on the percentage of xylene removed by activated carbon could be investigated to learn more about the adsorption of xylene by activated carbon. Another possible extension is to utilise the electrospinning of activated carbon to form nanofibers which possess superior mechanical and chemical properties.

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Appendix A

Where:
S is the volume (ml) of sodium thiosulfate used
M is the mass (g) of the AC sample.
A = (molarity of iodine solution)(12693.0),
DF = dilution factor = (I+H)/F
I = mass of iodine used/mL (from 9.2),

H = 5 % hydrochloric acid used/ml
F = filtrate/mL
C = residual iodine concentration, and
E = estimated iodine number of the carbon

Appendix B

C_e=equilibrium concentration of adsorbate

$Q_e = \frac{(Ci-Cf)\times V}{m}$ **,** equilibrium adsorption capacity of adsorbate

C_i = initial concentration of adsorbate

V= volume of solution containing adsorbate

m= mass of adsorbent used

Q_o= maximum adsorption capacity of adsorbent

K_f = Freundlich constant related to the total adsorption capacity of the solid

1/n = Freundlich sorption exponent.

Timeline

January 2019	· Research on Project Topics
February to March 2019	· Literature Review · Write up Proposal

March to May 2019	· Confirmation of Methods · Begin Experiments
May to June 2019	· Research Proposal · Continue Experiments
July to August 2019	· Complete Experiments · Analyse Results · Write up Report