

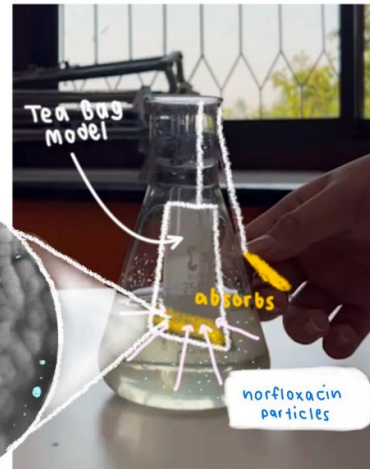
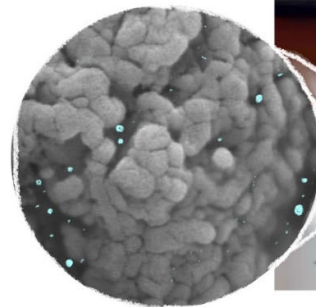
Entry to the Stockholm Junior Water Prize (2024)

Project

Norfloxacin Contaminated Wastewater Treatment using Porous Materials from Cassava Rhizomes: Tea Bag Model



Cassava Rhizomes



Project by

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I. Abstract: Norfloxacin Contaminated Wastewater Treatment using Porous Materials from Cassava Rhizomes: Tea Bag Model

This research focuses on studying the efficiency of Norfloxacin antibiotic adsorption in wastewater, which is one of the most widely used quinolone antibiotics and has been reported to contaminate water sources in many countries worldwide. The study utilizes a tea bag model filled with porous material derived from Cassava Rhizomes and compares its efficiency with commercial activated carbon. The porous material from Cassava Rhizomes, which is an agricultural waste product, was developed by doping with nitrogen gas, resulting in a BET surface area, pore volume, and average pore size of 181.3 m²/g, 0.128 cm³/g, and 30.9 Å, respectively. The percentage of mesopores was 86.10%, and the carbon content was 89.16%. The adsorption efficiency for Norfloxacin reached equilibrium in 57 hours at pH 6.21 and could be described by the Langmuir isotherm equation, indicating physical adsorption ($R^2 = 0.9886$) with a Gibbs free energy of -2991.46 kJ/mol. For synthetic wastewater, the adsorption percentage was 95.287%, and for contaminated wastewater samples, it was 93.949%.

Additionally, it was found that the tea bag model with porous material from Cassava Rhizomes significantly outperformed commercial activated carbon in Norfloxacin adsorption at a statistical significance level of 0.05. After six reuse cycles, the efficiency difference compared to the first adsorption was 49.39%, suggesting this method can replace hybrid porous carbon materials with magnetic nanoparticles. This method is cost-effective, easily accessible, and convenient for application, and it allows for the adjustment of the amount of porous material in the tea bag to suit the volume of wastewater. It is a promising approach to addressing water contamination, reducing the spread of antibiotics into the environment, and being environmentally friendly.

Keywords: Norfloxacin antibiotic, wastewater contamination, porous material from Cassava Rhizomes, nitrogen gas doping, tea bag model

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III. Abbreviations and Acronyms

Abbreviation

Abbreviations	Full Contexts
Å	Angstrom (<i>is equivalent to 10^{-10} m</i>)
cm ³ /g	Cubic centimeters per gram
°C	Degree Celsius
°C/min	Degree Celsius per minute
g/mg	Grams per milligram
K _d	Partition Coefficient
mL/min	Milliliters per minute
mL/mg	Milliliters per milligram
mL	Milliliters
mg	Milligrams
m ² /g	Square meters per gram
M	Molarity (mol/L)
pH _{pzc}	Point of Zero Charge
ppm	Parts per million (mg/L)
ppb	Parts per billion (µg/L)
µm	Micrometers
µg/mg	Micrograms per milligram
µg/L	Micrograms per liter (ppb)

Definition

-Adsorption is the process that accumulates substances or the concentration of the substance on the surface or between the surfaces of the adsorbent.

-Biochar is a material that contains carbon from the heat conversion of biomass under oxygenated conditions from sawdust biomass materials.

IV. Acknowledgement

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Chapter 1

Introduction

Statement of problems and significance

The contamination of wastewater with antibiotics is another water pollution problem. Antibiotics are drugs explicitly used to treat diseases caused by bacterial infections in humans, livestock, and aquaculture. The use of antibiotics has increased significantly. Between 2000 and 2018, the global usage rate of antibiotics increased by 46% and is expected to continue rising (Browne et al., 2021). According to global antibiotic usage reports, the quinolone group of antibiotics is among the most widely used. Data from the National Antimicrobial Resistance Surveillance Center of Thailand (NARST) reports antibiotic resistance, revealing that globally, approximately 700,000 people die annually from drug-resistant infections. If this issue is not promptly addressed, by 2050, the death rate from drug-resistant infections could rise to 10 million people per year. In Thailand, preliminary studies have found that there are about 88,000 cases of drug-resistant infections annually, with around 38,000 deaths per year. This results in an overall economic loss of USD 1.2 billion, or approximately 0.6% of the gross domestic product (GDP). From 2010 to 2017, the antibiotic resistance rate surged from 0.7% to 8.4% and will likely continue increasing rapidly. Consequently, the government has developed the Thailand National Strategic Plan on Antimicrobial Resistance 2017–2021 to address this issue urgently.

Antibiotics are extensively used in livestock and aquaculture, particularly in wastewater treatment systems that are not designed to remove antibiotic contaminants. These substances are persistent and difficult to degrade, leading to inefficient treatment, residual pollutants, and ecological impacts (Behera et al., 2011). All these factors contribute to the contamination of the environment with antibiotics and the development of antibiotic-resistant bacteria. Antibiotic treatments are more challenging when these bacteria spread to humans or animals (Nithima et al., 2015) (Figure 1).

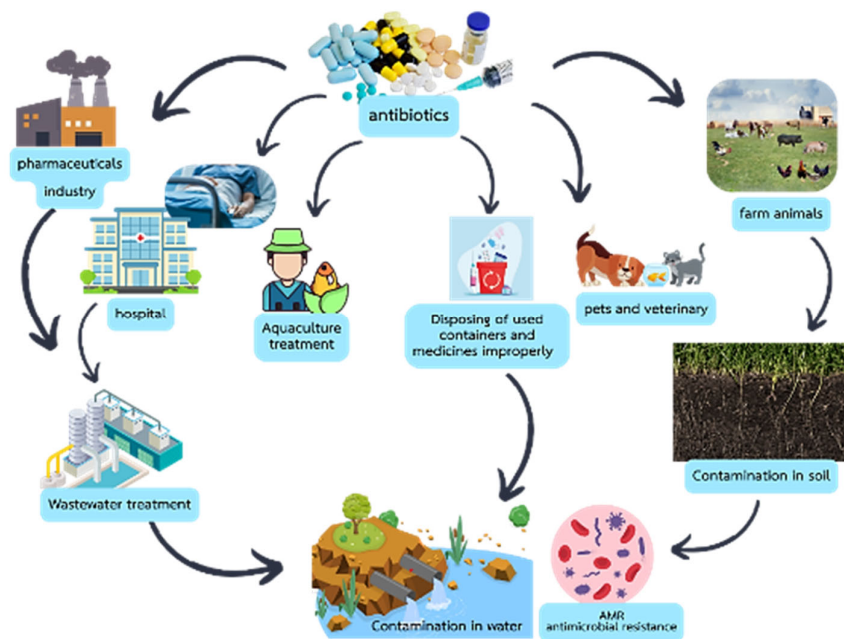
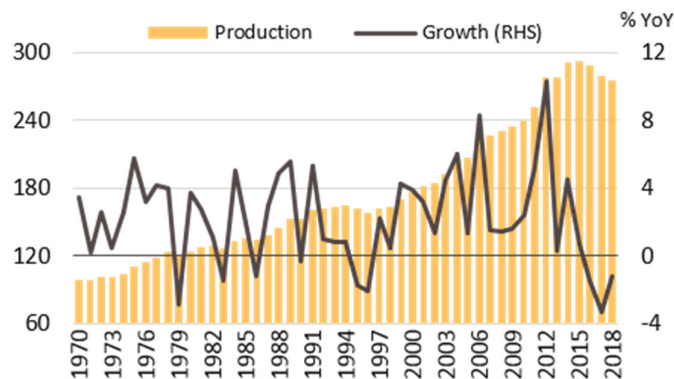


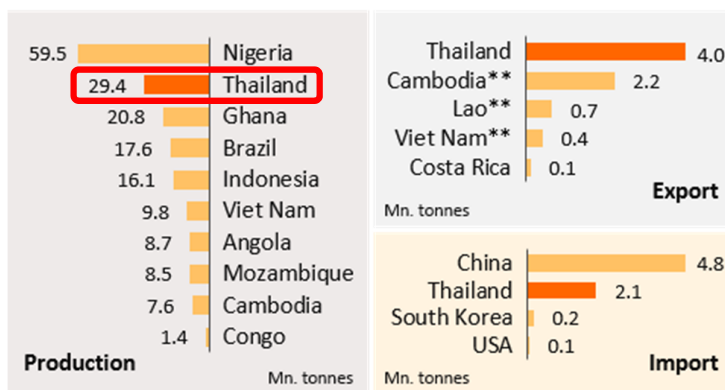
Figure 1: Contamination of water sources by antibiotics.

Current methods for removing antibiotic contaminants from water sources include advanced oxidation processes (AOPs). However, these methods require using chemicals such as hydrogen peroxide as the primary oxidizing agent in conjunction with catalysts like metal salts, ozone, UV radiation, or heat. Additionally, AOPs require complex and expensive equipment and cannot entirely and precisely remove all antibiotic contaminants. This research aims to develop porous materials from Cassava Rhizomes for the adsorption of antibiotics. Since the 1970s, global cassava production has been increasing, reaching up to 275 million tons in 2018 (Chaiwat Sowchatoensuk, 2020) (Figure 2). Thailand is the world's second-largest cassava producer (Figure 3). Cassava Rhizomes are an abundant, valueless agricultural waste material from the harvest.



Source: Food and Agriculture Organization of the United Nations (FAO)

Figure 2: World Cassava Production



Note: * Only Cassava Chip and pellet
 ** Latest Data on 2017 for Cambodia and Lao PDR, and 2015 for Viet Nam
 Source: FAO, Trade Map, Krungsri Research

Figure 3: Global Cassava Production and Cassava* Trade Countries (2018)
 Source: Chaiwat Sowcharoensuk (2020)

The researchers aim to upgrade Cassava Rhizomes into highly efficient porous materials using chemical activation compared to nitrogen doping. This will enhance the adsorption properties of the material for removing antibiotic contaminants from wastewater. The porous material is used with a tea bag model, which can replace hybrid porous carbon materials with magnetic nanoparticles. This method is cost-effective, accessible, and convenient to use, and it allows for adjusting the amount of porous material in the tea bag according to the volume of wastewater. It offers a new alternative for treating wastewater contaminated with antibiotics.

This research aligns with Thailand's Bio-Circular-Green (BCG) Economy and the Sustainable Development Goals (SDGs). Specifically, it supports SDG Goal 3: Good Health and Well-Being, sub-goal 3.9: Reduce the number of deaths and illnesses from hazardous chemicals and pollution in air, water, and soil significantly by 2030. SDG Goal 6: Clean Water and Sanitation, sub-goal 6.3: Improve water quality by reducing pollution, eliminating dumping, and minimizing the release of hazardous chemicals and materials. Halve the proportion of untreated wastewater and increase safe reuse and recycling globally by 2030. This innovation will lead to "Water Conservation Innovation toward Sustainability" under the theme "Bridging Borders: Water for a Peaceful and Sustainable Future."

Research Questions:

1. Does the tea bag model filled with porous material derived from Cassava Rhizomes effectively adsorb the antibiotic Norfloxacin from wastewater? If so, how?
2. Is there a significant difference in the efficiency of Norfloxacin adsorption from wastewater between the tea bag model filled with porous material derived from Cassava Rhizomes and the one filled with commercial activated carbon, potentially leading to a more cost-effective and sustainable solution? If so, how?

Hypotheses:

1. The tea bag model filled with porous material derived from Cassava Rhizomes is effective in adsorbing the antibiotic Norfloxacin from wastewater.
2. There is a difference in the efficiency of Norfloxacin adsorption from wastewater between the tea bag model filled with porous material derived from Cassava Rhizomes and the one filled with commercial activated carbon.

Objectives:

1. Study on the efficiency of Norfloxacin adsorption from wastewater using the Tea Bag Model filled with porous material derived from Cassava Rhizomes.
2. To compare the efficiency of Norfloxacin adsorption from wastewater using the Tea Bag Model filled with porous material derived from Cassava Rhizomes and commercial activated carbon.

Scope of Study:

1. Study Area

- 1.1 The research will be conducted in the laboratory at Monfort College Secondary School, Muang District, Chiang Mai Province.
- 1.2 The laboratory at the Faculty of Science, Chiang Mai University.
- 1.3 Synthetic wastewater.
- 1.4 Wastewater samples were taken from a hospital in the northern region of Thailand.

2. Relevant Factors for Measurement

- 2.1 Relevant factors affecting adsorption include equilibrium time, pH value, and the chemical and physical properties of the porous material.
- 2.3 Statistical analysis includes frequency distribution, percentage, mean, and standard deviation.

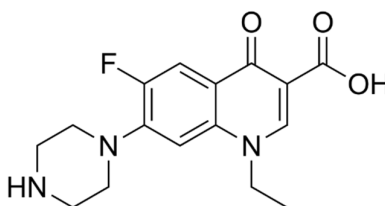
3. Research Period: July 5, 2023, to May 26, 2024.

Chapter 2

Literature Review

2.1 Antibiotic Norfloxacin

Norfloxacin belongs to the quinolone group of antibiotics. Quinolones, more commonly referred to today as fluoroquinolones, are a new group of synthesized antibiotics. They developed by modifying the structure of nalidixic acid, the first drug in this group, by adding a fluoride moiety. One widely used antibiotic in this group is Norfloxacin, which has the chemical formula $C_{16}H_{18}FN_3O_3$. Its chemical name is a 1-ethyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid and its structural formula is as follows:



The chemical structural formula of Norfloxacin (Source: Davis (2017))

2.2 Reporting of Norfloxacin Contamination in the Environment

Kümmerer (2003) reported that Norfloxacin is one of the fluoroquinolone antibiotics frequently found in the environment. Over the past several years, surveys conducted in China have shown that Norfloxacin is a widely used fluoroquinolone antibiotic in humans and animals, ranking second in usage after levofloxacin (Cui et al., 2011). The widespread use of Norfloxacin has led to its detection in various locations, raising concerns about its potential impact on ecosystems and human health. For instance, Zhao et al. (2010) surveyed the residual antibiotics in the manure of chickens, pigs, and cattle, finding Norfloxacin residues in chicken manure at levels as high as 225.45 mg/kg. Research by Xu et al. (2007) found contamination of Norfloxacin in the Harbor Bay area of Hong Kong and the Pearl River in Guangzhou Province, southern China, with levels ranging from 117–251 mg/L throughout the year. In other countries, such as Switzerland, Norfloxacin has been reported in sewage sludge with concentrations ranging from 1.54 to 2.37 mg/kg. It was also found in soil mixed with sewage sludge in concentrations ranging from 0.27 to 0.32 mg/kg. Additionally, several locations of community wastewater treatment systems effluents have reported Norfloxacin concentrations ranging from 39–489 ng/L (Golet et al., 2003).

Additionally, data collection on antibiotic concentrations in the WHO Western Pacific and WHO South-East Asia regions has found numerous water samples with quinolone antibiotic concentrations exceeding the predicted no-effect concentrations (PNECs) in both regions (Department of Global Public Health, 2023). Furthermore, there have been reports of quinolone antibiotic contamination in wastewater from hospitals in Nigeria, which affects plankton and algae in the water, impacting the food chain and ecosystem in water bodies (Akinranti et al., 2020). In Jordan, antibiotic contamination has been found in effluent concentrations as high as 510–880 ng/L (Shigei et al., 2021). Reports of antibiotic contamination in water sources continue to surface globally, with most cases found in underdeveloped or developing countries.

2.3 Related Research

Van-Truc Nguyen et al. (2022) studied the efficiency of biochar produced from used coffee grounds in adsorbing the antibiotic Norfloxacin in water. They found that the properties of the biochar conformed to the Langmuir isotherm model ($R^2 = 0.974$) with a maximum adsorption capacity of 69.8 mg g^{-1} . Analysis using the Response Surface Method (RSM) indicated that optimal adsorption occurred at pH 6.26, with a Norfloxacin concentration of 24.69 mg L^{-1} and an adsorbent dosage of 1.32 g L^{-1}

Joydeep Dutta and Aijaz Ahmad Mala (2020) studied the modification of rice husk ash, a low-cost material, to remove antibiotics contaminating the environment. They found that antibiotics are classified as emerging pollutants due to their toxicological properties, continuous-release, and persistence in aquatic environments. Antibiotics have been detected in almost every environment, and various techniques have been employed for their removal. However, the most suitable technology still requires further study.

Lalida Saeng-Athit (2011) conducted a groundbreaking study on the effect of pH on the adsorption process of the antibiotic Norfloxacin using rice husk ash. The study, conducted at a pH range of 5-8, revealed the remarkable effectiveness of rice husk ash. The rice husk ash sample used had a specific surface area of $36.78 \pm 0.58 \text{ m}^2/\text{g}$, surface functional groups with a total acidity of 1.72 mmol/g , mainly consisting of carboxylic groups at 1.45 mmol/g , and primary groups at 1.81 mmol/g . The adsorption of Norfloxacin by the rice husk ash sample reached equilibrium in 72 hours, occurring most effectively at pH 7.17, followed by pH 6.03, 7.76, and 4.93, respectively. This was consistent with the sorption edge results, which showed maximum adsorption at pH 7.21.

Saran Chittawanichprapa (2011) experimented with adsorbing the antibiotic ciprofloxacin using activated carbon prepared from coffee grounds. It was found that CG500 carbon, which was carbonized at 500 degrees Celsius, had the highest specific surface area of $124.50 \text{ m}^2/\text{g}$ and the smallest average pore size of 29.64 angstroms. This carbon could adsorb up to 50% of the antibiotic ciprofloxacin at pH 5.86, which the Langmuir equation can explain.

Yang Huang, Chaoran Li, and Zhang Lin (2014) experimented on paraquat adsorption using a tea bag model. They developed 3DG synthesis at 95 degrees Celsius during the EDTA integration process. The experimental results showed that 3DG exhibited excellent adsorption properties, capable of adsorbing paraquat up to 119 mg/g at pH 6.0, indicating that 3DG has better adsorption capabilities than typical herbicide adsorbents.

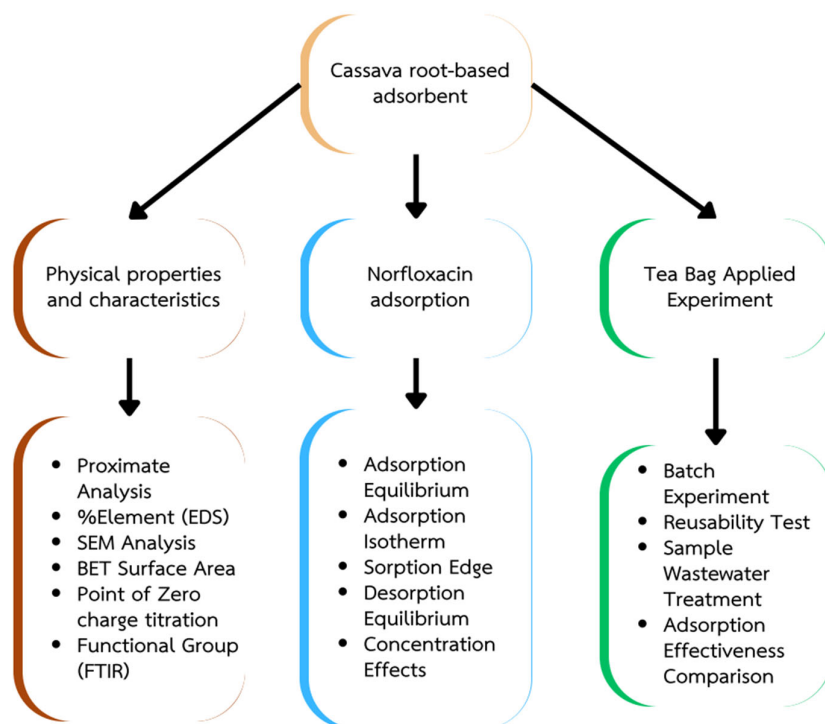
Samantha Macchi et al. (2021) developed porous carbon materials for dye adsorption using cigarette filters doped with ammonium polyphosphate using microwave techniques and the tea bag model. It was found that this method could remove more than 90% of methylene blue dye, providing a low-cost and accessible alternative to commercial activated carbon and platinum catalysts. Additionally, using PNCF can help reduce pollution from cigarette butts simultaneously.

Chapter 3 Materials and Methods

Materials

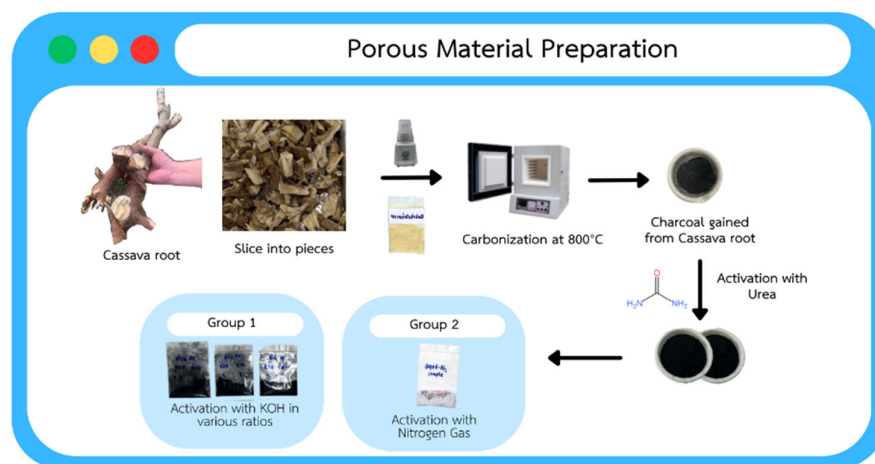
Chemical reagents	Material support
1. Cassava Rhizomes 2. Norfloxacin (C ₁₆ H ₁₈ FN ₃ O ₃) 3. Potassium hydroxide (KOH) 4. Sodium chloride (NaCl) 5. Disodium Ethylenediaminetetraacetate (Na ₂ (EDTA)) 6. Urea ((NH ₂) ₂ CO) 7. Sodium hydroxide (NaOH) 8. Hydrochloric acid (HCl) 9. Nitrogen (N ₂)	1. UV-Vis Spectrophotometer 2. Hot air oven 3. Precision balances (2 positions and 4 positions) 4. Stirrer 5. Shaker 6. pH meter 7. X-ray diffraction spectrometer 9. Scanning electron microscope (SEM) 10. High-temperature furnace 13. BET Surface Area Analysis apparatus 14. Fourier-transform infrared spectrometer (FTIR)

Method

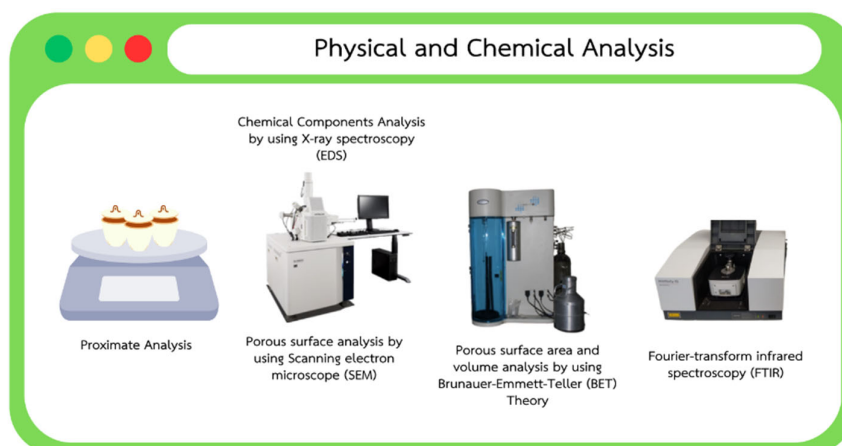


1. Preparation of Porous Material from Cassava Rhizomes and Physical Characterization

Preparing involves stimulating the material with different ratios of potassium hydroxide (KOH) solution compared to nitrogen doping. The ratios of Cassava Rhizomes to KOH are 1:0.5, 1:1, and 1:2.



2. Analysis of the Physical and Chemical Characteristics of the porous Cassava Rhizome material.



3. Study of Norfloxacin Antibiotic Adsorption by the porous Cassava Rhizome material. The experimental plan is presented in Table 3.1.

Table 3.1: shows the variables used in studying the adsorption efficiency.

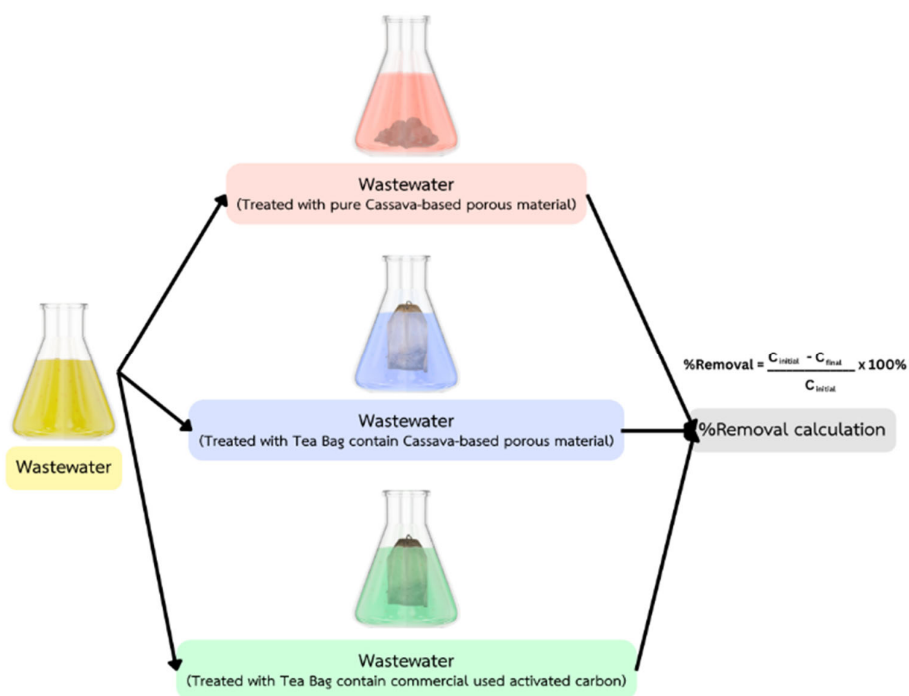
Experiment	pH	Initial concentration of Norfloxacin (ppm)	Adsorbent dosage (mg)	Time used (hr)	Additional Procedure Information
pH _{pzc} titration	1-12	-	5.0	24	Standard solution 0.01 M NaCl adjust pH 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12

Experiment	pH	Initial concentration of Norfloxacin (ppm)	Adsorbent dosage (mg)	Time used (hr)	Additional Procedure Information
Initial concentration of Norfloxacin (ppm)	6.8	0.5, 1.0, 1.5, 2.0, 2.5, 3.0	20	24	-
Adsorbent dosage (mg)	6.8	2.0	5.0, 10.0, 15.0, 20.0, 25.0, 30.0	24	-
Adsorption Equilibrium	-	2.0	20	every 3 hours from 0 – 72 hours	-
Sorption Edge	1-12	2.0	20	t _{eq}	-
Adsorption Isotherm	6.2	0.5, 1.0, 1.5, 2.0, 2.5, 3.0	20	t _{eq}	-
Desorption Equilibrium	1-12	2	20	Results every 24 hours from 24 – 192 hours	DI water, 0.01 M NaCl, EDTA 0.01 M

*every experiment was done at 25°C and wavelength detected at 278 nm

4. Batch Testing with the Tea Bag Model

A study was conducted to compare the efficiency of Norfloxacin antibiotic adsorption in wastewater using a tea bag model filled with the porous Cassava Rhizome material and commercial activated carbon.






Chapter 4 Results

4.1 Study on the Efficiency of Norfloxacin Antibiotic Adsorption in Wastewater Using a Tea Bag Model Filled with Porous Cassava Rhizome Material

4.1.1 Proximate Analysis of Porous Cassava Rhizome Material

The porous material from Cassava Rhizomes doped with nitrogen gas exhibits more favorable properties than activation with potassium hydroxide (KOH). This is due to its moisture content, ash content, and volatile matter meeting the standards for porous materials. Additionally, it has the highest fixed carbon content compared to other ratios, as shown in Table 4.1.

Table 4.1: Proximate Analysis of Charcoal Prepared by Different Methods

Activation	Ratio of Charcoal : Activation	Moisture content (%)	Ash content (%)	Volatile content (%)	Fixed Carbon (%)	Appearance
Raw	-	-	-	-	-	
KOH	1 : 0.5	12.9132	7.7889	1.0598	78.2381	
	1 : 1	11.9258	7.0135	1.4743	79.5864	
	1 : 2	11.0217	6.0394	0.9857	81.7532	
N ₂		10.4764	5.7614	0.8544	82.9078	

4.1.2 Chemical Composition Analysis with Energy-Dispersive X-ray Spectroscopy (EDS)

The porous Cassava Rhizome material stimulated by passing through N₂ gas showed a percent carbon content of 89.16, higher than stimulation with KOH. The %C is the standard specified for commercial activated carbon, which requires a %C greater than 80%, as shown in Table 4.2.

Table 4.2: presents the outcomes of the chemical composition analysis, a process conducted using the energy-dispersive X-ray spectroscopy method.

Activation	Ratio of Charcoal : Activation	Elements (%)				
		C	O	Na	Cl	Si
KOH	1 : 0.5	84.69	8.34	6.42	6.40	-0.69
	1 : 1	86.13	9.19	5.60	5.68	-0.22
	1 : 2	87.09	6.96	3.55	3.73	-0.28
N ₂		89.16	5.98	3.71	3.35	-0.43

4.1.3 Surface Characterization and Pore Size Analysis of Adsorbent Material Using SEM

The cassava ash's surface morphology and pore structure were analyzed using scanning electron microscopy (SEM) at various magnifications. The SEM images reveal the material's porous nature, as shown in Figure 4.1. These images illustrate the distinct porous structure of the Cassava Rhizome material, highlighting its potential as an effective adsorbent.

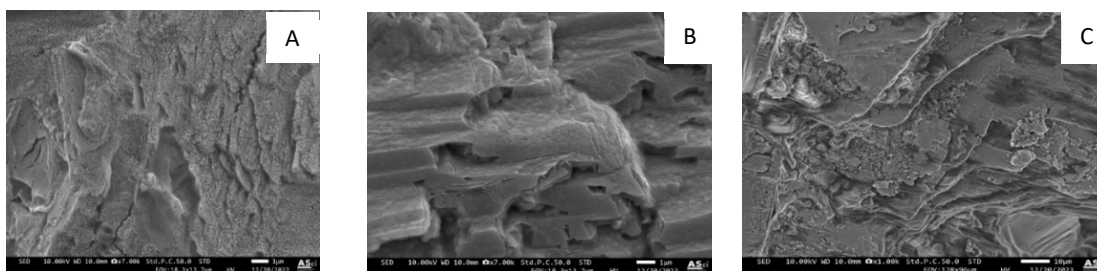


Figure 4.1: SEM Images of the porous Cassava Rhizome material at Various Magnifications (A) 700x magnification, (B) 7,000x magnification and (C) 10,000x magnification.

4.1.4 Study of Surface Area and Porosity of the Adsorbent

The adsorbent's BET surface area, pore volume, and average pore size are 181.3 m²/g, 0.128 cm³/g, and 30.9 Å, respectively, with a % Mesopore of 86.1%. As shown in Table 4.3, these results indicate that the prepared adsorbent material has potential for use as an effective adsorbent, comparable to other adsorbents. Detailed data is provided in Table 4.3. The results from the specific surface area and pore size distribution study suggest that the N₂-doped Cassava Rhizome material will likely be an effective adsorbent, similar to other commercially available adsorbents.

Table 4.3: BET Surface Area, Specific Surface Area, Pore Size Distribution, and Pore Volume of N₂-Doped Cassava Rhizome Material

Parameter	Value
BET Surface Area (m ² /g)	181.3
Pore Volume (cm ³ /g)	0.128
% Mesopore	86.1%
Average Pore Size (Å)	30.9

4.1.5 Determination of the pH at the Point of Zero Charge (pHpzc)

The pH_{pzc} of the porous Cassava Rhizome material, determined from the graph, is 6.38. This value indicates the pH at which the surface of the adsorbent has a neutral charge, which is crucial for understanding the adsorption behavior of the material in different pH environments.

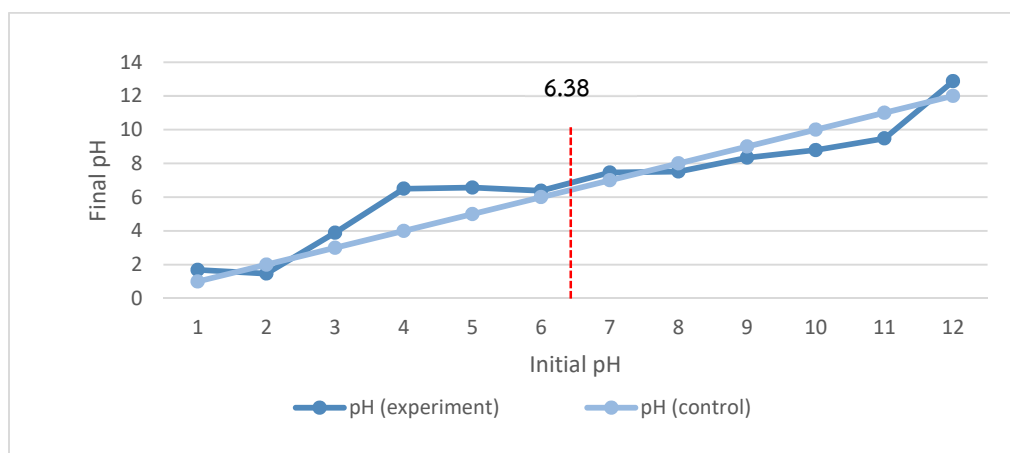


Figure 4.2: Graph of pH_{pzc} Value of Porous Cassava Rhizome Material

4.1.6 Analysis of Functional Groups of Porous Cassava Rhizome Material Using the FTIR Technique

The porous Cassava Rhizome material, after nitrogen doping, exhibits carboxylic and hydrosilane functional groups, which influence the adsorption of Norfloxacin through the formation of hydrogen bonds and π - π interactions. Peaks at wave numbers 3640 cm^{-1} , 3448 cm^{-1} , 1634 cm^{-1} , and 1360 cm^{-1} correspond to overlapping peaks of N-H and O-H stretching vibrations, stretching vibrations of C=O and C=C functional groups, and N-O symmetric stretch, respectively. Additionally, vibrations of C-C bonds are observed at 668 cm^{-1} . After adsorption of Norfloxacin, significant changes are observed in the peaks at 3640 cm^{-1} , 3448 cm^{-1} , 1634 cm^{-1} , and 668 cm^{-1} , indicating the occurrence of adsorption on the surface of the porous material.

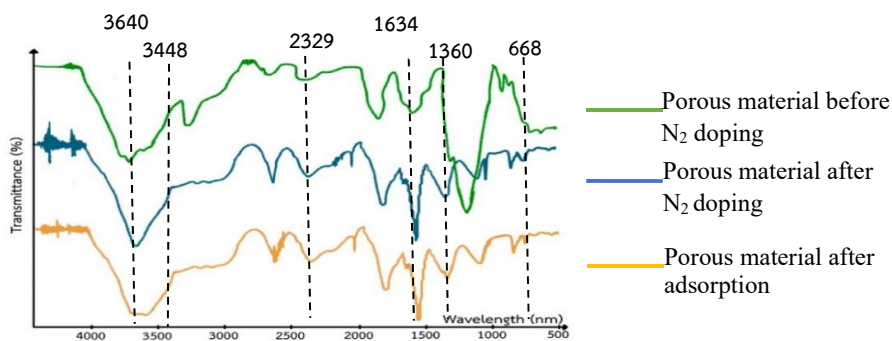


Figure 4.3: FTIR Graph Analyzing the Functional Groups of Porous Cassava Rhizome Material

4.1.7 Study of Adsorption Material Properties and Norfloxacin Antibiotic Adsorption

4.1.7.1 Equilibrium Adsorption of Norfloxacin Antibiotic

The porous Cassava Rhizome material reaches equilibrium after 57 hours at a temperature of $25\text{ }^{\circ}\text{C}$, as depicted in Figure 4.4.

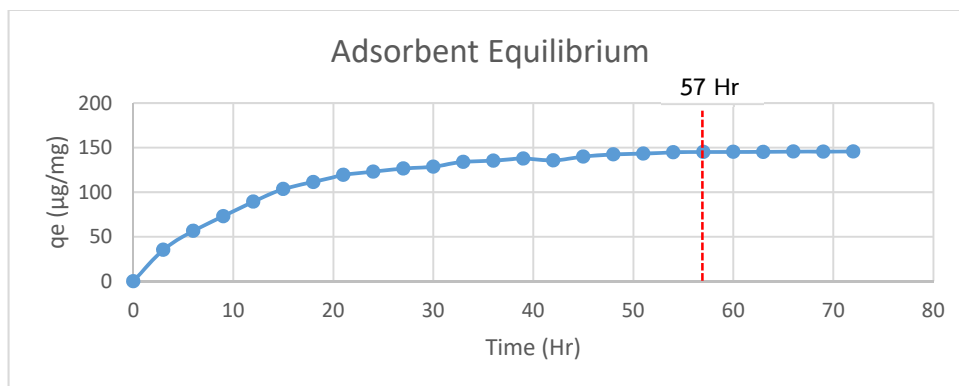


Figure 4.4: Graph showing the experiment to determine the adsorption equilibrium of Norfloxacin two ppm solution.

4.1.7.2 Isotherm Analysis of Norfloxacin Antibiotic Adsorption

The Langmuir isotherm equation provides a better explanation than the Freundlich equation. Considering the R^2 value of 0.9886, adsorption occurs predominantly on the single-layer surface of the adsorbent material. The Langmuir constant can be used to calculate the Gibbs free energy at $25\text{ }^{\circ}\text{C}$, resulting in -2991.46 kJ/mol , as shown in Figure 4.5 and Table 4.4.

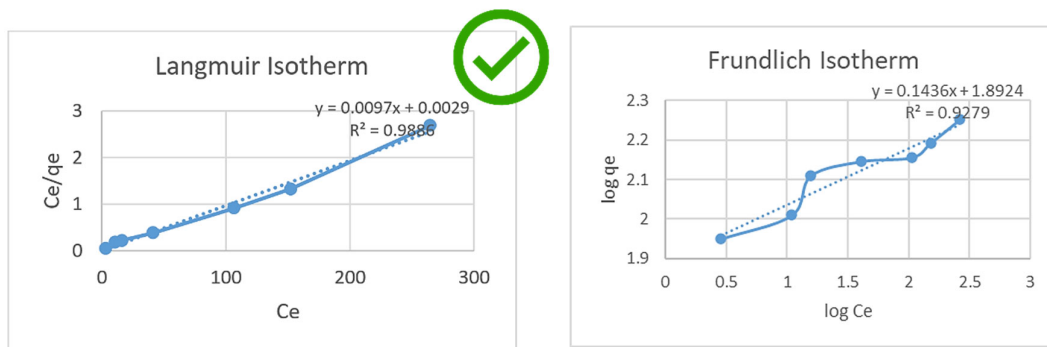


Figure 4.5: Graph of the Langmuir equation (left) and Freundlich equation (right).

Table 4.4: Showing the constants of the Langmuir and Freundlich equations.

sample	q_m ($\mu\text{g}/\text{mg}$)	K_L	R^2	ΔG^\ddagger 25°C
Langmuir adsorption isotherm	103.0927	3.34	0.9886	-2991.46
sample	n_F	K_F	R^2	
Freundlich adsorption isotherm	6.96	78.05	0.9279	

The porous Cassava Rhizome material had q_{\max} values higher than or equal to those previously researched at equal concentrations. This indicates that the porous Cassava Rhizome material are valuable waste materials that can be turned into adsorbents, and nitrogen doping is an effective method of enhancing the adsorbent, as shown in Table 4.5.

Table 4.5: Adsorbents' adsorption capacities compared to past papers and researches

Adsorbents	Amount of adsorbents	Initial Concentration of Norfloxacin	q_m (mg/g)	Reference
Peanut Shell	15 mg	10 ppm	11.74	Zhang, 2023
Wheat Straw	15 mg	10 ppm	10.75	Zhang, 2023
Magnetic graphene oxide	1 g/L	100 ppm	127.8	Zhang, 2016
Fe ₃ O ₄ /CD/AC/SA beads	10 g/L	35 ppm	2.55	Yadav, 2021
Macroporous resin	0.5 g/L	100 ppm	144.9	Yang, 2012
TiO ₂ @C	0.05 g/L	20 ppm	190	Wang, 2019
N-doped Cassava Rhizome	20 mg	3 ppm	103.09	This study

4.1.7.3 Determining the Adsorption Capacity of Norfloxacin Antibiotic at Various pH Levels or Sorption Edge

The graph illustrating the relationship between the adsorption coefficient of Norfloxacin antibiotic (K_d) and the pH of the solution exhibits a concave downward curve. Importantly, the maximum adsorption coefficient of the Norfloxacin antibiotic (K_d) is observed at pH 7.9, a result that aligns with the previously conducted experiment to determine the pH_{pzc} . This consistency in our findings adds to the reliability of our results. It can be concluded that the Cassava Rhizomes-derived adsorbent exhibits the highest adsorption capacity for the Norfloxacin antibiotic at pH 6.21, as depicted in Figure 4.6.

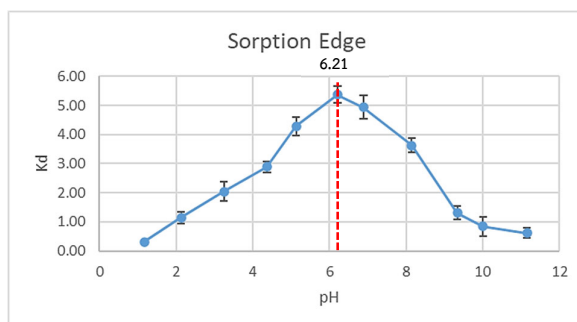


Figure 4.6: displays the relationship between pH values and the Kd values obtained from the experiment.

4.1.7.4 Study of Norfloxacin Antibiotic Desorption from the porous Cassava Rhizome material

The solution that could desorb Norfloxacin antibiotic most effectively from the adsorbent material is 0.01 M EDTA, which acts as a chelating agent and exhibits the highest desorption capacity in the solution, with a maximum Norfloxacin concentration of 109.67 $\mu\text{g/L}$, as illustrated in Figure 4.7.

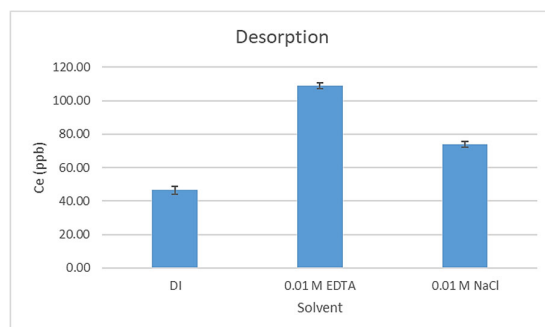


Figure 4.7: Illustrates the study of Norfloxacin desorption in the adsorbent material.

4.1.8 The tea bag model containing adsorbent material from Cassava Rhizomes has proven effective in adsorbing Norfloxacin antibiotics in synthetic and natural wastewater.

The efficiency is demonstrated in Table 4.6.

Table 4.6: A comparison table of initial and equilibrium concentrations of Norfloxacin antibiotic and % removal in synthetic and hospital wastewater.

Parameter	Unit	Synthetic Wastewater	Hospital Wastewater
Solution pH	–	6.8	6.8
Solution Temperature	$^{\circ}\text{C}$	25.0	25.0
Solution Volume	mL	100.0	100.0
Solutes and Solvent	–	Norfloxacin Water NaCl	Norfloxacin Water Other constituents such as sediment, dust, and microorganisms
The initial concentration of Norfloxacin	ppb	3,288	3,288
The equilibrium concentration of Norfloxacin	ppb	154.96	198.96
% Removal	%	95.287	93.949

4.1.9 The relationship between the initial concentration and the adsorption.

Capacity is such that as the initial concentration increases, the adsorption capacity (% removal) decreases. This is illustrated in Figure 4.8.

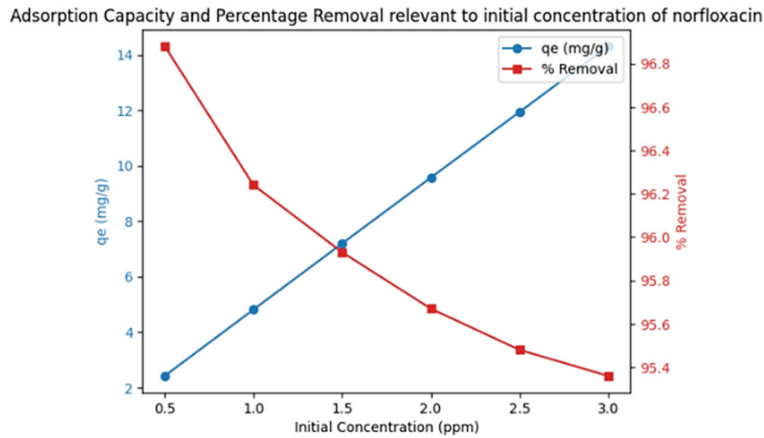


Figure 4.8: The graph illustrates the relationship between the initial concentration of Norfloxacin and q_e and % Removal.

4.2 Comparative Study of Norfloxacin Antibiotic Adsorption Efficiency in Wastewater Using a Tea Bag Model Loaded with Porous Cassava Rhizome Material and Commercial Activated Carbon.

4.2.1 Efficiency of Norfloxacin Antibiotic Absorption in Wastewater Using the Tea Bag Model Containing Porous Material from Cassava Rhizomes and Commercial Activated Carbon

The Porous Cassava Rhizome material effectively removes norfloxacin contaminants from natural wastewater, achieving equilibrium in 57 hours with an efficiency of 96.85%, higher than the removal efficiency of commercial activated carbon, which is 93.69%.

4.2.2 Removal Efficiency After Reuse

The porous Cassava Rhizome material shows a significantly higher removal efficiency than commercial activated carbon at a statistical significance level of 0.05. After six reuse cycles, compared to the first absorption, the difference is 49.39, while the commercial activated carbon shows a difference of 67.17, as shown in Figure 4.9.

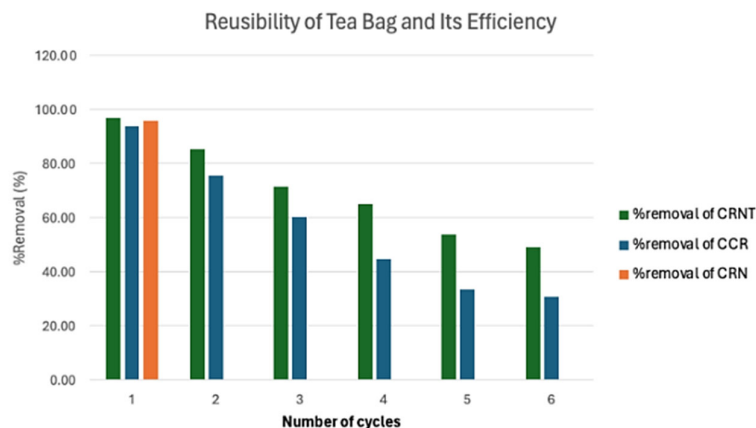


Figure 4.9: The graph illustrates the reusability and performance in the reuse of the adsorbent material packed in the Tea Bag Model.

4.2.3 The cost of a tea bag per 1 liter of wastewater is:

The cost of adsorbent material from Cassava Rhizomes is THB 57 per 100 grams, which is cheaper than commercial activated carbon, which is priced at THB 100–180 per 100 grams. The price of the tea bag containing 30 grams of adsorbent material is THB18.08 (0.49USD), as demonstrated in Table 4.7.

Table 4.7: Cost Price of the Tea Bag with Adsorbent Material

Line	Component/part	Material description	Location	Usage/piece	Unit Price	Total THB
1	Cassava Rhizome	porous material	Chiang Mai, Thailand	30 g	3 THB/Kg	0.18
1	Tea bag	package	Chiang Mai, Thailand	6 pieces	15 THB/100 pieces	0.90
Total Material Cost						
2	Labor Cost				500 THB	5.00
2	Overhead Cost				1,200 THB	12.00
2	Profit				0	
Total Tea Bag Containing Adsorbent Material						18.08 (0.49USD)

Chapter 5

Conclusion and Discussion

Conclusions:

1. Study on the Efficiency of Norfloxacin Antibiotic Adsorption in Wastewater Using a Tea Bag Model Filled with Porous Cassava Rhizome Material

1.1. Material Composition: An alternative approach in wastewater treatment involves using porous Cassava Rhizome material doped with nitrogen gas. This material has a higher carbon content than activated with potassium hydroxide, with a %C aligning with ISO standards for activated carbon.

1.2. Surface Area and Porosity: The BET technique reveals that the BET surface area, pore volume, and average pore size are 181.3 m²/g, 0.128 cm³/g, and 30.9 Å, respectively, with %Mesopore at 86.1%.

1.3. pH_{pzc} Value: The point of zero charge (pH_{pzc}) for the porous Cassava Rhizome material doped with nitrogen gas is 6.38.

1.4. Functional Group Analysis: FTIR analysis shows significant changes in peaks at 3640, 3448, 1634, and 668 cm⁻¹ after Norfloxacin adsorption, indicating adsorption occurring on the porous material's surface.

1.5. Adsorption Equilibrium: The precise adsorption equilibrium is reached after a meticulously timed 57 hours at a temperature of 25 °C.

1.6. Adsorption Isotherm: The adsorption isotherm fits the Langmuir equation better than the Freundlich equation, with an R² value of 0.9886, indicating monolayer adsorption on the adsorbent surface. The Langmuir constant was used to calculate the Gibbs free energy at 25 °C, yielding a -2991.46 kJ/mol value.

1.7. K_d and pH Relationship: The relationship between the adsorption coefficient (K_d) of Norfloxacin and the solution pH is bell-shaped, with the highest K_d value at pH 6.21.

1.8. Desorption Efficiency: The solution that most effectively desorbs Norfloxacin from the adsorbent is 0.01 M EDTA, a highly efficient chelating agent, which desorbs up to an impressive 109.67 µg/L of Norfloxacin.

1.9. Tea Bag Model Performance: The Tea Bag Model filled with porous Cassava Rhizome material achieves removal efficiencies of 95.287% and 93.949% in synthetic and natural wastewater, respectively. The study also finds an inverse relationship between initial concentration and adsorption capacity: as the concentration increases, the adsorption capacity decreases.

2. Comparative Study of Norfloxacin Antibiotic Adsorption Efficiency in Wastewater Using a Tea Bag Model Filled with Porous Cassava Rhizome Material and Commercial Activated Carbon

2.1. Removal Efficiency after Reuse: The porous Cassava Rhizome material demonstrated a significantly higher removal percentage than commercial activated carbon at a statistical significance level of 0.05. After six reuse cycles, the difference in removal efficiency compared to the first adsorption was 49.39% for the porous Cassava Rhizome material and 67.17% for the commercial activated carbon.

2.2 Cost Analysis: The production cost of the porous Cassava Rhizome material is a mere THB 57 per 100 grams, significantly undercutting the cost of commercial activated carbon. Moreover, a tea bag containing 30 grams of this material is a mere THB 18.08 (less than USD 0.5), making it a highly cost-effective solution.

Discussion:

Cassava Rhizomes doped with nitrogen gas exhibit increased porosity and improved surface functional groups. Tea bags filled with porous Cassava Rhizome material are highly effective in treating synthetic and natural wastewater contaminated with the antibiotic Norfloxacin. This method offers a low-cost, accessible, and convenient alternative to hybrid porous carbon materials with magnetic nanoparticles. The porous material in the tea bags can be adjusted as needed.

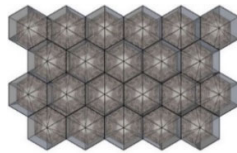
The experimental results validate the hypothesis that porous Cassava Rhizome material is more effective at adsorbing Norfloxacin in wastewater than commercial activated carbon, offering a new, viable option for treating antibiotic-contaminated wastewater. This solution is in perfect alignment with Thailand's Bio-Circular-Green (BCG) Economy and Sustainable Development Goals (SDGs), particularly SDG Goal 3 (Good Health and Well-being) and Goal 6 (Clean Water and Sanitation). It contributes to 'Water Conservation Innovation toward Sustainability' under the theme 'Bridging Borders: Water for a Peaceful and Sustainable Future.'

Future study:

Implementation of Porous Cassava Rhizome Material and Tea Bag Models in Real Wastewater Treatment Systems
System Design:



- Practical tea Bag Specifications: Each tea bag, measuring 7x8 cm, is designed to efficiently hold up to 30 grams of porous Cassava Rhizome material, ensuring optimal use of space in the system.



- Hexagonal Cell Structure: Tea bags filled with porous Cassava Rhizome material are placed in hexagonal cells (simple tessellation). Each hexagonal cell comprises triangular sub-cells with dimensions of 25.3x16.0x2.0 cm, each having a volume of 224 cm³. The total volume of the hexagonal cell is 1,344 cm³, accommodating up to 6 tea bags.

Advantages of the Hexagonal Cell Design:

1. Increased Surface Area: The hexagonal cell structure maximizes the contact area with water, enhancing the interaction between the wastewater and the adsorbent material.
2. Efficient Water Flow: The design facilitates better water flow through the system, ensuring thorough wastewater exposure to the adsorbent material.
3. High Adsorption Potential: The porous Cassava Rhizome material in the tea bags efficiently adsorbs Norfloxacin from the wastewater.

Scalability and Adaptation:

The system's design is efficient for small-scale treatment and highly adaptable for large-scale wastewater treatment. The number of hexagonal cells can be increased proportionally to handle larger volumes of wastewater, demonstrating its versatility and adaptability.



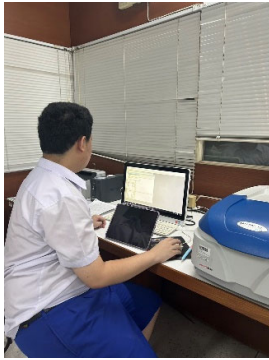
Tea Bag Model in Hexagonal Cell Structure in a Wastewater Treatment Tank

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VI. Annexation



Conduct an analysis of porous materials



Study the hospital's wastewater treatment system.