

**BATCH AND OPTIMIZATION STUDIES OF CIPROFLOXACIN
REMOVAL FROM AQUEOUS SOLUTION BY SPENT TEA LEAVES**

By

LEE SHAO KEN

A project report submitted to the Department of Chemical Science

Faculty of Science

Universiti Tunku Abdul Rahman

in partial fulfilment of the requirements for the degree of

Bachelor of Science (Hons) Chemistry

SEPTEMBER 2023

ABSTRACT

BATCH AND OPTIMIZATION STUDIES OF CIPROFLOXACIN REMOVAL FROM AQUEOUS SOLUTION BY SPENT TEA LEAVES

LEE SHAO KEN

The feasibility of spent tea leaves (STL) for the removal of ciprofloxacin (CIP) from aqueous solution was examined in this project. The effect of several experimental conditions was studied, including initial concentrations of adsorbate, adsorbent dosage, contact time, pH and agitation rate. Chemical modifications such as esterification and nitric acid modification were carried out to determine the influence on the adsorption performance. The equilibrium data of the adsorption of CIP by STL conform to both Langmuir and Brunauer-Emmett-Teller (BET) isotherm models, with R^2 value of 0.9941. Furthermore, the experimental data fitted well into pseudo-second-order kinetic model with R^2 values close to unity. The functional groups present on STL were determined using Fourier Transform Infrared Spectrophotometer (FTIR), and the surface morphology and topography were analyzed using Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM), respectively. Response Surface Methodology (RSM) was also employed in this work to determine the optimum conditions for the adsorption process. The optimum experimental conditions were found to be 40 mg/L of CIP concentration, 0.03 g of STL, pH 6.5, 150 rpm agitation rate and 182.5 minutes of contact time.

ABSTRAK

KAJIAN KUMPULAN DAN PENGOPTIMUMAN UNTUK PENYINGKIRAN CIPROFLOXACIN DARIPADA LARUTAN AKUEUS OLEH DAUN TEH SISA

LEE SHAO KEN

Kegunaan daun teh sisa (STL) untuk penyingkiran ciprofloxacin (CIP) daripada larutan akueus telah dikaji dalam projek ini. Kesan beberapa faktor eksperimen telah dikaji, termasuklah kepekatan awal CIP, dos bahan penjerap, masa sentuhan, pH dan kadar pengadukan. Pengubahsuaian kimia seperti pengesteran dan pengubahsuaian asid nitric telah dijalankan untuk menentukan pengaruh terhadap prestasi penjerapan. Data keseimbangan penjerapan CIP oleh STL lebih berpadanan dengan kedua-dua model isoterma Langmuir dan Brunauer-Emmett-Teller (BET), iaitu nilai R^2 0.9941. Tambahan pula, kajian kinetik menunjukkan kadar kinetik bagi penyingkiran CIP adalah mematuhi model kinetik tertib kedua. Kumpulan berfungsi yang terdapat pada STL telah ditentukan dengan menggunakan Spektroskopi Inframerah Fourier Transformasi (FTIR), dan morfologi permukaan serta topografi telah dianalisis menggunakan Mikroskop Elektron Pengimbasan (SEM) dan Mikroskop Kekuatan Atom (AFM), masing-masing. Response Surface Methodology (RSM) juga dilaksanakan dalam projek ini untuk menentukan parameter proses yang optimum untuk proses penjerapan ini. Parameter eksperimen optimum didapati

ialah 40 mg/L larutan CIP, 0.03 g STL, pH 6.5, kadar pengadukan 150 rpm dan 182.5 minit masa sentuhan.

ACKNOWLEDGEMENT

Throughout my final year project, I received a lot of help and support from different individuals. First of all, I would like to express the upmost gratitude to my supervisor, Dr. Ong Siew Teng for the guidance throughout my final year project. With her invaluable comments and advice, I am able to correct my mistake immediately and complete my project successfully. In addition to that, deepest thanks for her moral support that encouraged me throughout the journey.

I would also like to acknowledge with much appreciation to all the laboratory officers for their assistance, as well as their sharing of knowledge that has been inspired me. Their precious point of view allows me to view my problems in different perspectives, and this really helps to improve my project.

Nevertheless, I am extremely grateful to my friends and family who have been so tolerant and support during my project days. Appreciate for the continuous encouragement and emotional support, as well as useful suggestions that had given to me all this time. Their involvement has certainly inspired and energized me to give the best that I could.

Lastly, the research facilities provided by UTAR are acknowledged as well. A sincere thank you from the bottom of my heart to all that have been involved in my project.

Thank you.

DECLARATION

I hereby declare that this final year project report is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.



LEE SHAO KEN

APPROVAL SHEET

The final year project report entitled “**BATCH AND OPTIMIZATION STUDIES OF CIPROFLOXACIN REMOVAL FROM AQUEOUS SOLUTION BY SPENT TEA LEAVES**” was prepared by LEE SHAO KEN and submitted as partial fulfilment of the requirements for the degree of Bachelor of Science (Hons) Chemistry at Universiti Tunku Abdul Rahman.

Approved by:

 S7 Ong

(Dr. ONG SIEW TENG)

Date: 16/10/2023

Supervisor

Department of Chemical Science

Faculty of Science

Universiti Tunku Abdul Rahman

FACULTY OF SCIENCE
UNIVERSITI TUNKU ABDUL RAHMAN

Date: 19 September 2023

PERMISSION SHEET

It is hereby certified that **LEE SHAO KEN** (ID No: **20ADB04572**) has completed this final year project thesis entitled “BATCH AND OPTIMIZATION STUDIES OF CIPROFLOXACIN REMOVAL FROM AQUEOUS SOLUTION BY SPENT TEA LEAVES” under the supervision of Dr. ONG SIEW TENG from the Department of Chemical Science, Faculty of Science.

I hereby give permission to the University to upload the softcopy of my final year project thesis in pdf format into the UTAR Institutional Repository, which may be made accessible to the UTAR community and public.

Yours truly,



(LEE SHAO KEN)

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ACKNOWLEDGEMENTS	v
DECLARATION	vi
APPROVAL SHEET	vii
PERMISSION SHEET	viii
TABLE OF CONTENTS	ix
LIST OF TABLES	xi
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS	xiv
CHAPTER	
1 INTRODUCTION	1
1.1 Background	1
1.2 Ciprofloxacin	3
1.3 Adsorption technique	5
1.4 Adsorbents	6
1.5 Spent tea leaves	7
1.6 Objectives of the research	9
2 LITERATURE REVIEW	10
2.1 Heavy metal removal	10
2.2 Antibiotics removal	14
2.3 Dyes removal	19
2.4 Comparative study	22
2.5 Characteristics of STL for adsorption	24
3 MATERIALS AND METHODS	27
3.1 Chemicals and reagents	27
3.2 Methodology	28
3.2.1 Preparation of adsorbent	28
3.2.2 Preparation of adsorbate	28
3.2.3 Batch adsorption experiment	29
3.2.3.1 Effect of initial concentrations of CIP	31
3.2.3.2 Effect of contact time	31
3.2.3.3 Effect of STL dosage	31
3.2.3.4 Effect of pH	32
3.2.3.5 Effect of agitation rate	32
3.2.4 Determination of isoelectric point of STL (pH_{pzc})	32
3.2.5 Esterification of STL	33
3.2.6 Nitric acid (HNO_3) modification of STL	33

3.3	Characterization analysis	33
3.3.1	UV-visible Spectroscopy	33
3.3.2	Fourier Transform Infrared Spectroscopy	34
3.3.3	Scanning Electron Microscopy	34
3.3.4	Atomic Force Microscopy	34
4	RESULTS AND DISCUSSION	35
4.1	Batch adsorption experiment	
4.1.1	Effect of initial concentrations of CIP solution	35
4.1.2	Effect of contact time	37
4.1.3	Effect of agitation rate	38
4.1.4	Effect of STL dosage	40
4.1.5	Effect of pH	42
4.2	Characterization analysis	46
4.2.1	Fourier Transform Infrared Spectroscopy (FTIR)	46
4.2.2	Scanning Electron Micrograph (SEM)	50
4.2.3	Atomic Force Microscopy (AFM)	52
4.3	Adsorption isotherm	53
4.3.1	Langmuir isotherm	54
4.3.2	Freundlich isotherm	59
4.3.3	Brunauer-Emmett-Teller isotherm	62
4.4	Adsorption kinetic studies	65
4.4.1	Pseudo-first-order	65
4.4.2	Pseudo-second-order	69
4.4.3	Theoretical model	73
4.5	Surface modification	75
4.5.1	Esterification	76
4.5.2	Nitric acid modification	77
4.5.3	Comparison of adsorption effectiveness between native, esterified and nitric acid-modified STL	78
4.6	Response Surface Methodology (RSM)	80
4.6.1	Interactive effect of pH and initial CIP concentrations on uptake removal	82
4.6.2	Interactive effect of pH and contact time on uptake removal	84
4.6.3	Interactive effect of pH and agitation rate on uptake removal	85
4.6.4	Interactive effect of pH and STL dosage on uptake removal	87
4.6.5	Verification of Response Surface Methodology Models	89
5	CONCLUSIONS	91
5.1	Conclusion	91
5.2	Future prospect	92
	REFERENCES	93
	APPENDICES	102

LIST OF TABLES

Table		Page
2.1.1	Main functional groups loaded on tea wastes	12
2.2.1	Important functional groups and peaks in FTIR spectra of UTC	17
2.2.2	FTIR spectral characteristics of activated STL before and after adsorption of aspirin	18
2.4.1	Maximum CIP adsorption capacity of various adsorbents	23
2.4.2	Adsorption of different adsorbate by tea-leaf based adsorbent	24
3.1.1	Chemicals and reagents used in this project	27
4.2.1.1	Important peaks and functional groups in FTIR spectra	49
4.3.1.1	R_L value for different concentration	58
4.3.3.1	Isotherm parameter and correlation of determination of different isotherm models	65
4.4.1.1	Parameter of pseudo-first order kinetics for CIP adsorption onto STL	69
4.4.2.1	Parameter of pseudo-second order kinetics for CIP adsorption onto STL	72
4.6.5.1	Observed and predicted uptake removal for 23 sets of experiment	90

LIST OF FIGURES

Figure		Page
1.1.1	Component structure of members of fluoroquinolones	3
1.2.1	Chemical structure of CIP	4
1.3.1	Cycle and application of contaminants removal techniques in wastewater	6
1.5.1	Different types of tea	7
2.1.1	FTIR spectra of tea waste before (red line) and after (blue line) adsorption	12
2.1.2	SEM diagram of (a) native tea waste, (b) extruded tea waste (5,000×), (c) extruded tea waste (20,000×), and (d) zirconium-bonded tea waste	14
2.2.1	SEM micrograph of UTC before (a) and after (b) adsorption	15
2.2.2	FTIR spectra of UTC before (UTC) and after adsorption (UTC _{ad})	16
2.2.3	FTIR spectra of activated STL before and after adsorption of aspirin	18
2.3.1	SEM image of unadsorbed tea waste (a) and Acid Blue 25 adsorbed tea waste (b)	21
3.2.3.1	Overview of batch adsorption experiment	30
4.1.1.1	Effect of initial concentrations of CIP solution and contact time	36
4.1.3.1	Effect of agitation rate	39
4.1.4.1	Effect of STL dosage	41
4.1.5.1	Behavior of CIP as a function of pH	42

4.1.5.2	Effect of pH	45
4.2.1.1	FTIR spectrum of STL before and after adsorption	48
4.2.2.1	SEM micrograph of STL before (a) and after (b) adsorption	51
4.2.3.1	AFM image of STL before (a) and after (b) adsorption	53
4.3.1.1	Langmuir isotherm of CIP onto STL	56
4.3.2.1	Freundlich isotherm of CIP onto STL	60
4.3.3.1	BET isotherm of CIP onto STL	63
4.4.1.1	Pseudo-first-order of CIP adsorption onto STL	68
4.4.2.1	Pseudo-second-order of CIP adsorption onto STL	71
4.4.3.1	Theoretical model of CIP adsorption onto STL	74
4.5.1.1	Proposed mechanism of esterification with methanol	77
4.5.3.1	Uptake removal of CIP by different types of STL	79
4.6.1.1	3D surface plot of pH and initial CIP concentrations on uptake removal	83
4.6.2.1	3D surface plot of pH and contact time on uptake removal	85
4.6.3.1	3D surface plot of pH and agitation rate on uptake removal	87
4.6.4.1	3D surface plot of pH and STL dosage on uptake removal	88

LIST OF SYMBOLS/ABBREVIATIONS

C_e	Concentration of CIP solution at equilibrium
C_o	Initial CIP concentration
C_s	Saturation concentration of CIP
C_t	CIP concentration at time, t
K_1	Pseudo-first-order kinetics rate constant
K_2	Rate constant of pseudo-second-order model
K_B	BET constant
K_L	Adsorption equilibrium constant
K_f	Freundlich isotherm constant for adsorption
R_L	Dimensionless equilibrium parameter
q_e (expt)	experimental q_e value
q_e	Amount of CIP adsorbed at equilibrium
q_{max}	Maximum adsorption capacity of STL
q_t	Amount of CIP adsorbed at time, t
AFM	Atomic Force Microscopy
BET	Brunauer-Emmett-Teller
Cd	Cadmium
CIP	Ciprofloxacin
Cu	Copper
FTIR	Fourier Transform Infrared Spectroscopy
h	Initial adsorption rate

HCl	Hydrochloric acid
HNO ₃	Nitric acid
MB	Methylene blue
NaCl	Sodium chloride
Ni	Nickel
Pb	Lead
pH _{pzc}	pH of zero-point charge
R ²	Correlation of determination
RSM	Response surface methodology
SEM	Scanning Electron Microscopy
STL	Spent tea leaves
UTC	Used tea-leaf biochar
UV/Vis	Ultraviolet-visible
Zn	Zinc
<i>n</i>	Freundlich intensity parameter

Chapter 1

INTRODUCTION

1.1 Background

In 1928, Sir Alexander Fleming synthesized the first ever antibiotic in the world, namely penicillin. This achievement has successfully kicked start the antibiotic era, which marks a significant milestone for the world (Adedeji, 2016). The advancement of sciences and research continuously promote the development of health care industries, as abundant of new class of antibiotics have been discovered over the time. They are particularly important in human society, as they are able to prevent or treat some types of bacterial infections. Because of these pharmaceutical properties, the consumption of pharmaceutical compounds increased significantly over the past years, as people have relied extensively on antibiotics in hope of better health and immune protection. The use of pharmaceutical products is not only restricted for human use, instead the application in livestock and aquaculture due to intensive farming are commonly known as well. According to Browne, et al. (2021), the global antibiotic consumption rate covering 204 countries has increased by 46 % from year 2000 to 2018, and the value is expected to increase from time to time. In consequence, pharmaceutical wastes are found in large quantities in water systems and sewage.

There are many classes of antibiotic. Specifically, fluoroquinolones, being the third-largest group of antibiotics, cover a broad-spectrum of antibiotics that are responsible to hinder or treat various pathogenic diseases like urinary tract infections, pneumonia, gastroenteritis and so on. The most common members of fluoroquinolones include ciprofloxacin (CIP), norfloxacin, levofloxacin, and so on (Bhatt & Chatterjee, 2022). Figure 1.1.1 shows the chemical structure of several members under fluoroquinolones antibiotic class (Singh, Parwate and Shukla, 2009). However, despite their ability to benefit the community so greatly, they come at a price: they cause significant side effects when being released excessively into water systems, as pollutants. Conventionally, antibiotics are being released into water systems through various pathways, which include hospital effluents, discharge from industrial pharmaceutical plants, improper disposal by the community, excretion and so on (Zuccato et al., 2010).

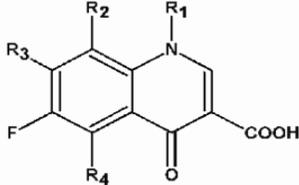
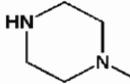
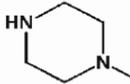
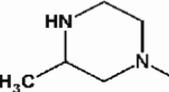
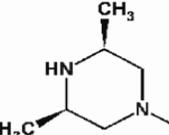
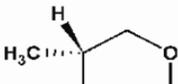
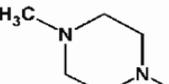
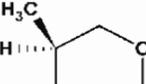
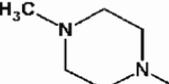
				
Compound	R ₁	R ₂	R ₃	R ₄
Norfloxacin	—C ₂ H ₅	—H		—H
Ciprofloxacin		—H		—H
Gatifloxacin		—OCH ₃		—H
Sparfloxacin		—F		—NH ₂
Levofloxacin				—H
Ofloxacin				—H

Figure 1.1.1: Component structure of members of fluoroquinolones (Singh, Parwate and Shukla, 2009)

1.2 Ciprofloxacin

In the class of fluoroquinolones, CIP is one of the most popular antibiotics, owing to its superior pharmaceutical properties. CIP is an FDA-approved antibiotic used to treat a variety of bacterial illnesses, such as urinary tract infections, pneumonia, gonorrhoea, chancroid, and so on. The chemical structure

of ciprofloxacin is shown in Figure 1.2.1 below. However, only 15% of CIP is being metabolized by human body, while up to 50% is excreted out as an unchanged drug (Movasaghi, Yan and Niu, 2019). The discharge concentration of CIP in wastewater is determined at about 30 mg/L, with higher concentration detected in drug manufacturing plant and pharmaceutical industry (Zhang et al., 2017). Medication released into water systems is proven to harm wildlife significantly, and the situation worsens when it enters human water supplies, whereby humans may suffer from adverse health effects such as respiratory disorders, cancer, reproductive issues, and many more (Ibrahim & Ho, 2023). The most noted consequence of antibiotic pollution and misuse of drugs is the development of antibiotic resistance in human body. In this context, the bacterial species may evolve and generates a defend mechanism to resist the effect of antibiotics, making them ineffective in most treatments (Movasaghi, Yan and Niu, 2019). In addition, long term introduction of these compounds into the environment may have detrimental effect to the ecosystem. Therefore, it is essential to tackle this issue before it becomes worsen.

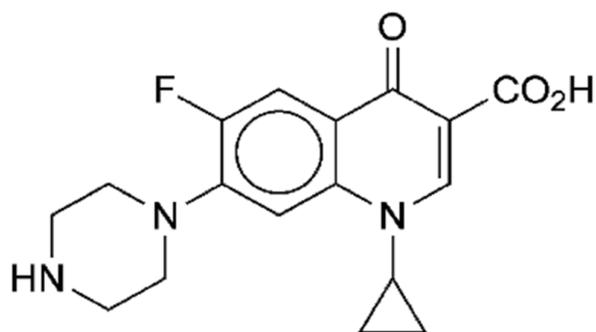
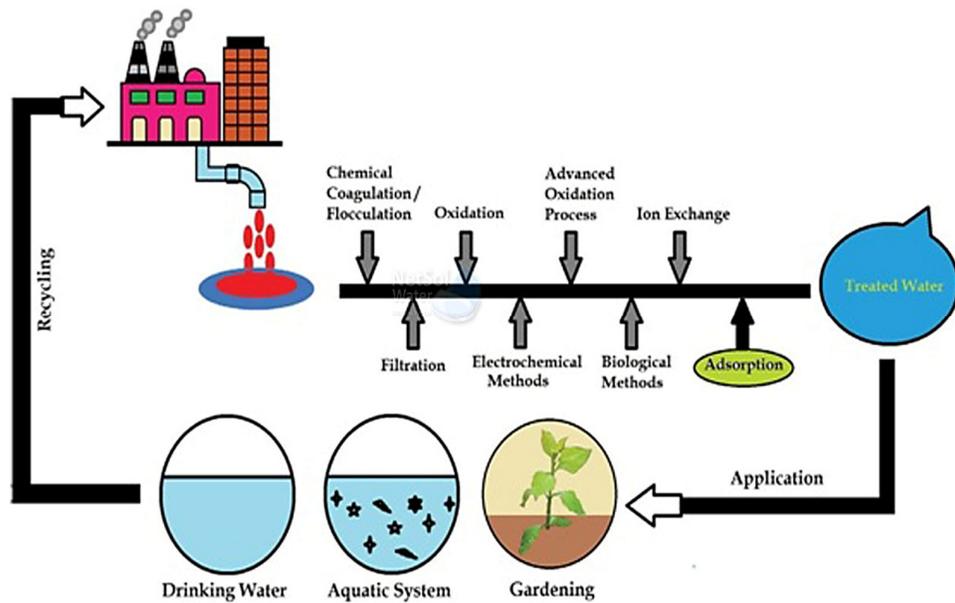


Figure 1.2.1: Chemical structure of CIP

1.3 Adsorption technique

Unfortunately, many researchers have discovered that many contaminants including pharmaceuticals are not eliminated during wastewater treatment process due to the limitation of sewage treatment plant. On top of that, they are incapable to self-degrade and can be quite persistent in wastewater. Considering the downsides possessed by these contaminants in water systems, it is vital to discover sustainable methods to tackle the issues. For this reason, several techniques and mitigations were designed and implemented, such as advanced oxidation technique, photocatalytic degradation, biological treatment and many more. Figure 1.3.1 illustrates the cycle and application of various techniques for wastewater treatment. But most of them show significant drawbacks in its application (Dutta & Mala, 2020). For instance, some of these advanced treatments require enormous amount of energy and it is extremely costly to remediate the wastewater on a large scale. Other than that, most of the materials involved and the degradation products are toxic and harmful to environment. On the other hand, adsorption has proven to be one of the optimistic approaches to remediate the wastewater from contamination due to ease of operation, low installation expenses, environmentally friendly, as well as high potential to regenerate the used adsorbent (Bhatnagar & Anastopoulos, 2017). It relies on the surface phenomenon with common mechanism to realise surface accumulation of pollutants on adsorbent. The liquid-solid intermolecular force of attraction initiates the attachment of pollutant molecule from the solution onto the solid surface, thus achieving removal purpose (Nageed, 2013).



Adapted from NetSol Water (2023)

Figure 1.3.1: Cycle and application of contaminants removal techniques in wastewater

1.4 Adsorbents

Given the advantages of adsorption process in the removal of contaminants, it is crucial to explore suitable yet sustainable adsorbent materials sensible to remove CIP in wastewater. In recent years, many economical adsorbents have been identified and reviewed to examine their pollutant-binding capacities. The popular options include locally available materials such as agricultural wastes, industrial wastes, and manufacturing by-products. Activated carbon, zeolites, biochar and so on with proven superior ability are also getting more attention. Unquestionably, most scientists opt to perform activation processes on native materials due to their improved capacity and efficiency of adsorption. In other words, the ability of native adsorbents for contaminants removal is often

overlooked or underestimated. However, most of the activation processes require tremendous amount of energy, and this simultaneously increases the operation cost and investment (Dutta & Mala, 2020). By weighing up the pros and cons of the activation process, it is considered worthy to perform the adsorption technique by using untreated adsorbents, as it is much more environmentally and economically sustainable. Therefore, this study focuses on the evaluation of spent tea leaves (STL) as a potential adsorbent to remove CIP from the aqueous solution.

1.5 Spent tea leaves

Tea plant (*Camellia sinensis*) is a species of evergreen, medium sized woody shrub or tree, under the family of Theaceae. Its leaves were utilized and consumed by people for medicinal purposes. This fragrant beverage was originated from China in 2737 BC, and there are various types of teas (Figure 1.5.1), depending on the withering and oxidation process.



Figure 1.5.1: Different types of tea

Tea offers a wide range of benefits to human's health such as prevention of cardiovascular diseases, antidiabetic, lower risk of atherosclerosis and so on (Bag, Mondal, Majumder & Banik, 2022). This has significantly escalated tea's popularity as it becomes one of the most welcoming yet in-demand beverages in the world. Statistics published by Statista Research Department (2023) shows that about 6.7 billion kilograms of tea were consumed worldwide in 2023, and the demand is expected to increase from time to time, estimated to achieve 7.4 billion kilograms by year 2025.

In terms of the composition of tea, the cell wall of the tea wastes contains both soluble and insoluble components. After being brewed, the properties and composition of spent tea leaves that believed to facilitate the adsorption process remained such as insoluble cellulose, hemicellulose, lignin, and structural protein. Therefore, it is definitely a wastage if the brewed tea leaves are being disposed without utilizing them. The high consumption of tea has created considerable amount of waste over time. Given the waste's surplus availability, spent tea leaves have gained many attentions to be considered as adsorbent. In other words, they are always readily accessible and available. In addition to that, they are nontoxic and could be easily obtained at low cost.

1.6 Objectives of the research

1. To assess the adsorption performance of STL for the removal of CIP.
2. To study the effect of different experimental conditions that influence the adsorption such as initial concentrations of adsorbate, contact time, agitation rate, adsorbent dosage, and pH.
3. To analyze the kinetic studies and adsorption isotherm models for the adsorption of CIP by STL.
4. To perform the characterization studies on the adsorbent by using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) to observe the differences in the adsorbent after the adsorption process.
5. To optimize the CIP removal by employing the Response Surface Methodology (RSM) experimental design.

Chapter 2

LITERATURE REVIEW

2. Literature review

The feasibility of using STL as the potential adsorbent in the removal of various pollutants has been studied and published by several researchers. This chapter highlighted and discussed some of the published works related to the removal of different types of waste by tea leaves-based adsorbent.

2.1 Heavy metal removal

STL were determined as a potential adsorbent to remove toxic heavy metal ions. Çelebi et al. (2020) evaluated the usefulness of brewed tea leaves as the adsorbent to remove several heavy metal ions such as lead (Pb), zinc (Zn), nickel (Ni), and cadmium (Cd). The experiment was performed under several experimental variables such as pH, medium temperature, dosage of adsorbent, and contact time to determine their effect towards the adsorption performance. As a results, optimistic adsorption capacities for each heavy metal ion were obtained, which were 1.197, 1.457, 1.163 and 2.468 mg/g for Pb, Zn, Ni and Cd ions, respectively. The adsorption process was able to reach equilibrium within relatively short time, indicating the effectiveness of the adsorbent. The result has proven that tea waste is a great adsorbent as they are capable to eliminate

considerable amount of toxic heavy metal ions from waste stream effectively. The authors also suggested that the adsorption process follows three steps: adsorption, surface precipitation and finally fixation. This is most probably due to the availability of surface functional groups (predominantly hydroxyl group) on tea leaves that are actively involved in the physicochemical reactions with the heavy metals such as complexation. By performing FTIR analysis on the tea wastes involved, and it was found out that there were several peaks experienced obvious shifting such as peaks at 2916.62, 2849.35 and 1516.44 cm^{-1} which represent aliphatic C-H groups and symmetric bending of alkyl group, respectively. This suggests that the functional groups on STL are particularly involved in physicochemical reaction and adsorption with metal ions, resulting in removal.

Tea leaves also possessed an added advantage of extensive porous surface and rough surface area that facilitated the adsorption process. As cellulose and hemicellulose are the main components of tea leaves, they contain widely distributed pores in large surface area, which are favorable in interacting with the contaminants. Figure 2.1.1 and Table 2.1.1 below show the spectra of FTIR of tea leave wastes before and after adsorption process, as well as the summary of main functional groups of tea, respectively.

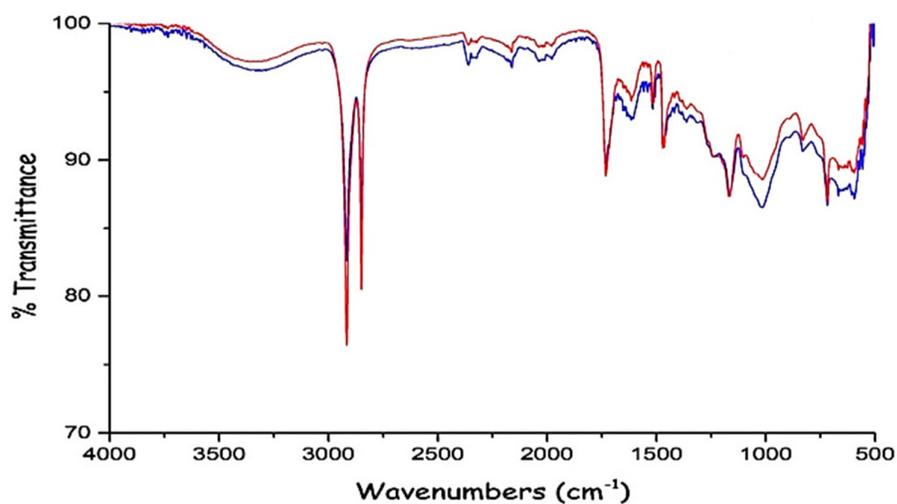


Figure 2.1.1: FTIR spectra of tea waste before (red line) and after (blue line) adsorption

Table 2.1.1: Main functional groups loaded on tea wastes

Frequency / cm^{-1}		Assignment
Before adsorption	After adsorption	
2916.62	2916.42	Aliphatic C-H group
2849.35	2849.23	Aliphatic C-H group
2160.69	2161.07	C=O stretching, C=O/C=C stretching
1615.38	1614.97	C-H alkanes in aromatic rings
1516.44	1471.66	-CH ₃ symmetric bending
1165.56	1167.43	C-O stretching
718.33	718.31	C-O-H stretching

Similar study on the adsorption of toxic Cu^{2+} ions was carried out by Etim et al. (2022). In this particular research, tea fibre and tea leaves were utilized to remove Cu^{2+} ions. Similarly, the impacts brought by the changes in pH, concentration of metal solution and the adsorbent dosage were studied. The authors were able to achieve maximum percentage removal of Cu^{2+} for both tea fibre and tea leaves at 99.97%, which is highly efficient and attractive. This has further proven the capability of tea leaves as a promising adsorbent.

Another notable research was carried out by Mei et al. (2019) who studied on the elimination of fluoride ions by modified tea waste. The authors conducted a comparison study on the adsorption efficiency between native tea leaves, extruded tea and zirconium-loaded tea waste. The characterization analysis of extruded tea waste showed greater pore size, and this could promote the binding of zirconium for better removal of fluoride ions from wastewater. As a result, 20.56 mg/g of adsorption capacity was able to be attained by zirconium-loaded tea waste. In order to have a clearer picture of the adsorption of fluoride ions, SEM was performed, and Figure 2.1.2 displayed the SEM micrographs of (a) tea waste, (b) extruded tea waste at $5,000 \times$ magnification, (c) extruded tea waste at $20,000 \times$ magnification and (d) zirconium-bonded tea waste. The porous structure was highly apparent in extruded tea waste, and this structure offered an added advantage on exposing their surface functional group to enhance the adsorption process. Although the native spent tea leaves performance is weaker than the extruded ones in terms of the removal efficiency, it is still believed that the native tea leaves have its own potential in the removal of various pollutants.

This is because the surface functional groups and physiochemical properties that originated from native spent tea leaves were the key factors in driving the adsorption process.

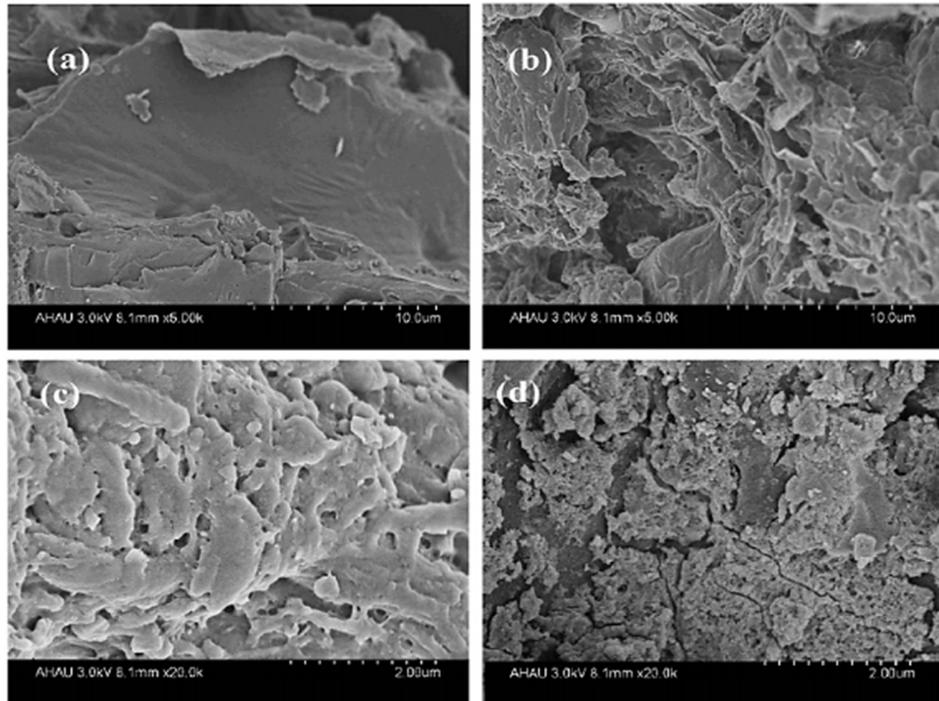


Figure 2.1.2: SEM diagram of (a) native tea waste, (b) extruded tea waste (5,000 \times), (c) extruded tea waste (20,000 \times), and (d) zirconium-bonded tea waste

2.2 Antibiotics removal

The usefulness of STL as natural adsorbent is further demonstrated by Li et al. (2018) who utilized spent tea leaves to produce tea-leaf biochar for the removal of ciprofloxacin through adsorption process. In this case, used tea leaves were utilized as precursor to produce biochar which possess greater carbon content.

In terms of the structure, tea-leaf biochar owns higher surface area and extensive porous structures, which are the ideal properties that favored adsorption process. This was proven as the authors were able to achieve a maximum adsorption capacity of 238.10 mg/g. In addition to that, the system obeyed Langmuir model. This optimistic result is largely due to the existence of irregular surface with non-uniform pores possessed by tea-leaf biochar. Figure 2.2.1 presents the SEM micrographs of tea-leaf biochar to show its surface morphology before and after adsorption. It could be clearly seen that after adsorption, there are abundant of foreign particles agglomerated within the pores and surfaces.

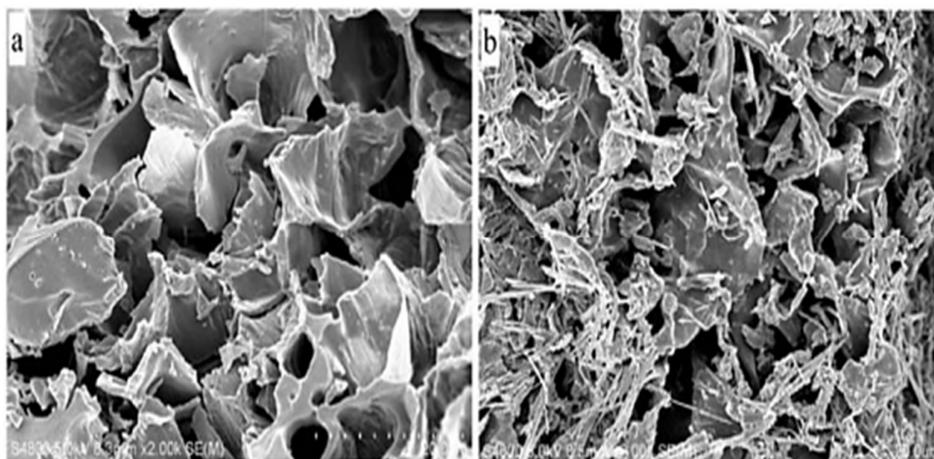


Figure 2.2.1: SEM micrograph of UTC before (a) and after (b) adsorption

From the result above, it could be confidently suggested that the spent tea leaves are capable on binding foreign particles, and the pore structure of biochar further enhances their binding ability, contributing significant impact towards the adsorption of contaminants. The authors proposed that the adsorption of tea-leaf

biochar and CIP was based on chemisorption. This is evidenced by the FTIR spectra of the adsorbent that displayed significant differences after adsorption. Therefore, it is suggested that there was chemical interactions and bonding occurred between the surface functional groups of STL with the contaminants. The FTIR spectra (Figure 2.2.2) before and after adsorption, as well as a table (Table 2.2.1) that includes important functional groups and peaks are displayed below. Through comparison, there are several new peaks and shifted peaks observed after adsorption process, such as 3400 cm^{-1} to 3413 cm^{-1} for -OH groups, symmetric bending of CH_3 from 1435 cm^{-1} to 1456 cm^{-1} , as well as new peaks such as 3038 cm^{-1} , 1490 cm^{-1} and 1309 cm^{-1} that representing N-H stretching vibrations, secondary amine groups and C-H stretching vibrations, respectively.

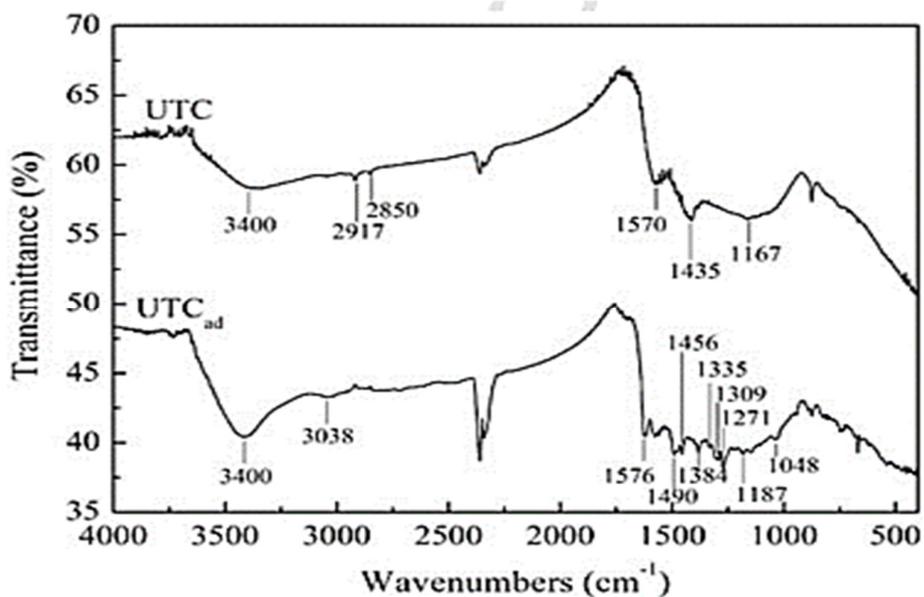


Figure 2.2.2: FTIR spectra of UTC before (UTC) and after adsorption (UTC_{ad})

Table 2.2.1: Important functional groups and peaks in FTIR spectra of UTC

Frequency (cm ⁻¹)		Functional groups
UTC	UTC _{ad}	
3400	3413	Stretching vibrations of -OH groups
	3038	N-H stretching vibration
2917		Aliphatic CH ₂ asymmetric stretch
2850		Aliphatic CH ₂ symmetric stretch
1570	1576	C=C band of the aromatic ring or highly conjugated C=C bond
	1490	Secondary amine group
1435	1456	Symmetric bending of CH ₃
	1384	Bending vibration of methyl
	1335	Aromatic nitro compound
	1309	C-H stretching vibration
	1271	Phenolic C-OH stretch
1167	1187	C-O in phenol
	1048	C=O stretching

Similar phenomenon was detected by Wong et al. (2018) who focused on the application of activated tea leaves to remove aspirin from aqueous solution. An optimistic adsorption removal of aspirin was detected at 94.28 %, after 1 hour of contact time, by using 0.5 g of adsorbent and 100 mg/L of aspirin solution at pH 3 and 30 °C. The experimental data fitted pseudo-second-order kinetic model nicely, giving a R² value of 0.9999 which was close to unity. This suggested that the adsorption of aspirin by the activated STL is dominated by chemical adsorption, which is in accordance with the study discussed above. The outcome was further supported by the result of FTIR. The spectra of the adsorbents are

presented in Figure 2.2.3, and significant bands were summarized in Table 2.2.2. It was determined that the frequency of symmetric bending of CH₃ and asymmetric stretching of C=O experienced certain shifting after the adsorption of aspirin. The changes in frequency have been suggested due to the interaction between aspirin and activated spent tea leaves. In addition, the authors proposed that this adsorption system obeyed to Freundlich isotherm, where heterogenous and multilayer adsorption takes place.

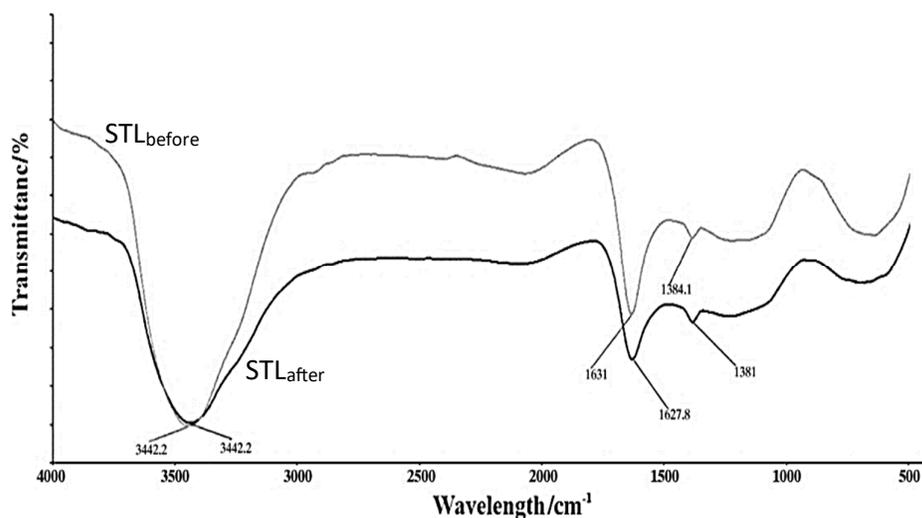


Figure 2.2.3: FTIR spectra of activated STL before and after adsorption of aspirin (Wong, et al., 2018)

Table 2.2.2: FTIR spectral characteristics of activated STL before and after adsorption of aspirin (Wong, et al., 2018)

Frequency (cm ⁻¹)		Functional groups
Before adsorption	After adsorption	
3442	3442	Bonded -OH group
1628	1631	C=O stretching
1381	1384	Symmetric bending of CH ₃

2.3 Dyes removal

Besides from heavy metal ions, dyes are one of the most emerging contaminants found in the environment. Many treatments have been applied to tackle the issue, including solar photo-Fenton degradation, photocatalytic degradation and so on. Amongst these, adsorption process is proved to be the most optimistic methods for removal of dyes. Hameed (2009) conducted a study to determine the effectiveness of STL in removing Methylene Blue (MB) dye from wastewater. The outcomes have demonstrated that the adsorption system is best described by Langmuir isotherm theory, where the adsorption of MB is monolayer onto homogenous sites of STL. To be more specific, a maximum monolayer adsorption capacity of 300.052 mg/g was accomplished in this adsorption system. In order to further validate the feasibility of using STL as a potential adsorbent in its native form, a comparison study of monolayer equilibrium capacity of MB with different adsorbents was carried out. The results shown that STL owned the highest adsorption capacity, as compared with coffee husk, *Luffa cylindrica* fibres, dehydrated wheat bran carbon and oil palm fibre activated carbon with adsorption capacity of 90.09, 47.0, 185.2 and 277.78 mg/g, respectively. The adsorption kinetics were also studied, and pseudo-second-order model was found to be more accurately represented the experimental data. All the results calculated at different MB concentrations were able to achieve coefficient of determination, R^2 of nearly unity. Therefore, it was proposed that adsorption process was controlled by chemisorption. This was supported by the FTIR results, where significant shifts in FTIR peaks were observed after the adsorption process, due to the chemical bonds formation between functional groups of STL and adsorbates.

Reza et al. (2016) studied the adsorption of Reactive Blue 21 dye by using tea leaves waste. They conducted the batch adsorption experiment by varying different parameters, including pH, mass of adsorbent, contact time, and concentration of dye solution to investigate their effects towards the adsorption performance. They concluded that the tea waste performed optimally at pH 6.0 and 90 minutes of contact time where equilibrium was attained. In addition to that, this adsorption system obeys to Langmuir isotherm, which led to a monolayer adsorption capacity of 28.99 mg/g.

In another work, Nasar (2021) reviewed the usefulness of raw tea wastes for the remediation of toxic dyes from polluted water. Figure 2.3.1 represented the SEM micrographs of un-adsorbed tea waste and Acid Blue 25 adsorbed tea for comparison purposes. A change of surface morphology was detected after adsorption as fewer cavities were observed as compared to the one before adsorption. This phenomenon was believed due to the penetration and attachment of Acid Blue 25 onto tea residues, filling up the pores and cavities. Another work involving the remediation of MB dye was also highlighted by Jain et al. (2020). The adsorption system was shown to obey to Langmuir isotherm and pseudo-second-order kinetic model, suggesting a monolayer adsorption (300.052 mg/g) and chemisorption of MB dye by the adsorbent.

Assembling the findings from the above studies, it is evident that tea waste could be one of the ideal adsorbents for dye removal due to the occurrence of strong interactions between dyes molecules with tea residues. This statement was highly supported by Liu, Fan and Li (2018) who suggested that the adsorption was accomplished by many different mechanisms, including hydrogen bonding, electrostatic interactions, complexation of functional groups, as well as other interactions like π - π interactions and ion exchange. This shows that the organic functional groups on tea waste played a vital role in contaminant removal. Therefore, tea leaves have been suggested as a potential adsorbent due to its beneficial contribution in the removal of contaminants. In this work, the authors were able to achieve a great adsorption capacity of tea waste in the removal of MB, which was 113.1461 mg/g.

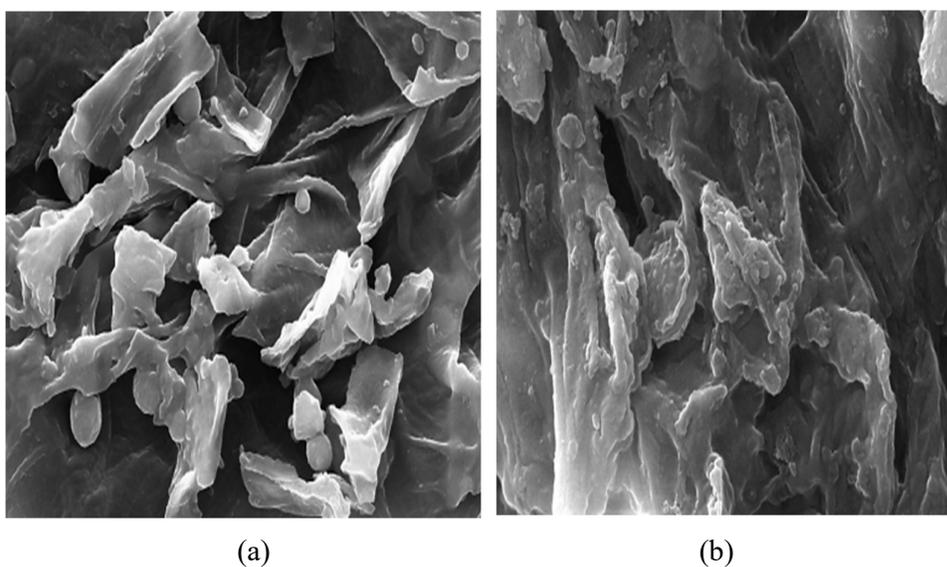


Figure 2.3.1: SEM image of unadsorbed tea waste (a) and Acid Blue 25 adsorbed tea waste (b)

Another notable study was performed by Sikdar, Goswami and Das (2020) who utilized tea waste to produce activated carbon to remove Indigo Carmine from wastewater. Different environmental variables were studied, including adsorbent dosage, concentration of dye, temperature and agitation speed. The optimized condition was determined by using RSM. As a result, it was determined that conditions set at pH 6, 0.05 g of adsorbent and 120 minutes reaction time obtained the highest percentage removal, which was 89 %. The data demonstrated that the system followed Langmuir isotherm and pseudo-second-order kinetic model, with maximum uptake capacity of 20 mg/g. The result was compared with different adsorbents on similar dye, and it was proven that tea waste-based carbonaceous material owned better adsorption capacity, as compared to Brazil nut shells, activated carbon from *Acacia nilotica* (babool) sawdust and citrus reticulate peels cellulosic waste, which possessed 1.1, 4.8 and 15 mg/g of adsorption capacity, respectively. This shows that tea leaves-based adsorbent is considered as more powerful and valuable biosorbents in adsorption technique.

2.4 Comparative study

The tables summarized the adsorption capacity of multiple adsorbents for the removal of CIP from aqueous solution (Table 2.4.1), as well as the adsorption performance of tea-leaf based adsorbents in removing different types of adsorbates (Table 2.4.2). Based on the results, it was clearly shown that tea-leaf biochar performed the best in removing CIP as compared to the others, and also

possessed the greatest adsorption capacity, which is 238.10 mg/g. This shows that the STL possessed powerful characteristics and properties that actively involved in adsorption process, resulting in great adsorptive performance. The removal of different types of adsorbates by tea-leaf based adsorbents also shown promising results. This further demonstrated that STL is indeed an “all-rounder” whereby its efficiency in contaminant removal have been shown these studies. They own crucial features such as capable to interact with a wide variety of substance and achieving the purpose of contaminant-separation from aqueous medium. In summary, STL is a highly efficient adsorbent to purify the aqueous medium from contamination.

Table 2.4.1: Maximum CIP adsorption capacity of various adsorbents

Adsorbent	Maximum adsorption capacity (mg/g)	References
Tea-leaf biochar	238.10	(Li, et al., 2018)
Aged-microplastics	46.91	(Zheng, et al., 2023)
Biochar derived from bamboo sawdust	78.43	(Wakejo, et al., 2022)
Porous graphene granules	235.60	(Ma, Yang, Yu and Zheng, 2015)
Yam peel powder	42.81	(Akpomie, et al., 2023)
Chitosan-modified graphene oxide	102.00	(Parashar, et al., 2022)

Table 2.4.2: Adsorption of different adsorbate by tea-leaf based adsorbent

Adsorbent (Tea-leaf based)	Adsorbate	Maximum adsorption capacity (mg/g)	References
STL activated carbon	Aspirin	178.57	(Wong, et al., 2018)
Black tea wastes	Lead ions	115.20	(Zuorro and Lavecchia, 2010)
Green tea wastes		83.80	
Waste black tea	Nickel ions	90.91	Malakahmah, Tan and Yavari, 2016)
	Zinc ions	166.67	
Tea waste	Reactive Blue 25 dye	28.99	(Reza, et al., 2016)

2.5 Characteristics of STL for adsorption

In general, soluble polysaccharides and proteins, as well as insoluble lignin, cellulose, and structural protein, make up the cell walls of tea leaves. After being brewed, the remaining insoluble components could facilitate the adsorption process for the purpose of contaminants removal (Nazir, Raoov and Mohamad, 2020). On dry weight basis, phenolic substances, fibers and proteins are the major constituents of STL. Due to the existence of these constituents, STL are well-known as carbonaceous materials, and this offers them outstanding physiochemical characteristics for adsorption. Based on the FTIR, it was evident that functional groups like carboxyl, hydroxyl, amine, and alkyl are present in abundance on the tea leaves surface. According to Nazir, Raoov and Mohamad

(2020), it has been proposed that these functional groups were involved actively in certain interactions with CIP to aid the adsorption process. The proposed interactions involve hydrogen bonding, π - π interactions and electrostatic attraction. CIP molecules consist of moieties like aromatic heterocyclic groups, benzene ring and fluorine. Such moieties are believed to act as important role in its interaction with the functional group present on STL such as C-OH, COOH, C-N and so on. For instance, the high electron-withdrawing property of fluorine on benzene ring makes it a π -acceptor, while the amine groups in tea leaves serve as electron-donating groups. As a result, π - π interaction is initiated. In addition to that, hydrogen bonding possesses significant contribution in the adsorption of CIP onto STL due to the presence of hydroxyl and carboxyl group that are capable to form hydrogen bonding. Other than that, electrostatic interaction is another possible mechanism as CIP exists as zwitterion in nature, and they are easily protonated or deprotonated at different pH on carbonyl and amine group, respectively (Igwegbe, et al., 2020). In summary, there are a great number of possible mechanisms between CIP and STL, and therefore it is confident that the adsorption of CIP by STL could be carried out effectively and efficiently.

Based on the studies reviewed above, it can be concluded that STL are potential adsorbent to remove a wide range of contaminants in wastewater, not only restricted to antibiotics, but also heavy metal ions and dyes. Although many works were performed by using activated tea wastes, it is evident that native STL still own the fundamental physiochemical properties and important surface functional groups that are useful in adsorption process. Not only this, the

application of adsorption technique by using STL in its native form depict an effective and successful green technology approach.

Chapter 3

MATERIALS AND METHODOLOGY

3.1 Chemicals and reagents

The chemicals and reagents used throughout the final year project were tabulated in the Table 3.1.1.

Table 3.1.1: Chemicals and reagents used in this project

Chemicals / Reagents	Manufacturer	Assay
Ciprofloxacin hydrochloride hydrate	Acros Organics	-
Concentrated hydrochloric acid	Quality Reagent Chemical (QRëC)	37 %
Concentrated nitric acid	Fisher Scientific	68 %
Methanol	Merck KGaA	-
Sodium hydroxide pellet	GENE Chemicals	99 %

3.2 Methodology

3.2.1 Preparation of adsorbent

STL were obtained from a Chinese restaurant in Kampar, Perak. The tea leaves were washed with distilled water to remove adhering dirt and impurities. The collected tea leaves were boiled at 80 °C in distilled water to remove any soluble components. The STL were then filtered, and the boiling process was repeated until the final solution was completely clear and achieved neutral pH. The boiled tea leaves were then filtered, washed, and dried in oven at 60 °C overnight to remove the moisture content completely. The dried tea leaves were grounded into powder form and screened through 250 µm sieve before stored in a sealed bottle containing silica gel for future use.

3.2.2 Preparation of adsorbate

CIP was chosen as the adsorbate in this project. The CIP used in the project was purchased from Acros Organic, in the form of ciprofloxacin hydrochloride hydrate, 98%. CIP has molecular formula of $C_{17}H_{18}FN_3O_3$ with molecular weight of 331.346 g/mol. A 500 mg/L stock solution was prepared in a volumetric flask. The solution was kept in dark to avoid photodegradation. Dilution technique was employed to prepare the working solution in the future.

3.2.3 Batch adsorption experiment

0.02 g of STL was added into 20 mL of CIP solution in a centrifuge tube. The mixture was agitated at 150 rpm using orbital shaker for 4 hours. The batch experiment was prepared in duplicates, as well as a control set without STL to prove that the adsorption of CIP was due to STL, instead of the wall of centrifuge tube. After the desired contact time was attained, the mixtures were centrifuged at 7500 rpm. The absorbance of the supernatant was measured using UV/vis spectrophotometer at wavelength of 276 nm. This is the maximum wavelength of CIP. The concentration of CIP could be calculated using the equation from the calibration curve, which shown in the Appendix A. The mean result for each experimental set was obtained, and the uptake removal, as well as the adsorption capacity of CIP could be calculated using the equations below:

$$Uptake\ removal = \frac{(C_o - C_t)}{C_o} \times 100\%$$

where C_o = initial CIP concentration (mg/L), C_t = CIP concentration at time, t (mg/L)

$$Adsorption\ capacity = \frac{(C_o - C_t)V}{m}$$

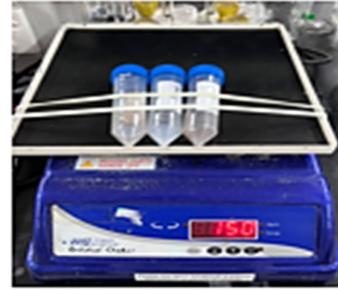
where C_o = initial CIP concentration (mg/L), C_t = CIP concentration at time, t (mg/L), m = adsorbent mass, V = volume of CIP solution

01



0.02 g of STL was added to 20 mL of CIP solution in 50 mL centrifuge tube

02



Agitated on orbital shaker at 150 rpm for 4 hours.

03



Centrifuge at 7500 rpm for 5 minutes

04



Measurement of absorbance using UV/vis spectrophotometer at 276 nm

Figure 3.2.3.1: Overview of batch adsorption experiment

The influences of several variables on CIP adsorption were investigated as follows:

3.2.3.1 Effect of initial concentrations of CIP

The effect of initial CIP concentrations was examined by using different concentrations of CIP solution, which were 20, 30 and 40 mg/L. The agitation rate and STL dosage were fixed at 150 rpm and 0.02 g, respectively. After certain time intervals, the samples were collected and measured for its concentration using UV/vis spectrophotometer.

3.2.3.2 Effect of contact time

In order to investigate the effect of contact time, the samples were withdrawn at different time intervals, which were 5, 10, 15, 30, 60, 120, 180, 240, 300 and 360 minutes for three different concentrations of CIP (20, 30 and 40 mg/L). The agitation rate and STL dosage were fixed at 150 rpm and 0.02 g, respectively.

3.2.3.3 Effect of STL dosage

The effect of STL dosage was evaluated by adding different amounts of STL into 20 mL of 20 mg/L CIP solution in the centrifuge tube. The amount of STL was ranging from 0.01 to 0.06 g, with 0.01 g intervals. The mixture was then agitated at 150 rpm by orbital shaker for 4 hours to attain the equilibrium before being measured for its concentration using UV/vis spectrophotometer.

3.2.3.4 Effect of pH

The influence of pH on the CIP adsorption by STL, the pH of the CIP solution was adjusted to the desired pH (pH 2-11) using various concentrations (0.1, 0.5 and 0.1 M) of hydrochloric acid (HCl) or sodium hydroxide (NaOH) solution. The agitation rate and contact time, as well as the STL dosage were fixed at 150 rpm, 4 hours and 0.02 g, respectively.

3.2.3.5 Effect of agitation rate

The effect of agitation rate was investigated using different agitation rates, which were 100, 150 and 200 rpm. The initial concentration of CIP and STL dosage were fixed at 20 mg/L and 0.02 g, respectively.

3.2.4 Determination of isoelectric point of STL (pH_{pzc})

20 mL of 0.1 M NaCl solution were prepared and the pH of the NaCl solution was adjusted using 0.1 M HCl solution or NaOH solution to produce solution with varying pH from pH 2 – 12. The initial pH of each solution was measured and recorded as pH_i . For each pH, 0.02 g of STL was added into each solution, and the mixtures were agitated at 150 rpm for 24 hours. After 24 hours, the final pH values of each supernatant were measured and denoted as pH_f .

3.2.5 Esterification of STL

The esterification of STL via acidic methanol method was performed by using 3.00 g of STL and added in 210 mL of 99.9 % methanol and 1.8 mL of concentrated HCl. The esterified STL was then rinsed with distilled water several times until neutral pH was obtained. Then, the esterified STL was dried in oven at 50 °C for 24 hours.

3.2.6 Nitric acid (HNO₃) modification of STL

2 g of STL was mixed with 50 mL of 5 M HNO₃ solution. The suspension was heated at 80 °C and continuously stirred for 4 hours. After 4 hours, the modified STL were washed with distilled water several times until neutral. Then, the STL were dried in oven at 50 °C overnight to remove all the moisture.

3.3 Characterization analysis

3.3.1 UV-visible Spectroscopy

The absorbance of the supernatant of CIP solution after the adsorption process was determined at wavelength of 276 nm using UV/vis spectrophotometer, model Thermo Scientific GENESYS 50.

3.3.2 Fourier Transform Infrared Spectroscopy

The surface functional groups present on the STL could be determined using Fourier Transform Infrared Spectrophotometer (FTIR), model Spectrum RX1 by Perkin Elmer. The tea leaves were grinded with KBr powder to form homogeneous mixture. Then, the powder was made into pellet for analysis. The FTIR analysis was performed in the range of wavenumber from 4000 – 400 cm⁻¹.

3.3.3 Scanning Electron Microscopy

The surface morphology of the STL was analyzed at emission current of 4.0 kV using SEM model JEOL-JSM-6701F.

3.3.4 Atomic Force Microscopy

The surface topography of the STL was examined using AFM model Park XE-70 AFM.

Chapter 5

CONCLUSION

5.1 Conclusion

In conclusion, STL were proven to be an effective yet potential adsorbent for the removal of CIP from aqueous solution in this study. The adsorption system was believed to obey pseudo-second order kinetic model, which suggested that chemical adsorption was involved in the adsorption process, with a R^2 close to unity. In addition to that, the experimental data fitted well to both Langmuir and BET models with R^2 value of 0.9941 as compared to Freundlich isotherm model. This suggested the adsorption extended beyond monolayer coverage over homogeneous surface. In FTIR analysis, there were several peak shifts after adsorption process, proving that certain interactions were occurred between particular surface functional groups of STL and CIP. Furthermore, SEM and AFM analysis further confirmed successful adsorption by showing significant changes of surface morphology and topography of STL after the adsorption of CIP, by comparing with the STL before adsorption. In the adsorption system of CIP by STL, initial concentrations of adsorbate, contact time, dosage of adsorbent and pH were determined as the significant factors that influence the adsorption strongly. The optimum level of each parameter to achieve maximum adsorption of CIP by STL was investigated using RSM, and a model equation was generated. The optimum condition was determined at 40 mg/L of CIP concentration, 0.03 g of STL, pH 6.5, 150 rpm agitation rate and 182.5 minutes

of contact time. The percentage of differences calculated for the experiments was within 8 %, which proven the validity and reliability of the equation.

5.2 Future prospects

For future studies, it is advisable to utilize STL as the adsorbent to remove different types of adsorbates, not only restricted to antibiotics, but also dyes and heavy metal ions, to examine their adsorption performance. Other than that, it is recommended to carry out modifications on the STL as it is believed that modified or activated STL could resulted in better adsorption performance.

REFERENCES

- Abegunde, S. M., Idowu, K. S., Adejuwon, O. M. and Adeyemi-Adejoly, T., 2020. A review on the influence of chemical modification on the performance of adsorbents. *Resources, Environment and Sustainability*, [e-journal] 1. <https://doi.org/10.1016/j.resenv.2020.100001>.
- Adedeji, W. A., 2016. The Treasure Called Antibiotics. *Annals of Abidan Postgraduate Medicine*, 14(2), pp. 56 – 57.
- Akpomie, K. G., Ofomatah, A. C., Chukwuemeka-Okorie, H. O., Ani, J. U., Agbo, S. C., Odewole, O. A., Ojo, F. K. and Alum, O. L. and Conradie, J., 2023. Equilibrium isotherm investigation on sequestration of ciprofloxacin from solution via adsorption onto yam peel powder. *IOP Conf. Series: Earth and Environmental Science*, [e-journal] 1178(2023). <https://doi.org/10.1088/1755-1315/1178/1/012020>.
- Aljeboree, A. M., Alshirifi, A. N. and Alkaim, A. F., 2017. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Arabian Journal of Chemistry*, 10(2), pp. S3381 – S3393.
- Al-Musawi, T. J., Mahvi, A. H., Khatibi, A. D. and Balarak, D., 2021. Effective adsorption of ciprofloxacin antibiotic using powdered activated carbon magnetized by iron(II) oxide magnetic nanoparticles. *Journal of Porous Materials*, 28(3), pp. 835 – 852.
- Ayawei, N., Angaye, S. S., Wankasi, D. and Dikio, E. D., 2015. Synthesis, Characterization and Application of Mg/Al Layered Double Hydroxide for the Degradation of Congo Red in Aqueous Solution. *Open Journal of Physical Chemistry*, 5(3), pp. 56 – 70.
- Bag, S., Mondal, A., Majumder, A. and Banik, A., 2022. Tea and its phytochemicals: Hidden health benefits & modulation of signaling cascade by phytochemicals. *Food Chemistry*, [e-journal] 371. <https://doi.org/10.1016/j.foodchem.2021.131098>.
- Belhachemi, M. and Djelaila, S., 2017. Removal of Amoxicillin Antibiotic from Aqueous Solutions by Date Pits Activated Carbons. *Environmental Processes*, 4(3), pp. 549 – 561.

Bhatnagar, A. and Anastopoulos, I., 2017. Adsorptive removal of bisphenol A (BPA) from aqueous solution: A review. *Chemosphere*, 168, pp. 885 – 902.

Bhatt, S. and Chatterjee, S., 2022. Fluoroquinolone antibiotics: Occurrence, mode of action, resistance, environment detection, and remediation – A comprehensive review. *Environmental Pollution*, [e-journal] 315. <https://doi.org/10.1016/j.envpol.2022.120440>.

Browne, A. J., Chipeta, M. G., Haines-Woodhouse, G., Kumaran, E. P. A., Hamadani, B. H. K., Zarea, S., Henry, N. J., Deshpande, A., Reiner, R. C., Day, N. P. J., Lopez, A. D., Dunachie, S., Moore, C. E., Stergechis, S., Hay, S. I. and Dolecek, C., 2021. Global antibiotic consumption and usage in humans, 2000-18: a spatial modelling study. *The Lancet Planetary Health*, [e-journal] 5(12). [https://doi.org/10.1016/S2542-5196\(21\)00280-1](https://doi.org/10.1016/S2542-5196(21)00280-1).

Brunauer, S., Emmett, P. H. and Teller, E., 1938. Adsorption of Gases in Multimolecular Layers, *Journal of the American Chemical Society*, 60, pp. 309 – 319.

Çelebi, H., Gök, G. and Gök, O., 2020. Adsorption capability of brewed tea waste in waters containing toxic lead(II), cadmium (II), nickel (II), and zinc (II) heavy metal ions. *Scientific Reports*, 10, pp. 17570.

Chang, K. L., Chen, C. C., Lin, J. H., Hsien, J. F., Wang, Y., Zhao, F., Shih, Y. H., Xing, Z. J. and Chen, S. T., 2014. Rice straw-derived activated carbons for the removal of carbofuran from an aqueous solution. *New Carbon Materials*, 29(1), pp. 47 – 54.

Chen, Y. G., Ye, W. M., Yang, X. M., Deng, F. Y. and He, Y., 2010. Effect of contact time, pH and ionic strength on Cd(II) adsorption from aqueous solution onto bentonite from Gaomiaozi, China. *Environmental Earth Sciences*, 64(2), pp.329 – 336.

Chung, W. Y. and Ong, S. T., 2021. Effective Removal of Reactive Brown 10 from Aqueous Solution by Using Chitosan Beads: Batch and Experimental Design Studies. *Journal of Physical Science*, 32(1), pp. 91 – 108.

Dutta, J. and Mala, A. A., 2020. Removal of antibiotic from water environment by the adsorption technologies: a review. *Water Science & Technology*, 82(3), pp. 401 – 426.

Enyoh, C. E., Wang, Q. and Ovuoraye, P. E., 2022. Response surface methodology for modelling the adsorptive uptake of phenol from aqueous solution using adsorbent polyethylene terephthalate microplastics. *Chemical Engineering Journal Advances*, [e-journal] 12(1). <https://doi.org/10.1016/j.ceja.2022.100370>.

Etim, E. E., Asuquo, J. E., Ogofotha, G. O., Nzubechukwu, M. C., 2022. Adsorption Studies of Cu²⁺ using Tea Leaves and Tea Fibre (*Camellia Sinensis*) as Adsorbents. *International Journal of Advanced Research in Chemical Science (IJARCS)*, 9(2), pp. 1 – 10.

Freundlich, H. M. F., 1906. Over the Adsorption in Solution. *The Journal of Physical Chemistry*, 57, pp. 385 – 471.

García-Alonso, J. A., Sulbarán-Rangel, B. C., Bandala, E. R. and Real-Olvera, J., 2019. Adsorption and kinetic studies of the removal of ciprofloxacin from aqueous solution by diatomaceous earth. *Desalination and Water Treatment*, 162, pp. 331 – 340.

Genç, N., Can Dogan, E. and Yurtsever, M., 2013. Bentonite for ciprofloxacin removal from aqueous solution. *Water science and technology: a journal of the International Association on Water Pollution Research*, 68(4), pp. 848 – 855.

Hamdaoui, O., 2006. Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Materials*, 135(1-3), pp. 264 – 273.

Hameed, B. H., 2009. Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *Journal of Hazardous Materials*, 161(2-3), pp. 753 – 759.

Hii, H. T., 2021. Adsorption Isotherm and Kinetic Models for Removal Of Methyl Orange and Remazol Brilliant Blue R by Coconut Shell Activated Carbon. *Tropical Aquation and Soil Pollution*, 1(1), pp. 1 – 10.

Ho, Y. S. and McKay, G., 1999. Pseudo-Second Order Model for Sorption Processes. *Process Biochemistry*, 34, pp. 451 – 465.

Huang, B., Liu, G., Wang, P., Zhao, X. and Xu, H., 2019. Effect of Nitric Acid Modification on Characteristics and Adsorption Properties of Lignite. *Processes*, [e-journal] 7(3). <https://doi.org/10.3390/pr7030167>.

Ibrahim, J. and Ho, J. W., 2023. Dispose of used meds properly. *The Star*, [Online] 16 Jun. Available at: <https://www.thestar.com.my/news/nation/2023/06/16/dispose-used-meds-properly> [Accessed: 25 August 2023].

Ighalo, J. O. and Adeniyi, A. G., 2020. A mini-review of the morphological properties of biosorbents derived from plant leaves. *SN Applied Sciences*, [e-journal] 2(3). <https://doi.org/10.1007/s42452-020-2335-x>.

Igwegbe, C. A., Oba, S. N., Aniagor, C. O., Adeniyi, A. G. and Ighalo, J. O., 2020. Adsorption of Ciprofloxacin from Water: A Comprehensive Review. *Journal of Industrial and Engineering Chemistry*, 93, pp. 57 – 77.

Jain, S. N., Tamboli, S. R., Sutar, D. S., Jadhav, S. R., Marathe, J. V., Shaikh, A. A. and Prajapati, A. A., 2020. Batch and continuous studies for adsorption of anionic dye onto waste tea residue: Kinetic, equilibrium, breakthrough and reusability studies. *Journal of Cleaner Production*, [e-journal] 252. <https://doi.org/10.1016/j.jclepro.2019.119778>.

Kurniawati, D., Bahrizal, Sari, T. K., Adella, F. and Sy, S., 2021. Effect of Contact Time Adsorption of Rhodamine B, Methyl Orange and Methyl Blue Colours on Langsat Shell with Batch Methods. *Journal of Physics: Conference Series*, [e-journal] 1788(1). <https://doi.org/10.1088/1742-6596/1788/1/012008>.

Lagergren, S., 1898. About the Theory of So-Called Adsorption of Soluble Substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 24, pp. 1 – 39.

Langmuir, I., 1918. The Adsorption of Gases on Plane Surface of Glass, Mica and Platinum. *Journal of the American Chemical Society*, 40, pp. 1361 – 1402.

Li, J., Yu, G., Pan, L., Li, C., You, F., Xie, S., Wang, Y., Ma, J. and Shang, X., 2018. *Study of ciprofloxacin removal by biochar obtained from used tea leaves* [Online]. Available at: <https://doi.org/10.1016/j.jes.2017.12.024> [Accessed: 26 August 2023].

Li, M., Wang, S., Luo, W., Xia, H., Gao, Q. and Zhou, C., 2014. Facile synthesis and in site magnetization of carbon-decorated lignocellulose fiber for highly efficient removal of methylene blue. *Journal of Chemical Technology*, 90(6), pp. 1124 – 1134.

Liu, L., Fan, S. and Li, Y., 2018. Removal Behaviour of Methylene Blue from Aqueous Solution by Tea Waste: Kinetics, Isotherms and Mechanism. *International Journal of Environmental Research and Public Health*, [e-journal] 15(7). <https://doi.org/10.3390/ijerph15071321>.

Ma, C. M., Hong, G. B. and Wang, Y. K., 2020. Performance Evaluation and Optimization of Dyes Removal using Rice Bran-Based Magnetic Composite Adsorbent. *Materials*, [e-journal] 13(12). <http://dx.doi.org/10.3390/ma13122764>.

Ma, J., Yang, M., Yu, F. and Zheng, J., 2015. Water-enhanced Removal of Ciprofloxacin from Water by Porous Graphene Hydrogel. *Scientific Reports*, [e-journal] 5. <https://doi.org/10.1038/srep13578>.

Malakahmah, A., Tan, S. & Yavari, S., 2016. Valorization of wasted black tea as a low-cost adsorbent for nickel and zinc removal from aqueous solution. *Journal of Chemistry*, 2016, pp. 1 – 8.

Mei, L., Peng, C., Qiao, H. and Ke, F., 2019. Enhanced removal of fluoride by zirconium modified tea waste with extrusion treatment: kinetics and mechanism. *RSC Advances*, 9(57), pp. 33345 – 33353.

Mishra, S. P., 2022. Insights into the Recent Use of Modified Adsorbents in Removing Heavy Metal Ions from Aqueous Solution. *Biointerface Research in Applied Chemistry*, 12(2), pp. 1884 – 1898.

Mondal, N. K. and Kar, S., 2018. Potentiality of banana peel for removal of Congo red dye from aqueous solution: isotherm, kinetics and thermodynamics studies. *Applied Water Science*, [e-journal] 8(6). <https://doi.org/10.1007/s13201-018-0811-x>.

Movasaghi, Z., Yan, B. and Niu, C., 2019. Adsorption of ciprofloxacin from water by pretreated oat hulls: Equilibrium, kinetic, and thermodynamic studies. *Industrial Crops and Product*, 127(2019), pp. 237 – 250.

Nageed, M., 2013. *Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater* [Online]. Available at: <http://dx.doi.org/10.5772/54048> [Accessed: 15 July 2023].

Nasar, A., 2021, *Utilization of tea wastes for the removal of toxic dyes from polluted water – a review* [Online]. Available at: <https://sci-hub.se/https://doi.org/10.1007/s13399-020-01205-y> [Accessed: 20 August 2023].

Nazir, N. A. M., Raoov, M. and Mohamad, S., 2020. Spent tea leaves as an adsorbent for micro-solid-phase extraction of polycyclic aromatic hydrocarbons (PAHs) from water and food samples prior to GC-FID analysis. *Microchemical Journal*, [e-journal] 159 (2020). <https://doi.org/10.1016/j.microc.2020.105581>.

NetSol Water, 2023. *What is adsorption in waste water* [online]? Available at: <https://www.netsolwater.com/treatment-of-waste-water-by-adsorption.php?blog=1498> [Accessed: 19 September 2023].

Ong, S. T. and Lee, W. N., 2015. Evaluation on the efficiency of ethylenediaminetetraacetic acid (EDTA)-modified rice husk as a low-cost sorbent for various dyes removal under continuous flow condition. *Desalination and Water Treatment*, 57(39), pp. 18157 – 18167.

Ong, S. T. and Seou, C. K., 2015. Removal of reactive black 5 from aqueous solution using chitosan beads: optimization by Plackett-Burman design and response surface analysis. *Desalination and Water Treatment*, 52(40-42), pp. 7673 – 7684.

Ooi, S. L. and Ong, S. T., 2019. Remediation of lead (II) and malachite green from aqueous solution using palm oil fruit fibre. *Stud. UBB Chem.*, 4, pp. 55 – 70.

Parashar, D., Harafan, A., Achari, G. and Kumar, M., 2022. Ciprofloxacin and Metronidazole Adsorption on Chitosan-Modified Graphene Oxide as Single-Compounds and Binary Mixtures: Kinetics, Isotherm and Sorption Mechanism. *Journal of Hazardous, Toxic, and Radioactive Waste*, [e-journal] 27(1). [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000724](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000724)

Putra, W. P., Kamari, A., Yusoff, S. N. M., Ishak, C. F., Mohamed, A., Hashim, N. and Isa, I. M., 2014. Biosorption of Cu(II), Pb(II) and Zn(II) Ions from Aqueous Solutions Using Selected Waste Materials: Adsorption and Characterization Studies. *Journal of Encapsulation and Adsorption Science*, 4(1), pp. 25 – 35.

Ramli, N. A. S., Amin, N. A. S. and Hidayah, N., 2016. Esterification of renewable levulinic acid to levulinate esters using amberlyst-15 as a solid acid catalyst. *Jurnal Teknologi*, [e-journal] 79(1). <http://dx.doi.org/10.11113/jt.v79.8095>.

Rao, H. J., 2021. Characterization Studies on Adsorption of Lead and Cadmium Using Activated Carbon Prepared from Waste Tyres. *Nature Environment and Pollution Technology*, 20(2), pp. 561 – 568.

Reza, A., Sheikh, F. A., Kim, H., Zargar, M. A. and Abedin, M. Z., 2016. Facile and efficient strategy for removal of reactive industrial dye by using tea waste. *Advanced Materials*, 7(11), pp. 878 – 885.

Rostami, E., Norouzbeigi, R. and Kelishami, A. R., 2018. Thermal and chemical modification of bentonite for adsorption of an anionic dye. *Advances in Environmental Technology*, 1, pp. 1 – 12.

Saini, S., Chawla, J., Kumar, R. and Kaur, I., 2019. Response surface methodology (RSM) for optimization of cadmium ions adsorption using C₁₆₋₆₋₁₆ incorporated mesoporous MCM-41. *SN Applied Sciences*, [e-journal] 1(894). <https://doi.org/10.1007/s42452-019-0922-5>.

Shakir, I. K. and Ghazy, R. N., 2019. Adsorptive Removal of Furfural from Wastewater on Prepared Activated Carbon from Sawdust. *Journal of Engineering*, 1(25), pp. 51 – 63.

Sikdar, D., Goswami, S. and Das, P., 2020. Activated carbonaceous materials from tea waste and its removal capacity of indigo carmine present in solution: synthesis, batch and optimization study. *Sustainable Environment Research*, [e-journal] 30(30). <https://doi.org/10.1186/s42834-020-00070-8>.

Singh, B. K., Parwate, D. V. and Shukla, S. K., 2009. Rapid Color Test Identification System for Screening of Counterfeit Fluoroquinolone. *E-Journal of Chemistry*, 6(2), pp. 377 – 384.

Sivakumar, S., Khatiwada, C. P., Sivasubramanian, J., Jini, P., Prabu, K., Venkateson, A. and Soundararajan, P., 2014. FT-IR study of green tea leaves and their diseases of Arunachal Pradesh, North East, India. *The Pharmaceutical and Chemical Journal*, 1(3), pp. 17 – 24.

Sobhanardakani, S., Zandipak, R., Bonyadi, M., Parvizimosaed, H., Moslemi, M., Tahergorabi, M. and Hosseini, S. M., 2015. Evaluation of Removal Efficiency of Cr (VI) Ions from Aqueous Solution Using Chitosan. *Journal of Chemical Health Risks*, 5(1), pp. 29 – 38.

Statista Research Department, 2023, *Global: Annual tea consumption 2012-2025* [Online]. Available at: <https://www.statista.com/statistics/940102/global-tea-consumption/> [Accessed: 22 July 2023]

Ternero-Hidalgo, J. J., Rosas, J. M., Palomo, J., Valero-Romero, M. J., Rodriguez-Mirasol, J. and Cordero, T., 2016. Functionalization of activated carbons by HNO₃ treatment: Influence of phosphorus surface groups. *Carbon*, 101(2016), pp. 409 – 419.

Wakejo, W. K., Meshasha, B. T., Kang, J. W. and Chebude, Y., 2022. Enhanced Ciprofloxacin Removal from Aqueous Solution Using a Chemically Modified Biochar Derived from Bamboo Sawdust: Adsorption Process Optimization with Response Surface Methodology. *Adsorption Science & Technology*, [e-journal] 2022. <https://doi.org/10.1155/2022/2699530>.

Wang, J. and Guo, X., 2020. Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere*, [e-journal] 258. <https://doi.org/10.1016/j.chemosphere.2020.127279>.

Wong, S., Lee, Y., Ngadi, N., Inuwa, I. M. & Mohamed, N. B., 2018. Synthesis of activated carbon from spent tea leaves for aspirin removal. *Chinese Journal of Chemical Engineering*, 26(5), pp. 1003 – 1011.

Yin, D., Xu, Z., Shi, J., Shen, L. and He, Z., 2018. Adsorption characteristics of ciprofloxacin on the schorl: kinetics, thermodynamics, effect of metal ion and mechanisms. *Journal of Water Reuse and Desalination*, 8(3), pp. 350 – 359.

Zbair, M., Anfar, Z. and Ahsaine, H. A., 2019. Reusable bentonite clay: modelling and optimization of hazardous lead and p-nitrophenol adsorption using a response surface morphology approach. *RSC Advances*, [e-journal] 9(10). <http://dx.doi.org/10.1039/c9ra00079h>.

Zhang, B., Han, X., Gu, P., Fang, S. and Bai, J., 2017. Response surface methodology approach for optimization of ciprofloxacin adsorption using activated carbon derived from the residue of desilicated rice husk. *Journal of Molecular Liquids*, 238, pp. 316 – 325.

Zheng, M., Wu, P., Li, L., Yu, F. and Ma, J., 2023. Adsorption/desorption behavior of ciprofloxacin on aged biodegradable plastic PLA under different exposure conditions. *Journal of Environmental Chemical Engineering*, [e-journal] 11(1). <https://doi.org/10.1016/j.jece.2022.109256>.

Zuccato, E., Castiglioni, S., Bagnati, R., Melis, M. and Fanelli, R., 2010. Source, occurrence and fate of antibiotics in the Italian aquatic environment. *Journal of Hazardous Materials*, 179(1-3), pp. 1042 – 1048.

Zuorro, A. and Lavecchia, R., 2010. Adsorption of Pb(II) on spent leaves of green and black tea. *American Journal of Applied Sciences*, 7(2), pp. 153 – 159.

