HYDROTHERMAL CARBONIZATION OF COCONUT HUSK AS AN ADSORBENT FOR THE REMOVAL OF CHLORAMPHENICOL COMPOUNDS

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by

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List of Abbreviations

AC	Activated carbon
BET	Brunauer–Emmett–Teller
CAP	Chloramphenicol
CHAC	Coconut husk activated carbon
CV	Crystal violet
FTIR	Fourier-transform infrared spectroscopy
HTC	Hydrothermal carbonization
PAC	Powdered activated carbon
PFO	Pseudo first order
PSO	Pseudo second order
RCH	Raw coconut husk
SEM	Scanning electron microscopy
TO	Typha orientalis
UV-vis	Ultraviolet-visible

Table of Contents

List of Tables

List of Figures

KARBONISASI HIDROTERMA SABUT KELAPA SEBAGAI PENYERAP UNTUK PENYINGKIRAN SEBATIAN KLORAMFENIKOL

Abstrak

Pencemaran air yang disebabkan oleh penggunaan bahan-bahan farmaseutikal secara berlebihan kini menjadi isu yang membimbangkan kerana ia berisiko memberikan komplikasi yang boleh mengancam keselamatan alam sekitar dan kesihatan awam. Dalam konteks ini, rawatan air kumbahan yang tidak efektif bagi air yang mengandungi sebatian kloramfenicol (CAP) sebelum pelepasannya telah menjadi isu yang serius, kerana pengumpulan CAP mungkin menjadi ancaman serius kepada orang ramai dan hidupan akuatik. Kajian ini mencadangkan penggunaan karbon teraktif daripada sabut kelapa (CHAC) yang disediakan melalui pengkarbonan hidroterma dan pengaktifan $ZnCl_2$ untuk penyingkiran sebatian CAP daripada campuran air. Kecekapan CHAC yang disediakan telah dinilai berdasarkan beberapa faktor utama yang berbeza seperti pH larutan (3, 5, 7, 9 dan 11) dan kepekatan awal larutan CAP (100 mg/L, 200 mg/L, 300 mg/L dan 400 mg/L), dimana hasil kajian menunjukkan penyingkiran CAP tertinggi sebanyak 99.99% pada kepekatan 200 mg/L dan pH optimum 9. Penjerapan CAP pada permukaan CHAC paling baik ditakrifkan oleh isoterma Langmuir ($R^2 = 0.9999$) yang dikaitkan dengan lapisan tunggal kapasiti penjerapan, q_{max} sebanyak 263.158 mg/g. Kajian kinetik penjerapan juga mendedahkan bahawa sistem penjerapan yang dibentangkan dalam kajian ini paling sesuai dengan model kinetik pseudo second order (PSO). Prestasi CHAC yang luar biasa pada penyingkiran CAP sepadan dengan luas permukaan BET dan isipadu liang sebanyak 740.7451 m^2/g dan 0.2476 cm^3/g. Penemuan yang diperoleh daripada kajian ini mencadangkan bahawa CHAC mempunyai prestasi penjerapan dan ciri-ciri yang sangat baik, dan ia juga boleh dilaksanakan dari segi ekonomi kerana kapasiti penjerapan yang tinggi, kos pengeluaran yang lebih rendah dan mesra alam.

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Abstract

The contamination of water caused by the extensive use of pharmaceutical components has become a concerning matter as it brings about a lot of complications that are threatening environmental safety and public health. In this case, the improper treatment of Chloramphenicol (CAP) compounds prior to its discharge has become a serious issue, as the buildup of CAP may become a serious threat to the public and aquatic lives. This study suggests the utilization of coconut husk-derived activated carbon (CHAC) prepared via hydrothermal carbonization and $ZnCl_2$ activation for the effective removal of CAP compounds from a water mixture. The efficiency of the prepared CHAC were assesed at different key parameters such as solution pH (3, 5, 7, 9 and 11) and initial concentrations of CAP solution (100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L), in which the results exhibit the highest CAP removal of 99.99% at 200 mg/L with an optimum pH of 9. The adsorption of CAP on the surface of CHAC was best defined by the Langmuir isotherm ($R^2 = 0.9999$) which attributes to the monolayer adsorption capacity, q_{max} of 263.158 mg/g. The adsorption kinetic study also revealed that the adsorption system presented in this study fits pseudo second order (PSO) kinetic model the most. The remarkable CHAC performance on CAP removal corresponds to the BET surface area and pore volume of 740.7451 m^2/g and 0.2476 cm^3/g, respectively. The findings acquired from this study strongly suggest that CHAC has excellent adsorption performance and properties, and it is also economically feasible due to high adsorption capacity, lower production cost and environmentally friendly.

Chapter 1: Introduction

1.1 Project background

The use of Chloramphenicol (CAP) has significantly grown to a great extend, especially in the pharmaceutical industry, where it is not only used as a main ingredient for eye ointments and ear drops, but also for making mouthwashes, toothpastes, moisturizers and more (National Center for Biotechnology Information, 2021). CAP, which is also known as chloromycetin, is an antibiotic that possesses great antibacterial properties and was primarily obtained from a filamentous bacterium known as *Streptomyces venezuelae* in 1947 (Xia, et al., 2014). CAP contains three (3) functional groups that control its biological activity, namely p-NO_2 group, dichloroacetyl moiety group and a primary alcohol group located at carbon number 3 of a propanediol chain (Yunis, 1988). In medical uses, CAP prevents the growth of bacteria by attacking the bacterial chromosome. Since CAP is a lipid-soluble component, this allows it to easily permeate the bacterial cell membrane and bind to the protein structure of the bacterial chromosome, which consequently inhibits protein synthesis of the bacterial cell (Drugbank, 2021).

Although CAP is very useful, the extensive use of this antibiotic has now become a serious concern as it brings about numerous contamination issues in water environments. Generally, CAP and other pharmaceutical components are released to the environment via several pathways, including direct discharge from pharmaceutical production facilities, discharge of treated sewage effluent from a sewage treatment facility, the use of animal manure on agricultural lands, discharge of undesired pharmaceutical components and more (Mansour, et al., 2018). Even though the concentration of CAP is considerably low in wastewater, the build-up of this active component in water will eventually cause its carcinogenicity, mutagenicity, toxicity, and other ecological parameters to become significant and perturbing

(Mansour, et al., 2018). In addition, as the world's population continues to grow over time, the demand of clean water will grow just as much as well. Thus, complete purification of water has become crucial, following the standard guidelines for different water application, to fill up the needs of the growing population.

In the matter of removing antibiotic components from wastewater, the ultrafiltration membrane, electrocoagulation, adsorption and ozonation are several method options that have been widely used in numerous industries to perform the purification action. However, the adsorption method has been proven to be the simplest, inexpensive, and most versatile method to eliminate the contaminants (Aljeboree & Alshirifi, 2018). Referring to the adsorbent, activated carbon (AC) has been known to be the best adsorbent for adsorption processes due to its highly porous structure that enables it to capture a variable amount of contaminants or solutes from a mixture (Johnson, 2014). In general, the interactions between the AC and the adsorbed contaminants are formed via Van der Waals and induced dipole forces. When the molecules interact, they will stick together and form an induced dipole at the adsorption pores that will eventually cause them to precipitate out of the solution (Nowicki, 2016). However, some researchers have remarked some issues that raised from the use of an AC prepared from coal, with respect to the environment. The combustion of the materials to produce ACs is associated with the generation of carbon dioxide (CO_2), which is a primary greenhouse gas. Thus, a new alternative of preparing ACs from lignocellulosic biomasses or agricultural wastes is now being widely investigated and utilized as they are biodegradable, environmentally friendly, widely available, and inexpensive (Man, et al., 2015).

Coconut husk is a lignocellulosic biomass that is widely available, cheap, and biodegradable. It is actually a part of a coconut that made up of about 60% cellulose and lignin (Man, et al., 2015). In Malaysia, approximately 6,000 to 10,000 nuts per hectare are produced each year (Yun, 2019), whereas nearly 10 million hectares of nuts are produced worldwide by

92 different countries, with 75% of the production is contributed by Asian countries (Ahmad, et al., 2021). The growing demand of coconuts husk has greatly increased ever since 10-20 years ago, with 100-220 million coconut fruits being imported worldwide each year, especially during festive seasons (Yun, 2019).

As of 2015, the growing demand of coconut husk in Malaysia for numerous industrial applications has urged MARDI to produce a mechanical machine to separate coconut husk from the endocarp, which is sold for RM 25,000 per unit (Daily Express, 2015). The use of coconut husk as an AC allows the conversion of agricultural wastes into useful applications and reduce water pollutions. Although many studies have utilized different types of biomasses such as rice husk and empty oil palm fruit bunches in the manufacture of AC, coconut husk has been one of the most preferred options as it has numerous favourable characteristics, including high carbon content, great strength, lower ash content and high volatile content (Man, et al., 2015).

The preparation of biomass-derived ACs generally includes two-main steps, namely the carbonization and activation steps, respectively. An improved carbonization step known as hydrothermal carbonization (HTC) provides an improvement in the manufacture of ACs, whereby it involves carbonization of biomass component in water medium under an autogenous pressure, done in an autoclave. This method generally operates at a temperature between 180-250˚C, which is lower than the conventional carbonization method that operates at 500-1000˚C (MacDermid-Watts, et al., 2019). In addition, the drying requirement prior to treatment is also eliminated with the use of water medium in this process. The effectiveness of HTC is not only seen on the operating condition and process intensification aspects, but it is also observed in chemistry aspect, whereby this method has been proven to maintain the chemical functional groups of the biomass (Zhao, et al., 2010). Nonetheless, this method is still tied to a few limitations when it comes to widespread applications, including being inflexible due to high temperature and pressure requirements; thus, making it hard to integrate this method into a continuous HTC reactor, and also high energy requirement, especially to heat up water for the reaction (MacDermid-Watts, et al., 2019).

1.2 Problem Statement

The excessive use of CAP and improper post-treatments prior to its effluent discharge has become very concerning as the build-up of the residual CAP industrial water effluents will eventually cause their carcinogenicity, mutagenicity, toxicity, and other ecological parameters becomes more significant and worrying. As a way to solve this issue, the removal of CAP from wastewater is crucial to avoid the consequential risks that may arise from the build-up of this chemical. The use of biomass-derived ACs for the removal of antibiotics residuals in wastewater has been determined to be a promising alternative as it also contributes to the sustainability of the environment. The preparation of the coconut husk-derived AC via HTC, followed by chemical activation of hydrochar have been widely utilized by a lot of researchers due to lower operating conditions and excellent AC properties. Many research studies have presented the productivities of other biomass-derived activated carbon with $ZnCl_2$ activation such as coconut shell, bagasse, soybean dregs and more. Nonetheless, the study on the productivity of coconut husk-derived activated carbon with $ZnCl_2$ activation still lacks investigation for comparative analysis. Thus, this study aims to observe the efficiency of coconut husk-derived activated carbon with $ZnCl_2$ activation by observing its physicochemical properties and adsorption performance on the removal of CAP compounds from a water mixture.

1.3 Research Objectives

i. To prepare activated hydrochar from coconut husk via hydrothermal carbonization in the presence of $ZnCl_2$.

ii. To examine the physical and chemical properties including surface morphology of the prepared hydrochar using BET, SEM and FTIR.

iii. To investigate the capability of the prepared hydrochar on the removal of CAP at different pH of solution and initial concentration of CAP solution.

Chapter 2: Literature Review

2.1 Hydrothermal carbonization (HTC) of coconut husk

The HTC method has now been widely used in many industries as it brings about a lot of benefits over the conventional carbonization methods. HTC has been proven to be more economically and environmentally friendly, as it operates at lower conditions (between 180-250˚C), compared to pyrolysis and gasification that operates at greater conditions that range between 500-800˚C and 550-1600˚C, respectively (Walling, et al., 2019). In relation to the greater demand of operating conditions for both pyrolysis and gasification processes, this correlates with higher investment, operating and maintenance costs. Thus, with respect to the environmental and sustainability concerns, HTC method shows better potential and greater benefits for the synthesis of ACs compared to the other options.

Many studies have reported considerably productive findings on hydrochar yield from HTC of biomass-derived ACs. Yay, et al., (2021) presented the preparation of olive pomace hydrochar via HTC at varying temperatures from 220˚C, 240˚C, 260˚C, 280˚C, to 300˚C. Based on the finding, it was found that the yield of hydrochar from 220˚C to 300˚C decreased between 43% to 70.24% with increasing temperature. Amongst all studied temperatures, the highest hydrochar yield was obtained at 220˚C with 70.24%. On the other hand, Sharma, et al., (2020) also reported a similar pattern for Eucalyptus bark-derived hydrochar yield at varying HTC temperatures, in which the study observed a drop in hydochar yield from 46.6% to 40% when the HTC temperature was varied from 220˚C to 300˚C. In this case, the study achieved a maximum yield of 46.6%, at HTC temperature of 220˚C. Another study on the preparation of coffee husk-derived hydrochar via HTC by Hien, et al., (2016) reported a yield of 50.2% for hydrochar prepared at 220˚C. The studies aforementioned generally agree that the observable varying hydrochar yields are affected by the operating conditions for the HTC itself, such as carbonization time or carbonization period and carbonization temperature. Further justification on the factors affecting the hydrochar yield will be further discussed in the discussion section.

2.2 Coconut husk-derived activated carbon

The carbon or hydrochar that is produced via HTC is generally activated prior to use, using several methods including; i) physical activation, whereby the carbon is carbonized in a partially oxidized atmosphere such as steam or carbon dioxide, ii) chemical activation, whereby the prepared carbons are mixed with chemical activating agents such as $ZnCl_2$, KOH or NaOH, iii) physicochemical activation, which combines both physical and chemical activation steps, and iv) microwave activation (Hao, 2014). Amongst all the methods mentioned, chemical activation is a promising method to yield ACs with improved surface morphologies and area.

The chemical activation of coconut husk hydrochar assisted by microwave-assisted gasification has been widely implement in numerous studies due to the great observable improvements on the prepared ACs. In general, the microwave-assisted gasification method is incorporated in the preparation step to trigger the pore development of pores in the sample. According to Tan, et al., (2008), the preparation of coconut husk-derived activated carbon (CHAC) KOH activation with microwave-assisted CO_2 gasification at 816˚C and 811˚C activation temperatures has yielded a maximum CHAC yield of 15.50% and 19.20%, respectively. Meanwhile, Foo & Hameed, (2012) reported a maximum CHAC yield of 80.75% for CHAC with KOH activation and microwave-assisted CO_2 gasification. The difference in CHAC yields observed between the findings presented by Tan, et al., (2008) and Foo & Hameed, (2012) are affected by several factors, such as the KOH:husk ratio, microwave power, and activation temperature. Further justification on the factors affecting the CHAC yield will be further discussed in the discussion section.

2.3 Adsorption of Chloramphenicol (CAP)

In many studies, the evaluation of an activated carbon's performance is determined based on its capability to remove contaminants or dye from a water mixture. This study also observes the performance of CHAC prepared via $ZnCl_2$ activation on CAP removal. The evaluation of its performance are done based on two (2) different parameters, which are pH of CAP solution and the initial concentration of CAP solution.

2.3.1 Effect of solution pH

As a matter of fact, the pH of solution possesses a very significant impact on the removal performance of CAP compounds using activation carbons. This is because, the pH of solution has the potential to trigger interactions between the adsorbate and adsorbent particles. Thereby, the optimum pH which correlates to the highest removal efficiency depends on the types of adsorbents and adsorbates used, respectively. Theoretically, CAP particles which are cationic in nature will naturally bind to negatively charged surface of CHAC. In the case of CAP removal, several research studies have reported that the successful binding between CAP and adsorbent is observed at higher solution pH, rather than at lower pH.

According to Yu, et al., (2019), the highest CAP removal using ZVI MPs catalyst was attained at solution pH of 9, due to the reduction of H^+ ions concentration at higher pH, which allows the negatively charged surface of ZVI MPs catalyst to successfully bind with the positively charged CAP molecules. Moreover, Zhang, et al., (2021) reported a similar finding, at which the highest CAP removal was achieved at pH of 10.36. The finding presented by Idris, et al., (2020) concluded that the highest CAP removal was achievable at pH of 7. On the other hand, Sultana, et al., (2022) denoted a similar observation using CHAC for crystal violet (CV) removal, in which the removal efficiency increases with increasing pH from 1 to 5. The studies aforementioned are generally in agreement that the removal of CAP increases with increasing pH. Nonetheless, a slight reduction in removal efficiency is observed by all studies above when the pH is further increased due to the excessive concentration of negatively charged particles in the solution which impedes the interactions between the CAP particles and the negatively charged surface of AC.

2.3.2 Effect of initial concentration

The initial concentration of CAP solution is another useful factor to evaluate the removal efficiency of CAP compounds using CHAC. Generally, the adsorption capacity of an activated carbon increases with increasing concentration, due to increasing adsorbate uptakes on the adsorbent surface. At higher concentrations, more adsorbates will be captured by the adsorbent, causing them to adhere to the surface of the adsorbent until the surface is fully occupied. When this happens, the adsorbent performance is expected to drop, due to the unavailability of active sites which retards the ability of the adsorbent to adsorb further. Hence, a drop in the removal efficiency of the adsorbent will be observed as well.

According to Zhang, et al., (2021), the adsorption capacity of powdered activated carbon (PAC) increases from 99.62 mg/g, 149.23 mg/g and 197.84 mg/g with increasing CAP concentrations from 100 mg/L, 150 mg/L and 200 mg/L, respectively. In addition, Li, et al., (2018) also reported a similar observation on the adsorption capacity of Typha orientalis (TO)-based AC with increasing CAP concentration, in which the adsorption capacity increases from 0.215 mmol/g, 0.265 mmol/g to 0.320 mmol/g when the CAP concentration was increased from 0.15 mmol/L, 0.2 mmol/L and 0.3 mmol/L, respectively. Moreover, Yu, et al., (2019) also reported that the highest CAP removal efficiency is observed with increasing concentration. This study attained a maximum CAP removal of 100% at CAP concentration of 20 mg/L. On the other hand, Sultana, et al., (2022) also observed an increase in CV dye removal efficiency with increasing dye concentration, whereby the highest removal using

CHAC was achieved at concentration of 100 mg/L, and its efficiency significantly drops to 63% when the concentration increased to 400 mg/L.

2.4 Efficiency of $ZnCl_2$ activation

As part of the objectives, the efficiency of the CHAC prepared via $ZnCl_2$ activation in this study will be further assessed and compared with other biomass-derived ACs which are also chemically activated by $ZnCl_2$ activation. Briefly, $ZnCl_2$ activation will trigger the breaking of lateral bonds between the cellulose molecules, leading to the occurrence of a swelling effect on the adsorbent surface, and consequently promotes the pore developments on the surface. Hence, an enhancement on the adsorbent morphology will be observed, making it more suitable for adsorption purpose.

Generally, the efficiency of CHAC prepared from this study is evaluated based on its synthesis condition and highest maximum adsorption capacity, q_{max}. According to Jain, et al., 2015, the preparation of coconut shell-derived AC via $ZnCl_2$ activation is done at 275˚C, for 12 hours. The resulting coconut shell-derived AC produced from the study is associated with q_{max} of 264 mg/g for the adsorption of phenol compounds. On the other hand, Kristianto, et al., 2020 denoted that the preparation of bagasse-derived AC via $ZnCl_2$ activation was performed at 250˚C for 2 hours, and the corresponding q_{max} for the adsorption of Cr(VI) was 88.880 mg/g, which is apparently lower than the findings presented by Jain, et al., 2015. Li, et al., (2020) and Idris-Hermann, et al., (2018) reported a similar synthesis condition for the preparation of soybean dregs- and bitter kola nut shells-derived ACs, in which both samples are prepared at 500˚C for 1 hour. Nonetheless, the highest achievable q_{max} for both ACs are different, whereby the qmax attained by soybean dregs-derived AC and bitter kola nut shells-derived AC for dye removals are 255.10 mg/g. and 72.590 mg/g, respectively. On the flip slide, the preparation of guava seed-derived AC via $ZnCl_2$ requires synthesis condition of 400˚C for 2 hours which correlates to the q_{max} of 80.5 mg/g for green dye removal.

2.5 Adsorption of Chloramphenicol (CAP) using biomass-derived AC

The removal of CAP compounds from wastewater or water mixture has been getting a lot of attentions. Based on a study on CAP removal using lignocellulosic material-derived AC, a surface area of 794.8 m^2/g is observed for TO-based AC, which is then correlated to the maximum CAP adsorption capacity, q_{max} of 137.1 mg/g. The study also remarks that the adsorption capacities obtained for every sample fit both pseudo-second-order kinetic model and Freundlich isotherm model (Li, et al., 2018). Another study on CAP removal using modified corn stalks-chitosan-derived AC resulted in a maximum adsorption capacity of 58.75 mg/g (from Langmuir model). The adsorption capacity is then associated with the CAP removal efficiency of 95.49%. Compared to the results presented by Li, et al., (2018), the lower results obtained by this study is correlated with lower surface area of the activated char, which is 168.55 m^2/g (a, n.d.).

On the other hand, a study reported by Zhang, et at., (2021) on CAP removal using Powdered AC (PAC) observed a maximum adsorption capacity of 304.878.08 mg/g. This maximum value is associated with BET surface area of 1296.08 m^2/g. In addition, the study also presented that the adsorption capacity of PAC at CAP concentration of 100 mg/L was achievable at 99.60 mg/g. Apparently, the BET surface area obtained by Zhang, et at., (2021) is significantly higher than results mentioned previously (without the regards of experimental preparation). Meanwhile, Lach, (2019) reported the highest achievable q_{max} for the removal of CAP at 214.91 mg/g using Picabiol-derived AC. This finding correlates with BET surface area of Picabiol-derived AC of 1692 m^2/g. On the other hand, Idris, et al., (2020) evaluated the efficiency of CAP removal using three (3) different adsorbents, namely NIPs-CAP, Si@MIPs-

CAP and Si@NIPs-CAP. Based on BET analyses, the NIPs-CAP, Si@MIPs-CAP and Si@NIPs-CAP adsorbents had surfaces areas of 21.02 m^2/g, 58.99 m^2/g and 41.52 m^2/g, respectively. The highest qmax obtained for each adsorbent corresponds to 62.5 mg/g, 29.59 mg/g and 32.26 mg/g for NIPs-CAP, Si@MIPs-CAP and Si@NIPs-CAP adsorbents, respectively. This study also reported that the adsorption capacity attained by NIPs-CAP, Si@MIPs-CAP and Si@NIPs-CAP adsorbents at CAP concentration of 100 mg/L are 62.5 mg/g, 29.59 mg/g and 32.26 mg/g, respectively.

Chapter 3: Materials and methods

3.1 List of materials and equipment

The list of materials and equipment for the experiment are as shown on Table 1 and Table 2 below.

Table 1: List of materials for the project.

Materials	
Component	**Use**
Coconut husk	Raw material for the synthesis of AC
$ZnCl_2$ solution	Used for the chemical activation of AC
HCl solution	Additive to adjust the pH of CAP solution
NaOH solution	Addictive to adjust the pH of CAP solution
CAP	Main component for adsorption
CO_2 gas	Used for hydrochar activation
Distilled water	Washing agent

Table 2: List of equipment for the project.

Equipment	
Component	**Use**
Mechanical grinder	To grind the raw material into smaller sizes
Molecular sieves (10-20 mesh)	To maintain uniform size range of particles
Oven	For heating purpose
Stainless steel reactor	To carry out HTC process
Pyrex glass tube	To contain/load the hydrochar for char activation
BET surface analyzer	To determine the BET surface area of hydrochar
UV-vis spectrophotometer	To determine the concentration of CAP
SEM	To observe the surface morphology and properties of hydrochar
FTIR	To determine the functional groups of the hydrochar
Thermostatic shaker bath	To mix/stir the adsorbent-CAP mixture

3.2 Research Methodology

The general idea of this project involves two main steps, including the preparation of hydrochar via HTC and the actual experiment to examine the performance of the hydrochar on the removal of CAP. Figure 1 below shows the overall flow diagram of the project, starting with literature reviews, to gain as much data and information from literatures to be compared with the experimental data later, followed by the design of the experiment, which is divided into two parts; the preparation of hydrochar and the adsorption of CAP using the prepared hydrochar. Next, the flow continues with experimental data collection and analysis, whereby the data collected will be thoroughly analyzed and compared with literatures and finally, thesis and report writing. The procedures involved follows the methodology suggested by Jain, et al., (2015) and Li, et al., (2018).

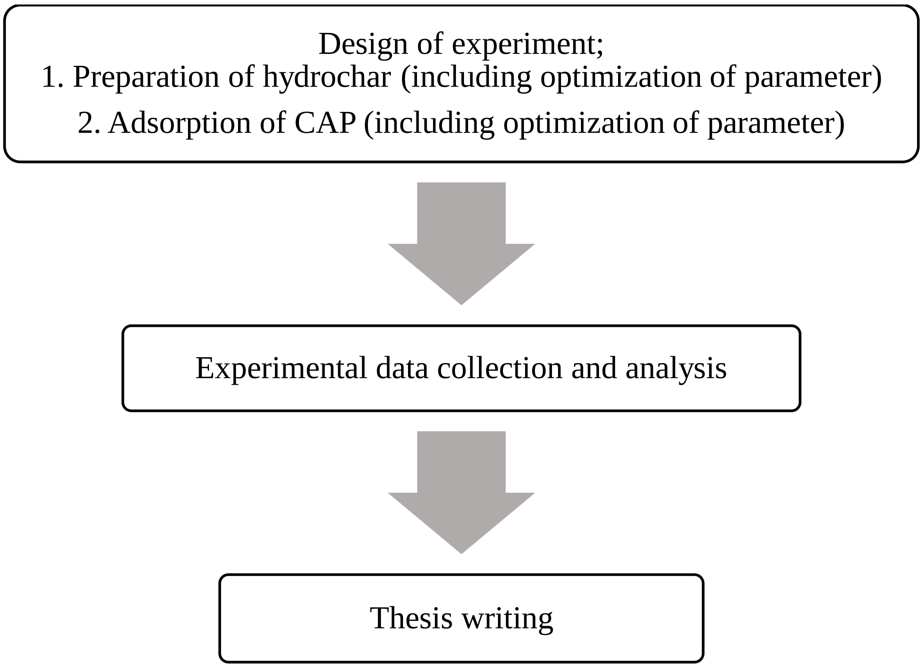

Figure 1: Overall flow diagram of the project.

3.3 Experimental procedure

3.3.1 Preparation of hydrochar

The overall flow diagram for the preparation of hydrochar is shown on Figure 2 below. The coconut husk, which is the raw material for the experiment is obtained locally around Nibong Tebal and is labelled as RCH.

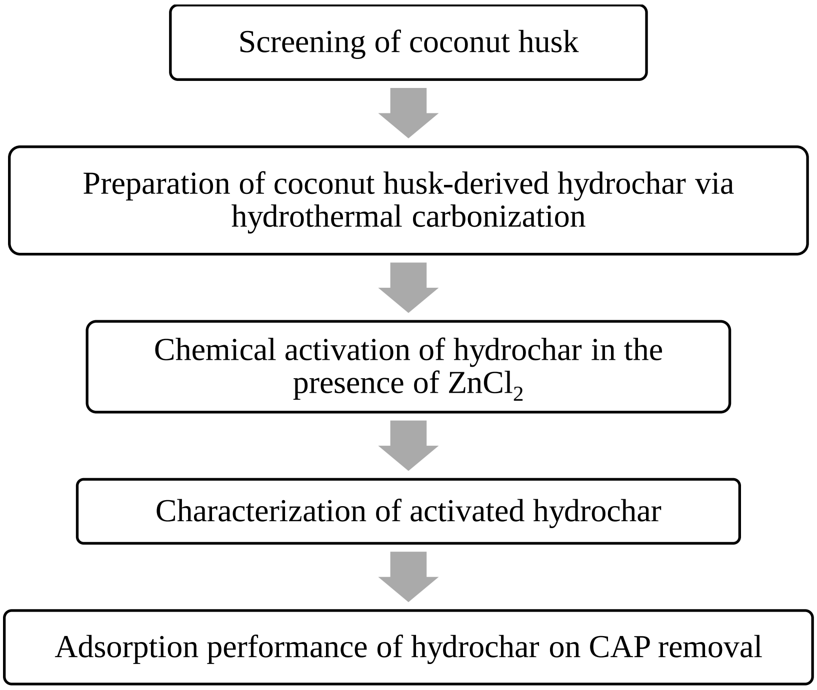

Figure 2: Flow diagram on the preparation of hydrochar.

a) Screening of raw material

The coconut husk is washed with distilled water and dried at 120˚C for 5 hours. Then, the raw coconut husk is ground into small particles using a grinder. To ensure uniform sizes of particles, the crushed particles are sieved into 10-20 mesh sizes.

b) Hydrothermal carbonization (HTC) of coconut husk

The hydrothermal carbonization (HTC) of the prepared coconut husk samples are done in a 200 ml stainless-steel reactor. 5 g of the coconut husk and 150 ml of distilled water are mixed and placed in the reactor, and the treatment is conducted at a fixed HTC temperature of 220˚C for 2 hours. Then, the reactor is let to cool down to room temperature before the hydrochar is taken out and filtered using a filter paper. The hydrochar obtained is then thoroughly washed using distilled water twice to remove water-soluble volatile matters and then dried at 120˚C over the night before it is chemically impregnated with $ZnCl_2$ (Islam, et al., 2017). The yield of hydrochar is then determined using Equation 1 below.

$$Hydrochar\ yield\ (\%) = \frac{W_{char}}{W_{ch}} \times 100\% \tag{1}$$

Where W_{char} and W_{ch} are the weight of hydrochar and coconut husk, respectively.

c) $ZnCl_2$ activation and microwave-assisted CO_2 gasification

Following the objective of the study, the precursor is mixed together with $ZnCl_2$ solution in appropriate quantities to ensure the desired $ZnCl_2$:husk ratio of 3:1 is achieved. After mixing, the hydrochar is recovered and dried in an oven at 120˚C for 5 hours. After drying, the dried hydrochar is subjected to the microwave irradiation activation method. Approximately 2 g of dried hydrochar is loaded inside a Pyrex glass tube, and placed inside the microwave's chamber. The microwave is run at fixed radiation power of 515 W for 6 minutes. During this step, CO_2 gas is allowed to flow through the chamber at a flow rate of 150 cm^3/min to give a gasification impact on the sample. After activation, the resulting AC produced is collected and labelled as CHAC. The yield of CHAC is determined using the formula as shown below.

$$CHAC\ yield\ (\%) = \frac{W_f}{W_i} \times 100\% \tag{2}$$

Where W_f and W_i are the weight of CHAC and dried coconut husk, respectively.

d) Characterization of activated hydrochar

The characterization of samples are performed to assist the determination of surface area, pore characteristic, surface morphology and existing functional groups on the surface of CHAC and RCH. The BET, SEM and FTIR analyses are conducted prior to the adsorption experiments.

i. Brunauer–Emmett–Teller (BET) analysis

The surface areas and pore volumes of CHAC and RCH are determined using a volumetric adsorption analyzer (Micromeritics ASAP 2020) which is available in the Analytical laboratory of School of Chemical Engineering, USM. Prior to the analysis, 0.5 g of CHAC and RCH samples are prepared and sent to the technician in charge at the laboratory. This determination is done based on the nitrogen (N_2) gas adsorption at 77K, and the corresponding surface area of each sample is determined from the adsorption isotherm using BET equation. Upon analysis completion, the results obtained are then used for further analysis and discussion.

ii. Scanning Electron Microscopy (SEM) analysis

The surface morphologies of CHAC and RCH are determined using a scanning electron microscopy (SEM) (FEI Quanta 450) which is available in the Process Control laboratory of School of Chemical Engineering, USM. Prior to the analysis, 0.5 g of CHAC and RCH samples are prepared and sent to the technician in charge at the laboratory. The observations on surface morphologies of CHAC and RCH samples are done using four (4) different magnifications; 500X, 1000X, 3000X and 5000X.

iii. Fourier Transform Infrared (FTIR) Spectroscopy analysis

The determination of existing functional groups that are present within the molecules of CHAC and RCH are determined using a iii. Fourier Transform Infrared (FTIR) Spectroscopy (IR prestige 21) which is available in the Analytical laboratory of School of Chemical Engineering, USM. Prior to the analysis, 1 g of CHAC and RCH samples are prepared and sent to the technician in charge at the laboratory. Briefly, when IR radiation passes through a sample, it triggers the vibrations of covalent bonds within the molecules of the sample. In this case, the vibrations may indicate stretching vibration or bending vibration. The IR spectrum obtained from FTIR analysis can be divided into two (2) approximate regions, namely the functional group region which is noted between 4000-1000 cm^{-1}, and the fingerprint region which is observed at a range of <1000 cm^{-1} (Hunt, 2019).

3.3.2 Adsorption of CAP

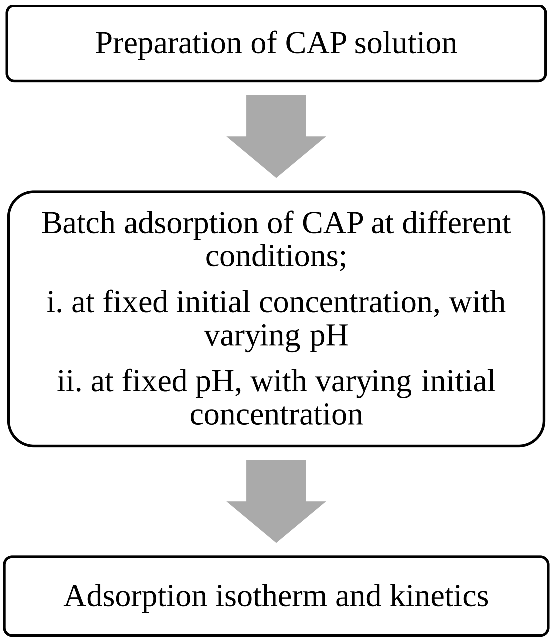

Figure 3: Flowchart for batch adsorption of CAP using CHAC.

a) Preparation of CAP solution

Chloramphenicol (CAP, purity of > 98%) is purchased from Aladdin (Shanghai, China). 1 L of 100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L of CAP stock solutions are prepared by mixing 0.1 g, 0.2 g, 0.3 g and 0.4 g of CAP powder with 1 L of distilled water, respectively. Each mixture is mixed at 30˚C for 1 hour to obtain equilibrium before it can be used for adsorption experiments.

b) Batch adsorption of CAP

All batch adsorption experiments are conducted in 250 ml stoppered conical flasks, containing a mixture of 0.1 g of CHAC with 100 mL of CAP solution. The adsorption capacity and removal efficiency of CAP are determined by using Equation (3) and (4):

$$Adsorption\ capacity, Q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

$$Removal\ efficiency\ (\%) = \frac{C_0 - C_e}{C_0}\ x\ 100 \tag{4}$$

Where

Q_e = adsorption capacity (mg/g)

C_0 = initial concentration of CAP solution (mg/L)

C_e = equilibrium concentration of CAP solution (mg/L)

V = volume of solution (L)

W = mass of adsorbent (g)

3.3.3 Calibration curve

Calibration curve is constructed prior to the parameter study. The calibration curve generally assists the prediction of CAP concentration from the experiment. 100 ml of 100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L CAP solutions are prepared, and their respective absorbance values are measured using UV-vis spectrophotometer using 400 nm wavelength as suggested by main reference (Sultana, et al., 2022). The corresponding curve of concentration vs absorbance are then plotted and ready to be used.

3.3.4 Parameter study

a) Adsorption at different pH of CAP solution

The adsorption capacity of CHAC is observed at different pH of CAP solution by adding either 0.1 M HCl or NaOH solution. In this experiment, the pH of CAP solution is adjusted at 3, 5, 7, 9 and 11, with a fixed CAP concentration of 200 mg/L (Sultana, et al., 2022). 0.1 g of CHAC is added to each flask containing 100 ml of CAP solution of different pH. The mixture is agitated at 25˚C in a thermostatic shaker bath for 3 h at a stirring speed of 100 rpm to ensure adsorption equilibrium. During the experiment, a small amount of sample (approximately 4.5 ml) is taken out of each flask using a nylon syringe filter (0.45 μm) at different contact time intervals to determine the concentration of CAP solution at the respective contact time. The concentration of CAP is determined using ultraviolet-visible (UV-vis) spectrophotometer (Li, et al., 2018). The optimum pH is then determined and fixed for the next parameter study.

b) Adsorption at different initial concentrations of CAP solution

The adsorption capacity of CHAC is observed at different initial CAP concentrations (100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L) at optimum pH which is determined from the earlier parameter study. The pH of CAP solution is adjusted by adding either 0.1 M HCl or NaOH solution, and the pH is fixed throughout the experiment. The mixture is agitated at 25˚C in a thermostatic shaker bath for 3 h at a stirring speed of 100 rpm to ensure adsorption equilibrium. Similarly, a small amount of sample (approximately 4.5 ml) is taken out of each flask using a nylon syringe filter (0.45 μm) at different contact time intervals during the experiment to determine the concentration of CAP solution at the respective contact time. The concentration of CAP is determined using ultraviolet-visible (UV-vis) spectrophotometer (Li, et al., 2018).

3.3.5 Adsorption isotherms

The adsorption isotherm study is conducted to gain information on the mobility or retention of adsorbate on the surface of the adsorbent. The adsorption isotherm correlates the equilibrium data from the experiment to further assist the understanding of the adsorption system. In this study, two (2) adsorption isotherm models are considered to determine the adsorption process of CAP using CHAC. The isotherm models are Langmuir isotherm and Freundlich isotherm.

a) Langmuir isotherm

According to Langmuir isotherm model, the adsorption occurs on a finite number of surface sites of the adsorbent through monolayer adsorption with no transmigration of adsorbate in the surface plane (Tan, et al., 2008). Briefly, the Langmuir isotherm assumes that a monolayer (single layer) is formed when adsorbate adheres on the surface site of an adsorbent without involving any interaction between the absorbed particles, and maximum adsorption is achieved when the surface of the adsorbent is completed covered by the monolayer of adsorbed particles (Hammond & Conner Jr., 2013). The non-linear form of Langmuir isotherm is given by (Langmuir, 1916):

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \tag{5}$$

Upon linearization, the Langmuir isotherm can be simplified to:

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \tag{6}$$

Where q_e refers to the amount of CAP adsorbed at equilibrium (mg/g), q_0 is the saturated monolayer sorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg), and C_e is the concentration of adsorbate at equilibrium (mg/L). From the equation, the values of q_0 and K_L can simply be obtained from the plot of C_e/q_e vs C_e.

b) Freundlich isotherm

The Freundlich isotherm model is an empirical equation that explains the multilayer and non-ideal adsorption process that occurs on heterogeneous surface of adsorbent (Freundlich, 1906). The isotherm model is generally derived based on the assumption that both cations and anions of adsorbate are adsorbed onto the same surface of adsorbent simultaneously (Nakahara, 1996). The non-linear form of Freundlich is given by (Freundlich, 1906):

$$q_e = K_F {C_e}^{\frac{1}{n}} \tag{7}$$

Upon linearization, the Freundlich isotherm can be simplified to:

$$ln\, q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

Where q_e refers to the amount of CAP adsorbed at equilibrium (mg/g), K_F is the Freundlich isotherm constant ((mg/g).(L/mg)$^{1/n}$), n is the adsorption intensity, and C_e is the concentration of adsorbate at equilibrium (mg/L). From the equation, the values of n and K_F can simply be obtained from the plot of ln q_e vs ln C_e.

3.3.6 Adsorption kinetics

The adsorption kinetic study is conducted to determine the rate-determining step of the adsorption process, alongside the adsorption mechanism of CAP particles onto CHAC (Sultana, et al., 2022). It generally describes the extent of adsorption with respect to time, and is used to determine the diffusion of adsorbate onto the adsorbent surface. In this study, two kinetic models, namely the pseudo first order kinetic model and pseudo second order kinetic model are used to test the kinetic data obtained from the experiment.

a) Pseudo first order kinetic model

Briefly, a pseudo first order reaction can be referred to as a second-order reaction that behaves like a first-order reaction. This kinetic model describes an adsorption process through the diffusion of particles across a boundary (BYJU'S, 2022). The pseudo first order kinetic model can be expressed using Lagergren kinetic equation as shown below (Lagergren, 1898):

$$\frac{dq}{dt} = k_1(q_e - q) \tag{9}$$

Upon integration, the Lagergren kinetic equation above can be further derived to obtain the non-linear and linear equations as shown below (Sultana, et al., 2022):

$$q_t = q_e(1 - e^{-k_1 t}) \tag{10}$$

$$\ln(q_e - q_t) = \ln q_t - \frac{k_1}{2.303} t \tag{11}$$

Where q_e refers to the amount of CAP adsorbed at equilibrium (mg/g), q_t is the amount of CAP adsorbed at time, t (mg/g), k_1 is the rate constant for first order kinetics (min^{-1}), and t is the contact time (min). From the equation, the value of k_1 can simply be obtained from the plot of ln (q_e - q_t) vs t.