CORNCOB MODIFIED BY CuFe LAYERED FOR OXYTETRACYCLINE REMOVAL FROM AQUEOUS SOLUTION

by

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List of Abbrevation

AC	AC
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
CC	Corncob
CCAC	Corncob AC
FTIR	Fourier Transform Infrared
IR	Impregnation ratio
IUPAC	International Union of Pure and Applied Chemistry
OTC	Oxytetracycline
CIP	Ciproflaxacin
MG	Malachite green
MSDS	Material Safety Data Sheet
RMSE	Root Mean Square Error
RSM	Response surface methodology
SEM	Scanning electron microscopy
STA	Simultaneous thermogravimetric analyzer

List of Symbols

Symbol	Description	Unit
B_t	Constant for Boyd model	-
C	Solute/outlet concentration	mg/L
C_e	Concentration of adosrbate at equilibrium	mg/L
C_t	Concentration of adosrbate at time	mg/L
C_o	Initial/inlet adsorbate concentration	mg/L
Ea	Arrhenius activation energy of adsorption	-
F	Fraction of solute adsorbed for Boyd model -	-
k_1	Adsorption rate constant for pseudo-first order	-
k_2	Adsorption rate constant for pseudo-second order	-
K_F	Adsorption or distribution coefficient for Freundlich	-
K_L	Rate of adsorption for Langmuir isotherm	L/mg
n_F	Constant for Freundlich isotherm	-
n_{KC}	Adsorption intensity Koble-Corrigan isotherm	-
Q_m	Maximum adsorption capacity of adsorbent	mg/g
ΔG_o	Changes in standard free energy	kJ/mol
ΔH_o	Changes in standard enthalpy	kJ/mol
Δq_t	Normalized standard deviation	%
ΔS_o	Changes in standard entropy	J/mol K

KARBON TERAKTIF TONGKOL JAGUNG DIUBAHSUAI OLEH CuFe BERLAPIS UNTUK PENYINGKIRAN OXYTETRACYCLINE DARIPADA LARUTAN AKUAS

ABSTRAK

Dalam kajian ini, karbon teraktif (CCAC) berasaskan tongkol jagung telah disediakan daripada biojisim sisa untuk mengkaji penyingkiran OTC dalam larutan akueus. Reka bentuk eksperimen mendapati bahawa CCAC dipengaruhi terutamanya oleh nisbah impregnasi Cu-Fe, kuasa sinaran dan masa sinaran. Keadaan optimum penyediaan CCAC dengan kuasa sinaran 364 W, dan masa sinaran selama 20 minit, menghasilkan penyingkiran OTC dan hasil CCAC sebanyak 13.6431 mg/g dan 20.85%. Pencirian CCAC ditentukan bersifat mesoporous, dengan luas permukaan yang tinggi dan jenis struktur liang yang heterogen. Kefungsian permukaan CCAC tersedia berbilang kumpulan berfungsi sebagai tapak aktif untuk pengikatan kimia dan fizikal OTC. Untuk kajian kelompok, kesan kepekatan awal, jumlah OTC yang dikeluarkan oleh keadaan optimum CCAC, meningkat dari semasa ke semasa. Kajian tentang kesan suhu mempunyai kesan penyingkiran yang semakin meningkat. pH keseimbangan 8 menghasilkan peratusan penyingkiran tertinggi dalam kesan kajian pH larutan. Analisis model isoterma menghasilkan Freundlich sebagai model paling sesuai untuk kapasiti monolayer maksimum. Kajian kinetik mendedahkan bahawa penjerapan OTC ke CCAC mengikut model kinetik pseudo-second-order dengan nilai k_2 minimum. Termodinamik penjerapan OTC-CCAC membuktikan sifat endotermik seperti berikut kesan kajian suhu.

CORNCOB MODIFIED BY CuFe LAYERED FOR OTC REMOVAL FROM AQUEOUS SOLUTION

ABSTRACT

In this study, corncob-based activated carbon(CCAC) was prepared from waste biomass to study the removal of OTC in an aqueous solution. The experimental design discovered that the CCAC is mainly influenced by Cu-Fe impregnation ratio, radiation power and time. The optimal condition of CCAC preparation with radiation power of 364 W, and radiation time of 20 min, resulted in OTC removal and CCAC's yield of 13.6431 mg/g and 20.85%. The characterization of CCAC is determined mesoporous in nature, high surface area and heterogeneous types of pore structures. The surface functionality of CCAC is available multiple functional groups function as active sites for OTC chemical and physical binding. For the batch studies, the effect of initial concentration, the amount of OTC removed by the optimized condition of CCAC, increases over time. The study of the effect of temperature has an increasing removal effect. Equilibrium pH of 8 yields the highest removal percentage in the effect of the solution pH study. Isotherm model analysis resulted in Freundlich as the best-suited model for the maximum monolayer capacity. The kinetic study revealed that the adsorption of OTC onto CCAC follows a pseudo-second-order kinetic model with minimal k_2 value. The thermodynamics of OTC-CCAC adsorption proves the endothermic nature as follows the effect of temperature study..

CHAPTER ONE
INTRODUCTION

1.1. Overview of antibiotics in wastewater

The demand for high quality water as in global demand has been steadily increasing whether for drinking, sanitation, irrigation, or industrial usage. However , there has been widespread concern about water treatment and water reuse involving the strictest standards in recent years (Tatjana et al 2020). As in the industrial sector, wastewater is restricted for discharge to open water bodies or for other domestic usage before fine treatment which satisfies existing water contamination standards by the health ministry. Among all the industries available, pharmaceutical and aquaculture industry are rapidly developing industries correlation to global population, relatively discharging higher volume wastewater effluent compared to previous years (Šimatović, Ana ,2019;Gadipelly et al 2014). According to Yu et.al (2020), the worlds fish demand reached around 170 million ton in 2016, depicts the uprising trend in aquaculture industry. Instinctively, this situation levels up the challenges to ensure wastewater effluent safe to the environment without releasing high-impact chemical substances that disturbs the ecosystem and existing life forms (Šimatović, Ana ,2019).

Antibiotics are pharmaceuticals to prevent and control diseases for humans and animals in general (Kumar et al., 2012), as they are known to be highly efficient bacteriostatic. In these subsequent years, antibiotics such as norfloxacin, sulfamethoxazole, nalidixic acid and trimethoprim has already been discovered in wastewater effluent, river water, and groundwater, with quantities ranging from nanograms per litre to micrograms or even milligrams per litre (Kaixin Yi et al 2017). These pharmaceutical residues, especially antibiotics renowned for its potential toxic effects which is similar physio-chemical behavior compared to other xenobiotics, even the environmental concentrations at low concentration could cause toxic effects to micro-life forms. Among the impacts of antibiotics in open water sources, antibacterial resistance among the natural bacterial population concerns environmentalist and health organizations the most (Hermando et al. 2006). This means certain harmful species of bacteria can no longer be controlled by certain antibiotics. As this situation is feared to may cause more serious problems as a variety of antibiotics suspends in water-sources and affects the microbial behavior as well the organisms around affected bodies. As shown in Figure 1.1, the flow of antibiotics is to aquatic and terrestrial environment is mainly summarized due to inefficient wastewater treatment plants, veterinary purpose, and aquaculture industries. (Antibiotic in aquaqulture-seabos, 2022)

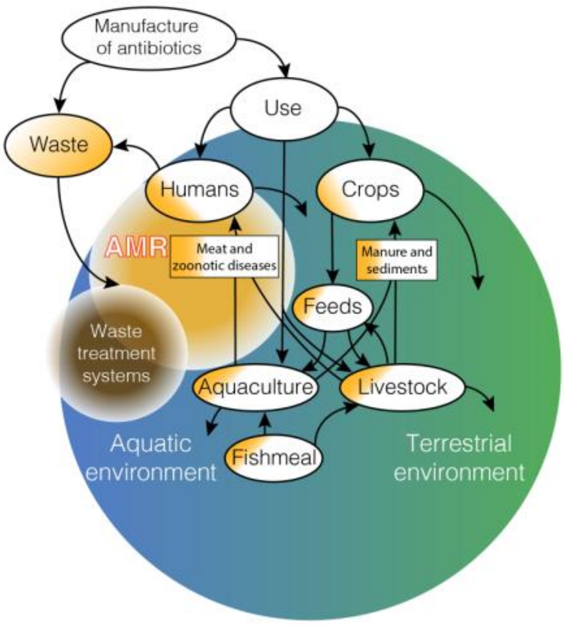


Figure 1. 1 Environmental pathways of antibiotics and their link to AMR

Antimicrobial-resistant (AMR) bacteria, antibiotics, metals, and emerging contaminants (CECs) are mostly obtained from effluents of wastewater treatment plants, hospitals, and other healthcare institutions (pharmaceutical), industry, agriculture, and aquaculture (Galvin et. al 2010). Specified AMR is a phenomenon results when prolonged exposure of antibiotic to pathogens where consumption of effected resources may results in infections that requires special treatment or advanced antibiotics. Galvin et al, 2010 estimated by the year of 2050, if issues prolonged without new antibiotics, 10 million deaths are likely to occur because of AMR. Without any argument it is argued to be a serious threat where this mortality by AMR is higher than predicted future cancer mortality (Galvin et al, 2010).

Among surging concentration of antibiotics in waste effluent, Tetracyclines are one of them as they belong to a class of antibiotics known as broad-spectrum drugs that have numerous applications in human medicine, veterinary medicine, and aquaculture. Tetracyclines, often known as TCs, are a class of antibiotics that limit the production of proteins in microorganisms by binding to the 30S subunit of the ribosomes in those microorganisms (Scaria et al 2021). Oxytetracycline falls under this spectrum of antibiotics as its classified by WHO as a critically important antibiotic in 2019 because it is used as an alternate treatment for serious infections in people and to treat diseases caused by bacteria that can be transmitted from non-human sources to humans (Munoz et al 2017). During the period 2008–2018, OTC reported to be applied over 73% of the top 15 aquaculture-producing countries (Lulijwa et al., 2019). Following the usage of vast majority of OTC, it is suspected to be large concentration can be released into water bodies.

Among the effected pathogens by this antibacterial resistance study, the Enterobacteriaceae family, E. coli one of affected pathogen as it lives in the guts of both people and animals. Even tough E. coli are mostly good bacteria that live in the large intestine, pathogenic strains, on the other hand, can cause infections in the gut and urinary tract, meningitis, and sepsis. Most of the time, people get sick from contaminated water, food, or animals (Grevskott et. al, 2017). This

AMR phenomenon of E.coli species due to OTC can shields some strains from elimination as causes the development of severe symptoms and potentially fatal consequences such hemolytic uremic syndrome(*E.coli,*2022). This *E.coli* potentially fatal strains soon no longer treatable with OTC as resistance gene survives through water and terrestrial bodies or even through meat sources and much stronger antibiotics is needed as to control medical concerns. As per importance given by World Health Organization itself, OTC control needed an immediate and effective approach that lowers OTC concentration in aquatic and terrestrial environment (WHO, 2016)

The OTC control in wastewater effluent becomes very essential as to ensure the drug-resistant bacteria developed in the common environment. This statement more reasons for the refining of OTC removal in wastewater effectively to zero concentration as possible. There are various wastewater remediation methods conventionally used for antibiotic removal including electrochemical processes, oxidation, ozonation, photolytic processes, membrane filtration and adsorption processes (Phoon et al, 2020). In industry adsorption process is more preferred due to its simplicity and waste utilization property from biomasses used for production of AC as adsorbent. AC as adsorbent is considered inexpensive and non-toxic , yet standalone. AC still not much effective due to less active functional groups on adsorbent surface (Zubair et al, 2021). This leads to surface modification approaches for higher removal efficiency as multiple studies indicates integration with metals such as Mg, Zn, Cu and Fe results in improved surface functionalities and better performance. Hence, LDHs composite adsorbent promises a fast and high efficiency removal of multiple pollutants and antibiotics. LDHs have competent properties for wastewater treatment such as versatile composition, large specific area, low toxicity, and excellent capability with the purpose of accommodating a wide spectrum of anions in the interlayers. When compared to other examined adsorbents, these LDHs demonstrated a high anionic pollutant removal efficiency as well as a rapid sorption rate (Ling et al 2016). Besides, exceptional reusability potential is an added benefit that demonstrates its efficacy in real-world wastewater treatment systems (Zubair et al, 2021;Lesbani et al, 2021).

Yet, even with various functionalities of LDHs, use of these composites is greatly restricted by the dissolution and agglomeration of LDHs in aqueous solution. Aggregation of LDHs makes this composites incapable in wastewater treatment for effective antibiotic removal (Zubair et al 2021). However, recent studies show that the drawbacks of LDHs can be eliminated with competent support like AC which enriches surface functionality and increase porous nature that requires larger and reactive surface for highly effective intercalation of metal hydroxides that overcomes the LDH drawbacks in overall (Zubair et al 2021). This narrows down this study to find suitable adsorbent for LDH composite and its adsorption properties experimental evaluation

1.2. Problem Statement

Due to high increase in global population, the pharmaceutical and aquaculture industry has surging development. Antibiotics releasing from these industries results a significant change in microbial behavior of interested microorganisms develops antibiotic resistance that eventually bring harm to humans. Due to the fact even small concentration of antibiotic can bring harm, removal of antibiotic from wastewater become more crucial. Adsorption process by using activated carbon (AC) is known for the best removal technique for antibiotic removal form aqueous solution. The adsorption method promises a relatively similar removal percentage to other high-priced methods with high reusability and stability which makes the method of interest. Precursors are investigated especially from agricultural wastes which are renewable, cheap and abundantly available. Waste utilization concept is applied by converting disposable biomass to industrial use products that can be used in antibiotic wastewater treatment steps. Due to the abundance of corncob waste from corn-food industry, an attempt to convert corncob into ACs for removal of Oxytetracycline has been made in this study.

1.3. Research Objectives

This study is mainly focused based on these stated objectives:-

i. To prepare corncob based activated carbon (CCAC) by using physiochemical activation
ii. To optimize the operating parameters in the preparation of CCAC using response surface methodology.
iii. To characterize CCAC in terms of surface are, surface morphology, proximate content and surface chemistry.
iv. To study the effects of antibiotic initial concentration, temperature and solution pH for adsorption of OTCon CCAC for equilibrium, kinetic and thermodynamic studies. .

CHAPTER TWO
LITERATURE REVIEW

2.1. Background of OTC antibiotic

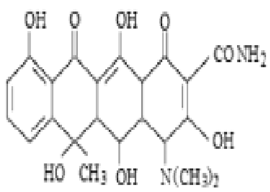
This antibiotic resistant gene (ARG) bacteria have been a treat not only to Oxytetracycline (OTC) but to various type of antibiotics that escapes either in hospital or other livestock industries. This situation is getting no more insignificant to ignore, as in farmland soil of Canada and Britain, tested contained a high level of OTC which is at about 513 µg/kg and 1691 µg/kg (Mengya et al.2020). Besides, there detected as much as 300 mg/kg of OTC in the sediments near a Chinese aquaculture facility (Huang et. al, 2013). As in aquaculture, around 100 to 200 tons of antibiotics are reportedly used every year, and there is evidence from studies that over 90% of OTC is not metabolized and is excreted in the urine and feces in a bioactive form. Today, more than 75% of OTC products are discharged into the environment following treatment at wastewater treatment plants (Li Qi et. al, 2021). The unconsumed antibiotics are secreted to the surrounding which affects the ecosystem and microbial behavior of microorganisms which alters drug resistance, interrupt key cycles critical to marine ecosystem which is nitrification cycle , soil fertility and rudimentary processes (Watkins et al 2007). Looking to the details of OTC concentration released in environment, research done by Igbinosa, Etinosa O. (2015) where to determine the antibiogram profiles of Vibrio isolates obtained from four distinct fishpond facilities in Benin City, Nigeria, and evaluate their presence. Vibrio species were detected at all the study sites as PCR test has run to identify the resistance gene for 20 antibacterial agents. At the end of study, it has been identified that a high level of resistance found for AMP , ERY , NAL , SUL , TMP , SXT , TET , OTC, and CHL.(Igbinosa, 2015).

Table 2. 1: Percentage Profiles of the Antimicrobial Resistance of Selected Vibrio Isolates Recovered from Fish Pond Sources (Igbinosa, 2015)

Antibiotics	V. fluvialis (n = 52) (%)	V. parahaemolyticus (n = 43) (%)	V. vulnificus (n = 47) (%)	Other Vibrio species (n = 25)(%)	Resistant Strain (%)
AMP	77	71	100	80	85
ERY	77	93	75	87	91
NAL	38	30	32	35	50.8
SUL	94	45	47	79	68.8
TMP	87	58	64	70	72.5
SXT	67	12	36	30	29.9
OTC	96	100	96	85	99.4
CHL	98	76	36	60	73.1

Reviewing the study and obtained result of percentage of resistant strain, OTC has the highest percentage of 99.4% in all Vibro species. This statement indicates the criticalness of surging OTC resistant among pathogens, as it becoming obvious that it is very crucial to eliminate antibiotic residues from wastewater before releasing them to open water sources.

Table 2. 2: Physiochemical properties of OTC

Molecular structure	Molecular Formulae	Molecular Weight	Log_{Kow}	pKa	Cross Area
	$C_{22}H_{24}N_2O_9$	460.45	-0.9	3.27	4.074

2.2. Abatement methods for OTC removal

Throughout history, pharmaceutical and aquaculture wastewater treatment cultivated traditional methods in removing OTCs and other same sort antibiotics. Traditional treatment methods can be grouped into three which are biological, chemical, and physical methods. Electrochemical processes, oxidation, ozonation, photolytic processes, membrane filtration processes are the well-known conventional remediation processes (Watkinson et al 2007). These traditional processes have their advantage and disadvantages and according to studies these wastewater treatment plants can perform partial removal of targeted antibiotics which is between 20-90%. This shows several percentages of antibiotics still escape from wastewater remediation plants to the environment which even a small concentration can put up the antibacterial resistance. For that matter, studies were done by proving metabolites present in WWTPs can be synthesized back to their original form upon registering to open waters (Watkinson et al 2007). Besides, advanced oxidation processes and membrane separation itself promises adsorption efficiency around 90-99% of antibiotics. Yet, these methods are not favored due to their high cost and harsh conditions (Peng et al 2016).

Among all the stated treatment methods, researchers claim adsorption is one of the significant techniques for wastewater contaminant removal. This technique is a mass transfer process as it is considered most effective due to its simplicity, low toxicity, and low cost for the removal of targeted components in wastewater treatment. The adsorption can be driven by physical or chemical reactions between adsorbate and surface adsorbents. Hydrogen bond, dipole-dipole interaction and Van der Waals forces are the common and prime attraction forces for physical adsorption meanwhile, chemical adsorption operates by linking chemically. This physical adsorption can be reversed yet in chemical adsorption it is done and specific (Sharma and S.K., 2015).

In those treatment plants that use adsorption technique, various adsorbents have been used to remove contaminants from wastewater, including carbon nanostructures, magnetic nanomaterials, and polymer nanocomposites. However, adsorbents practical application is limited due to their limitations, which include a high cost, non-biodegradability and poor adsorption and regeneration performance (Zubair et al 2021). For the past twenty years, AC usage has been a common adsorbent as they are renowned for its standalone high adsorption capacity. AC typically present a porous and solid form which can be produced by any carbonaceous solid based, natural, or synthetic. Biomass like coconut shell, sugarcane bagasse, rice husk can be precursors for AC which are obtained from simple pyrolysis and respective biomass have significant adsorption capacity especially for a specific type of antibiotics. In these carbon-based adsorbents, current research papers pointing out their various action mechanism such as hydrophobic effect, π-π interactions, hydrogen bonds, covalent and electrostatic interactions as their coexistent ensures competent adsorption efficiency itself (Peng et al. 2016).

2.3. Various adsorbents for OTC removal

A few studies were performed in the literature to investigate OTC adsorption with various adsorbents such as bentonite, zeolite , pumice, carbon nanotube, montmorillonite, graphene oxide(Pham et al, 2019). Yet, it is noted that most of these studies were related to the adsorption of OTC to AC and montmorillonite. In support of the effectiveness of using AC, removal of OTC, there is a comparative study on removal of OTC using commercial AC, activated sludge, graphene oxide magnetic nanoparticles and which are the comment pristine adsorbent used for removal of antibiotics especially for OTC. The outcomes have shown that sludge-derived materials, graphene oxide magnetic nanoparticles, AC, and alumina are compelling adsorbents for the OTC removal from an aqueous solution. With various convergence limits the adsorption limits of adsorbents were gotten as 55.9 mg g−1 (95%) for AC, 90.9 mg g−1 (70%) for activated sludge, 45 mg g−1 for graphene oxide (86%), 36.4 mg g−1 for zeolite (96%) and 653.3 mg g-1 for chitosan (>80%)(Pham et al, 2019). This shows adsorption of OTC can be very effective when moved on with AC as pristine or even with other integration approach.

Table 2. 3: Comparison the adsorption capacity values and percent sorption of adsorbents for the removal of OTC (Pham et al, 2019)

Adsorbents	**Adsorption capacity, mg/g**	**Removal Percentage, %**
Commercial AC	55.9	95
Activated Sludge	90.9	70
Graphene oxide	45	86
Zeolite (La-Z) (Desalination of water treatment, 2022)	36.377	96
Chitosan (Rivas et al, 2022)	653.3	80

Focusing on the targeted antibiotic of this paper, the removal of OTC promising removal efficiency when using AC synthesized from corncob. Corn cob is a type of lignocellulosic waste that has a significant potential for usage as adsorbents in Ecuador due to its widespread production and availability. In Ecuador, 0.186 kg of CC is obtained for every kilogram of corn harvested and about 1060 million corns produced in 2016 alone (Maria et al 2019; Juela et al 2021). The chosen CC for AC synthesis is limited in study as existing studies are based on ACs synthesized from corn residues which is corn stalks. The existing performance of corn stalk based pristine AC has results as when concentration increased from 10 mg/L, the removal efficiency of OTC reduced from 99.90 % to 49.21 %, which confirmed unsuitable effect of high initial concentration on the adsorption process (Razi University- OTC, 2022). Theoretically, the speculation of CCAC gives same results as corn stalk AC where these two precursors has relatively similar cellulose, hemicellulose, and lignin content. As the percentage is tabulated in table below, can be seen that the percentage difference for each content falls under 3%.

Table 2. 4: Percentage of Cellulose, Hemicellulose and lignin on corn farm residues (Fajardo et al 2015)

Corn Residues	Cellulose,%	Hemicellulose %	Lignin %
Stalk	41.2	36	15.9
Cob	39.6	35	18.4

Whereas, by implying the insignificant difference in content, it is speculated the corncob based pristine AC will have similar performance as pristine cornstalk-based AC performance with integration of LDH impregnation approach. Not only do these corn cob as adsorbents, utilize agricultural waste but they yield above 80% of the removal efficiency of OTC alone (Maria et al 2019).

2.4. Combination of treatment method

However, comparing other adsorbents available, standalone CCAC still relatively has lower adsorption performance. This study was caused by the less available number of active functional groups and low ion exchangeability. To overcome this barrier, surface modification is approached as an attractive method to alter surface characteristics of AC and enhance adsorption efficiency.(Huang et al. 2021;Tan et al. 2017). In this matter, significant levelled up removal performance of adsorbate when AC supported with metals such as Mg, Zn, Cu and Fe rather than pristine AC. This shows that this modification in surface functionalities, structure and textural properties adds up and make available huge active sorption sites. Layered double hydroxides (LDHs) are hydrotalcite clays with brucite layered structure which can be expressed by the general formula(Rathee et al 2021) :-

$$[M^{2+}{}_{1-x}\, M^{3+}{}_{x}\, (OH)_2\,]^{x+}.[A^{n-}{}_{x/n}.mH2O]^{x-}$$

M^{2+} and M^{3+} = metals with divalent and trivalent ions

x = molar ratio of trivalent cations,

An- = anion within the interlayer.

These LDHs resulted in relatively faster and far greater removal performance on removing various contaminants. The low cost of AC feedstock, abundant feedstock, and minimal energy usage during production made it ideal for bioremediation. ACs porous structure and enhanced surface functioning make it an attractive support material for intercalating metal hydroxides and preventing LDH aggregation (Zubair et al 2021). Among available synthesized LDH integration (Ni, Cu, Zn, Co), CuFe LDH promises relatively to have better performance than LDHs. According to study by Zubair et al (2021), CuFe LDH exhibited the highest and enormous adsorption capacity in contaminant(dye) removal which is around 212.35 mg/g at pH 2.5 and 25°C. Plus, in that study, CuFe exhibited exceptional reusability and affinity for specified adsorbate owing to its high crystallinity, wide surface area, and abundant oxygen functions. (Zubair et al 2021).

Supporting to this modification of AC from various biomass through impregnation of LDH has been studied in removal various aqueous solution contaminants such dye, heavy metals, minerals, and other organic contaminants. Zhang et al. (Zhang et al., 2013) employed a spontaneous high-mount technique to functionalize activated cotton-wood biochar with MgAl-LDH nanoparticles, then manage to remove phosphate with a maximum adsorption capacity of 410 $mg.g^{-1}$. The ultra-fine AC-MgAl-LDH composites synthesized shown a high capacity for phosphate sorption in aqueous solutions which higher than the adsorption capacity of any other LDH adsorbent. AC-MgAl-LDH ultra-fine composites have showed their potential applicability for pollutants removal, particularly in the removal of phosphate from waste effluent, as demonstrated by the results from Zhang et al study (Zhang et al., 2013).

Meili et al (2018) studied this AC-MgAl LDH for removal of methylene blue dye which mainly studied its pH influence, kinetic study, and regeneration capability. This composite reached a maximum adsorption capacity of 406.47 mg.g1at 40°C, and it has a rapid action on dye removal, reaching equilibrium in as little as 20 minutes and removing up to 95 percent of the dye at pH 12, indicating the materials feasibility in dye adsorption under basic solution conditions. The results of the regeneration experiments revealed that after six cycles, the removal capacity had decreased to levels that were comparable to those achieved with pure biochar.

In other study by Wang et al (2015), the AC-LDH method yielded high removal efficiency, about 98% in removing arsenic by using NiMn-LDH/ AC composite. This composite adsorbent studied its capability to adsorb arsenic in very low concentration with high efficiency with a high capacity for chemical regeneration in the presence of NaOH. At low arsenic concentrations (e.g., less than 12 mg/L), the adsorbent composite has a good arsenic removal effectiveness of more than 98%. The AC-NiMn/LDH is quickly desorbed by NaOH and attached with a high efficiency of more than 98 percent in the second and third desorption–resorption cycles. Thus, AC-NiMn/LDH is a highly effective sorbent for the removal of arsenic from aqueous solutions (Wang et al. 2015).

These studies proofed surface modification yield better removal efficiency and high regeneration properties that have potential to reduce cost of pharmaceutical wastewater remediation treatment plant. With choice of abundant biomass to be converted to AC and relatively better performance LDH metal composites, Corncob-CuFe LDH composites for removal of OTC are expected to yield competitively similar adsorption performance compared to other high-cost advanced treatment methods. This modified and integrated method need to be studied thoroughly considering all factor and varying adsorbent related properties. This study is targeted and expected to improve the pristine removal performance up to above 99%.

2.5. Adsorption Isotherm

Adsorption isotherms are fundamental because they represent how solutes interact with adsorbents and are critical for optimizing adsorbent utilization. Adsorption isotherms commonly studied using four isotherm models: Langmuir, Freundlich, Temkin, and Koble-Corrigan. The adsorption isotherm for the adsorptive removal of OTC by Corncob-LDH composite can be studied using these common isotherm models

2.5.1. Langmuir Model

The Langmuir model describes monolayer sorption on distinct localized adsorption sites. Uniform energies of monolayer sorption onto the sorbent surface is assumed while specifies no transmigration of the adsorbate in the plane of the surfaces (Mathias et al.1996) . The model ca be expressed as:-

$$q_e = \frac{Q_m K_L C_e}{1+K_L C_O} \tag{2.3}$$

Where C_e is the equilibrium constant (mg/L), q_e is amount of OTC adsorbed quilibrium (mg/g), Q_m is maximum monolayer coverage capacity(mg/g), K_L is Langmuir isotherm constant (L/mg)

2.5.2. Freundlich Model

The Freundlich isotherm is used to describe adsorption processes that occur on heterogeneous surfaces and active sites with different energies based on multilayer adsorption and equilibrium (Samarghandi et al.2009). The isotherm is expressed as:-

$$Q_e = K_f C_e^{\frac{1}{n}} \quad n > 1 \tag{2.4}$$

Where K_f is the Freundlich isotherm constant, n is adsorption intensity, C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the amount of phosphate adsorbed at equilibrium (mg/g).

2.5.3. Temkin Model

Based on the uniform distribution of binding energies, this model evaluates the influence of the adsorbate interaction on the adsorbent. Due to adsorbate/adsorbate interactions, the heat of adsorption of the molecules in the layer would drop linearly with coverage. (Samarghandi et al.2009). This model can be expressed in linear form which:

$$q_e = B_T ln A_T + B_T ln C_e \tag{2.5}$$

where B_T is RT/b_T constant related to the heat of adsorption (L/mg); q_e is amount of adsorbate adsorbed at equilibrium (mg/g); C_e is equilibrium concentration of adsorbate (mg/L); T is absolute temperature; R is universal gas constant and A_T is equilibrium binding constant (L/mg).

2.5.4. Koble-Corrigan Model

Koble-Corrigan (KC) model is a three-parameter empirical model for representing equilibrium adsorption data (Hamidpour et al.2011) which its equation expressed as

$$q_e = \frac{a_{KC} C_e^{nKC}}{1 + b_{KC} C_e^{nKC}} \qquad (2.6)$$

where q_e is the adsorbed amount at equilibrium (mg/g); *Ce* is the adsorbate equilibrium concentration (mg/L); a_{KC}, b_{KC} and n_{KC} are Koble-Corrigan parameters.

2.6. Adsorption Kinetics

Kinetic studies of batch adsorption processes offer information regarding the optimal circumstances, sorption mechanism, and possible rate regulating step. On adsorption data, linear forms of pseudo-first- and pseudo-second-order kinetics are common in adsorption of antibiotics which in this study OTC onto CCAC.

2.6.1. Pseudo first-order

pseudo-first-order kinetic model explains the relationship between the rate the sorption sites of the adsorbents are occupied and the number of unoccupied sites (Demirbas et al.2004). The equation gives:-

$$(q_e - q_t) = \ln q_e - k_1 t \qquad (2.1)$$

where qe and qt are the amounts of OTC adsorbed at equilibrium and at time t (mins), respectively, and k1 is the rate constant of adsorption (min^{-1})

2.6.2. Pseudo second order

The pseudo-second-order kinetic model describes the dependency of the adsorption capacity of the adsorbent on time (Ho and McKay, 1999) and can be expressed as:-

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2.2)$$

where qt and qe are the amounts of OTC adsorbed at equilibrium and at time t (mins), respectively, and k_2 is the pseudo-second-order rate constant (g/mg/min).

2.7. Boyd Kinetic Model

This model is mainly used to identify the slowest step in the adsorption process, which is expressed as (Boyd *et al*., 1947):

$$B_t = -0.4977 - \ln\,(1 - \frac{q_t}{q_e}) \quad (2.8)$$

where q_t is amount of adsorbate adsorbed at time t (mg/g); q_e is amount of adsorbate adsorbed at equilibrium (mg/g) and B_t is mathematical function of q_t/ q_e.

2.8. Thermodynamic study

Thermodynamic parameters are critical in determining the adsorption process's spontaneity and viability. They supply the data essential to develop an adsorption process (Raghav et al. 2018) . Thermodynamic of adsorption experiment was carried out at different temperature conditions and calculated parameters included enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG).

$$\Delta G° = \Delta H° - T\Delta S° \tag{2.9}$$

$$\ln K_C = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{2.10}$$

$$\Delta G = -RT\ln K_C \tag{2.11}$$

Where R is the natural gas constant and KC is the constant at equilibrium and is calculated as

$$K_C = \frac{C_e}{1-C_e} \tag{2.12}$$

where C_e is the concentration of sorbent at equilibrium condition.

2.9. Sustainability of design experiment

In 2015, the United Nations Member States adopted 17 Sustainable Development Goals (SDGs) with the objective of enhancing health and education, eliminating discrimination, and spurring economic development, all while battling climate change and protecting our coastlines and forests. There are 17 goals highlighted by this institution and which are:-

This antibiotic removal study is more focused to several goals stated as discussed in literature review this antibiotic relatively brings significant side effects to not only to aquatic organisms and environmental microbes and polluting the water to extent effecting the immunity of living humans. By removing this antibiotic which will prevent the effects will subsequently make the achievement of Goal 6: Clean water and Sanitation, Goal 3: Good Health and well-being, and Goal 14: Life below water.

Corncob is vast amount of waste that produced by food industries in tons per annum. This waste accumulation can bring to environmental impact and energy waste by dumping to environment with no approach of utilization. This study proves the use of corncob producing AC which promises effective use in wastewater treatment can promise the sustainability of food industry and economic growth by utilizing the biowaste produced, eventually achieves the Goal 9; Industry, innovation and infrastructure and Goal 12: Responsible consumption and production.

In conclusion, the experiment that was intended is able to meet a lot of the important goals of sustainable development. This includes good health and well-being, clean water and sanitation, decent employment income, responsible consumption and production, and life under the water.

CHAPTER THREE
MATERIALS AND METHODS

3.1. Introduction

This final year project is focused on the experiment of pharmaceutical wastewater treatment using corncob modified by CuFe layered for OTC antibiotic removal. Major focused factors effecting adsorbent properties has been highlighted in this chapter. Experimental flow has been displayed in simple block diagram as shown in figure below.

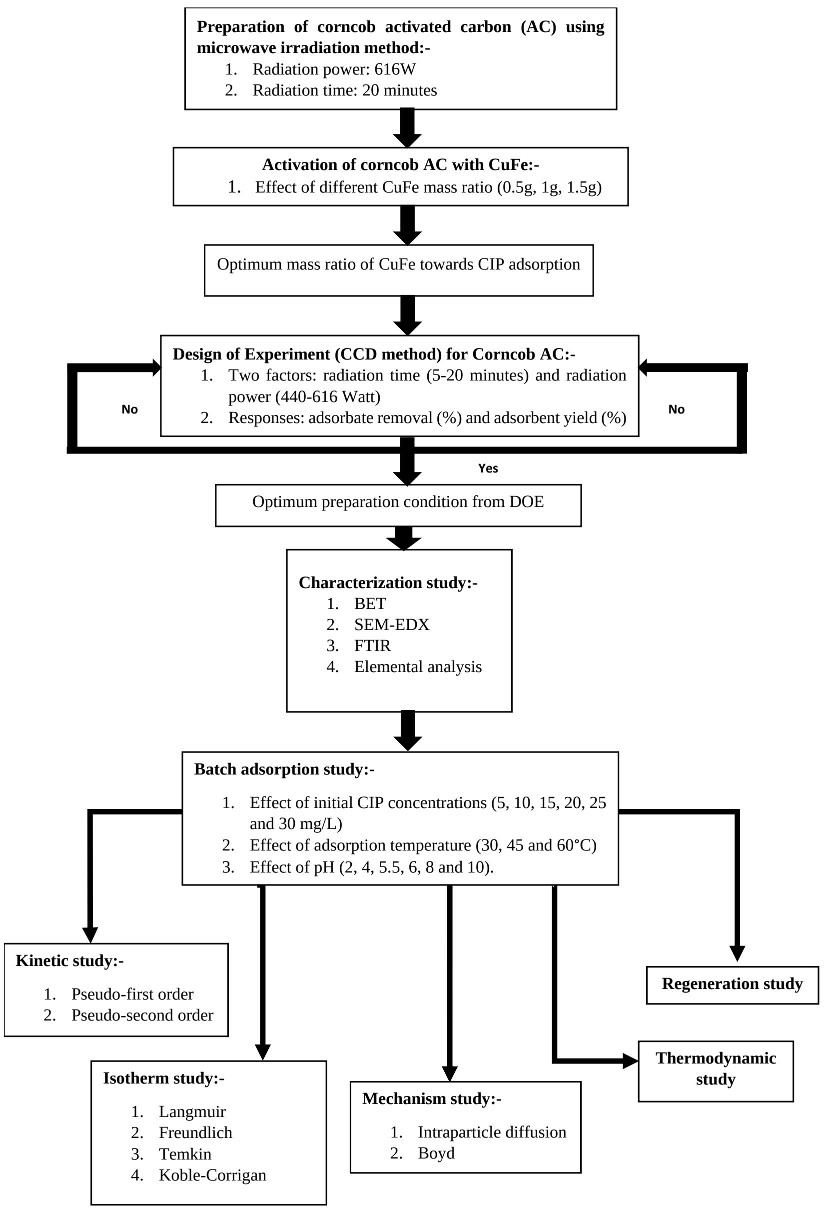


Figure 3. 1 : Overall Flowchart

3.2. Material and Chemicals

A list material and chemicals required, and equipment used for adsorption and regeneration study listed in tables below.

Table 3.1: List of Material and Chemicals

Materials and Chemicals	Purpose
OTC	Used as adsorbate for adsorption study
Deionized Water	To mix and dilute the solution
Sodium hydroxide	To increase the pH of solution
Hydrochloric Acid	To decrease the pH of solution
Corncob	Biomass for AC production.

Table 3.2 : List of Equipment Required

Equipment	Purpose
Grinder	Grind Corncob to homogenous particles.
Microwave	Heat up for AC production
Weighing Scale (mg)	Measure weight of sample
Magnetic Stirrer	Homogenous mixing
UV-Vis Spectrometer	Determine absorbance.
Centrifuge Machine	Centrifuge sample
Water bath Machine	Constant temperature control of mixture

3.3. Preparation of Corncob

Corncobs were sundried for 5 days before thoroughly grounded. The grounded particles rinsed twice with water at 40°C and dried in an oven at 60°C for 24 hours. The corncob particles were screened to eliminates the coarser sizes and to get a homogenous particle size ranging less than 0.4mm.

3.4. Preparation of AC using microwave assisted method

Grounded particles placed in test tube as CO_2 gas flowed in tube and let for 5 min to eliminate oxygen gas. Microwave is set at medium high; 616 watt and let heated for 20 minutes with interval rest for 5 minutes at every 5 minutes. This to avoid pressure buildup in test tube which may cause damage.

3.5. Preparation of Corncob-CuFe LDH Composite

A facile co-precipitation method was adopted to produce biochar-CuFe layered double hydroxides composites (B-CuFe). Initially, 4.82 g copper and 4.04 g iron salts (i.e., 2:1 mole ratio of $M^{3+:}M^{2+}$ salts) were added into a 500 mL reaction flask containing 100 mL of de-ionized water. Simultaneously, different mass of the corncob derived biochar pyrolyzed at 700 ◦C, was ultrasonicated (50 pulse amplitude) for 30 min in 50 mL of de-ionized water. The ultrasonicated biochar slurry was mixed with copper and iron salts in a reaction flash and vigorously agitated >800 rpm at 65 ◦C for about 5–10 min. By dropwise addition of freshly prepared 1 M sodium hydroxide, the mixture pH was gradually increased to 9–9.5 and kept at such value prior to refluxing for 24-hour at 65 °C. Afterwards, the synthesized Corncob-CuFe composite preOTCitate was centrifuged (4000 rpm and 5 min), then thoroughly washed with de-ionized water and finally by ethanol to eliminate all unreacted salts and any impurities. The as-synthesized Corncob-CuFe composite composites were oven-dried for 48 h at 60 °C and stored in a desiccator prior to use.