COCONUT HUSK BASED ACTIVATED CARBON PRODUCED VIA SODIUM BICARBONATE ACTIVATION FOR CHLORAMPHENICOL REMOVAL FROM AQUEOUS SOLUTION

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HALIMATUSAADAH BINTI ISMAIL

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LIST OF SYMBOLS

a	Constant of Koble-Corrigan isotherm	$L^n mg^{1-n}/g$
A	Arrhenius factor	-
A_i	Measured absorbance	
b	Constant of Koble-Corrigan isotherm	L/mg^n
B_T	Constant of Temkin isotherm	mg/g.h
B_t	Constant of Boyd model	-
C_e	Adsorbate concentration at equilibrium	mg/L
C_O	Initial adsorbate concentration	mg/L
E_a	Arrhenius activation energy	kJ/mol
k_1	Constant of pseudo-first-order kinetic model	1/h
k_2	Constant of pseudo-second-order kinetic model	$mg/g.h^{1/2}$
K_F	Constant of Freundlich isotherm	$mg/g.(L/mg)^{1/n}$
K_L	Constant of Langmuir isotherm	L/mg
K_T	Constant of Temkin isotherm	L/mg
l	Optical path length	1 cm
m_f	Dry mass of precursor	g
m_i	Dry mass of raw coconut husk	g
n_F	Constant of Freundlich isotherm	-
n_{KC}	Adsorption intensity of Koble-Corrigan isotherm	-
q_e	Adsorbate adsorbed per unit mass of adsorbent at equilibrium	mg/g
q_t	Adsorbate adsorbed per unit mass of adsorbent at time, t	mg/g
$q_{t,cal}$	Calculated adsorption uptake at time, t	mg/g

$q_{t,exp}$	Experimental adsorption uptake at time, t	mg/g
q_m	Monolayer adsorption capacity of adsorbent	mg/g
R	Universal gas constant	8.314 J.mol.K
R_L	Separation factor	-
R^2	Coefficient of determination	-
t	Time	h
T	Absolute temperature	K
V	Volume of solution	L
W	Mass of adsorbent	g
X	Activated carbon preparation variable	-
Y	Predicted response	-
	Greek letters	
$\Delta G°$	Change in standard Gibbs free energy	kJ/mol
$\Delta H°$	Change in standard enthalpy	kJ/mol
Δq_t	Normalized standard deviation	%
$\Delta S°$	Change in standard entropy	kJ/mol
ε_λ	Molar absorptivity coefficient of solute at wavelength	-
λ	Wavelength	nm

LIST OF ABBREVIATIONS

AC	Activated carbon
CHAC	Coconut husk activated by sodium bicarbonate
AOP	Advanced oxidation process
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CAP	Chloramphenicol
CCD	Central composite design
EC	Emerging contaminant
FTIR	Fourier Transform Infrared
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
MPSD	Marquadt’s percent standard deviation
MRPL	Minimum required performance limit
MSE	Mean square error
RSM	Response surface methodology
RMSE	Root mean square error
SEM	Scanning electron microscopy
TGA	Thermogravimetric analyzer
WHO	World Health Organization

LIST OF APPENDICES

KARBON TERAKTIF BERASASKAN SABUT KELAPA TERHASIL MELALUI PENGAKTIFAN SODIUM BIKARBONAT UNTUK PENYINGKIRAN KLORAMFENIKOL DARIPADA LARUTAN AKUAS

ABSTRAK

Penyelidikan yang dibentangkan mengkaji tentang penyingkiran kloramfenikol (KFK) daripada larutan akuas oleh karbon teraktif berasaskan sabut kelapa (KTSK). Hasil KTSK dikawal dengan ketara oleh suhu pengaktifan manakala prestasi penjerapan KFK banyak dipengaruhi oleh nisbah jerap isi (NJI), suhu pengaktifan dan masa pengaktifan $NaHCO_3$. Analisis melalui metodologi permukaan sambutan mendedahkan keadaan penyediaan optimum untuk suhu pengaktifan, masa pengaktifan dan NJI didapati masing-masing 500 ℃, 1 jam dan 0.5. KTSK yang dioptimumkan didapati adalah jenis liang homogen dan mesoporus dengan luas permukaan BET 438.2 m^2/g. Dalam kajian penjerapan kelompok, penjerapan KFK oleh KTSK meningkat apabila kedua-dua kepekatan awal KFK dan masa sentuhan meningkat. Untuk kesan pH larutan, penyingkiran KFK tertinggi didapati pada pH 2. dan yang paling rendah pada pH 13. Padanan terbaik untuk sistem penjerapan KFK ialah model isoterma Langmuir dan model kinetik pseudo-tertib-pertama. Proses penjerapan dikawal oleh mekanisma serapan-filem. Kajian termodinamik mendedahkan penjerapan KFK oleh KTSK adalah eksotermik dan bersifat spontan.

COCONUT HUSK BASED ACTIVATED CARBON PRODUCED VIA SODIUM BICARBONATE ACTIVATION FOR CHLORAMPHENICOL REMOVAL FROM AQUEOUS SOLUTION

ABSTRACT

The presented research studied on the removal of chloramphenicol (CAP) from aqueous solution by coconut husk based activated carbon (CHAC). The CHAC yield was significantly affected by activation temperature whilst CAP adsorption performance was greatly influenced by NaHCO3 impregnation ratio (IR), activation temperature and activation time. Analysis by response surface methodology revealed the optimum preparation conditions for activation temperature, activation time and IR were found to be 500 °C, 1 hour and 0.5, respectively. The optimized CHAC was found to be homogeneous and posed mesoporous type of pores with BET surface area of 438.2 m2/g. In batch adsorption study, the CAP uptakes onto CHAC increased as both CAP initial concentration and contact time increased. For effect of solution pH, the highest CAP removal was found at pH 2.and the lowest at pH 13. The best models for CAP adsorption system were Langmuir isotherm and pseudo-first-order kinetic. The adsorption process was governed by film-diffusion mechanism. Thermodynamic study revealed the CAP adsorption onto CHAC was exothermic and spontaneous in nature.

CHAPTER 1

INTRODUCTION

1.1 Pharmaceutical industry and its emerging contaminants

Pharmaceutical industries in Malaysia are rapidly growing from the persistent increase of investments from multinational companies in Malaysia. Consequently, Malaysia has come forth as one of the largest pharmaceuticals manufacturers and exporters globally (Praveena et al., 2019). Emerging contaminants (ECs), otherwise known as micropollutants, are derived from various sources, including the pharmaceutical industry and they are highly polluting. The presence of ECs in environment is contributed from various sources such as pharmaceutical effluent discharge, household and hospital waste, municipal wastewater treatment plant effluent and inappropriate discarding of expired pharmaceutical products and veterinary drugs (Praveena et al., 2018). As elucidated in Figure 1.1, various potential resources have led to the presence of antibiotics in the environment such as soil, groundwater and surface water. Antibiotics are non-biodegradable in nature and accumulation of these compounds in water bodies can contribute to the emergence of antibiotic-resistant bacteria (Kurt et al., 2017).

Malaysia being one of the developing countries is lacking in the wastewater treatment system and as a consequent, highly stable ECs and pharmaceutical residues cannot be removed effectively and sufficiently (Hashim et al., 2016). Additionally, Malaysia do not have any explicit regulations that issues the limit for pharmaceutical residues in source water as it is not considered as priority pollutants despite all the risky health effects towards the public and aquatic environment (Othman and Ariffin, 2019). The ignorance towards this matter could be attributed to the absence of pharmaceuticals as pollutants in drinking water quality by World Health Organization

(WHO) (Al-Odaini et al., 2013). Table 1.1 shows some of the pharmaceutical residues found in surface water in Selangor, Malaysia (Praveena et al., 2018).

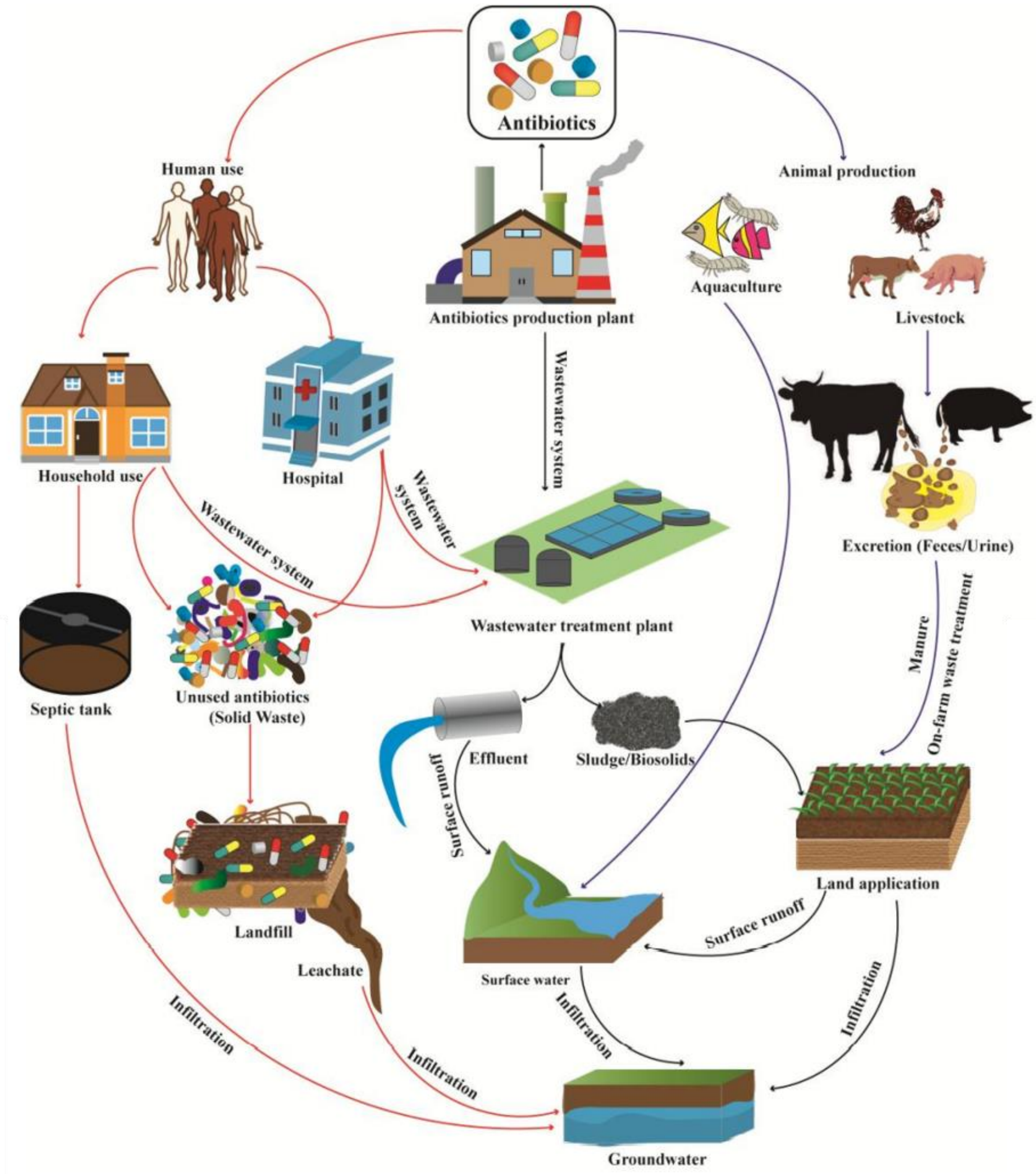

Figure 1.1 Potential pathways of antibiotics resources into the environment (Oberoi et al., 2019)

Table 1.1 Occurrence of pharmaceuticals residues in Selangor, Malaysia (Praveena et al., 2018)

Locations	**Concentration of pharmaceuticals residues (ng/L)**			
	Caffeine	**Chloramphenicol**	**Ciprofloxacin**	**Nitrofurazone**
Lui River	30.12	16.57	112.40	38.37
Selangor River	25.76	22.88	198.91	42.65
Gombak River	36.60	23.10	267.20	41.81

The increasing presence of these ECs in the aquatic environment annually has led to a serious concern of the potential adverse effects to the human health, environment and aquatic organisms (Agüera et al., 2013). If such pharmaceuticals residues are not removed sufficiently during wastewater treatment, they can migrate into the aquatic environment and eventually end up in the food chain (Kümmerer, 2009). Since a large number of pharmaceuticals are water-soluble, polar, non-volatile and non-biodegradable, they often escape the biological treatment in sewage water treatment plant and are released to the environment (Al-Odaini et al., 2013).

Chloramphenicol (CAP) is an active, broad-spectrum antimicrobial agent against many gram-positive and gram-negative baccili and cocci by inhibiting protein synthesis in microbes (Figure 1.2). Thus, making it once a popular choice to treat bacterial infection in human and animals. CAP was first discovered in 1947, isolated from *Streptomyces venezuelae* which is found in soil and compost (Balbi, 2004). Although CAP is broadly used as antibiotic to treat diseases including conjunctivitis, meningitis and plague cholera, it is very toxic and may adversely cause aplastic anemia, leucopenia, thrombocytopenia and gray baby syndrome (Dasgupta, 2012). European Union has underlined the minimum required performance limit (MPRL) for CAP in animal-origin products at 0.3 μg/kg (Li et al., 2018). Taking the harmful effects of CAP residues to public health into consideration, many countries such as the European Union, Australia, United States, Japan and Canada have banned its use in the food production (Zhou et al., 2014). Although the banning has been implemented, CAP is still one of the antibiotics that is frequently found in groundwater, surface water (rivers, ocean, lakes and reservoir) and even drinking water due to its low cost, effectivity and availability that attracts farmers and aquaculturists to use it despite the illegality (Liu et al., 2009; Tahrani et al., 2015). Therefore, a cost-effective, safe and sustainable treatment method to remove CAP from water-bodies is highly necessary and important.

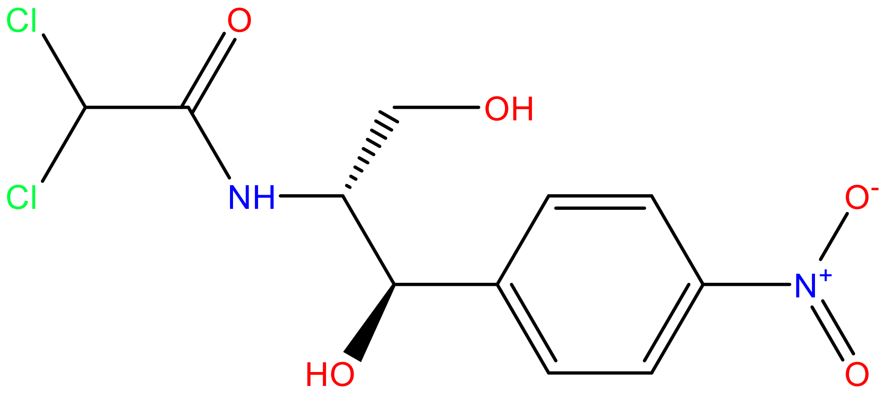

Figure 1.2 Molecular structure of chloramphenicol (CAP) (Abdollahi and Mostafalou, 2014)

1.2 Adsorption via activated carbon

Over the past years, some physicochemical methods have been employed for the removal of CAP from water or wastewater namely adsorption, advanced oxidation and nanoparticles treatment (Xiao et al., 2022). Owing to its highly complex bacterial structure, CAP cannot be removed effectively via conventional wastewater treatment methods which are through biological, chemical and physical methods (Ebele et al., 2017). Adsorption process has been reported to be a well-known practice for removal of antibiotic from water bodies owing to its well-developed surface area, high porosity and simplicity (Zubair et al., 2021a). Many efficacious adsorbents such as magnetic nanomaterials, polymer nanocomposites and carbon nanostructures have been utilized in the water treatment but they possess several limitations in terms of practicality in which they are costly, non-biodegradable and have low reusability performance besides producing more toxic CAP by-products which are potentially carcinogenic to human and animals (Zubair et al., 2021b; Li et al., 2018). Therefore, there has been a constant advancement in the adsorbent technology to develop a cost-effective, eco-friendly, high reusability and adsorption performance of an adsorbent.

Recently, adsorption process via activated carbon (AC) derived from biowaste has gained the attention of many researchers due to its abundant availability, sustainability and cost effectivity. Many studies have been conducted on the AC synthesis from biowaste, commonly agricultural waste such as date seeds (Ogungbenro et al., 2020), rice husk, corncob and wheat straw (Ratan et al., 2018), strawberry seeds and pistachio shells (Blachnio et al., 2020), oil palm empty fruit bunch (Tran Thi Dieu et al., 2020), bamboo stem (Sucipta et al., 2021), coconut shell (Den et al., 2021), banana peels (Ogbodo et al., 2021) and walnut shell (Yu et al., 2019). For instance, coconut (*Cocos nucifera*) husk (Plate 1.1) is one of the most abundant agricultural wastes in Southeast Asia which possess little to no economic value and thus, pose a disposal issue to the public. By utilizing coconut husk as precursor for the preparation of AC will help to cater the waste management issue of this waste and simultaneously, the AC can be employed as an adsorbent to remove pharmaceuticals residues from the water.

Plate 1.1 Coconut husk for AC precursor

1.3 Problem statement

Chloramphenicol (CAP) is a type of antibiotic that is extensively used for treating bacterial infections in human and veterinary medicine since late 1950s. Antibiotics are considered as emerging contaminants due to the harmful effects it can bring to not only human health but also to animals and environment too (Ahammad et al., 2021). Detection of CAP in water sources has been gaining attention due to its potentially detrimental effects to public health such as thrombocytopenia, leukemia, plastic anemia and hypoplastic. Correlating to this issue, owing to its selective extraction, high adsorption performance, cost effective and simplicity, adsorption is reported to show an efficient removal of emerging contaminants from an aqueous solution. Different materials have been used as adsorbent namely graphene, biochar, clay, minerals, metal oxides, chitosan, gels, polymeric resins and molecular imprinted polymers (Xiang et al., 2020). Out of all, carbon-based materials such as AC, carbon nanotube, graphene and biochar have gained the popularity among the researchers due to their high specific surface areas, abundant pore structures and highly adjustable functional groups. Hence, the adsorbent must be modified as to increase its adsorption capacity towards a specific contaminant. A few reported studies claimed that the highest uptake capacity for CAP by pristine biochar was only 8 mg/g, which is relatively low in order to meet the standard requirement for antibiotic removal (Liao et al., 2013). Therefore, numerous research studies had been performed over the past decades to enhance the AC surface functional groups thus improving its adsorption performance.

Implementation of AC for decontamination of water had always been a popular choice to remove pollutant whether its organic or inorganic pollutants, heavy metal ions, antibiotics or dyes (Xiang et al., 2020). The existing commercial AC is derived from petroleum coke, coal and peat, which is non-renewable and non-sustainable in the long run (Abuelnoor et al., 2021). Other than that, the AC reactivation process for these materials is highly energy-intensive which contributes to the expensive regeneration process (Rashidi & Yusup, 2017). Hence, in context of sustainable development, numerous researchers have been focusing on the AC production from renewable, and relatively cheaper resources such as agricultural waste (Bahamon et al., 2020).

As much as 998 million tonnes of agricultural waste is produced annually, and in Malaysia, 1.2 million tonnes of this waste are discarded into landfills per year. In Malaysia, coconut is one of the important crops amongst oil palm, paddy and rubber (Tahir & Hamid, 2012). The coconut husks (CH) are usually disposed of after the coconut water is sold. This was proven by a statistic reported by Kamal Baharin et al., (2020) whereby coconut husk contributes to almost 0.239 million tonnes of the agricultural wastes in 2012. Thus, this makes CH a potential precursor for AC due to its abundant availability, while at the same time mitigating the waste production from agricultural sector to achieve sustainable waste management. CH possess high carbon and low inorganic content which makes it suitable to be adopted as AC for wastewater treatment (Dabwan et al., 2015).

Some of the reported research on antibiotics removal by biowaste-derived ACs through adsorption had shown positive results; 256.29 mg/g removal of Caffeine by microwave-assisted $ZnCl_2$ ACs derived from sawdust (Thue et al., 2017) and 263.7 mg/g adsorption uptakes of Ciprofloxacin by phosphoric acid ACs derived from peach stone (Álvarez-Torrellas et al., 2017).

Considering all the reported studies on sodium bicarbonate ACs derived from biomass for antibiotics removal from water, still, there was no studies related to CAP. Thus, in this paper, an attempt was made to synthesize coconut husk-derived activated carbon produced via sodium bicarbonate activation (CHAC) and to study the performance towards CAP removal. The CHAC was synthesized via impregnation method at different mass ratios of activator and precursor and its respective adsorption performance on CAP was evaluated.

1.4 Research objectives

The objectives of this research are:

i. To synthesize coconut husk-derived activated carbon (CHAC) via impregnation with sodium bicarbonate ($NaHCO_3$) furnace activation to evaluate its adsorption performance on CAP.

ii. To optimize the synthesis parameters (activation temperature and activation time) of CHAC composite by using response surface methodology (RSM) and evaluate their effects towards the responses of CAP uptakes and CHAC's yield.

iii. To analyze the physicochemical properties of CHAC using various characterization techniques of surface area, pore characteristics, elemental analysis, proximate analysis and surface chemistry.

iv. To investigate the effect of initial concentration, contact time, pH, and solution temperature on CAP adsorption onto CHAC

CHAPTER 2

LITERATURE REVIEW

2.1 Insights into antibiotics

The term antibiotic is originated from Greek word ‘antibiosis’ which means ‘against life’. Antibiotics are compounds which are able to inhibit microbial growth or completely destroy it by terminating the synthesis of cell wall of the bacteria, hindering the synthesis of nucleic acid and lowering the permeability of bacteria’s cytoplasmic membrane to prevent the bacteria from reproducing, which allows the body’s natural defense mechanism to eliminate them (Buckle, 2015). Antibiotics are highly complex compounds which consists of multiple functional groups such as trienes, tetraenes, pentaenes, hexaenes, aromatic ring, polyene macrolide ring and beta-lactam ring. Antibiotic is commonly characterized by chemical structure, action mechanism or activity spectrum. Some of the classes according to chemical structure are beta-lactams (3-carbon and 1-nitrogen ring), penicillins (combination of beta-lactam with thiazolidine ring), carbanepems (beta-lactam fused with five-membered ring having carbon atom at position 1 instead of sulfur), sulfonamides (sulfonyl group fused with an amine group) and quinolones (bicyclic ring with a carboxylic and ketone group) (Etebu and Arikekpar, 2016). Classifications based on the action mechanism of antibiotics targeting the bacterial cell are cell wall synthesis inhibition, protein synthesis inhibition, nucleic acid synthesis inhibition, metabolic activity inhibition and plasma membrane disruption (Verma et al., 2022).

Table 2.1 Classification of antibiotics, mechanism action and potential side effects (Verma et al., 2022)

Antibiotics	Action of mechanism	Possible side effects
Amino glycosides		
Gentamicin Netilmicin Tobramycin	Bind to bacterial 30S subunit of ribosome and prevents the bacteria to synthesize vital proteins for its growth	Loss of hearing, Vertigo, Kidney damage
Penicillins		
Amoxicillin Ampicillin Penicillin G	Intervene with the bacterial synthesis of peptidoglycan layer in the cell wall	Allergy, Brain and kidney damage, Diarrhea
Sulfonamides		
Sulfadiazine Sulfamethizole	Inhibit bacterial folic acid synthesis which causes the cells incapable of producing nucleic acids and thus preventing cells from dividing	Allergy, Kidney failure, Nausea, Diarrhea, Lower white blood cell count
Others		
Chloramphenicol Thiamphenicol	Bind to bacterial ribosomal 50S subunit and inhibit protein synthesis	Aplastic anemia, Gray baby syndrome Pancytopenia

Although antibiotics are superior and effective in treating various microbial diseases, most of them have the potential to cause antimicrobial side effects, in which some is considered as life-threatening (Cunha, 2001). Some of the most common non-severe side effects includes headache, nausea, diarrhea, muscle/joint pain and vomiting (Mammadova et al., 2019). Meanwhile, the detrimental side effects include kidney damage, aplastic anemia, crystals in urine and decrease in white blood cell count (Awad et al., 2012). Table 2.1 shows the classification of antibiotics, its mechanism and possible side effects.

2.2 Removal techniques of antibiotics and CAP

With the rising awareness of the CAP potential risks to the ecosystem and public health, many researchers have explored various different decontamination methods to cater this issue. Present antibiotics removal methods from wastewater are generally characterized into chemical, biological and physical methods. As the name suggest, chemical treatment is carried out by chemical reactions between chemicals and contaminants in regards to the volatility and solubility or other properties that able to separate the targeted compounds from aqueous solution (Phoon et al., 2020). Typical examples of chemical treatment are coagulation, electrolysis, neutralization, chlorine disinfection and advanced oxidation process (AOP) (Mahdi et al., 2021). AOP is an attractive treatment method which has been applied widely owing to its high versatility, non-toxic and wide spectrum of application. However, the process is costly due to the expensive reagents (such as H_2O_2) and high energy intensity (UV radiation or generation of ozone) (Cuerda-Correa et al., 2019).

Biological method can be further classified into aerobic (requires oxygen), anaerobic (absence of oxygen) and combination of both aerobic and anaerobic. This method utilizes microorganism, such as bacteria, algae and nematodes to degrade organic compounds. Biodegradation of antibiotics by pure or mixed microbial culture can alter the chemical and structural properties of compounds into small and harmless molecules such as H_2O and CO_2. One of the conventional biological treatments is activated sludge process where under aerobic conditions, microbial culture suspension is used to degrade organic material and form floc that can be separated with ease in the settling unit. Though the process is widely used owing to its simplicity and easily operated process, the antibiotics removal varied remarkably for different types of antibiotics from -1% for Azithromycin, 25% for Norfloxacin, 52% for Sulfamethoxazole, 66% for Erythromycin to 71% for Ciprofloxacin (Verlicchi et al., 2013). Two critically important operating parameters which affect the contaminants removal efficiency are solids retention time and hydraulic retention time. Solids retention time and hydraulic retention time of more than 15 days and more than 4 to 6 hours, respectively, are required to achieve an efficient antibiotics removal from the water, hence indicating that this method is time-consuming (Oberoi et al., 2019). Moreover, it is reported that biological treatment may increase the accumulation of antibiotics resistance bacteria hence posing an alarming concern to the public as the existing medications will not be effective anymore (Zhu et al., 2021).

Physical method makes use of the natural interaction of the contaminants, such as van der Waals, gravity, electrostatic and hydrophobic interactions and it is the most widely used method in the wastewater treatment as it does not disrupt the chemical structure of the pollutant which may produce toxic by-products. Moreover, physical treatment is simple to design and operate as well as it is able to eliminate and decrease the abundance of antibiotics resistance bacteria (Liu et al., 2009). Common approaches of physical treatment include adsorption, filtration, sedimentation and ultraviolet disinfection (Lu et al., 2020). A study conducted by Li et al., (2018) has shown that CAP removal by adsorption onto AC able to achieve 80.9% and 83.4% removal rate from groundwater and distilled water, respectively. Additionally, the AC produced has high specific surface area of 794.8 m^2/g with porous structure.

Table 2.2 Various treatment methods used in the removal of Chloramphenicol from aqueous solution

Treatment methods	**Advantages**	**Challenges**	**Remarks**	**Reference**
Adsorption on activated carbon from *Typha orientalis*	Maximum adsorption capacity of 137.1 mg/g Removal rate of 66-83% in realistic water environment Economical and sustainable adsorbent	-	Pseudo-second-order kinetic model and Freundlich isotherm model	(Li et al., 2018)
Adsorption on ABA-16 (ordered mesoporous carbon)	Maximum adsorption capacity of 209.7 mg/g	-	Three-parameter adsorption isotherm models and pseudo-second order kinetic model.	(Mohd Din et al., 2015)
Adsorption on carbon dioxide activated wheat straw biochar	Maximum adsorption capacity of 11.3 mg/g Cost-effective and sustainable adsorbent	-	Langmuir isotherm model.	(Kozyatnyk et al., 2021)
Adsorption on MWCNT-10 (multi-walled carbon nanotubes)	Maximum adsorption capacity of 107.9 mg/g Excellent chemical and thermal stability, low-toxicity adsorbent	-	Freundlich isotherm model	(Zhao et al., 2016)

Electrochemical advanced oxidation (In situ H_2O_2 electrogeneration and activation by Fe atoms cathode)	Complete removal achieved in 210-300 min High reusability performance	Longer period is required for higher CAP initial concentrations Relatively high cost	Initial CAP concentration is 25 mg/L Removal efficiency was evaluated in an electro-Fenton-like system	(Song et al., 2021)
Synergy of *Geobacter* and metal oxide nanoparticles	100% removal efficiency Five-times higher removal rate and two-times higher removal efficiency compared to pure culture	Degradation product (CPD3) is large and toxic	*Geobacter metallireducens* culture supplied with $\mathrm{Fe_3O_4}$ and $\mathrm{MnO_2}$ nanoparticles Removal rate (0.71 $\mathrm{d^{-1}}$) and removal efficiency (100%)	(Xiao et al., 2022)
Electrochemical advanced oxidation	Complete CAP removal at very low current density and electric charge	Relatively high cost	Boron Doped Diamond as anode with current density and electric charge of 1.25 $\mathrm{mA\ cm^{-2}}$ and 8 $\mathrm{Ah\ dm^{-3}}$, respectively	(Herraiz-Carboné et al., 2020)

As presented in Table 2.2, various treatment has been employed to remove CAP from water and adsorption process was the most studied method by using carbon-based adsorbent. The maximum adsorption capacity of CAP onto various types of adsorbents namely AC, biochar, ordered mesoporous carbon and carbon nanotubes ranged from 11.3 mg/g to 209.7 mg/g and the methods are reported to be more economical and sustainable compared to other methods as the adsorbent resources can be derived from biowaste. Therefore, it can be deducted that adsorption via carbon-enriched matter exhibit promising advancement and opportunities in the water remediation.

2.3 Activated carbon

From the graphite family, AC has the most porous structure with specific surface area ranging from 500-3000 m^2/g (Oubagaranadin and Murthy, 2011). Over the past few decades, AC has shown to be a promising adsorbent for the removal of contaminants from wastewater due to its relatively large surface area, high adsorption capacity, high thermal stability and high mechanical strength (Xiang et al., 2020; Yahya et al., 2018). AC is an amorphous, porous and carbon-enriched material synthesized through heating of either naturally occurring or synthetic carbonaceous matter. AC has no distinctive chemical formula (Cuhadaroglu and Uygun, 2008) however, the chemical properties of AC are expected to be comparable of those in aromatic hydrocarbons as it consists of functional groups such as carboxyl, carbonyl, and phenols attached to polycyclic aromatic rings (Ao et al., 2018). AC is characterized by its physical appearance, and it is often classified into powdered AC, granulated AC, extracted AC, fibrous AC, pellet AC and AC cloths (Yahya et al., 2018). Other characterization of AC is based on its pore size where three classes has been underlined by International Union of Pure and Applied Chemistry (IUPAC); micropores (< 2 nm), mesopores (2 nm – 50 nm) and macropores (> 50 nm) (Figure 2.1). Both size and distribution of these pores in AC will determine its adsorptive properties (Ioannidou and Zabaniotou, 2007).

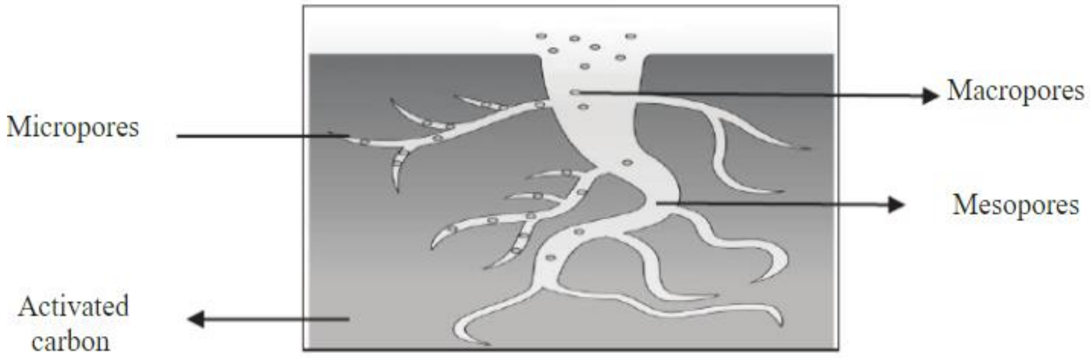

Figure 2.1 Internal structure of AC (Yahya et al., 2018)

The type of starting material as precursor has been a critical parameter that will affect the characteristics, properties and quality of the resulting AC. Commercial AC utilized non-renewable and expensive precursor such as coal, peat, and petroleum residues. Therefore, alternative resources from agricultural waste have become a popular alternative as they are economical, renewable and sustainable as well it is highly abundant in large quantity (Chayid and Ahmed, 2015). In recent years, many agricultural residues which possess high carbon and low inorganic contents have been utilized as precursor for the preparation of AC. Table 2.3 summarized the ultimate and proximate analysis of some agricultural residues which has the potential to be employed as precursor.

Many parts of the plant can be utilized, for instance, stem, bark, leave, shell, stone, fruit peel, husk and root. Table 2.4 underlines the surface area and total pore volume of AC prepared from agricultural residues. As can be seen, the surface area is relatively high hence making it advantageous in adsorptive removal for the remediation of water.

Table 2.3 Ultimate and proximate analysis of some agricultural residues (Yahya et al., 2018)

Agricultural residues	Ultimate analysis (% w/w)					Proximate analysis (% w/w)		
	C	H	O	N	S	Moisture	Volatiles	Ash
Almond shell	50.50	6.60	42.69	0.20	0.01	10.00	80.30	0.60
Bamboo	45.53	4.61	-	0.22	-	2.40	69.63	6.51
Corn cob	46.80	6.00	46.3	0.90	-	4.30	78.70	0.90
Coconut shell	48.63	6.51	44.64	0.14	0.08	8.21	73.09	0.10
Durian shell	39.30	5.90	53.74	1.00	0.06	11.27	-	4.84
Palm shell	50.01	6.90	41.00	1.90	-	7.96	72.47	1.10
Rice husk	36.52	4.82	41.10	0.86	-	-	67.50	16.70
Walnut shell	45.10	6.00	48.60	0.30	-	11.00	71.80	1.30

Table 2.4 Properties of activated carbons prepared from agricultural residues (Ioannidou and Zabaniotou, 2007)

Raw materials	Surface area (m^2/g)	Total pore volume (cm^3/g)
Almond shell	998	0.40
Apricot stone	1190	0.50
Cassava peel	1378	0.583
Corn cob	960	0.486
Corn hulls	1010	0.4348
Macadamia nutshell	1718	0.723
Oak	985	0.3792
Olive seed	1550	-
Rice straw	2410	1.4

Albeit AC shows an excellent performance due to its high porosity and surface area, different synthetization techniques of AC may limit its adsorption ability and specific application and thus, is usually activated or modified accordingly to alter its surface properties and consequently improve its adsorption performance towards multiple adsorbates.

2.4 Adsorption process

Adsorption process involves the transfer of molecules from bulk fluid to the surface of a solid bodies or liquids. Few common terms used in the process are adsorbent, the adsorbing phase and adsorbate, the solute that is adsorbed onto the adsorbent surfaces. In general, adsorption process proceeds through several phases; external mass transfer through the boundary layer in between the bulk solution and the outer surface of adsorbent, diffusion of adsorbate into the adsorbent particles and reaction between the adsorbate and the active sites in the adsorbent pores as depicted in Figure 2.2.

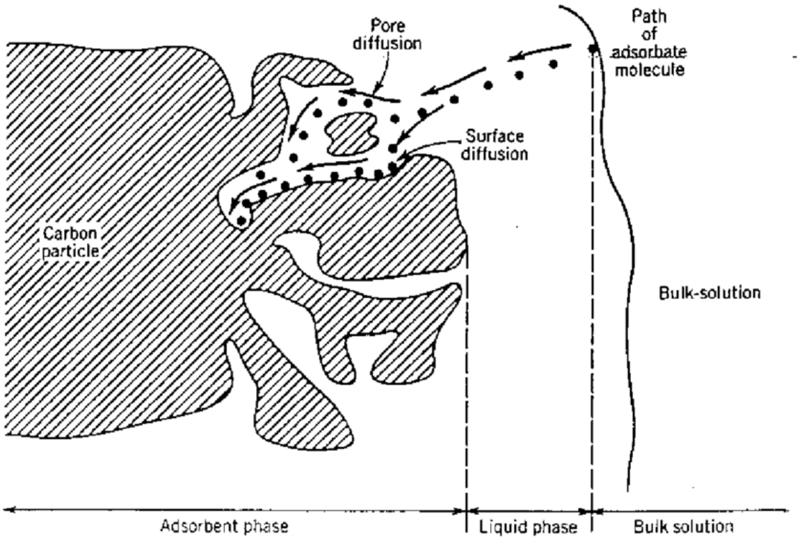

Figure 2.2 Mechanism of adsorption onto activated carbon (Hand et al., 1983)

Adsorption usually incorporates either physical or chemical interactions between the two phases. Physical adsorption, otherwise known as physisorption, only involves weak interaction forces such as van der Waals, electrostatic, hydrophobic interactions or hydrogen bonding between the adsorbate and the adsorbent and thus, the reaction is easily reversible (desorption). There is no alteration to the chemical structure of the adsorbate since the reaction only involve physical forces. In contrary to physical adsorption, chemical adsorption, also known as chemisorption, may involve chemical bonding alteration due to the strong interactions of covalent or ionic bonds between the adsorbate and atoms on the adsorbate surfaces. Thus, chemisorption may not be fully reversible and large energy is required for the regeneration of the adsorbent. Based on the thermodynamic parameter of enthalpy changes (ΔH°), it can be assessed whether the adsorption is via chemical or physical whereby ΔH° for physical adsorption is in the range of 2.1 - 20.9 kJ/mol whilst 80 - 200 kJ/mol indicating chemical adsorption (Rudi et al., 2020). Additionally, the enthalpy changes value is able to give indication on temperature range that is favorable for the adsorption process to occur. Positive value of enthalpy changes reveals that the reaction is endothermic which is caused by high temperature and thus, will drives the adsorption. On the other hand, negative value indicates an exothermic reaction and the adsorption capacity drops at higher temperature (Anastopoulos et al., 2019).

Studies have shown that water remediation by adsorption process via AC exhibit excellent performance (Xiang et al., 2020). The maximum adsorption capacity of some adsorbate namely Ciprofloxacin and Tetracycline by $NaHCO_3$ ACs was reported to be 27.40 and 154.45 mg/g, respectively (Table 2.5). The resources are limited as there were too little studies conducted on $NaHCO_3$ as the activation agent.

Table 2.5 Activated carbon-$NaHCO_3$ composite in adsorptive removal of different adsorbate

Adsorbent type	Adsorbate type	Maximum adsorption capacity (mg/g)	Isotherm model	Reference
Activated carbons-based *folium cycas*-$NaHCO_3$	Ciprofloxacin	27.40	Langmuir	(Kong et al., 2020)
Cassava ethanol sludge biochar-$NaHCO_3$	Tetracycline	154.45	Langmuir	(Zhang et al., 2021)

2.5 Preparation of activated carbon

In general, preparation of AC consists of two basic steps namely carbonization and activation. Carbonization is performed in an inert environment to reduce the volatile content of biowaste to produce char, i.e., via pyrolysis or microwave-induced hydrothermal carbonization whilst the purpose of activation is to enhance the pore volume and specific surface area (Gao et al., 2020; Nizamuddin et al., 2019). Since activation step is more crucial than carbonization as it will determine the AC properties and its adsorption performance, therefore, few different activation methods have been developed to fulfil the need. Activation of the precursor is widely performed via chemical, physical or physicochemical technique. Chemical activation, or also known as wet oxidation, is a single-stage activation method which is carried out in an inert environment and involve the usage of chemical additives such as zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH), phosphoric acid (H_3PO_4) or potassium hydroxide (KOH) which act as both dehydrating agents and oxidants to simultaneously carbonize and impregnate precursor at low temperature ranging from 300 to 800 ℃ (Yang et al., 2021).

The impregnation ratio (IR) is the weight ratio of chemical to the raw material. An optimum IR is one of the important factors to synthesize high-quality AC. On the other hand, physical activation, otherwise known as thermal activation is a two-stage process consists of carbonization in presence of inert gas (nitrogen or argon), and followed by activation stage in the presence of oxidizing gas (carbon dioxide or steam) as activator at temperature range of 800 - 1200 ℃ (Danish and Ahmad, 2018).

Few papers have outlined that chemical activation is more preferable as it resulted in more porous structure of adsorbents, higher yield along with lower activation time and is done at lower temperature than physical activation method (Feng et al., 2022). Nonetheless, physicochemical method, which combines both physical and chemical activation, is highly coveted owing to the high surface area of AC produced. Albeit the longer synthesis time and higher cost, this method was proven to yield a high fraction of mesopores (Liou et al., 2016). Molina-Sabio et al., (1996) have successfully produced AC derived from peach stones with high adsorption capacity and a broad range of pore size distribution through two-steps physicochemical method by using H_3PO_4 as chemical reagent and CO_2 as oxidizing gas. In another study, coconut shells and palm seeds derived ACs with large amount of mesopores present by a single-step physicochemical technique using KOH-CO_2 and $ZnCl_2$-CO_2 but it poses a serious environmental problem due to the heavy metal residues (Hu et al., 2003). Chemical impregnation can be done prior to the thermal treatment or after, although the latter is more recommended as impregnation on char brings the possibilities of; i) better formation of cross-linked structures between carbon atoms and chemical due to the higher chances of contact and reaction; ii) decrease the development of viscous slurry; and iii) lessen the unwanted reactions between chemical and impurities in the raw material (Mohd Din et al., 2009).

2.6 Adsorption isotherm

Adsorption isotherms are utilized to quantify the amount of adsorbate on the adsorbent's surface as a function of pressure or concentration at constant temperature as the adsorption process reaches equilibrium (Sandu et al., 2019). Some of the common adsorption isotherms models used for are Langmuir, Freundlich, Temkin and Koble-Corrigan.

2.6.1 Langmuir isotherm

Langmuir isotherm model is the most common model used to study the adsorption behavior of adsorbate onto adsorbent. This model assumes the adsorbate surfaces to be homogeneous or monolayer and hence it is invalid for non-homogeneous surfaces. This implies that this model assumes the adsorbate molecule is adsorbed onto adsorbent surfaces in a single molecular layer and no other molecules may attached on top of it (Alafnan et al., 2021). Further assumptions of this model are; 1) adsorption and desorption rates are equal at equilibrium, (2) the surface loading or fractional surface coverage is directly proportional to the rate of desorption and, (3) the adsorbent surface consists of a uniform two-dimensional array of similar adsorption sites (Hammond and Conner, 2013). The Langmuir isotherm equation is expressed as following (Langmuir, 1918):

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \text{Equation 2.1}$$

The linearized form is expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad \text{Equation 2.2}$$

where q_e is adsorbate amount at equilibrium (mg/g); C_e is the adsorbate equilibrium concentration; q_m is the monolayer capacity of adsorbent (mg/g) and K_L is the Langmuir constant which is related to the free energy adsorption (L/mg). Linear plot of Langmuir model on C_e/q_e against C_e will yield slope of $1/q_m$ and y-intercept of $1/K_L q_m$. An important parameter to further analysed the adsorption is the separation factor, R_L which defined as:

$$R_L = \frac{1}{1+K_L C_O} \qquad \text{Equation 2.3}$$

where C_O is the adsorbate initial concentration (mg/L). Four different scenarios are outlined for the separation factor value; favorable adsorption when R_L is between 0 and 1, unfavorable adsorption when R_L is more than 1, linear adsorption when $R_L = 1$ and irreversible adsorption when $R_L = 0$.

2.6.2 Freundlich isotherm

Freundlich isotherm model is usually applied for non-ideal adsorption on non-homogeneous surfaces. In contrast with Langmuir model, Freundlich model assumes there are many different active sites which acts simultaneously with different adsorption energy (Karami et al., 2022). The Freundlich isotherm model is defined as (Freundlich, 1906):

$$q_e = K_F C_e^{1/n_F} \qquad \text{Equation 2.4}$$

The linearized form of this model is obtained by taking the logarithmic on both sides as:

$$\log q_e = \frac{1}{n_F} \log C_e + \log K_F \qquad \text{Equation 2.5}$$

where q_e is adsorbate amount at equilibrium (mg/g); C_e is the adsorbate concentration at equilibrium (mg/L); K_L is the Freundlich constant which is related to the bonding energy of adsorbate onto adsorbent (mg/g).(L/mg)$^{1/n}$ and n_F is the heterogeneity factor. Linear plot of $\log C_e$ against $\log q_e$ will provide slope of $1/n_F$ and intercept of $\log K_F$. The value of $1/n_F$ will always lies between 0 and 1 in which it indicates the surface