MICROWAVE IRRADIATED RICE HUSK BASED ACTIVATED CARBON FOR ADSORPTION OF CHLORAMPHENICOL

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MICROWAVE IRRADIATED RICE HUSK BASED ACTIVATED CARBON FOR ADSORPTION OF CHLOROPHENICOL

by

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LIST OF SYMBOLS

	Symbol	Unit
A_T	Binding constant	L g^{-1}
B_T	Temkin constant	-
b_i	Linear coefficient	-
b_{ij}	Quadratic coefficient	-
b_o	Constant coefficient	-
C	Boundary layer	-
C_e	Equilibrium concentration of chloramphenicol	mg/L
C_o	Initial chloramphenicol solution	mg/L
E_a	Arrhenius activation energy	kJ/mol
k_1	Adsorption rate constant of pseudo-first order	1/min
k_2	Adsorption rate constant of pseudo-second order	g/mg.min
k_i	Rate constant	g mg^{-1} min^{-1}
K_F	Freundlich isotherm constant	mg/g $(L/mg)^{1/n}$
K_L	Langmuir isotherm constant	L/mg
K_P	Constant of intraparticle diffusion	mg/ $g^{-1}h^{-1/2}$
n_F	Heterogeneity factor	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_t	Amount of adsorbate adsorbed at time	mg/g
q_m	Maximum monolayer adsorption	mg/g
R	Universal gas constant	8.314 J/mol.K
R^2	Correlation coefficient	-
T	Temperature	K
t	Time	hr

V	Volume of chloramphenicol solution	L
W	Mass of adsorbent	g
x_1	Radiation power	W
x_2	Activation time	min
x_i	Coded value	-
x_j	Coded value	-
y_1	Chloramphenicol removal	%
y_2	Rice husk activated carbon yield	%
Δq_t	Error of adsorption capacity	%
$\Delta G°$	Changes in standard enthalpy	kJ/mol
$\Delta H°$	Changes in standard entropy	kJ/mol
$\Delta S°$	Changes in standard Gibbs free energy	kJ/mol

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CAP	Chloramphenicol
CCD	Central composite design
DF	Degree of freedom
FTIR	Fourier transform infrared
GAC	Granular activated carbon
IUPAC	International Union of Pure and Applied Chemistry
PAC	Powdered activated carbon
SDGs	Sustainability Development Goals
SEM	Scanning electron microscopy
RH	Rice husk
RHAC	Rice husk activated carbon
Rpm	Rotation per minute
RSM	Response surface methodology
UV	Ultraviolet

KARBON TERAKTIF PENYINARAN GELOMBANG MIKRO BERASASKAN SEKAM PADI UNTUK PENJERAPAN KLORAMFENIKOL

ABSTRAK

Industri farmaseutikal adalah salah satu penyumbang utama Kloramfenikol (CAP) kepada sumber air yang boleh menyebabkan pelbagai masalah persekitaran. Dalam beberapa tahun kebelakangan ini, karbon teraktif berasaskan bahan buangan pertanian telah digunakan sebagai penjerap dalam rawatan air sisa antibiotik. Tujuan kajian ini adalah untuk mengkaji prestasi karbon teraktif (AC) yang dihasilkan dari sekam padi untuk menyingkirkan kloramfenikol (CAP) dengan pengaktifan fizikal menggunakan gasifikasi karbon dioksida dan teknik radiasi gelombang mikro. Metodologi gerak balas permukaan digunakan untuk mengoptimumkan parameter penyediaan karbon teraktif sekam padi iaitu daya gelombang mikro dan masa pengaktifan untuk penjerapan kloramfenikol (CAP). Keadaan penyediaan optimum untuk karbon teraktif sekam padi diperhatikan pada daya radiasi 490 W dan masa pengaktifan 2 minit yang menghasilkan penyingkiran CAP sebanyak 92.15% dan hasil karbon teraktif sekam padi sebanyak 65.43%. Penjerapan CAP oleh karbon teraktif sekam padi meningkat dengan peningkatan kepekatan CAP awal dan masa sentuhan. Keseimbangan penjerapan CAP pada karbon teraktif sekam padi mengikuti garis sesuhu Freundlich. Kajian kinetik penjerapan CAP ke karbon teraktif sekam padi yang baik diwakili oleh model kinetik pseudo tertib kedua. Menurut analisis termodinamik, nilai $\Delta H°$ adalah negatif, menunjukkan bahawa penjerapan adalah proses eksotermik.

MICROWAVE IRRADIATED RICE HUSK BASED ACTIVATED CARBON FOR ADSORPTION OF CHLORAMPHENICOL

ABSTRACT

Pharmaceutical industry was one of the main contributors of Chloramphenicol (CAP) to the water sources which can causes various environmental problems. In recent years, agriculture waste based activated carbon has been employed as an adsorbent in the treatment of antibiotics wastewater. The purpose of this study is to investigate the performance of activated carbon (AC) generated from rice husk (RH) for the removal of Chloramphenicol (CAP) by physical activation utilizing carbon dioxide (CO_2) gasification and microwave irradiation technique. Response Surface Methodology (RSM) was used to optimize the rice husk based activated carbon's (RHAC) preparation parameters of radiation power and activation time for adsorption of Chloramphenicol (CAP). The optimum conditions for RHAC preparation were observed to be 490 W of radiation power and 2 minutes of activation time which resulted 92.15% of CAP removal and 65.43% of RHAC's yield. The CAP adsorption by RHAC increased as the initial CAP concentration and contact time increased. Adsorption equilibrium of CAP onto RHAC followed Freundlich isotherm. The kinetic studies of CAP adsorption onto RHAC was best represented by pseudo-second order kinetic models. According to the thermodynamic analysis, the value of $\Delta H°$ was negative, indicating that the adsorption was an exothermic process.

CHAPTER 1

INTRODUCTION

1.1 Research background

Over the past decades, antibiotic medications have been widely used in treatment and act as diseases preventive in humans and animals. Between the year 2000 and 2015, the consumption of antibiotic grows 65% from 21.1 to 34.8 billion daily doses. The percentage of antibiotic could rise higher than 202% from 42.3 billion daily doses by 2030 if the increases in antibiotic consumption rates continues (Friedrich, 2018). Antibiotic usage in animals can result in residues which can contaminate ground water or the air system (Lundborg & Tamhankar, 2017). Chloramphenicol (CAP) is one of the antibiotics that is widely used in humans and animal for disease treatment. However, some of the country has banned the uses of CAP in food animals due to its capability to cause the Aplastic anemia when expose to it (Hanekamp & Bast, 2015). Even though the uses of CAP in food animals are banned, the wastewater from antibiotic manufacturing and improper disposal into the aquatic ecosystems such as rivers, lakes and seas still pollute the water environment (Yiran Li et al., 2018). Several studies were reported that the CAP was found in fish in Bangladesh and shrimp in India and Indonesia (Lundborg & Tamhankar, 2017). Therefore, it is important to develop or to produce adsorbents for extracting CAP in contaminated waters. Extensive research has been reported on removing CAP from wastewater by using activated carbon (AC) derived from biomass.

AC such as granular activated carbon (GAC) or powdered activated carbon (PAC) has been proven to be an successful innovation or method for the elimination of organic compound (Fu et al., 2017). Adsorptive removal by AC has gain serious attention to the researcher due to its advantages such as simple in operation, low energy cost, high adsorption rate, high reliability and environmentally friendly (Guillossou et al., 2019; T. Zhang et al., 2019). The adsorption performances of the AC depends on the type and the dose of the AC, the operating conditions, and the composition of the water (Guillossou et al., 2019). Generally, only 60 to 90% of average removals range that could be achieved and it is highly depends on the molecule properties such as hydrophobicity, size, or charge (Guillossou et al., 2019).

AC is usually prepared via combination of physical and chemical activation technique. This technique is favoured because of its advantage to operate in a simple way, shorter activation time, higher yield and well development of the porous structure (Ao et al., 2018). This technique involves two processes which are carbonization and activation where they are performed simultaneously. Generally, chemical activation is implemented to woody biomass and the chemical agents used are phosphoric acid, sulphuric acid or zinc chloride. The function of chemical agents is to act as dehydrating agents and oxidants. In chemical activation process, the raw material is first impregnated with chemical agents for cellulose to break down and then, the impregnated sample is subjected through pyrolysis at temperature ranging from 500 to 800℃. At this level, the raw material is dehydrated by chemical activator which produce AC with porous structure. Then the AC being washed to remove the remaining activating agent on samples (Świątkowski, 1999).

Over the last few years, the used of microwave is gaining serious attention in preparing AC due to its capability to produce fast, uniform and accurate control of heating (Ao et al., 2018). When microwave radiation is applied to the object, the microwave energy induces the dipole rotation over a million times per second in atomic scale. This produce frictional interaction between molecules and atoms inside the object, thus generates rapid and volumetric heating (Lam et al., 2017). Microwave heating also can increase energy efficiency, increase the yield and product quality besides reducing hazardous product emissions (Y. Wang et al., 2015). Due to that, the use of microwave is more preferable over the conventional heating for producing AC.

As the price of current AC is high, recently numerous researches has been conducted to find low cost and environmental friendly materials to be transformed into AC for adsorption process (Menya et al., 2018). Examples of these low-cost materials that have been reported are African palm fruit (Abdulrazak et al., 2017), tobacco stems (Mudyawabikwa et al., 2017), coconut shell fibers (Yanyan et al., 2018) and rice husk (Ahiduzzaman & Sadrul Islam, 2016). Malaysia is one of the countries that consume rice as a staple food. In 2018, Malaysia produced approximately 1.7 million metric tons of rice and from that, rice husk as waste is produced as well. It is estimated that 25% of paddy weight is comes from rice husk (Kosseva, 2011). Unfortunately, abundance of rice husk is burned by farmers, thus creating environmental pollution. Although various studies on the production of AC from rice husk has been published, these studies only concern on application for removal of heavy metals (Mullick et al., 2018) and dyes (Ahmad et al., 2020). Until now, there is no studies have been reported on removing CAP by using RHAC. Thus, this study aimed to prepare RHAC to remove CAP in wastewater.

1.2 Problem statements

There are many cases where CAP has been found in water sources which directly cause problems on environment, aquatic ecosystem and humans' health. Conventional wastewater treatment is not effective to remove CAP. Hence, development of a new method and material focuses on effective chloramphenicol removal is very important. Adsorption is an effective method to remove CAP from aqueous solution besides it is a simple and eco-friendliness method (Yiran Li et al., 2018).

AC can be prepared using conventional method, however conventional heating consumes more energy and time. To overcome this problems, microwave heating was used as its beneficial to reduced pyrolysis time for activation as a result of fast temperature rise, as well as the significantly lower energy usage.

High adsorption and yield of AC are desirable, however due to the problems between AC's performance and yield, optimum preparation conditions are hard to achieve. Hence, response surface methodology (RSM) was utilised to find the optimum preparation conditions in this study.

Rice husk is one of the agricultural wastes that produce abundantly every year in Malaysia which can cause disposal problem. To reduce the volume of rice husk waste, it can be converted into various application such as ceramic, cements and plastic composites. Due to its good physical characteristics, rice husk can be used as precursor to produce low cost AC. Thus, the transformation of rice husk into activated carbon as adsorbent can help in minimize the unused rice husk and reduce the environmental problems.

1.3 Research objectives

1. To prepare AC from rice husk via microwave irradiation technique under the flow of CO_2 gas for the removal of CAP in aqueous solution.
2. To optimize adsorption removal of CAP and RHAC's yield by optimizing preparation conditions (radiation power and radiation time) using response surface methodology (RSM).
3. To evaluate CAP-RHAC adsorption system in terms of equilibrium, isotherm and kinetic studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Type of antibiotics

Many countries have undergone rapid industrialization with the high use of chemical which can results the rise of disease in humans. Due to that, pharmaceutical sector is one of the main role in producing more medicine such as antibiotics to overcome this problem. Approximately, there are 210 types of semisynthetic antibiotic produced in natural environment. With different chemical structure, antibiotic can be classified into many categories such as lincosamides, macrolides, sulfonamides, chloramphenicol, tetracyclines, fluoroquinolones, imidazoles, β-Lactams and others (Ahmed et al., 2015; Ben et al., 2019). About 120 types from these categories are used in livestock husbandry and health care where some of them may be disposed through the environment such as river and sea.

2.1.1 Chloramphenicol

Chloramphenicol (CAP) is a broad-spectrum antibiotic which derived from Streptomyces venezuelae in 1947 (Martelli et al., 1991; Shukla et al., 2011).The molecular formula of CAP is $C_{11}H_{12}Cl_2N_2O_5$. CAP is bacteriostatic but it can be bactericidal if use in high concentrations and it is mostly used for internal diseases treatment. The function of CAP is to stops bacterial growth by binding the ribosome and inhibiting protein synthesis of bacteria. However, most country banned CAP in animal industry due to its genotoxic property. Exposure of CAP can lead to Aplastic anemia and bone marrow suppression thus it is hardly used as human medication (Hanekamp & Bast, 2015). As CAP was used in human medicine, the wastes can contaminate the water sources (Hanekamp & Bast, 2015).

2.1.2 Drawback of CAP

Recently, CAP has been appraised as an arising type of pollutants in the environment. The existence of antibiotic in the environment is come from different sources such as pharmaceutical manufacturers, animals, agriculture and humans (Al-Riyami et al., 2018). CAP was found in the wastewater and seawater with the concentration up to 2430 ng/L. Even at low concentration, the effect on this type of antibiotic can cause a critical risk to the human health and environmental ecosystem (Palma et al., 2020). The exposure of aquatic life to antibiotic can cause some impact on their growth, weight and survival (Ahmed et al., 2015). The accumulation of antibiotic can lead to the mutagenic effects, nephropathy, arthropathy and can cause damage to central nervous system. Thus, removal of antibiotic residues in environment which can exposed to human and animals is needed due to its large usage nowadays (Ben et al., 2019).

2.1.3 Methods in removing CAP

With the rapid increase in antibiotic consumption in most countries, there are various technique to remove it from the water sources. Many researchers concern on the existence of CAP in water sources which can gives negative impact to aquatic ecosystem and human health. Currently, researchers are actively working to develop the efficient technology in removing CAP to ensure the water sources are clean and unpolluted. The technology includes bio-electrochemical treatment (Guo et al., 2019), photocatalytic degradation (Dong et al., 2017), ozonation (Cao et al., 2020), zero-valent iron (Tan et al., 2018), electro-irradiated system (Cotillas et al., 2018) and adsorption (Yiran Li et al., 2018). Among them, adsorption has been reported as an efficient technology, low cost and environmental friendly (Yiran Li et al., 2018).

2.1.4 Agricultural waste as adsorbent materials

Agricultural waste or also called lignocellulosic biomass contains three types of carbon based polymer which is lignin, cellulose and hemicellulose. It is the most abundant material in the world where it can be converted into various type of product and one of it is AC. Table 2.1 shows various agricultural wastes converted to adsorbent to remove antibiotic.

Table 2.1: List of agricultural wastes converted to adsorbents for antibiotics removal (Ouyang et al., 2020).

Agricultural waste	Antibiotic pollutants	Adsorbent properties	References
Pine sawdust	Sulfamethoxazole	Surface area = 125.8 m^2g^{-1} Pore volume = 0.14 cm^3g^{-1}	(Reguyal & Sarmah, 2018)
Giant reed	Amoxicillin	Surface area = 1372 m^2g^{-1} Pore volume = 0.760 cm^3g^{-1}	(Chayid & Ahmed, 2015)
Cassava waste	Oxytetracycline	Surface area = 128.4 m^2g^{-1} Pore volume = 0.01 cm^3g^{-1}	(Luo et al., 2018)
Garden waste	Trimethoprim	Surface area = 8.89 m^2g^{-1} Pore volume = 0.018 cm^3g^{-1}	(Yuan Li et al., 2019)
Palm tree	Tylosin	Surface area = 120 m^2g^{-1} Pore volume = 2.43 cm^3g^{-1}	(Guo et al., 2019)
Wheat straw	Norfloxacin	Surface area = 112.6 m^2g^{-1} Pore volume = 0.604 cm^3g^{-1}	(Jinghuan Zhang et al., 2018)
Wheat husk	Gemifloxacin	Surface area = 95.76 m^2g^{-1} Pore volume = 0.11 cm^3g^{-1}	(Gholami et al., 2020)
Tea waste	Sulfamethazine	Surface area = 576.1 m^2g^{-1} Pore volume = 0.109 cm^3g^{-1}	(Rajapaksha et al., 2016)

Rice husk (RH) is an external layer of the rice that being produce abundantly from rice manufacturing factories as a waste. Approximately, around 80 million tons of rice husk produced yearly and causing disposal problem (Shamsollahi & Partovinia, 2019). The composition of the RH contains around 50% of cellulose, 25% to 30% of lignin, 15% to 20% of silica and 10% to 15% of moisture (Singh, 2018). RH has many potentials in agriculture and various industries because of its advantage such as granular structure, high chemical stability, and high mechanical strength. RH has a potential to be a good low cost adsorbent and effective in removing CAP.

2.2 Activated carbon

Activated carbon (AC) is a porous substance usually used for adsorption of organic and inorganic compound, polar and non-polar compound in the aqueous or gas environment (Ao et al., 2018). Activated carbons AC's come from versatile group of adsorbents that have high level of porosity and very good formation of surface area getting up to thousand square meters per gram (Ao et al., 2018; T. Zhang et al., 2019). The adsorption capacity of the materials depends on the nature of the sorbent and the preparation method (Tehrani-Bagha & Balchi, 2018). Apart from carbon it also contains other element such as sulphur, nitrogen, hydrogen and oxygen which are existing from elementary material or occurred during the production process (Kaåomierczak et al., 2013). AC is usually produced from wood and agricultural wastes such as sawdust, coconut shells, nut shells, palm kernel and coal through pyrolysis and activation at higher temperature (Ao et al., 2018).

The adsorption capacity is not only depending on the surface area of the AC and distribution of the pore size but porous structure also gives significant role in determination of the adsorption capacity (Park et al., 2003). Generally, pores are being classified into three group which are micropores, mesopores and macropores (Mays, 2007). Table 2.2 shows the pore size classification recommended from IUPAC and Figure 2.1 shows the structure of pore classification. These classifications are depending on the precursor, process and operating condition used.

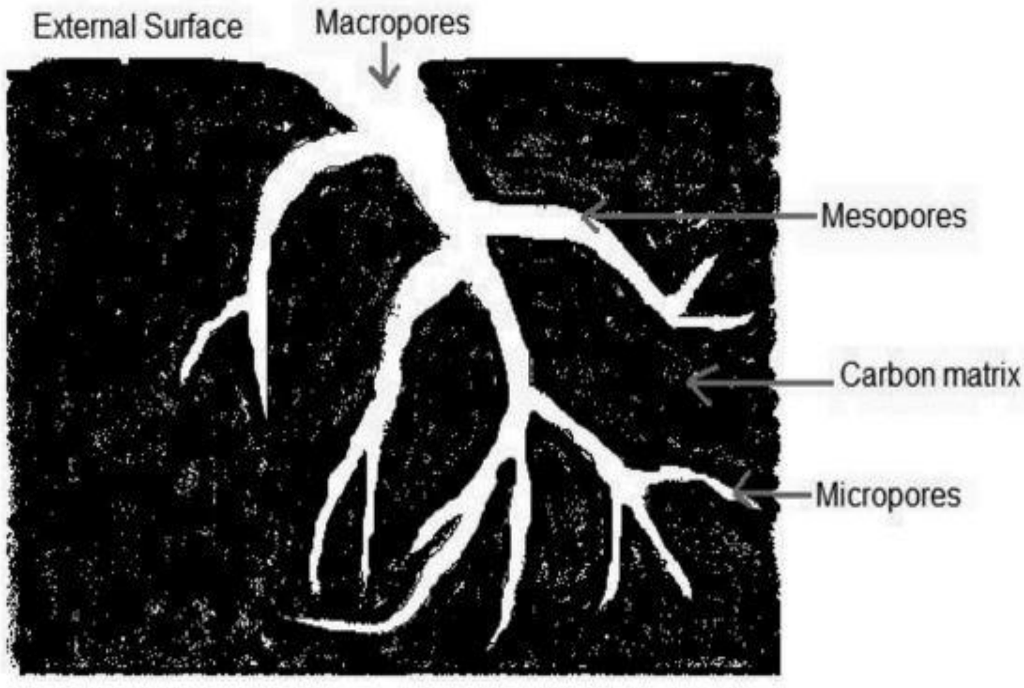

Figure 2.1: The structure of porous material of activated carbon (Ali et al., 2018).

Table 2.2: The pore size classification recommended by IUPAC (Mays, 2007).

Pore classification	**The size of the pore**
Micropore	The diameter of the pore is smaller than 2 nm
Mesopore	The diameter of the pore is between 2 to 50 nm
Micropore	The diameter of the pore is bigger than 50 nm

2.2.1 Removal of antibiotics by AC

AC is used to remove antibiotics usually being characterized depending on the production process, operating condition and type of biomass used. The production process means method of activation process, the type of activating agent and the procedure of the carbonization used which all of this will contribute to the efficiency in removing antibiotics. In addition, the operating condition such as temperature, the amount of activating agent and the pH value also highly contribute to the AC's adsorption capacity (Mansour et al., 2018). Removal of antibiotics by AC has many benefits because the precursors are renewable, diverse and abundant. The cost of preparing AC is also cheap and the preparation is simple because of high reactivity of biomass (González-García, 2018).

There are many type of adsorbents used to remove antibiotic residues including, polymeric resin, chitosan and gels, clay and minerals, metal oxides and carbon-based materials. Among them, carbon based materials the most widely used because of their great surface area, high number of pore structures and excellent surface functionality. There are different types of adsorbent which are based on carbon materials such as carbon nanotube-based materials, graphene-based material, bio char-based material and AC. AC is the most popular among this type of carbon-based material as an alternative technology in removal antibiotic based on the number of paper published from 2007 to 2017 according to Figure 2.2 (Xiang et al., 2019)