TAMARIND SEED BASED ACTIVATED CARBON PREPARED VIA CuFe LAYERED FOR CAFFEINE REMOVAL FROM AQUEOUS SOLUTION

by

MOHAMAD FAZRUL IKMAL BIN AZIZ

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Mohamad Fazrul Ikmal bin Aziz

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LIST OF SYMBOLS

Symbol	**Description**	**Unit**
q_e	Caffeine uptakes at equilibrium/Adsorption capacity	mg/g
C_o	Initial concentration of caffein	mg/L
C_e	Concentration of caffein at equilibrium	mg/L
V	Volume of solution	mL
m	Mass of TSAC used	g
Q_m	Maximum adsorption capacity	mg/g
K_L	Langmuir constant	L/mg
K_F	Freundlich constant	mg/g
n_F	Freundlich constant	
R^2	Coefficient of determination	
W_{chem}	Mass of chemicals	g
W_{char}	Mass of char	g
m_{TSAC}	Mass of dry TSAC	g
m_{TS}	Mass of dry TS	g
M_1	Concentration of stock solution	mg/L
M_2	Concentration of desired solution	mg/L
V_1	Volume of stock solution	L

V_2	Volume of desired solution	L
IR	Impregnation ratio	g/g
RMSE	Root mean square error	

LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmet-Teller
BPA	Bisphenol-A
BPS	Bisphenol-S
C	Carbon
CH_3	Methyl
CO_2	Carbon dioxide
CuFe	Copper iron
DNA	Deoxyribonucleic acid
EC	Emerging contaminant
H	Hydrogen
H_3PO_4	Phosphoric acid
IUPAC	International Union of Pure and Applied Chemisrty
KOH	Potassium hydroxide
N	Nitrogen
N_2	Nitrogen gas
O	Oxygen
PAH	Polycyclic aromatic hydrocarbon

PCB	Polychlorinated biphenyls
SEM	Scanning electron microscope
TGA	Thermogravimetric analyzer
TS	Tamarind seed
TSAC	Tamarind seed based activated carbon
UV-Vis	Ultraviolet-visible
$ZnCl_2$	Zinc chloride

KARBON TERAKTIF BERDASARKAN BIJI ASAM JAWA TERHASIL MELALUI LAPISAN CuFe UNTUK PENYINGKIRAN KAFEIN DARI LARUTAN AKUAS

ABSTRAK

Kafein merupakan bahan cemar yang terdapat dalam sisa air. Dalam kajian ini, karbon teraktif berdasarkan biji asam jawa (KTBAJ) yang diubah suai oleh lapisan CuFe melalui pemanasan gelombang mikro di bawah aliran gas karbon dioksida telah dihasilkan untuk penjerapan kafein dari larutan akuas. Pencirian KTBAJ dilaksanakan dari segi morfologi permukaan, analisis unsur dan analisis prosimat. Selain itu, kajian isoterma juga telah dijalankan pada nisbah impregnasi (IR) yang berbeza. KTBAJ dihasilkan daripada sisa tani biji asam jawa melalui pengaktifan pemanasan dengan gelombang mikro disertai dengan aliran gas CO_2. KTBAJ yang terhasil turut dijayakan dalam pembuangan kafein dengan kapasiti penjerapan lapisan tunggal Langmuir yang membawa angka 214.25 mg/g. Luas permukaan BET yang agak tinggi diperoleh untuk KTBAJ ialah 498.53 m^2/g serta diameter liang ialah 2.19 nm. Di samping itu, penjerapan kafein pada KTBAJ meningkat apabila IR CuFe turut meningkat. Tambahan pula, nilai optimum IR didapati 1.50 dengan pengambilan kafein 65.48 mg/g dan peratusan pembuangan 69.84%. Seterusnya, kajian isoterma turut membongkar bahawa penjerapan kafein pada KTBAJ telah mematuhi model Freudlich. Hal ini demikian, menandakan liputan berbilang lapisan dan penguasaan penjerapan fizikal.

TAMARIND SEED BASED ACTIVATED CARBON PREPARED VIA CuFe LAYERED FOR CAFFEINE REMOVAL FROM AQUEOUS SOLUTION

ABSTRACT

Caffeine is an emerging contaminant in wastewater. In this study, tamarind seed based activated carbon (TSAC) modified by CuFe layered via microwave heating under the flow of carbon dioxide gas was produced for adsorption of caffeine from aqueous solution. Characterization of TSAC was conducted in terms of surface morphology, elemental analysis and proximate analysis. Besides, isotherm study was also carried out at different impregnation ratio (IR). TSAC was synthesized from agrowaste of tamarind seed through microwave heating activation under the flow of CO_2 gas. Resulted TSAC was also succeeded in caffeine removal with Langmuir monolayer adsorption capacity of 214.25 mg/g. Relatively high BET surface area obtained for TSAC was 498.53 m^2/g and the pore diameter was 2.19 nm. Furthermore, adsorption of caffeine onto TSAC increased when IR of CuFe increased. In addition, the optimum IR value was found to be 1.50 with caffeine uptakes of 65.48 mg/g and percentage removal of 69.84%. Moreover, isotherm study also revealed that adsorption of caffein onto TSAC followed Freundlich model. This signifies multilayer coverage and the dominance of physisorption.

CHAPTER ONE

INTRODUCTION

1.1 Emerging contaminants (ECs)

Rapid industrial development in various sector has been causing wide range of pollutants to enter the environment through wastewater. These pollutants include dyes (methylene blue, malachite green, Remazol brilliant blue R and metanil yellow) (Aichour et al., 2022), heavy metals (zinc, lead and cadmium) (Dey et al., 2021), organic contaminants which include polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and brominated organic compounds, pharmaceutical and endocrine disruptor substances. Apart from these well-established groups of pollutants, the world is facing with another class of contaminant, known as emerging contaminants (ECs). By definition, ECs are organic and inorganic contaminants that originated from substances that are not regulated yet or just been regulated recently, but posing a serious threat to the environment and human health (Cundy et al., 2022). Some examples of ECs are personal care products residues, pharmaceuticals residues, perfluoroalkyl compounds, plasticizers such as bisphenol-A (BPA) and bisphenol-S (BPS), pesticides and so on. The residues of these contaminants are moving from one destination to another via many ways such as ineffective wastewater treatment work, recycling process of e-wastes, hospital and pharmaceutical centres and run-off from agricultural land (Richardson and Ternes, 2018). Although the existence of ECs in water are usually low (0.001 ppm), their exposure towards organism have been reported to cause biological disruption and generational effects (Chen et al., 2018, Thomas et al., 2018). Over time, persistence ECs can accumulate to cause harmful effects toward human and aquatic creatures (Snow et al., 2017).

1.2 Caffeine

Caffeine or also known as 1,3,7-trimethylxanthine is an alkaloid that comes from methylxanthine family and has been classified as ECs due to its function as a stimulant and biological marker for pollution discovery (Li et al., 2020). Although caffeine is popular with coffee, this substance can be found at other plants as well such as tea leaves and cocoa fruit. In fact, large amount of caffeine is accumulated at the seeds, leaves and fruits section where they act as a natural pesticides to paralyze and kill insects that feed on these plants (Junior et al., 2020). Caffeine can prevent human from being sleepy because caffeine is able to stimulate the central nervous system of human which momentarily putting off the drowsiness effect. In some studies, moderate consumption of caffeine in human for years might causing a mild positive effect towards certain diseases namely Parkinson, heart disease and certain cancers (Bandookwala et al., 2019). Accumulation of caffeine in environment is caused by the fact that human excretes un-degraded caffein and other compounds such as theophylline, paraxanthine and trimethyluric acid through urine, besides the microorganisms in wastewater are not effective in metabolizing caffeine (Junior et al., 2020). The existence of caffeine in water bodies can be harmful towards aquatic creatures and ecosystem due to its stability towards degradation. At high concentration, caffeine can cause irritability, mutation effects such as inhibition of DNA, tremors, anxiety (Zhang et al., 2011), bone mass loss through calcium mobilization from cells and a risk factor for cardiovascular diseases (Ali et al., 2012, Torres, 2014). Some studies also revealed that caffeine at moderate level can reduce fine motor coordination and sleep disorder like insomnia (Aly, 2013, Habibi et al., 2012).

1.3 Problem statements

The existence of caffein in water bodies can cause many health issues towards human and aquatic animals. Besides that, caffeine is not biodegradable and unable to be catalysed by microorganism. Therefore, an attempt was made in this study to remove caffeine from aqueous solution via adsorption process using activated carbon (AC).

AC is known to be effective in removing many pollutants. However, commercially available AC is expensive since it is derived from non-renewables resources such as bituminous coal. Therefore, an attempt was made in this study to produce AC from agricultural waste of tamarind seed.

The performance of AC in adsorbing pollutant can be limited by many factors including pores sizes, surface area and surface chemistry. To enhance the adsorption performance even further, CuFe is added as a layer to the AC.

Conventional heating process to activate the precursor of AC is very time consuming and energy extensive. Therefore, microwave irradiation technique was employed to save activation time, activation power and gas used.

1.4 Research objectives

The objectives of this research are:

i) To convert tamarind seed into tamarind seed based activated carbon (TSAC) via chemical activation using CuFe to remove caffeine from aqueous solution.

ii) To characterize precursor and TSAC in terms of surface morphology, elemental analysis and proximate analysis.

iii) To study the effect of CuFe impregnation ratio (IR) onto caffeine uptakes and caffeine percentage removal.

iv) To conduct isotherm study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Adsorption process

Adsorption is defined as the process where a solid holds molecule of a gas or liquid to its surface as a thin film. The solid that holds the molecules is known as an adsorbent while the molecules that are held by the adsorbent are known as an adsorbate. Adsorption is one of the methods of chemical separation. There are diverse applications that use adsorption to separate the chemical substances. There are many types of adsorbents used in adsorption process such as zeolite, char, bio-sorbent, activated carbon (AC) and so on. Adsorption process comprises of three steps. The first step occurs when adsorbate molecules move from the bulk phase to the adsorbent's external surface. The second step involves the transport of adsorbate molecules to the inside of adsorbent. The last step is the sorption process where the process can be either physical adsorption (physisorption) or chemical adsorption (chemisorption). Figure 2.1 shows the adsorption of adsorbate molecules onto adsorbent while Figure 2.2 shows the image for physisorption versus chemisorption. Physisorption is relatively weak as compared to chemisorption and involved Van der Waals force. On contrary, chemisorption is irreversible, stronger and involves electron sharing (covalent bond) or electron exchanged (ionic bond).

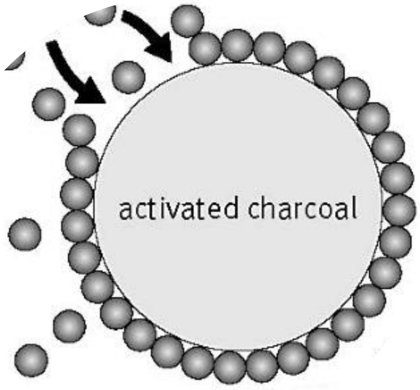


Figure 2.1 Adsorption of adsorbate molecules onto adsorbent (AC)

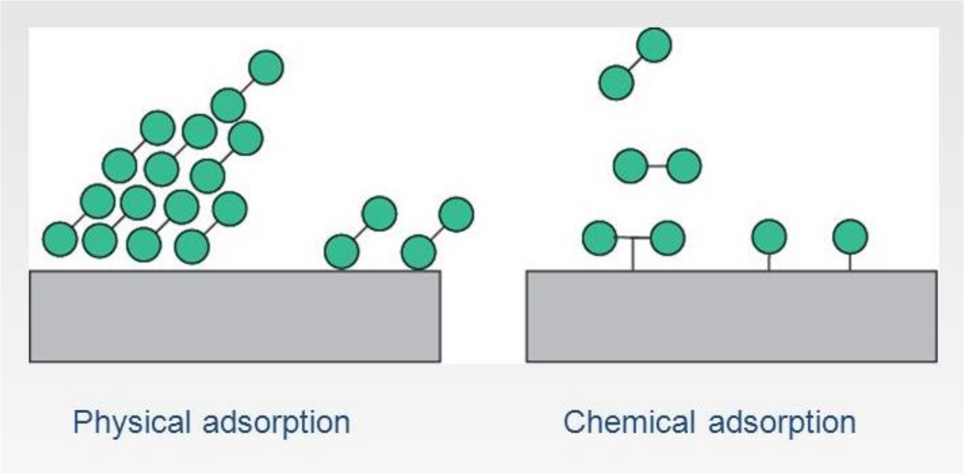


Figure 2.2 Physical adsorption and chemical adsorption

2.2 Activated carbon

AC is a type of adsorbent that can be characterized from its highly porous nature and tremendously high in surface area (>500 g/m^2). Therefore, numerous active sites are available inside the pores AC to enable adsorption process to happen. International Union of Pure and Applied Chemisrty (IUPAC) has been classified pores into three main groups namely micropores, mesopores and macropores which corresponded to pore size below 2 nm, pore size between 2 to 50 nm and pore size above 50 nm, respectively, as shown in Figure 2.3.

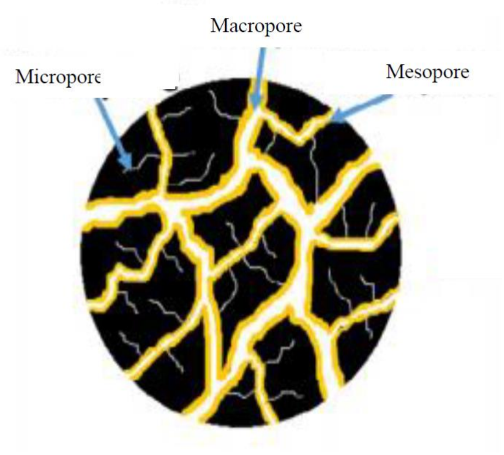


Figure 2.3	Types of pores inside adsorbent

Adsorption process using AC can be regarded as a superior method as compared to other methods such as oxidation, catalytic degradation and biodegradation due to low efficiency, long process and high operating cost (Khanday et al., 2017a, Khanday et al., 2017b). Besides relatively simple in design, AC was proven to be effective in treating many types of pollutants including dyes (Aichour et al., 2022, Soh et al., 2022, Gao et al., 2021), heavy metals (Yusop et al., 2022, Mandal et al., 2021), antibiotics (Khanday et al., 2019), pesticide (Aziz et al., 2021), ECs (Kozyatnyk et al., 2021) and others. Unfortunately, the production of AC is limited by expensive non-renewables feedstocks such as petroleum coke and bituminous coal. Due to this, many researchers have been producing AC from renewable sources, mostly from agricultural wastes such as coconut shell (Yusop et al., 2022), date palm bark (Haghbin and Niknam Shahrak, 2021), Alpinia galanga stem (Ahammad et al., 2021), peanut shell (Ahmad et al., 2021), date stone (Jabbar, 2020), date pits (Mohammed et al., 2018) and others.

2.3 Tamarind seed

Tamarind seed (TS) obtained from *Tamarindus indica* is a leguminous tree from the family of *Fabaceae* and native to tropical Africa. Tamarind trees yield edible pod-like fruit that is widely utilised. The tamarind tree is a slow-growing, long-lived, enormous tree that may reach heights of 80 or even 100 feet (24-30 metres) under ideal conditions, with a spread of 40 feet (12 metres) and a trunk circumference of 25 feet (7.5 m). It has dark-gray, rough, fissured bark and is exceptionally wind-resistant, with robust, elastic limbs that gently droop at the ends. The leaves are typically evergreen, but during the hot season, they may be lost short in extremely dry places. TS contains nutrients such as protein and it is rich in many essential amino acids such as isoleucine, leucine, lycine, methionine, phenylalanin and valine. It also composes of lipids which are a good source of essential fatty acids and has a high number of polysaccharides. Other than that, the seed has high content of minerals such as calcium, phosphorus, magnesium and potassium (Bagul et al., 2015). For so long, TS has been always considered as agricultural waste, but recent discoveries had found some medical drug applications, preparing gum and bio-nanocomposites for bone tissue engineering (Eriki Ananda et al., 2019). However, utilization of TS in medical field is still a long way to go. Most of TS is dispose in the environment, therefore, by converting it into AC, it will add some value to this agricultural waste. Figure 2.4(a) and (b) show the image of tamarind fruit and tamarind seed respectively.

(a)

(b)

Figure 2.4 (a) Tamarind fruit and (b) tamarind seed

2.4 Methods of preparing AC

The production of AC starts with a carbonization step and followed by activation process. Carbonization step is to prepare the precursor into becoming a material that is high in carbon content. This can be achieved via heat treatment under inert gas or also known as a pyrolysis process (Gao et al., 2020). The products generated from this pyrolysis process includes moisture, volatile matter which comprised of lignin, cellulose and hemi-cellulose, tar compound and few gases. At the end of carbonization process, precursor will be transformed into char. Char was found to be effective to treat many pollutants in various studies such as dental clinic pollutant adsorption by bone char (Elvir-Padilla et al., 2022), 17-α-ethinylestradiol adsorption by plastic waste char (Lai et al., 2022), carbon dioxide, CO_2 adsorption by biomass-activated char (Goel et al., 2021), aquatic pollutants by bone chars (Yang et al., 2022), methylene blue dye by activated char (Hu et al., 2021), dichloromethane and toluene adsorption by bio-char (Pi et al., 2021) and so on. However, the pores development inside char is not at the optimum level, therefore the real potential of char can be further enhanced via activation process.

Activation process is a process to convert char into a material that is extremely high in porosity, high in surface area and posing functional groups in its surface. This material is better known as AC. Activation process can be conducted via three ways namely physical activation, chemical activation and physicochemical activation. In physical activation, char is subjected with a subsequent heat treatment under the flow of activating gas such as steam, CO_2 or combination of both at activation temperature between 800 to 1000 °C (Zaini et al., 2021, Ma et al., 2020, Pallarés et al., 2018). Physical activation is desired by researchers because there is no need to use any chemicals. However, physical activation requires higher activation temperature as compared to chemical treatment. In chemical treatment, the char is impregnated with chemicals such as potassium hydroxide, KOH, phosphoric acid, H_3PO_4, zinc chloride, $ZnCl_2$ and so forth (Mbarki et al., 2022). Chemical and char will be impregnated between 8 hours to 24 hours before being heated at moderate temperature between 400 and 600 °C under inert gas of nitrogen, N_2. In a physicochemical activation, both physical and chemical approached were combined and the resulted AC will have a better pores characteristic. The physicochemical activation is relatively more expensive and consume more resources.

2.5 Adsorption study

Under equilibrium study, the effect of IR was verified towards the caffeine uptakes and caffeine percentage removal. 0.2 g of prepared TSAC was added into 200 mL of caffein solution with a concentration of 50 mg/L. After 24 hours, a sample of caffein solution was withdrawn to measure its concentration using UV-Vis spectrometer. The amount of caffein adsorbed by TSAC at equilibrium was determined from the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where qe, Co, Ce, V and m are caffein uptakes at equilibrium (mg/g), initial concentration of caffein (mg/L), equilibrium concentration of caffein (mg/L), volume of solution (mL) and mass of TSAC used (g). On contrary, the percentage removal of caffeine is calculated as follows:

$$Removal\ (\%) = \frac{(C_o - C_e)}{C_e} \times 100\% \tag{2}$$

2.6 Adsorption isotherm

Adsorption isotherm is important to describe the relationship between adsorbate molecules in the bulk phase with adsorbate molecules in solid phases a function of pressure (or concentration) at a constant temperature (Karri and Sahu, 2018). Adsorption isotherms give researchers and engineers useful estimation data under various operating conditions that may be used for the design, optimization, and troubleshooting of an adsorption process (Mozaffari Majd et al., 2022). Two most popular isotherm models are Langmuir and Freundlich.

2.6.1 Langmuir isotherm

The most widely employed isotherm model is Langmuir. This model assumes monolayer coverage on homogenous surface of adsorbent. Langmuir is usually associated with chemisorption where one active site can hold one adsorbate molecule only, thus explaining the monolayer coverage. The equation for this isotherm model is given as follows:

Langmuir (Langmuir, 1918):

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where Q_m is maximum adsorption capacity (mg/g) and K_L is the constant of Langmuir.

2.6.2 Freundlich isotherm

Contradicted to Langmuir isotherm, Freundlich model assumes multilayer coverage on a heterogenous surface of adsorbent which associated with physisorption where one active sites can holds more than one adsorbate molecules. The equation for this isotherm model is given as follows:

Freundlich (Freundlich, 1906):

$$q_e = K_F C_e^{1/n_F} \tag{4}$$

where K_F and n_F are constants of Freundlich. The correlation coefficient, R^2 generated by these isotherms were compared to determine which isotherm represents the adsorption system the best.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The precursor used in this study which is TS was collected from a nearby local market in Nibong Tebal, Pulau Pinang. Upon receiving it, TS was washed thoroughly with tap water before being dried in an oven for 24 hours at 110 °C. The chemicals used in this study were caffeine, iron(III) nitrate nonahydrate and copper (II) nitrate trihydrate which were purchased from Sigma Aldrich Sdn. Bhd. Activating gas of carbon dioxide, CO_2 gas (99.80%) was obtained from Air Product, Malaysia. Deionized water was utilized in the preparation of caffeine solution. Figure 3.1 shows the molecular structure of caffeine and Table 1 shows the physical and chemical properties of caffeine.

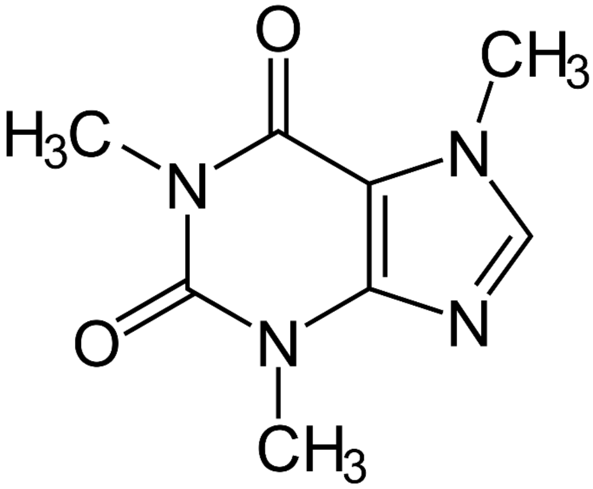


Figure 3.1 Molecular structure of caffeine

Table 3.1 Physical and chemical properties of caffeine

Physical properties	
Physical form	Odourless white powder
Colour	White, prismatic crystals
Odor	Odorless
Taste	Bitter taste
Boiling point	177.78 °F at 760 mm Hg
Melting point	237.78 °F
Solubility	2.17 g/100mL
Desity	1.23 g/cm^3

Chemical properties	
Molecular formula	$C_8H_{10}N_4O_2$
Molecular weight	194.19 g/mol

3.2 Preparation of TSAC

The obtained TS was subjected with carbonization process. The schematic diagram of the char preparation unit is given in Figure 3.2. A 50 g of TS was inserted inside the tubular cylinder and then, loaded inside the vertical furnace. Then, the temperature was increased to 500 °C and hold for 1 hour under the flow of N_2 gas at a flowrate of 150 cm^3/min. Once the carbonization process was done, the sample was let to cool down to room temperature under the flow of N_2 gas. The sample now was called char. The chemical mixture, W_{chem} consisting of 1.0 g iron(III) nitrate nanohydrate was added to 0.5 g, 1.0 g and 1.5 g of copper(II) nitrate. Then, the char was impregnated with the chemical mixture at impregnation ratio of 0.5, 1.0 and 1.5 by using the formula as follows:

$$\frac{W_{chem}}{W_{char}} \tag{5}$$

where Wchem and Wchar are the mass of chemicals (g) and the mass of char (g), respectively.

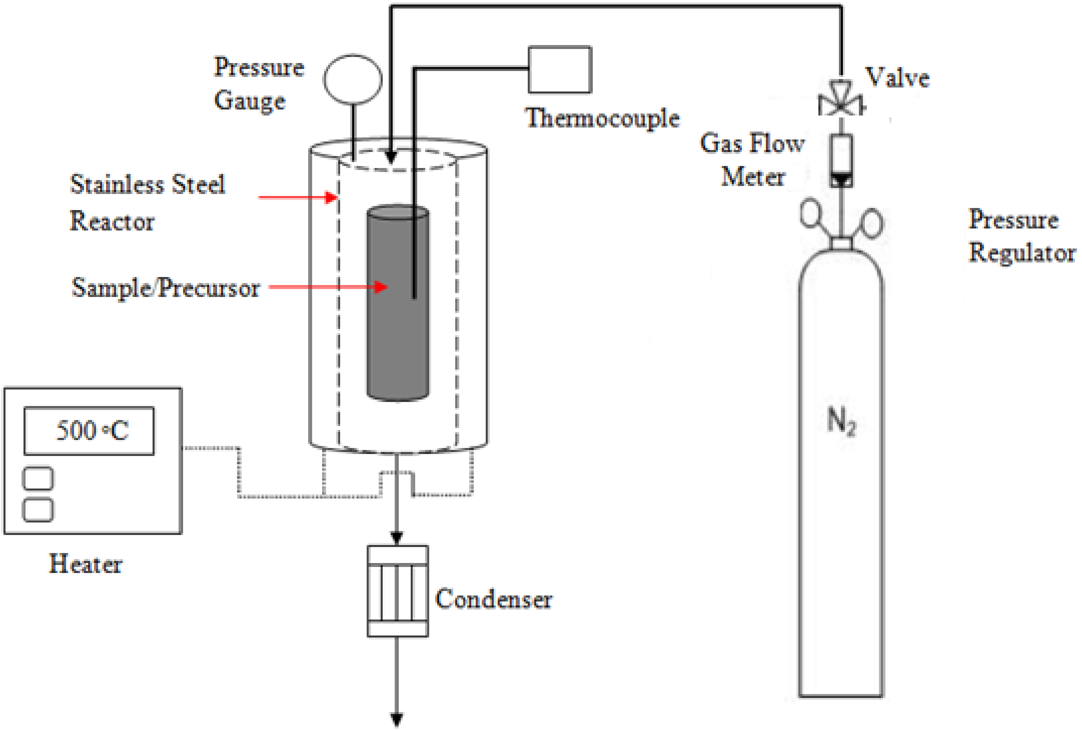


Figure 3.2 Schematic diagram of char preparation unit

The char was impregnated with chemicals for 24 hours inside oven at 110 °C. After that, the impregnated char was heated using modified microwave at radiation power and radiation time of 616 W and 20 minutes, respectively, under the flow of CO_2 gas at 150 cm^3/min. The schematic diagram for microwave irradiation technique is given in Figure 3.3. Once activation process is done, the resulted sample was known as tamarind seed-based AC, TSAC. The yield of TSAC can be calculated from the following formula:

$$Yield\ (\%) = \frac{m_{TSAC}}{m_{TS}} \tag{6}$$

where m_{TSAC} and m_{TS} are mass of dry TSAC and TS, respectively. TSAC was kept inside air-tight container to be used for characterization and adsorption studies.

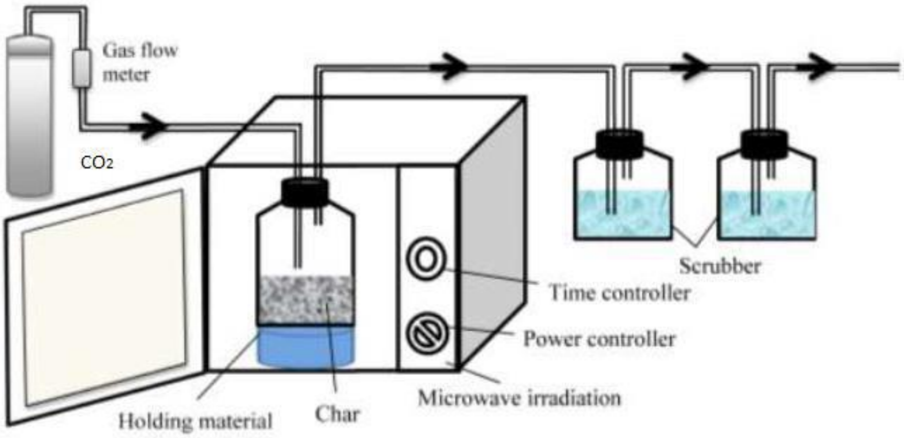


Figure 3.3 Schematic diagram for microwave irradiation technique

3.3 Batch adsorption and analysis system

200 mL of caffein solution with a concentration of 50 mg/L was prepared inside 250 ml conical flask and then, 0.2g of TSAC was added inside it. The conical flask was assembled inside water bath shaker. The solution temperature and shaking speed of the water bath shaker were set to be 30 °C and 80 rpm, respectively. The concentration of adsorbate under investigation was measured using a double beam UV-Visible spectrometer (Model Shimadzu UV-1800, Japan). The wavelength of caffeine was set to be 272 nm.

3.4 Preparation of caffein solution

The preparation of caffein solution starts with preparation of caffein stock solution. Accurately 1.00 g of caffeine was weighted and then was dissolved in a 1000 mL of deionized water inside volumetric flask. The resulted caffeine stock solution was 1000 mg/L. For equilibrium and isotherm studies, the concentration of caffeine used was 50 mg/L. Therefore, the stock solution was diluted by using the following formula:

$$M_1V_1 = M_2V_2 \tag{7}$$

where M_1 and M_2 are concentration of stock solution and desired solution, respectively, whereas V_1 and V_2 are volume of stock solution and desired solution, respectively.

3.5 Characterization system

Characterization of the samples were made in terms of surface area, surface morphology, elemental analysis and proximate analysis.

Surface area developed inside AC provides the necessary spaces or sites for adsorption process to occur. The surface area together with pore volume and average pore diameter of the samples were quantified by using Micromeritics ASAP 2020 volumetric adsorption analyser. The analysis was conducted based on the adsorption of N_2 gas at the temperature of 77K. The isotherm model of Brunauer-Emmet-Teller (BET) was employed to calculate the surface area whereas total pore volume was determined by estimating it to be a liquid volume of N_2 at relative pressure of 0.99.

The surface morphology of samples was inspected using a scanning electron microscope (SEM) (Quanta 450 FEG, Netherland). The samples were attached to a plate before being layered with a thin layer of gold for electron reflection using Polaron Division Bio-RAD SEM sputter coater. The magnification level is between 500 – 4000x.

Last but not least, ultimate analysis was carried out by using elemental analyzer (Perkin Elmer 2400 Series II CHNS/O) whereas proximate analysis was performed by using thermogravimetric analyzer (TGA) (Perkin Elmer STA 6000, USA). Ultimate analysis revealed the elemental composition of the samples whilst proximate analysis determined the composition of moisture, volatile matter, fixed carbon and ash content of the samples.

3.6 Overall experimental activities

Figure 3.4 shows the overall experimental activities.

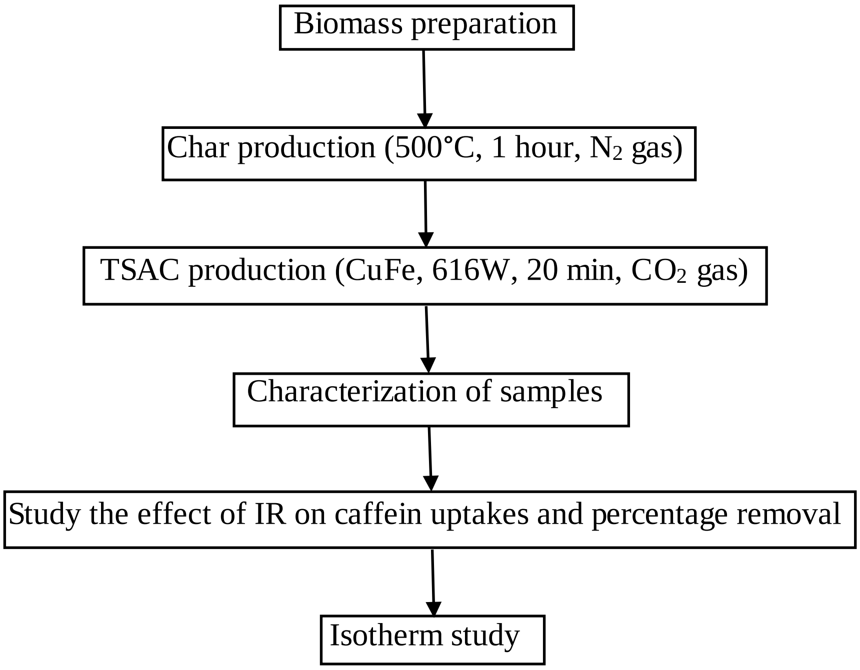


Figure 3.4 Overall experimental activities

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characteristics of samples

The characteristics of TSAC and precursor were characterized in terms of surface area and pore characteristics, SEM images, ultimate and proximate analysis.

4.1.1 Surface area and pore characteristics

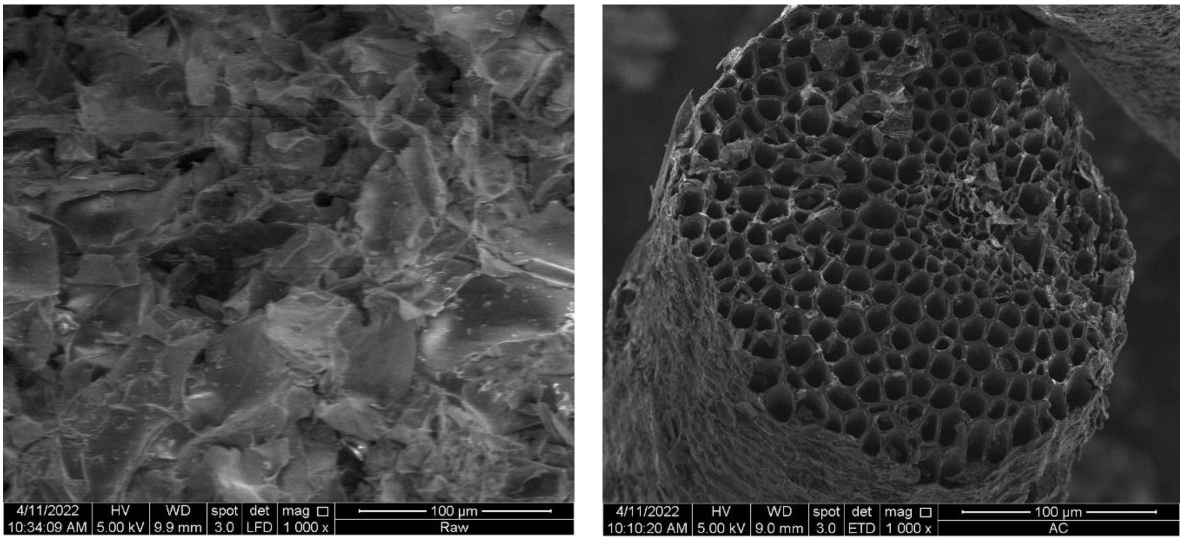
The surface area and pore characteristics for samples are given in Table 4.1. It was found that BET surface area of TS increased from 1.52 m^2/g to 125.42 m^2/g after carbonization process took place. The heat treatment from carbonization process promotes the thermal degradation process which removes moisture and volatile components in TS. As a result, these components evaporated and leave the sample, providing the necessary space for pores network to form. After chemical activation with CuFe and microwave heating, the BET surface of TSAC increased tremendously to 498.53 m^2/g from 125.42 m^2/g in TS char. Microwave irradiation technique further enhancing the thermal degradation process especially polar volatile compounds such as moisture, cellulose and lignin in TS char. On the other hand, the metals of CuFe moves freely to penetrate deep into the skeleton of TS char, thus causing more pores to be developed. Both thermal degradation and CuFe penetration contributed to the increment of total pore volume from 0.06 cm^3/g in TS char to 0.37 cm^3/g in TSAC and an increment in average pore diameter from 2.11 nm in TS char to 2.19 nm in TSAC. Based on IUPAC classification, the pores in TSAC belongs to the mesopores region which is suitable for water treatment applications.

Table 4.1 Surface area and pore characteristics of samples

	BET surface area (m^2/g)	**Total pore volume (cm^3/g)**	**Average pore diameter (nm)**
Tamarind seed, TS	1.52	-	-
TS char	125.42	0.06	2.11
TSAC	498.53	0.37	2.19

4.1.2 Surface morphology

The SEM image is given in Figure 4.1(a) and (b) for TS and TSAC, respectively. It can be seen that the surface of TS was rough with no pores can be detected. On contrary, the surface of TSAC was spotted to be filled with numerous pores. These pores were once filled with moisture together volatile matter such as lignin, cellulose and hemicellulose. Then, these components evaporated due to heat treatment during carbonization and microwave heating during activation. Penetration of CuFe also improved the pores development in TSAC.



(a) (b)

Figure 4.1 SEM images for (a) TS and (b) TSAC with 1000x magnification

4.1.3 Elemental and proximate analysis

The elemental and proximate analysis for TS and TSAC is given in Table 4.2. It was found that the C, N, H and O elements of TS were 50.20, 33.85, 2.45 and 13.50%, respectively. These values were comparable with elemental analysis on TS made by Ramesh et al. (2015) where C, N, O and H elements were found to be 51.70, 35.50, 12.40 and 0%, respectively. It was found that C element and fixed carbon percentage rose significantly from 50.20 to 66.85% and from 31.26 to 60.92%, respectively, after carbonization and microwave activation took place. Conversely, as expected, the volatile matter and moisture percentages dropped significantly from 55.04 to 31.98% and 10.30 to 5.12%, respectively from TS to TSAC. High increment in fixed carbon percentage and significant reduction in volatile matter and moisture percentage of TSAC proved the effectiveness of carbonization and activation steps employed in this study. High fixed carbon percentage was desired as it made up the skeleton of carbon matrix of TSAC whereas low ash was desired since ash contains no pores and playing no roles in adsorption process.

Table 4.2 Elemental and proximate analysis of the samples

	Elemental analysis (%)				**Proximate analysis (%)**			
	C	**N**	**H**	**O**	**Moisture**	**Volatile matter**	**Fixed carbon**	**Ash**
TS	50.20	33.85	2.45	13.50	10.30	55.04	31.26	3.40
TS char	55.42	31.52	-	13.06	5.53	40.40	51.92	2.15
TSAC	66.85	27.86	-	7.77	5.12	31.98	60.92	1.98

4.2 Adsorption study – effect of IR

Figures 4.2 and 4.3 show the plots of adsorption capacity and percentage removal for caffeine-TSAC adsorption system at 30 °C, respectively. It was found that both caffeine uptakes and caffeine percentage removal increased from 56.19 to 65.48 mg/g and from 60.86 to 69.84%, respectively, when the IR of CuFe increased from 0.50 g/g to 1.50 g/g. At higher

IR, more metals of CuFe were available to penetrate the skeleton matrix of TSAC at higher intensity. As the result, more pores were developed, hence, providing more active sites to be occupied by caffein molecules. Consequently, adsorption capacity and percentage removal of caffeine by TSAC were increased.

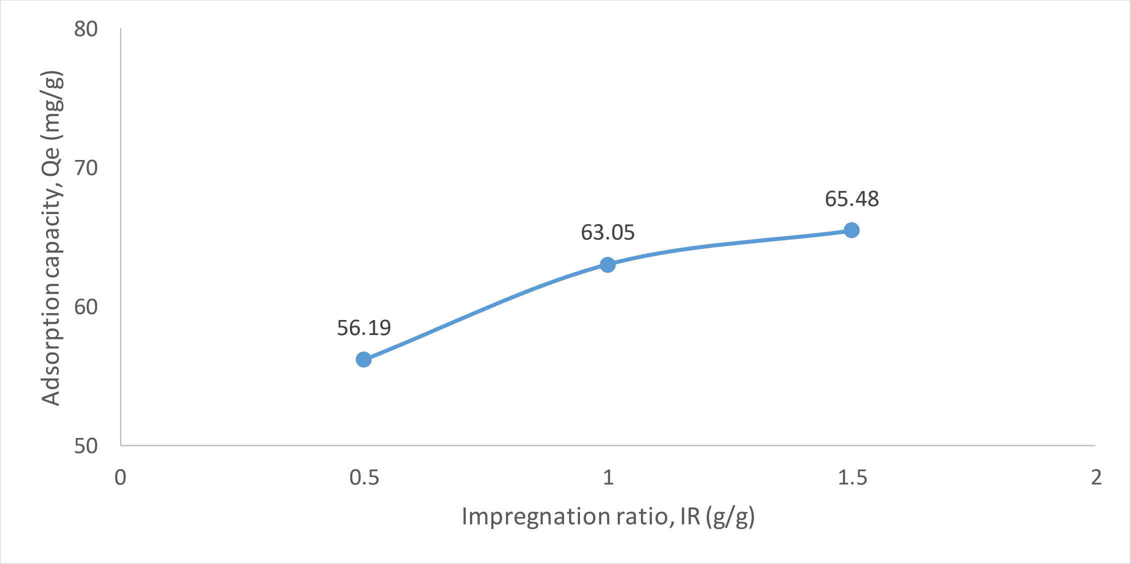


Figure 4.2 Plot of adsorption capacity of caffeine by TSAC versus IR at 30 °C

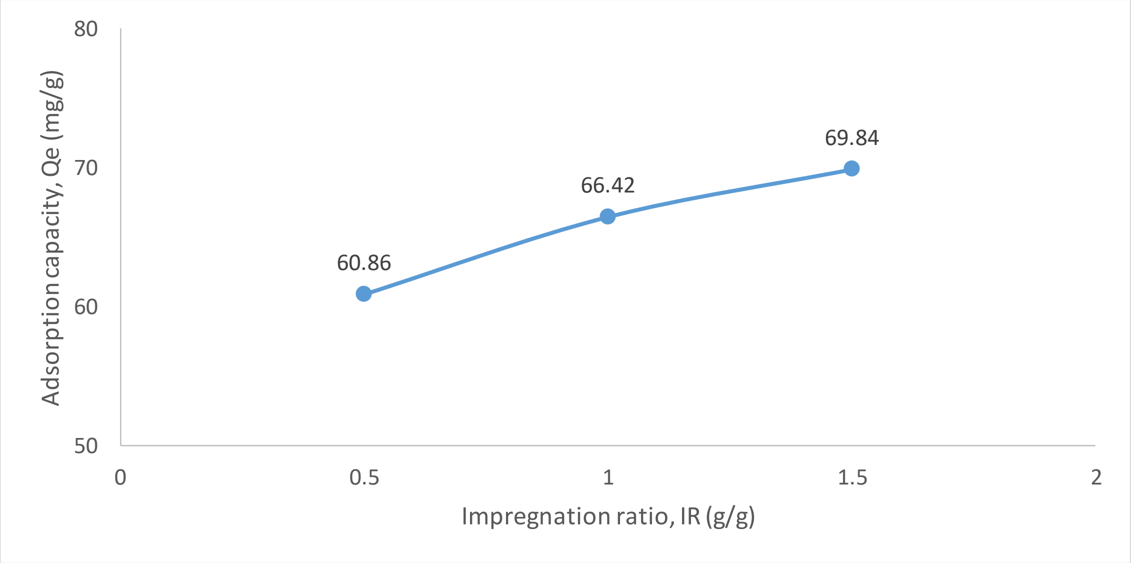


Figure 4.3 Plot of percentage removal of caffeine by TSAC versus IR at 30 °C

4.3 Isotherm study

Figure 4.4 shows the isotherm plot for Langmuir and Freundlich isotherms whilst Table 4.3 summarized the isotherm parameters obtained in this study. Both Langmuir and Freundlich models were found to produce high R^2 value of 0.9997 and 0.9991, respectively. However, caffeine adsorption onto TSAC can be concluded to follow Freundlich due to its lower RMSE and average error percentage of 4.93 and 7.39%. Therefore, it signified that caffein molecules formed a multilayer coverage on TSAC with main forces were contributed by physisorption. The Langmuir monolayer adsorption capacity, Qm was found to be 214.25 mg/g. This adsorption process was confirmed to be favourable since n value is between 1 to 10 (Yusop et al., 2022).

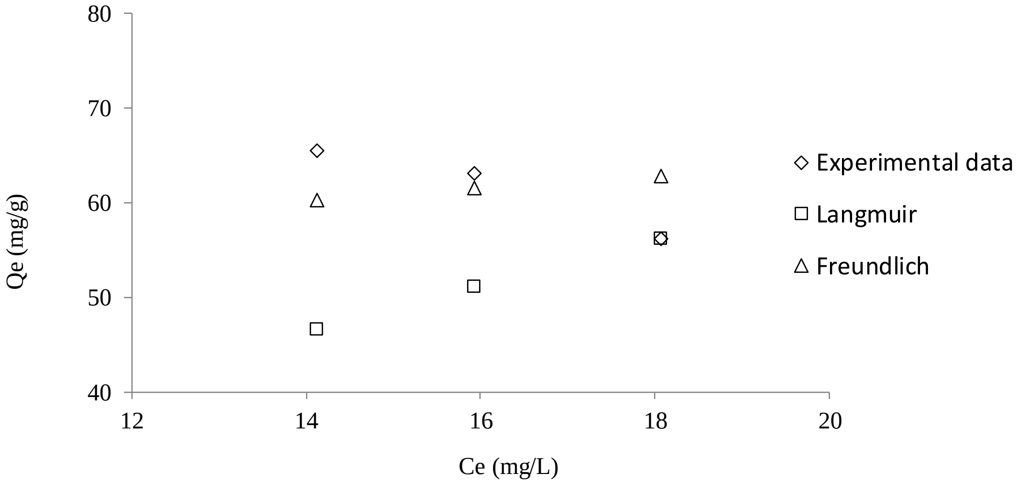


Figure 4.4 Isotherm plots for caffeine-TSAC adsorption system at 30 °C

Table 4.3 Summary of isotherm parameters

	Langmuir		Freundlich
Q_m	214.25	**K_L**	38.77
K_L	0.020	**n**	6.00
RMSE	12.88	**RMSE**	4.93
Average error (%)	15.90	**Average error (%)**	7.39
R^2	0.9997	**R^2**	0.9991

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The findings of this research are as follows:

i) TSAC was successfully synthesized from agrowaste of tamarind seed by employing CuFe activation coupled with microwave heating activation under the flow of CO_2 gas. Resulted TSAC was succeeded in removing caffeine with Langmuir monolayer adsorption capacity of 214.25 mg/g.

ii) Relatively high BET surface area was obtained for TSAC of 498.53 m^2/g and pore diameter of 2.19 nm.

iii) Adsorption of caffeine onto TSAC increased when IR of CuFe increased. The optimum IR value was found to be 1.50 with caffein uptakes and percentage removal of 65.48 mg/g and 69.84%, respectively.

iv) Isotherm study revealed that adsorption of caffein onto TSAC followed Freundlich model which signifies multilayer coverage and the dominance of physisorption.

5.2 Recommendations:

Some recommendations for the future works are as follows:

i) To conduct equilibrium study in terms of initial concentration effect, temperature effect and solution pH effect.

ii) To conduct kinetic and thermodynamic studies.

iii) To study the regeneration of TSAC.

iv) To test the adsorption performance of TSAC using different adsorbates.

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