BATCH ADSORPTION STUDY FOR REMOVAL OF CHLORAMPHENICOL USING ACTIVATED CARBON

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By

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TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

Symbol	Description	Unit
C_0	Initial concentration of adsorbate in liquid phase	mg/L
C	Final concentration of adsorbate in liquid phase	mg/L
C_e	Equilibrium concentration of adsorbate in liquid phase	mg/L
q_e	Adsorbate adsorbed per weight of adsorbent at equilibrium	mg/g
q_m	Adsorbate adsorbed per weight of adsorbent at saturation	mg/g
q_t	Adsorbate adsorbed per weight of adsorbent at time instant	mg/g
q_{exp}	Experimental adsorption capacity	mg/g
q_{cal}	Calculated adsorption capacity	mg/g
K_L	Langmuir constant	L/mg
K_F	Freundlich constant	mg/g
n	Adsorption intensity	dimensionless
k_1	Pseudo first order kinetic rate constant	min^{-1}
k_2	Pseudo second order kinetic rate constant	g/mg.min
V	Volume of adsorbate solution	L
W	Weight of adsorbent	g
R^2	Correlation coefficient	dimensionless

LIST OF ABBREVIATIONS

AC	Activated carbon
CPC	Chloramphenicol
UV-Vis	Ultraviolet-visible

KAJIAN PENJERAPAN SECARA BERKELOMPOK UNTUK PENYELESAIAN KLORAMFENIKOL MENGGUNAKAN KARBON TERAKTIF

ABSTRAK

Kloramfenikol ialah sejenis antibiotik bakteria spektrum luas yang digunakan untuk penyakit seperti wabak, taun, dan demam kepialu. Akibatnya, kloramfenikol boleh menyebabkan pencemaran kepada sumber air apabila dilepaskan ke alam sekitar menyebabkan gangguan kepada ekosistem akuatik dan membawa kepada rintangan mikrob. Objektif penyelidikan adalah untuk menilai prestasi penggunaan karbon teraktif komersial untuk penyingkiran kloramfenikol dan menentukan parameter optimum untuk penyingkiran CPC. Kapasiti penjerapan bahan penjerap didapati meningkat sehubungan dengan peningkatan kepekatan CPC awal. Ini disebabkan kepekatan larutan yang tinggi mewujudkan kecerunan kepekatan yang memberikan daya penggerak untuk pemindahan jisim berlaku, peningkatan suhu disebabkan tenaga kinetik yang lebih tinggi dibekalkan dan peningkatan tapak penjerapan dos penjerap lebih dibekalkan. Walau bagaimanapun, mengambil kira faktor seperti kos, keadaan optimum akhir ialah suhu 30 °C, kepekatan awal 10 mg/L dan dos penjerap 1 g/L. Model tertib pertama pseudo dan model tertib kedua pseudo kinetik penjerapan telah dinilai dan disiasat. Dapatan ujian dengan pekali R^2 yang lebih tinggi dicirikan oleh persamaan kinetik tertib pseudo-saat dalam semua eksperimen yang dijalankan. Isoterma penjerapan telah dimodelkan dengan menggunakan isoterma Freundlich, Langmuir, Temkin. Berdasarkan keputusan yang diperoleh, model Langmuir memberikan padanan terbaik kepada data ujian, diikuti oleh Freundlich dan akhirnya Temkin. Sifat termodinamik juga telah dikaji di mana proses penjerapan CPC pada karbon teraktif adalah proses endotermik yang spontan secara termodinamik dan proses penyerapan sorben adalah proses tidak boleh balik kerana ΔS

lebih besar daripada 0. Keputusan menunjukkan bahawa karbon teraktif adalah penjerap yang menjanjikan untuk rawatan kloramfenikol dalam air terjejas.

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ABSTRACT

Chloramphenicol (CPC) is a broad-spectrum bacterial type of antibiotic used for diseases such as plague, cholera, and typhoid fever. Consequently, chloramphenicol can cause pollution to the water sources when releases to the environment causing disruption to aquatic ecosystems and leading to microbial resistance. The objective of the research is to evaluate the performance of the application of commercial activated carbons for the removal of chloramphenicol and determine the optimum parameters for the CPC removal. The adsorption capacity of adsorbent is found to increase with respect to the increasing initial CPC concentration. This is due to high solution concentration create concentration gradient that provide driving force for mass transfer to occur, increasing temperature due to higher kinetics energy supplied and increasing adsorbent dose adsorption sites are more supplied. However, considering factor such as cost, the final optimum conditions are temperature 30 °C, initial concentration 10 mg/L and adsorbent dosage 1 g/L. The pseudo first order and pseudo second order models of adsorption kinetics was assessed and investigated. The findings of tests with a higher coefficient R_2 were characterised by the pseudo-second order kinetics equation in all experiment carried out. The adsorption isotherm was modelled by using the Freundlich, Langmuir, Temkin isotherm. Based on the result obtained, the Langmuir model provided the best match to the test data, followed by Freundlich and finally Temkin. The thermodynamics properties also been studied where adsorption process of CPC onto activated carbon is a thermodynamically spontaneous, endothermic process and the sorbent uptakes processes is irreversible

process since ΔS is greater than 0. The results revealed that activated carbon is a promising adsorbent for treatment of chloramphenicol in affected water.

1. CHAPTER 1: INTRODUCTION

1.1 Background Information

1.1.1 Active pharmaceutical ingredients (APIs)

The word "active pharmaceutical ingredient" (API) refers to the physiologically active component of a drug product, such as a tablet or capsule. Drug goods typically contain a variety of components where API is the most important among them. Excipients are other substances found in pharmaceuticals. These compounds must be biologically safe because they make up a variable percentage of the medication product. Formulation is the process of optimising and modifying the mixture of components used in a medicine. APIs are employed in the diagnosis, cure, mitigation, therapy, or prevention of disease, or to influence the structure or function of the body. Pharmaceutical production is divided into two stages. Manufacturers turn raw ingredients into APIs in the first phase. The second stage is to create the final formulation by mixing APIs and excipients into tablets, capsules, solutions, and other forms, and then packaging the medicine for end consumers. APIs are either sold on the open market (also known as the merchant market) or used as inputs in final formulations by manufacturers.

APIs are prevalent endocrine disruptors present in medications and personal care products. Due to its application, they are regularly observed in especially in water for drinking purposes. Current water treatment technologies, on the other hand, are ineffective at eliminating new endocrine disruptors, potentially contaminating tap water (Wee et al., 2020). Humans are thus exposed to the health risk caused by API through drinking tap water. APIs are significant for environmental and human health protection because they are act as water quality monitoring indicators for safe water supply from organic pollutants.

1.1.2 Active Pharmaceutical Ingredients (APIs) in Malaysian Tap Water

To establish if pharmaceutical contaminants should be listed, they should be assessed on the following six qualities: (Othman et al., 2021)

- Causes negative health consequences
- Quantity of APIs production with respective purposes
- Predominant of APIs in water
- Tenacity
- Ingestible sources, such as food and water
- Frequency and duration of APIs exposure.

Active pharmaceutical components are the only pharmaceutical pollutants that are dangerous to humans and aquatic organisms. The "degradability performance”, life span, and persistence in the aquatic environment are all features and attributes of APIs that are harmful to humans and the environment.

In the instance of Malaysia, there were more than 250 pharmaceutical manufacturers; more than 30 therapeutic categories containing more than 50 different medications were used. The Putrajaya drinking water system (Praveena et al., 2019), Langat River (Omar et al., 2019a), Klang River (Omar et al., 2019b), the Lui, Gombak, and Selangor rivers (Praveena et al., 2018), all been discovered to have pharmaceutical pollutants. However, because the waste from pharmaceutical products is regarded a non-priority environmental policy in Malaysia, no clear law oversees the situation and the laws solely addresses pharmaceutical pollutants in general, with special attention paid to hazardous waste generated by medical facilities or services. There is currently no parameter value defined for the pharmaceutical product that eventually ended up tap water that potentially endanger human health.

Wee et al. (2020) carried out studies to examines tap water in Malaysia for the distribution and prevalence of APIs to mitigate the threat of new organic contaminants polluting drinking water. Ten APIs from seven distinct medicinal classes were investigated, which comprises of anti-inflammatory drugs, antibiotics, antiepileptics antibacterial agents, beta-blockers, psychoactive stimulants, and antiparasitic drugs, genotoxic, neurotoxic with endocrine system disfunction effects.

As indicated in Table 1.1 Analysis of APIs in tap water, nine target chemicals were found at concentrations ranging from 0.03 to 21.39 ng/L, but chloramphenicol was below the MDL (0.23 ng/L) at all sampling points (Wee et al., 2020). APIs were found in tap water at amounts greater than the MQLs, indicating contamination. Table 1.1 shows the general API that can be found in Malaysia's tap water while Table 1.2 indicates some of their consequences.

Table 1.1 Analysis of APIs in tap water (Wee et al., 2020)

Classes	**Compound**	**Concentration (ng/L)**	
		Min	Max
Anti-inflammatory drug	Dexamethasone	< 0.36	2.11
	Diclofenac	< 2.56	21.39
Antibiotic	Chloramphenicol	< 0.23	< 0.23
	Sulfamethoxazole	< 0.03	0.9
	Triclosan	< 1.29	9.74
Antiepileptic	Primidone	< 0.14	2.99
Antibacterial agent	Ciprofloxacin	< 0.05	8.69
Beta-blocker	Propranolol	< 0.03	0.69
Psychoactive stimulant	Caffeine	0.27	5.33
Antiparasitic drug	Diazinon	< 0.08	1.8

Table 1.2 APIs and health effects (Othman et al., 2021)

APIs	Possible Health Effects
Endocrine disrupting compounds (EDCs)	• Endocrine dysfunction, physiological function • Aggressive effects on gene expression • Abnormal cell proliferation • Metabolic disruption, morphological and functional effects in the human system • Infertility as well as abnormal prenatal and childhood development
Caffeine, Sulfamethoxazole, Propranolol	• Acute and chronic damages • behavioural changes • accumulation in tissues • Reproductive damage • Inhibition of cell proliferation
Diclofenac and dexamethasone	• linked to oxidative stress and decreased steroid hormone (i.e., testosterone) levels • lead to reproductive impairment in aquatic organisms

1.1.3 Activated Carbon

Activated carbon (also called activated charcoal, activated coal or active carbon) contains carbonaceous material derived from charcoal. It is produced by pyrolysis of organic materials of plant origin such as coal, coconut shells and wood, sugarcane bagasse, soybean hulls and nutshell (Sabir et al., 2015). Generally, activated carbon is a very useful adsorbent. It is a low-cost material with distinguishable properties like high specific surface area, high porosity, and desired surface functionalization (Bhat, 2021). Due to its a promising characteristic, it has been extensively studied by many researchers.

Few types of activated carbon commonly available as shown below:

- Nut shell based activated carbon
- Coal-based activated carbon
- Wood based activated carbon
- Petroleum based activated carbon

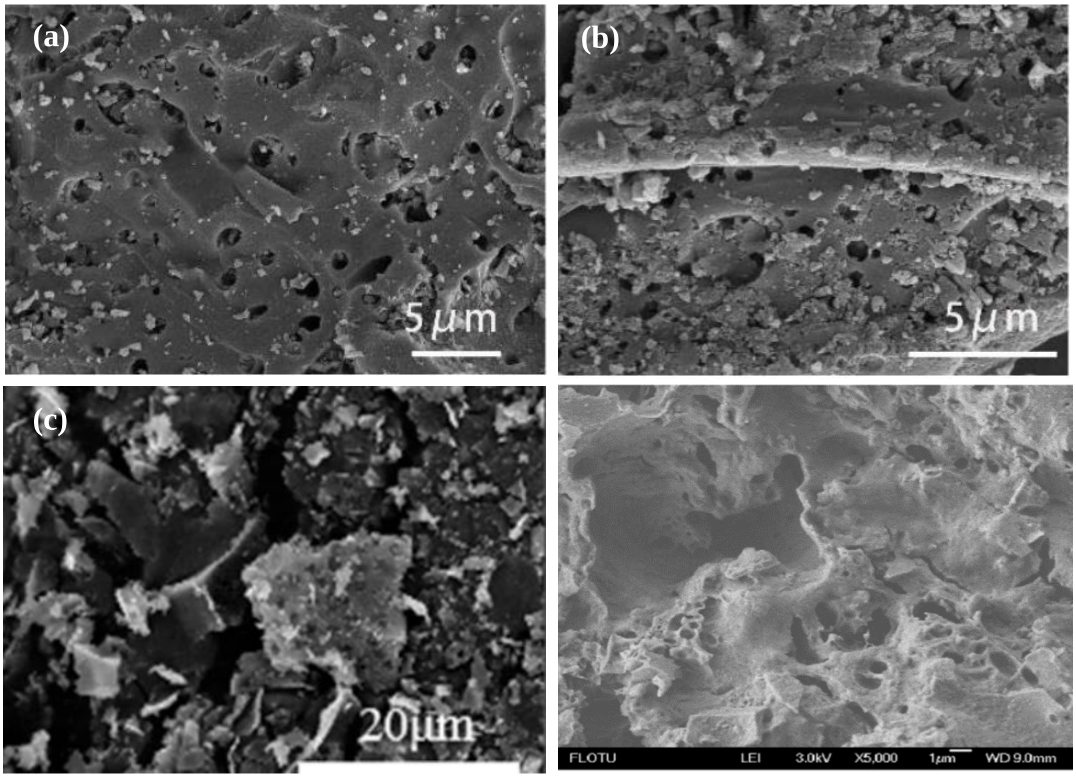


Figure 1.1 SEM images of examples of activated carbon

Figure 1.1 shows the scanning electron microscope (SEM) images of activated carbon where Figure 1.1 (a) and (b) are the coconut shell-derived powdered activated carbons and coal-derived powdered activated carbons (Xie et al., 2020), Figure 1.1 (c) is wood-derived carbon after air oxidation (Ren et al., 2019) and Figure 1.1 (d) is carbonized and sulfonated vegetable oil asphalt catalyst (Shu et al., 2009).

1.2 Problem Statement

Chloramphenicol has been extensively approved for use in underdeveloped countries due to its dual advantages of low production cost and excellent stability. This chemical has been found in water sources such as rivers, lakes, and sea because of agri- and aquaculture activities. Chloramphenicol may be found in hospital wastewaters, influents and effluents of wastewater treatment plants in response of human or animal medicinal benefits (Nguyen et al., 2022).

Chloramphenicol exposure could have major consequences for the environment and human health. In addition, it is extremely harmful to aquatic organisms. Through specialised protein regulation, this chemical inhibits and limits the growth and development of algae for instance green algae, blue-green algae, marine algae, and freshwater green algae. Chloramphenicol is recognised to play a role in the development of in a rare disease, aplastic anaemia in rats, cats, dogs, and pigs, as well as humans. A shortage of red and white blood cells causes this illness, which results in blood problems and a high death rate. Furthermore, several studies have suggested that chloramphenicol may be carcinogenic to humans (Nguyen et al., 2022). Many nations, including the United States, European Union, Australia, Canada, Japan, and China is no longer use CPC as an ingredient in animal feed due to these harmful consequences negative repercussions. Decontaminating water with chloramphenicol is a difficult task, given its extensive prevalence and detrimental consequences on the environment and humans. As a result, developing a sustainable and green technique to eradicate chloramphenicol from the environment is critical. The capacity of activated carbon to adsorb particles from wastewater is among its many appealing qualities. Thus, the performance of synthesized activated carbon in adsorption requires investigation in detail. Also, to ensure the activated carbon capable of performing at its best, the effect of operating conditions such as initial concentration temperature and amount of adsorbent needed to be studied.

1.3 Objective

The following are the study's goals:

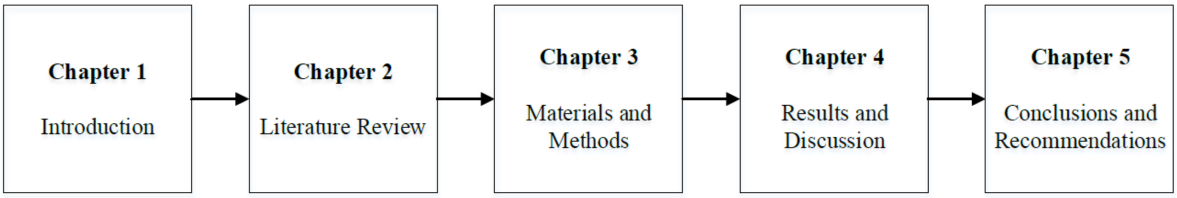
I. To study the effect of concentration, temperature and amount of adsorbent on chloramphenicol adsorption.

II. To compare the behavior of CPC adsorption by using adsorption isotherms and adsorption kinetics model.

III. To investigate the dynamics of the adsorption through thermodynamics approach such as the Gibb's free energy, enthalpy, and entropy.

1.4 Thesis Organization

The presentation of the project report has been organized using a thesis that is quite clear and typical. The project report essentially consists of five chapters: an introduction to the general project, a literature assessment of related research, the materials and equipment to be utilized in the project, discussions of the results gained, and conclusions to wrap up the whole project. To make the illustrations easier, the arrangement of the thesis is as indicated below.

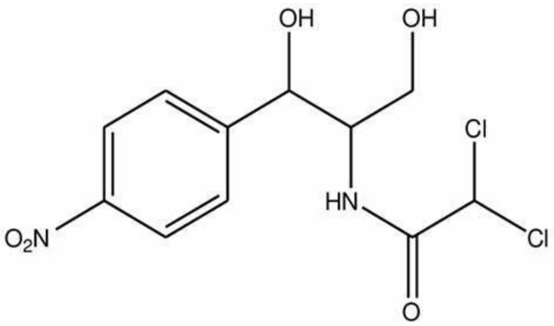


2 CHAPTER TWO: LITERATURE REVIEW

2.1 An insight to Chloramphenicol

Chloramphenicol (CPC) is a drug that is used to treat infections of the eyelids, such as bacterial conjunctivitis and otitis externa. Typhoid and cholera have also been treated with it. Chloramphenicol is a protein-inhibiting antibiotic. This antibiotic is a broad-spectrum antibiotic where it was obtained from the bacteria *Streptomyces venezuela*. Chloramphenicol can destroy the bacterium through attaching of the bacterial ribosomal subunit that can prevent of production of protein. As a result, chloramphenicol is preferred for treatment of bacterial infections by gram-positive, gram-negative, and anaerobic bacterial. Table 2.1 shows the molecular properties of chloramphenicol.

Table 2.1 Molecular Properties of Chloramphenicol

Chemical Formula	Molecular weight	Molecular Structure
$C_{11}H_{12}Cl_2N_2O_5$	323.13	

Emergent antibiotic contaminants include chloramphenicol. Aquaculture, hospital wastewaters, human and livestock therapeutic activities, and pharmaceutical production are all major contributors of chloramphenicol contamination. Chloramphenicol is released into the water through aquaculture activities, sewage, and wastewater (household, industrial, and a portion of agricultural), all of which are treated at wastewater treatment plants. Many environmental pollutants, such as chloramphenicol, can be found in wastewater treatment plant influents and effluents. Praveena et al., 2018 in their studies of pharmaceuticals residues, found in the presence of chloramphenicol in the 3 selected water bodies sources of Selangor (Malaysia) where the result is summarized in Table 2.2.

Table 2.2 Presence of chloramphenicol in the Malaysia's River

Study Location	Water Source	Chloramphenicol concentration
Lui River	Surface of water	15.80 to 18.03 ng/L
Gombak River	Surface of water	22.72 to 23.37 ng/L
Selangor River	Surface of water	21.48 to 24.35 ng/L

Adsorption on activated carbon can be used to remove several pollutants for a variety of applications. It permits both inorganic and organic chemicals to be removed from water and wastewater. This approach can be used to successfully remove a variety of antibiotics and is widely applied in the removal of chloramphenicol.

2.2 Common technology used for pollutants treatment

In general, physicochemical and/or biological methods are used to remove contaminants from effluents, with research focusing on more cost-effective methods or new alternatives. As a result, the effluent parameters will define the procedure to be used. Each treatment has its own set of constraints, including cost, feasibility, efficiency, practicability, dependability, environmental impact, sludge production, difficulty of operation, pre-treatment needs, and the formation of potentially harmful by-products (Grégorio & Eric, 2018). Table 2.3 shows some treatments for pollutants with each advantage and disadvantages.

Table 2.3 Summary of several techniques for the pollutant's removal

Methods	Characteristics	Advantages	Disadvantages
Chemical precipitation	Uptake and remove of the pollutants with separation of the products formed	• Technologically simple (simple equipment) • Economically advantageous and efficient • Adapted to high pollutant loads	• Chemical consumption • High sludge production, handling and disposal problems (management, treatment, cost)
Chemical oxidation	Use of an oxidant	• Simple, rapid, and efficient process	• Production, transport and

		• No sludge production	management of the oxidants • Several dyes are more resistant to treatment and necessitate high ozone doses
Adsorption /filtration	Non-destructive process	• Variety of commercial products • Variety of target contaminants • Highly effective process	• Relatively high investment • High cost of material
Membrane filtration	Semipermeable barrier	• Small space requirement • Simple, rapid and efficient, even at high concentrations	• Investment costs are often too high for small and medium industries • High energy requirements