REMOVAL OF SELECTED PHARMACEUTICAL COMPOUNDS FROM HOSPITAL WASTE WATER USING AN ADSORBENT PREPARED FROM *Jatropha curcas* WASTE CAKE

BY

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DECEMBER, 2019

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DEPARTMENT OF CHEMISTRY,
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ZARIA, NIGERIA

DECEMBER, 2019

DECLARATION

I declare that the work in this Thesis entitled"**Removal of Selected Pharmaceutical Compounds from Hospital Wastewater Using an Adsorbent Prepared from *Jatrophacurcas* Waste Cake**" has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

ADEGBE, Abakpa Elijah Date

CERTIFICATION

This Thesis entitled "REMOVAL OF SELECTED PHARMACEUTICAL COMPOUNDS FROM HOSPITAL WASTEWATER USING AN ADSORBENT PREPARED FROM *Jatropha curcas* WASTE CAKE" by Elijah Abakpa ADEGBE, meets the regulations governing the award of Doctor of Philosophy in Analytical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my late father Mr Emmanuel Adegbe.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
BET	Brunauer-Emett-Teller
Conc	Concentration
CAC	Commercial Activated Carbon
CCD	Central Composite Design
CV	Correlation of Variance
FTIR	Fourier Transform Infra-red
HPLC	High-Performance Liquid Chromatography
JAC	Jatropha Activated Carbon
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
Min	Minutes
PET	Polyethylene Terephthalate
PhAC	Poly(3-hydroxylalkanoate) polymerase subunit
r^2	Correlation of Regression
UV	Ultra Violet
WWTP	Wastewater Treatment Plant
SEM	Scanning Electron Microscopy
SOF	Surface Oxygen Functionalities
SPE	Solid Phase Extraction

ABSTRACT

Samples collected from the Ahmadu Bello University Teaching Hospital Zaria Wastewater treatment plant were extracted using the solid phase extraction method and analysed based on the drug usage in Nigeria, using High-Performance Liquid Chromatography (HPLC). In the wastewater matrices investigated, amoxicillin had the highest concentration of 8066 µg/L while ibuprofen had a concentration of 165.50 µg/L. Acetaminophen had the lowest concentration of 34.31 µg/L. This study showed that some pharmaceutical compounds were not effectively removed during the wastewater treatment.The present work also investigated the use of *Jatropha* waste cakes, a by-product of the manufacturing process of biofuels, as a potential feedstock for the preparation of activated carbon. Chemical activation of the precursor, using phosphoric acid as dehydrating agent, was conducted. The Jatropha waste cake was carbonized at 400^{o}C and activated with H_3PO_4at 450^{o}C respectively. The microstructural and structural properties of the prepared adsorbent were studied using Brunauer-Emett-Teller (BET), Scanning Electron Microscope (SEM) and Fourier Transform Infra-Red (FTIR). The BET results revealed that the surface areas and pore size of the jatropha activated carbon were868 m^2g^{-1} and 2.128 nm respectively.The FTIR results showed changes in the absorption band of the precursor material compared to that of the *Jatropha* activated carbon. This showed that the activation process was successful. The central composite design was used to optimize the effects of contact time, concentration, adsorbent dosage and pH on the adsorption process. This resulted in the successful adsorption of acetaminophen (99.98%), amoxicillin (99.96%), and ibuprofen (100 %). The prepared adsorbent compared favourably with the commercial activated carbon.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Pharmaceuticals are substances used in the diagnosis, treatment, or prevention of disease and for restoring, correcting, or modifying organic functions (EncyclopædiaBritannica, 2018).Pharmaceuticals are detected constantly in aquatic environments including surface water, groundwater and drinking water (Lin and Li, 2015; Lin and Tsai, 2009).This has raised environmental concerns because of the health risks associated with the exposure of aquatic life to them and the possible health risks to humans when they reach drinking water (Matongo *et al.*, 2015). Environmental concerns were triggered when the occurrence of pharmaceuticals in river water was associated with the feminization of fish living downstream of a wastewater treatment plant (WWTP) outfalls (Ternes *et al.*, 1999).

Different authors have reported the occurrence of pharmaceuticals in water sources in Europe, Asia and the USA (McQuillan*et al.*, 2002; Heberer, 2002; Loffler and Ternes, 2003; Fatta-Kassinos *et al*., 2011; Rehman *et al*., 2013; Manickum and John, 2013; Camacho-Muñoz *et al*., 2014; Luo *et al.*, 2014). However, there is scanty information about their presence in African water bodies although literature indicates that types of pharmaceuticals and their metabolites commonly detected are dependent on social, cultural, technological and agricultural factors (Dehghani *et al*., 2011; Agunbiade and Moodley, 2014); hence, it will be unique for different geographical areas and water bodies (Matongo *et al*., 2015).A study in Kenya reported the occurrence of ibuprofen, paracetamol, sulfamethoxazole and zidovudine at a high concentration (~ 10-30 μgL^{-1}) in the Nairobi River basin (K'oreje *et al.*, 2012).

The pharmaceuticals which are often detected in wastewater include antibiotics, antacids, steroids, antidepressants, analgesics, anti-inflammatories, antipyretics, beta-blockers, lipid-lowering drugs, tranquillizers and stimulants (Rivera-Utrilla *et al*., 2013). Various studies have reported the presence of these pharmaceuticals in river water (Ternes *et al*., 2002; Lin and Reinhard, 2005; Ellis, 2006).

After administration, the active substances of the pharmaceuticals are metabolized, but only to some extent. The unmetabolized active substances are excreted, largely in urine (generally 55–80% of the total with few exceptions) as reported in Ternes and Joss, (2006) and partially in faeces, as unchanged substances, as a mixture of metabolites or conjugated with an inactivating compound attached to the molecule (Halling-Sorensen *et al*., 1998; Lienert *et al*., 2007), thus entering the water cycle.

Hospitals are important sources of these compounds: a great variety of microcontaminants result from diagnostic, laboratory and research activities on one side and medicine excretion by patients on the other. These contaminants include active principles of drugs and their metabolites, chemicals, heavy metals, disinfectants and sterilants, specific detergents for endoscopes and other instruments, radioactive markers and iodinated contrast media. Residues of pharmaceuticals can also be found in wastewater treatment plant (WWTP) effluents through disposal and inefficient removal by conventional systems (Kummerer, 2001; Petrovic *et al*., 2003; Carballa *et al*., 2004; Onesios *et al*., 2009).

Despite their specific nature, quite often hospital effluents are considered to be of the same pollutant load as urban wastewaters (UWWs) and are discharged into public sewer networks, connected to a WWTP and co-treated with UWWs. Before entering into the

public sewer, chlorination is sometimes required for the wastewater coming from infectious disease wards (Emmanuel *et al*., 2004).These conventional plants have a limited capacity to remove pharmaceutical products from urban wastewater. This is because a lot of these compounds cannot be metabolized by microorganisms as a source of carbon and may inhibit the activity of the microorganisms (Rivera-Utrilla *et al*., 2013).

Therefore, more effective and specific treatment options are required to adequately reduce the amount of these pollutants in effluents, and hence minimize their effects on the environment.With this background, this study seeks to identify and quantify some selected pharmaceuticals in the Ahmadu Bello University Teaching Hospital Liquid Waste Treatment Plant and to remove them using adsorbent prepared from *Jatropha* waste cake.

1.2 Statement of Research Problem

Pharmaceutical compounds and their metabolites are constantly discharged into the environment in large quantities primarily through excretion (mainly through urine and faeces), and also through the disposal of unused and expired drugs either directly into domestic sewage system, in landfills or by burial (Azzouz*et al*., 2010). This has raised concerns because of the dangers associated with exposure of the environment to them and the possible risks to human health. The presence of pharmaceutical compounds in water has been reported for Europe, Asia and the USA (Matongo*et al*., 2015), but there is little data in the chemical literature detailing their presence in African water bodies especially in Nigeria.

The conventional wastewater treatment technologies have not effectively removed pharmaceutical compounds from wastewater before their discharge into the environment (Okuda *et al*., 2009).

1.3 Justification of the Study

Pharmaceutical compounds are detected in wastewater discharged from hospitals. This has raised environmental concerns because of the health risks associated with the exposure of aquatic life to them and the possible health risks to humans when they reach drinking water. The limited data on the pharmaceutical compound pollution in the wastewater discharged from hospitals in Nigeria prompted this study.

Jatropha waste cake, which is an agricultural waste generated by the biofuel industry, can be considered as a potential low-cost adsorbent for the removal of pharmaceutical compounds from hospital effluents. Research has been carried out using *Jatropha* seed hull for the adsorption of a dye (malachite green) and heavy-metal ions, such as zinc and cadmium, and it has shown a remarkable adsorption capacity. Due to its high lignin content, *Jatropha* hull has the potential to be a good precursor for the production of activated carbon (Masita *et al.*, 2013).

Activated carbon possesses a large surface to volume ratio and this makes ita viable option to effectively treating wastewater.Therefore, activated carbons are the most commonly used adsorbents. Different pollutants such aspesticides, phenolic compounds, dyestuffs, and metals can be removed from liquid streams using these solids (Le Cloirec and Faur, 2006; Yin *et al*., 2007).

Thus, activated carbon prepared from *Jatropha* waste cake is being proposed as a probable adsorbent for removing pharmaceutical compounds from wastewater before their eventual discharge into water bodies.

1.4 Aim of the Study

The aim of this research is to investigate the effectiveness of an adsorbent derived from *Jatropha* waste cakein the removal of some selected pharmaceutical compounds present in hospital wastewater.

1.5 Objectives of the Study

The following are the objectives of this study:

i. to preconcentrate and extract some pharmaceutical compounds from the hospital wastewater using Solid Phase Extraction method;

ii. to determine the concentration of the extracted pharmaceutical compoundsin the wastewater using the High-Performance Liquid Chromatography(HPLC);

iii. to prepare adsorbent from *Jatrophacurcas* waste cake by carbonization and impregnation methods using H_3PO_4 as an activating agent;

iv. to determine the surface area, structural and morphological characteristics of the *Jatropha* activated carbon using BET, SEM and FTIR;

v. to study the effect of contact time, initial concentration, adsorbent dosage and pH of the adsorption of prepared solutions of acetaminophen, amoxicillin and ibuprofen using a commercial adsorbent and the prepared *Jatropha* activated carbon; and

vi. to optimize the adsorption process.

CHAPTER TWO

LITERATURE REVIEW

2.1 Pharmaceutical Compounds in Environment

The major sources of pharmaceutical compounds in the environment include municipal Wastewater Treatment Plants (WWTPs), WWTPs of pharmaceutical production facilities, hospital effluents and agricultural run-off (Khetan and Collins, 2007, Mompelat *et al*., 2009). The unmetabolized pharmaceutical compounds are excreted in urine and faeces which are disposed of through the sewer system. Hence the pharmaceutical compounds will be more concentrated in the municipal treatment plants. Human excretion of unchanged or slightly changed pharmaceutical compounds conjugated to polar molecules such as glucuronides enter WWTPs and may be cleaved, thereby releasing the original pharmaceutical compound into the environment (Heberer, 2002).

2.1.1 Acetaminophen

Paracetamol (an international name used inEurope) and acetaminophen (an international nameused in the USA) are two official names of the samechemical compound derived from its chemical name:N-acetyl-para-aminophenol (the segment “cet” inserted between “para” and “amino”) and Nacetyl-para-aminophenol.It has analgesic and antipyretic properties similarlyto non-steroidal anti-inflammatorydrugs (NSAIDs), but contrary to them, it does not possessany anti-inflammatory activity. When applied inrecommended doses, it does not induce typical forNSAIDs gastrointestinal side effects. However, itsuppresses prostaglandin production likewiseNSAIDs.Due to lack of an anti-inflammatory component, paracetamol has not been regarded as a member of the NSAIDs family in pharmacological textbooks, although what is interesting, it has beenalways discussed together with these

drugs.Therefore, the discussion on the mechanism ofaction of paracetamol should begin from the analysis of NSAIDs action.

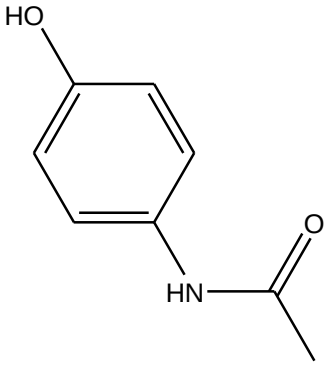


Figure 2.1: AcetaminophenStructure

2.1.2 Amoxicillin

Amoxicillin is a semi-synthetic drug, which belongs to a class ofantibiotics called the Penicillins (β-lactam antibiotics). It is shown to be effective against a wide rangeofinfections caused by wide range of Gram-positive and Gram-negative bacteria in both human and animals and is used for the treatmentand prevention of respiratory, gastrointestinal, urinary and skin bacterial infections due to itspharmacological and pharmacokinetic properties (Bush, 2003; Soussa, 2005; Rao *et al*,2011). Besides its use in humanmedicine, amoxicillin is also used for treating and preventing animal diseases as well as it isused as growth promoters for many domestic and food animals, including dogs, cats, pigeons,horses, broiler chickens, pigs, goats, sheep, pre-ruminating calves, cattle and fishes (Pfizer, 2004; Schering-Plough, 2007). Itis well absorbed from gastrointestinal tract. The apparent volume of distribution of amoxicillinis approximately 0.26-0.31L/Kg and widely distributed to many tissues, including liver, lungs,prostate muscle, bile, ascetic, pleural and synovial fluids, and ocular fluids, accumulates in theamniotic fluid and crosses the placenta but penetrates poorly into the central nervous systemunless inflammation is present. It is

approximately 17–20% bound to human plasma proteins,primarilytoalbumin (Shah et al, 1994; Eppes & Childs, 2002).Amoxicillin is very closely related to ampicillin with the same spectrum of activity and potencybut is much better absorbed when given orally, achieving blood concentrations approximatelytwice as high as those obtained with ampicillin (Rao *et al*, 2011).It acts binding to penicillin binding protein (PBP-1A) located inside the bacterial cell wall, theamoxicillin acylate the penicillin-sensitive transpeptidase C-terminal domain by opening thelactam ring causing inactivation of the enzyme, prevents the formation of a cross-link of twolinear peptidoglycan strands, inhibiting the third and last stage of bacterial cell wall synthesis,which is necessary for cell division and cell shape and other essential processes, producing asa consequence the lisis of the bacteria cells (Amin *et al*, 1994; Nagralli *et al*, 2002; Dousa & Hosmanova, 2005; Torres *et al*, 2010; Rao *et al*, 2011). The two major metabolites of amoxicillinare amoxicilloic acid and piperazine-2, 5-dione (diketopiperazine). These metabolites have lostantibacterial activity of the parent component, but the amoxicilloic acid could have potentialallergic properties (Reyns *et al*, 2008; Reyns *et al*, 2009; Fujiwara *et al*, 2011).

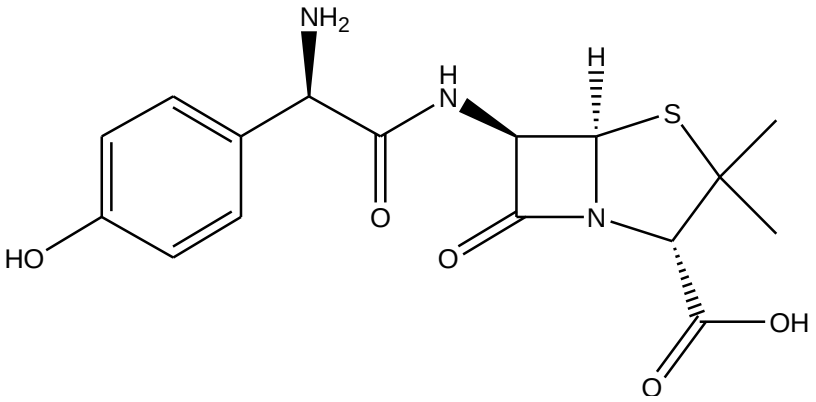


Figure 2.2: Amoxicillin Structure

2.1.3 Ibuprofen

Ibuprofen is a non-steroidal anti-inflammatory drug with a half-life of 1.8–2 h. It is one of thesafest drugs employed for treatment of inflammation, pain andfever (Rainford, 2009; Mazaleuskaya *et al*, 2015). Its oral dose is 200–400 mg (5–10 mg/kg in children),every 4–6 h to a maximum of 1.2 g per day in adults. Although itis not the most potent of the non-steroidal anti-inflammatorydrugs, it represents a good balance of efficacy and safety overa wide dosage range when compared with others in the groupand it is also readily available and cost-effective.Ibuprofen has analgesic and anti-inflammatory properties. Itis used in mild-to-moderate pain such as dysmenorrhea, headaches (including migraine), dental pain, postoperative pain andmusculoskeletal/joint disorders including osteoarthritis, rheumatoid arthritis and ankylosing spondylitis (Gigante& Tagarro, 2012; Kandreli *et al*, 2013).

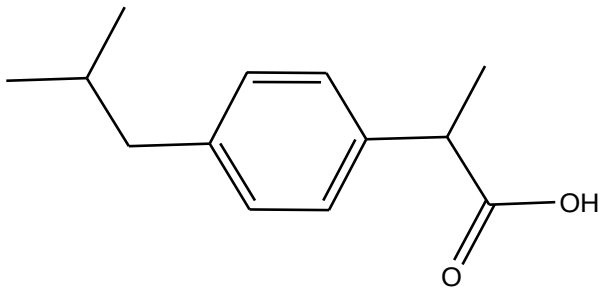


Figure 2.3: IbuprofenStructure

2.2 Determination of Pharmaceutical Compounds in Wastewater

The continuous entry of pharmaceutical compounds and their metabolites into the environment alongside their biological properties may have significant, long-term effects on the stability of ecosystems because they possess mutagenic, carcinogenic and toxic properties. To ensure human and environmental safety, robust and reliable screening and confirmatory tests capable of the low-level detection of pharmaceutical compounds are required (Wagil *et al*., 2015).

2.2.1 Sample preparation

The concentration of pharmaceutical compounds detected in water samples in the environment are generally too low to allow a direct injection into a chromatographic system. Therefore, efficient pre-concentration steps are necessary which should also result in some sample clean-up. The basic concept of sample-preparation methods is toconvert a real matrix into a sample suitable for analysis.This process almost inevitably changes the interactionsof compounds with their concrete chemical environment. These interactions are determined by the physicaland chemical properties of both analytes and matrices,and they affect the applicability of different samplepreparation techniques and analytical methods as wellas their efficiency and reproducibility. Hence, characterization of the initial physicochemical state of a sampleis a precondition of all further sample-preparation steps; it is very important to have information on thephysical and chemical properties of an analyte because that may help determinewhether a compound is likely to concentrate in some specific conditions(Paschke, 2003; Diaz-Cruz *et al*., 2003).

Matrix effects are major problem in extracting analytes (e.g. pharmaceuticals). A matrix effect can bedefined as the influence of a property of the sample,independent of the presence of the analyte, on recoveryefficiency and thereby on the quantity extracted (e.g.pharmaceuticals may sorb to organic matter in thesamples, causing the concentrations of freely dissolvedpharmaceuticals to be lower and therefore more difficultto detect).Sample preparation can be achieved by employing awide range of techniques, but all methods have the same goal (Smith, 2003):to remove potential interferences;to increase the concentration of an analyte;if necessary, to convert an analyte into a more suitable form; and,to provide a robust, reproducible method that is independent of variations in the

sample matrix.Although many traditional sample-preparationmethods are still in use, there have been trendstowardsthe use of smaller initial sample sizes, small volumes or noorganic solvents; greater specificity or greater selectivity in extraction;and, increased potential for automation (Smith, 2003).Sample preparation must also be tailored to the finalanalysis, considering the instrumentation to be used andthe degree of accuracy required, whether quantitative orqualitative (Ridgway *et al*., 2007).

2.2.1.1 Solid-phase extraction

Solid-phase extraction(SPE) has gradually replaced classical liquid-liquidextraction (LLE) and has become the most common samplepreparation technique in environmental areas. In SPE, the analytes to be extracted are partitioned between a solid phase and a liquid phase, and these analytes must have a greater affinity for the solid phase than for the sample matrix. SPE is mostly used to prepare liquid samples and extracts of semi-volatile or non-volatile analytes, though it can also be used for solids pre-extracted into solvents (Fontanals *et al*., 2005).

SPE products are excellent for extraction, concentration and clean-up. Clean-up procedures on SPE sorbents are not limited to extracts from solid samples but could also be used for all the extracts obtained from environmental samples, especially wastewater samples. Clean-up is an important step in determination of analytes at low levels and depends, of course, on the complexity of the sample matrix and detection mode, especially when the analysis is performed by liquidchromatography (LC) (Fontanals *et al*., 2005).

Choice of a sorbent is the key point in SPE because it can control parameters such as selectivity, affinity and capacity. This choice depends strongly on the analytes of interest

and the interactions of the chosen sorbent through the functional groups of the analytes. Also, itdepends on the kind of sample matrix and its interactions with both the sorbent and the analytes (Fontanals *et al.*, 2005). Classical SPE sorbents are either silica-based or polymeric. Silica sorbents include chemically-bonded silica with the C_8or C_{18} organic groupand ion-exchange materials.Silica sorbents have several disadvantages compared with polymeric sorbents. They are unstable in a broader pH range and contain the silanols, which are not a good choice for tetracyclines because they have been found tobind irreversibly (Lindsey *et al.*, 2001), but for estrogens, silica-gel cleanup is followed by C_{18} SPE enrichment (Beausse, 2004). Polymeric sorbents include polymeric materials (St-DVB), immunosorbents (ISS), molecularly-imprintedpolymers (MIPs) and restricted access materials (RAMs) (Fontanals *et al*., 2005; Leon-Gonzalez and Perez-Arribas, 2000). RAMs and MIPs are special types of very specific and selective sorbents. RAMs are SPE sorbents that are often used for the analysis of small drugs, their impurities and metabolites. MIPs are highly stable polymers that possess recognition sites adapted to the three-dimensional shape and functionalities of an analyte of interest (Majors, 2007). MIP sorbents have been used for sulfonamides (Zheng *et al.*, 2001), trimethoprim (Hu *et al*., 2005) and tetracyclines (Caro *et al*., 2005).

Pharmaceutical compounds of acceptable hydrophobicity can easily be preconcentrated using any reversed-phase material such as alkyl-modified silica or polymer-based materials. Deprotonation of acidic compounds and protonation of basic compounds should be suppressed to ensure sufficient hydrophobicity of the analytes. Therefore, acidic pharmaceuticals should be preconcentrated under acidic conditions, whereas basic analytes should be preconcentrated at an alkaline pH (Stolker *et al*., 2004). Alternatively, mixed-

mode SPE materials can be used which exhibit both reversed-phase and cation-exchange properties due to the presence of sulfonic acid groups on the hydrophobic surface of the particles (Stolker *et al*., 2004). Using acidified sample solutions, acidic and neutral analytes would be extracted by hydrophobic interactions, whereas protonated basic analytes would interact via ion exchange mechanisms (Stolker *et al*., 2004). Mixed-mode materials with reversed-phase and anion-exchange properties have been used under slightly basic conditions for antibiotics containing carboxylic acid functionality (Benito-Pena *et al*., 2006).

2.2.2 Previous studies on the determination of pharmaceuticals in water, sediments and wastewater

Yang and Carlson (2004 used solid-phase extraction (SPE) combined with high-performance liquid chromatography–ion trap tandem mass spectrometry (LC-MS-MS) for determination of trace concentrations of erythromycin-H_2O (ETM-H_2O), roxithromycin (RTM) and tylosin (TLS) in natural and wastewater matrices. These macrolides (MLS) were extracted from water samples using Oasis HLB cartridges,and the average recovery was 93.6 ± 8.6, 92.1 ± 10.0, and 94.3 ± 8.9% for ETM-H_2O, RTM and TLS in surface water, respectively. For water from the influent of a wastewater treatment plant (WWTP), the average recovery was 84.8 ± 14.0, 83.2 ± 13.1, and 86.1 ± 13.4% for ETM-H_2O, RTM and TLS, respectively.A study carried out by Weigel *et al*. (2004) determined the presence of some pharmaceuticals, among them analgesics, ß-blockers and anti-depressants as well as caffeine, the antibacterial triclosan and the insect repellent N,N-diethyl-3-toluamide (DEET) in different sewage samples (sewage treatment plants, hospital effluents) from Tromsø/Norway and in seawater from Tromsø-Sound, into which the sewage is discharged. Caffeine, triclosan, ibuprofen and its major metabolites hydroxy- and carboxyibuprofen

were present in all sewage samples. Additional pharmaceuticals were also observed in sewage containing hospital effluents.

Pailler *et al*. (2009) investigated four classes of veterinary and human pharmaceuticals (sulfonamides, tetracyclines, analgesics and hormones) in surface water and wastewater in Luxembourg. The selected eleven pharmaceuticals include four sulfonamides (sulfathiazole, sulfamethoxazole, sulfadimethoxine and sulfamethazine), two tetracyclines (tetracycline and oxytetracycline), two analgesics (ibuprofen and diclofenac), and three hormones (two naturals, estrone and β-estradiol, and one synthetic,17-α-ethinyl estradiol). The samples were pre-concentrated by solid-phase extraction using Oasis® HLB (Hydrophilic Lipophilic Balance). The analysis of the investigated pharmaceutical compounds was carried out by high-performance liquid chromatography coupled to a triple quadrupole mass spectrometer. Recovery rates ranged from 70 % to 94%, with relative standard deviations between 4 % and 19%.

Azzouz *et al*. (2010) studied the presence of 9 pharmaceuticals (clofibric acid, diclofenac, ketoprofen, ibuprofen, naproxen, carbamazepine, metoprolol, propranolol and triclosan) and 3 Hormones (estrone, 17-α-estradiol and 17-α-ethinylestradiol) in water samples using a semi-automatic flow-based method. The analytes were retained on a solid-phase extraction sorbent column and 1L of the eluate analyzed by gas chromatography in combination with electron impact ionization mass spectrometry in the SIM mode. The sorbent used, Oasis-HLB, provided near-quantitative recovery of all analytes. The method was validated with quite good analytical results including low limits of detection (0.01–0.06 ng/ L for 100mL of water) and good linearity (r^2> 0.993) throughout the studied concentration ranges.

Wagil *et al*. (2015) reported on the determination of Metronidazole (MNZ), an antibacterial and antiprotozoal drug in water, sediment and fish tissue samples using liquid chromatography– ion trap mass spectrometry (LC-MS/MS). MNZ was extracted from waters on Strata XC cartridges using solid-phase extraction (SPE), and from sediments and fish tissues by solid-liquid extraction. Absolute recoveries ranged from 89.3% to 97.2%, and the method detection limits were 3.4 ng L^{-1} (water samples), 0.4 ng g^{-1} (sediment samples) and 0.3 ng g^{-1} (tissue samples). These methods were used to determine MNZ in surface waters, sediments and fish tissues from the Polish River Gos´cicina; MNZ was found in all these matrices.

Gbylik-Sikorska *et al*. (2015) developed a sensitive liquid–chromatography-electrospray tandem mass spectrometry multiclass method for determination of 45 veterinary compounds belonging to 9 different antibiotic groups, including aminoglycosides, b-lactams, diaminopyrimidines, fluoroquinolones, lincosamides, macrolides, pleuromutilins, sulfonamides and tetracyclines, in water from breeding animal watering supply system. The isolation of the analytes was carried out by solid-phase extraction with heptafluorobutyric acid as an ion-pair agent on the Strata-X reversed-phase cartridges. All analytes were determined simultaneously in one single run on a C18 column with gradient elution and short analysis time (13 min). The method was validated, average relative recoveries were in the range of 84.3–109.3%. The applicability of the method was tested by determining antimicrobial compounds in real water samples collected from water supply systems in breeding animal farms. The average antibiotics concentration in real water samples were, respectively, in the range of 0.14–1670 µgL^{-1}.

Matongo *et al.* (2015) studied the occurrence of pharmaceutical residues in the water and sediment of Msunduzi River in the KwaZulu-Natal province of South Africa and in the Darvill wastewater treatment plant found in Msunduzi catchment using Solid Phase Extraction method. The antipyretic ibuprofen had the highest concentration of up to 117 µg L^{-1}, 84.60 µg L^{-1} and 659 ng g^{-1} in wastewater, surface water and sediment respectively in all the matrices investigated. Antibiotics were detected in generally low concentrations of <10 µgL^{-1} in surface water samples and up to 34.50 µgL^{-1} in wastewater; moreover, they were not completely removed during wastewater treatment. In surface water, Henley dam exhibited a high concentration of the pharmaceutical residues and the highest concentration of metronidazole in sediment (up to 1253.50 ngg^{-1}) detected. Metronidazole was only detected in sediment and bio-solids.

2.3 Activated Carbon

Activated carbon in the broadest sense is a wide range of heat-treated, porous carbon-based materials. Activated carbon (AC) is defined as a porous carbon material, a char which has been subjected to reaction with gases, sometimes with the addition of chemicals, e.g. $ZnCl_2$, before, during or after carbonization in order to increase its adsorptive properties (Fitzer *et al.*, 1995). Another definition is that activated carbon is porosity enclosed by carbon atoms (Marsh and Rodriguez-Reinoso, 2006a).

Activated carbons have a highly developed porosity which gives them an enormous surface area (Bansal and Goyal, 2005); typically, 1g of activated carbon will have a surface area between 500-3000m^2/g(Rodríguez-Reinoso and Molina-Sabio, 1998). It is this surface area that allows AC to adsorb large amounts of pollutants.

AC preparation follows two broad steps: the carbonization of the carbonaceous raw material at high temperatures (400 –850°C) in an inert atmosphere and the activation of the carbonized product(Bansal and Goyal, 2005). During the carbonization process, most of the non-C elements such as O, H, and N are eliminated as gaseous species (COx, NOx) by the pyrolysis of the parent material. The carbon atoms group themselves into stacks of flat, aromatic sheets cross-linked in a random manner in a nanocrystalline structure that chemists refer to as disordered and physicists refer to as defective layers. These aromatic sheets are irregularly arranged, which leaves free spaces. These spaces give rise to pores, which give the AC its high surface area. During carbonization, these pores are filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. This pore structure in carbonized char is further developed and enhanced during the activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended and extremely high surface area of the product. (Mazyck and Cannon, 2000;Bansal and Goyal, 2005).

The activation results in the oxidation of some of the regions within the char in preference to others so that as combustion proceeds, a preferential etching takes place. There is considerable diversity in how the pores and pore structure of an AC are described. The pores are generally classified into micropores (widths smaller than 2 nm), mesopores (widths between 2 nm and 50 nm) and macropores (widths larger than 50 nm) (Rouquerol *et al.*, 1994). Mesopores are often expressed as a methylene blue (MB) number as it is assumed that a large molecule such as MB cannot penetrate the micropores. Micropores capacity can be expressed as an iodine number. It is assumed that iodine can penetrate into the micropores while larger molecules such as MB cannot. By comparing the iodine and

methylene blue numbers of an AC it is possible to determine the relative microporosity to mesoporosity ratio. No comprehensive model of the microporous nature of carbons has been devised that can tie together all the properties of an AC (Marsh and Rodríguez-Reinoso, 2006).

Electron spin resonance studies have shown that the aromatic sheets in activated carbons contain free radical structure or structure with unpaired electrons. These unpaired electrons are remnants of the carbonization process; due to the breaking of bonds at the edges of the aromatic sheets create edge carbon atoms. These edge carbon atoms have unsaturated valences and can interact with elements such as O, H, N, and S (present in the parent material or added by the activating agent) creating surface oxygen functionalities (SOF) (Figure 2.1).

The surface of activated carbon can be characterized into three zones: the carbon basal planes (including basal edges and crystal defects), heterogeneous surface groups (mainly SOF, but includes sulphur groups) and inorganic ash (Franz *et al.*, 2000). The majority of the adsorption sites are on the basal planes, which form more than 90 % of the carbon surface. However, the much higher activity of the heterogeneous groups can affect the overall adsorption capacity. Heteroatoms (non-carbon atoms) may be combined both with peripheral carbon atoms at the corner and edges of crystallites, in intercrystalline spaces and even in defect zones of particular planes constituting the AC's crystalline structure. Most heteroatoms are grouped at the surface of the AC and they differ in terms of their reactivity. Surface bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds and to react in a similar way to reagents.

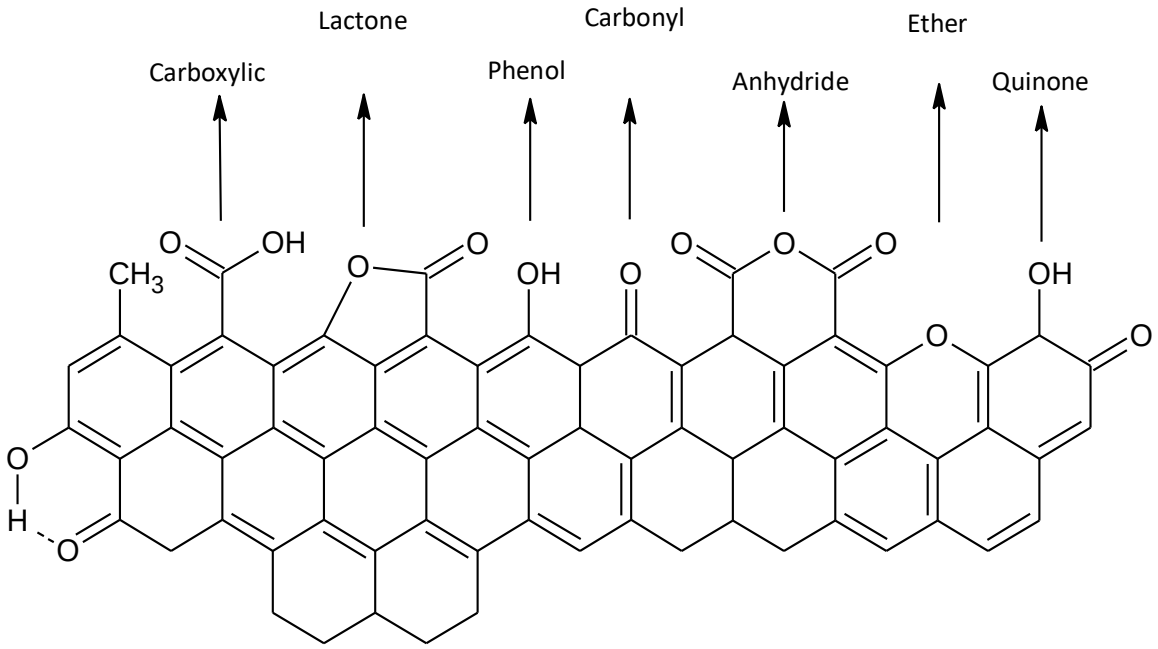


Figure 2.4: Diagram of Surface Oxygen Functionalities (SOF) on the edges of the aromatic sheets of an AC surface (Shen *et al.*, 2008).

If they are bound in the core of the crystalline structure, they are often inert due to their low accessibility and interaction with local atoms (Jankowska *et al.*, 1991).

Other factors can influence the adsorption of the AC. The point of zero charge of an AC is the pH at which the AC has no net charge (Hameed *et al.*, 2009). At a pH below this, the carbon is net positively charged and above this, it is negatively charged. This property significantly influences the adsorption on the carbon surface and is an important consideration for creating ACs as changes in pH will greatly influence adsorption (Khan, 2002). The elemental composition of a typical AC has been found to be 88 % C, 0.5 % H, 0.5 % N, 1 % S, and 6 to 7 % O, with the balance representing inorganic ash constituents (Bansal and Goyal, 2005). ACs used in applications where high purity is required are typically treated - usually acid washed - to reduce the ash content as it could leach into solution. The oxygen content of an AC can vary depending on the type of raw material and

the conditions of the activation process, ACs with more SOF will consequently have higher oxygen content. In theory, all carbonaceous materials can be made into AC, although the properties of the resulting AC will vary, depending on the raw material, the activating agent, and the conditions of the carbonization and activation processes.

The best AC for a particular application is usually determined empirically as there are many parameters that influence adsorption. Prediction of adsorption capacity in advance is limited to models that deal with idealized cases (Franz *et al.*, 2000). BET isotherms using N_2 is a very popular method for comparing ACs (Rolando, 2007, Rouquerol *et al.*, 2013).

2.3.1 Sources of activated carbon

A wide variety of carbons have been prepared from agricultural wastes; bamboo dust, groundnut shell, rice husk and straw (Kannan and Meepkshisundaram, 2001); coconut shell and groundnut shell (Gimba, 2001); coconut husk and goat hair (Babarinde, 2002); Hazelnut shell (Demirbas *et al*., 2002); silk cotton ball, coconut tree sawdust, maize cob and banana pith (Kadirvelu *et al*., 2003); pecan shells (Bansode *et al*., 2003); palm kernel (Abechi, 2011); *Delonix regia Pods* and *Khaya senegalensis* Fruits (Ocholi, 2006).

Activated carbon derived from coconut tree sawdust was reportedly used to remove Cr (VI) from aqueous solution (Selvi *et al*. 2001). Activated carbon developed from a rapidly renewable bio-resource was used for the removal of cadmium (II) and nickel (II) from dilute aqueous solutions (Bass *et al*., 2002). Neem cake was employed and converted to activated carbon by activating it with phosphoric acid. The carbons showed surface areas and total pore volumes of approximately 352 m^2/g and 34.26 ml/g respectively (Alau,

2015). Studies on agricultural waste from corn cob activated with $ZnCl_2$ produced an adsorbent with excellent microporosity (Tsai *et al*., 2001).

2.3.2 Adsorption process

Adsorption is the force of physical attraction between the surface of a porous solid and a component molecule being removed from the bulk phase. The most fundamental property of adsorbate-adsorbent interaction is the adsorption equilibrium. The equilibrium at a given temperature is usually presented under the form of adsorption isotherms, which are useful for selecting the most appropriate adsorbent and also for predicting the performance of the adsorption system. A physical-chemical process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface till the thermodynamic equilibrium of the adsorbate concentrations is attained with no further net-adsorption is a general expression for adsorption. It involves the interphase accumulation or concentration of substances at a surface or interface between any two phases such as liquid-liquid, gas-solid, or liquid-solid interfaces. The material that is adsorbed is called the adsorbate and the material upon whose surface adsorption takes place is called the adsorbent (Adamson, 1960; Atkins 2003).

2.3.2.1 Types of adsorption

There are two main types of adsorption namely,physisorption and chemisorption. Physisorption is an interaction between adsorbate and adsorbent in which nonspecific forces of attraction such as dispersion or dipole are involved and the binding energy of the adsorbate is less than 20kJ/mol (Adamson, 1960; Atkins 2003). These forces are non-specific since they do not depend on any property of either the adsorbate or the adsorbent

(Parfitt and Sing, 1976). It occurs in minutes and the process is reversible (Atkins, 2003). Multilayers areeasily formed at higher pressure/concentration in physisorption due to small heat of adsorption. Chemisorption is a type of adsorption in which some degree of specific chemical interaction between the adsorbate and adsorbent is involved though the energy of adsorption may be quite large compared to those of chemical bond formation. Typically, the enthalpy values are in the region of 200KJ/mol (Adamson, 1960; Atkins 2003). The enthalpy of adsorption depends on the extent of surface coverage, mainly because the adsorbate particles interact. If the particles repel each other, the adsorption becomes less exothermic as coverage increases. If the adsorbate particles attract one another, then they tend to cluster together in islands, and growth occurs at the borders (Adamson, 1960). The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than for physisorption. At low-temperature chemisorption may be so slow that for practical purposes only physisorption is observed, whereas chemisorption predominates at high temperature (Adamson, 1960). On a general note, the monolayer is formed in chemisorption due to the short-range chemical forces between the adsorbate and adsorbent (Atkins, 2003).

2.3.3 Previous studies on the use of activated carbon in the removal of pharmaceutical compounds

Méndez-Díaz *et al*. (2010) studied the adsorption kinetics of four nitroimidazoles (i.e. dimetridazole, metronidazole, ronidazole and tinidazole) on three ACs: two commercial ACs from Sorbo–Norit (S) and Merck (M) and a third prepared by chemical activation of petroleum coke (C). Nitroimidazole adsorption kinetics (initial concentration in mg/L) on ACs increase in the order C<S<M. It is related to the increase in AC hydrophobicity,

corresponding to an inverse relationship with their oxygen content and their total acid site concentration.

Cabrita *et al*. (2010) investigated the adsorption of acetaminophen (paracetamol) onto ACs prepared from polyetheneterephthalate (PET) recycling used plastic bottles, cork powder and peach stones. It was observed that the presence of oxygen on the AC surface decreases the strength of the acetaminophen adsorption. The authors indicated that the adsorbent–adsorbate affinity was stronger in hydrophobic ACs of basic character containing a well-developed microporosity.

Quesada-Peñate *et al*. (2009) studied the adsorption of levodopa, a Poly(3-hydroxylalkanoate) polymerase subunit (PhAC) used in the treatment of symptoms of Parkinson's disease by three ACs derived from different materials. It was observed that the adsorption of levodopa was clearly disfavored by the presence of acidic surface groups whereas basic surface groups in AC had a positive impact.

Mestre *et al*. (2009) studied the removal of ibuprofen from water using ACs obtained from chemical and physical activations of cork powder waste and Polyethylene terephthalate (PET) from used plastic bottles. The authors showed that pH played an important role in the adsorption process; the charge of the AC surface groups was modified with pH, leading to a net negatively charged AC surface for pH values higher than pH_{PZC} (point of zero charge) of the sample. Simultaneously, for solution pH values higher than the pKa of ibuprofen (4.91) the molecule was deprotonated. Consequently, as the pH increases for values higher than 5, the adsorption of ibuprofen was less favourable due to the electrostatic repulsion between the adsorptive anion and the surface of the AC that

gradually becomes more negatively charged. In contrast, at acidic pH the AC surface was neutral and ibuprofen was non-dissociated (solution pH < pKa), therefore repulsive electrostatic interactions were minimized and adsorption was enhanced. Moreover, the authors observed that ibuprofen adsorption was favoured with ACs having a basic character and large micropores. On the other hand, they concluded that adsorbents with a large fraction of micropores are not adequate to effectively remove ibuprofen. A pseudo-second-order kinetic model was used to describe the experimental kinetic data, which confirmed the faster adsorption kinetic in ACs with high mesopore volumes. Hence, mesopores can be considered as transport pores, which favour the adsorbate diffusion into the porous structure.

Mestre *et al*. (2011) studied the use of sisal (a native plant of Mexico) waste as the precursor to prepare ACs by chemical activation with K_2CO_3. The adsorption kinetics of ibuprofen and paracetamol were obtained using two ACs with an apparent surface area of 1038 and 985 m^2/g; a pore volume of 0.49 and 0.48 cm^3/g, and an almost neutral character of the surface according to the pH_{PZC} values measured 7.0 and 8.2 measured, respectively. The assays were made without pH control, resulting in approximately 4 for ibuprofen and 6 for paracetamol. The results showed that the adsorption process obeys a pseudo-second-order kinetic equation. Moreover, ibuprofen showed higher removal efficiency than paracetamol. The authors explained this result by the electrostatic interactions of the dissociated form of ibuprofen with the positive or neutral surface of the carbons, as well as by its lower solubility in the 10% methanol solution used in the assays. The authors also concluded that the removal efficiency was mostly dependent on the volume of the largest

micropores (i.e. supermicropores) of AC, as the solvation effect may enlarge the solute molecular dimensions thus hindering its access and packing in the narrower micropores.

Baccar *et al*. (2012) studied the adsorption of ibuprofen, ketoprofen, naproxen and diclofenac onto a low-cost activated carbon, prepared from olive-waste cakes. Single and mixture solutions of the drugs were considered. The adsorption capacities of the carbon for the four drugs were quite different and were linked essentially to their pKa and their octanol/water coefficient. The adsorption kinetics of the adsorbates were investigated and the results indicated that the adsorption process followed the pseudo-second-order kinetic model for the four tested drugs. The effect of pH and temperature on the drugs uptake by the adsorbent was also investigated. Increasing pH gradually reduced the uptake of the four drugs, and this effect was more perceptible when the pH became alkaline. The increase of temperature in the range 4–40 ºC did not have a perceptible effect on the adsorption process for all the studied drugs.

2.4. *Jatropha Curcas*

Jatropha curcas L. is a woody shrub which belongs to family Euphorbiaceaeand it is found across different regionsall over the world due to its strength. It has many names in different regions like the physic nut, goat nuts,(pinhão-manso in Brazil), Barbados nut, purging nut, nettle spurge (Wurdack *et al.*2005).*Jatropha* plant is also found in Nigeria and the local names are botuje pupa, lapalapa pupa, okpokporu, sherigun, among others.Previous researchesshowed that *Jatropha* is native to Central and South America (Pecina-Quintero*et al*. 2014).*Jatropha* curcas is a valuable multi-purpose crop, historicallyit was used as medicine for wounds and leaves used as drinksagainst malaria, *Jatropha* plants used to controlsoil degradation, alleviate erosion, desertification and increase soil fertility,

however, in last decades there ismore attention to use *Jatropha* oil for produce biodiesel, *Jatropha* curcas is easily propagated by seeds or stemcutting, it is tolerant for drought for longtime, it is grow well with treated wastewater, also, it can be grown onmarginal land. *Jatropha* curcas seed have about 32-40% valuable oil used to producebiofuel, therefore, it couldbe the source for biodiesel production particularly in arid and semiarid regions.The by-products of biodieselproduction (seed shell, seed coat, seed cake and glycerine) are also very useful. The seed coat is used as mulch and can be used for the removal of heavy metals from wastewater. The coats contain cellulose and lignin, and the surface of cellulose in contact with water is negatively charged that can attract cations such as Cu(II) ions. Lignin has various polar groups (alcohols, carbonyls, acids, amino, phenol,hydroxyls and ethers) as potential chemical bonding agents for chemisorptions (Jain *et al*., 2008).



Plate 2.1: *Jatropha* curcas plant

2.5 Overview of Techniques for Removal of Pharmaceutical Compounds

Pharmaceuticals have been detected in drinking water but are not as well documented as in wastewater or natural waters (Mompelat *et al.*, 2009). This is due to lower quantities of pharmaceuticals in the raw water used for drinking water abstraction (compared to wastewater), more efficient removal by water treatment processes and the breakdown of pharmaceuticals caused by residual chlorine in the water distribution system (Gibs *et al.*, 2007).

However, some pharmaceutical compounds are present in drinking water at detectable levels and the approaches used to remove them are not without limitations. There is no specific treatment that is presently available to assure the complete removal of various pharmaceutical compounds due to their diverse properties. Reliable processes that are able to eliminate both bulk substances, as well as pharmaceutical compounds, are yet to be developed (Luo *et al.*, 2014). An overview of the current removal techniques is presented belowto show the performance of each technique for pharmaceutical removal and to identify the need for improvement.

2.5.1 Coagulation–flocculation

Coagulation–flocculation is used for removing particulate matter, colloids as well as some dissolved substances. Generally, coagulation-flocculation processes result in inefficient elimination of most pharmaceutical compounds (Luo *et al*., 2014). Matamoros and Salvadó (2013) studied the micropollutant removal in a coagulation/flocculation–lamella clarifier for treating secondary effluent. The removals ranged from imperceptible elimination to

50%, among which the relatively high removals (20–50%) were observed for the compounds with K_{OW} - 4 at pH = 7–8 (e.g. galaxolide, tonalide, and octylphenol).

Suárez et al.(2009) observed a significant reduction (around 80%) of musks (e.g.galaxolide and tonalide) during coagulation-flocculation treatment ofhospital wastewater. The other compounds that showed identifiable elimination were diclofenac (max. 46%), naproxen (max. 42%) andibuprofen (max. 23%).

landfill leachate has been considered as an important source of some EDCs, Asakura and Matsuto (2009) noted that treatment of landfill leachate by coagulation and sedimentation could not remove biphenol A but achieved much higher removals for DEHP and nonylphenol (70% and 90% respectively). As a whole, most micropollutants, have been reported to be poorly removed during coagulation-flocculation processes (Luo *et al*., 2014). Exceptions were some musks, a few pharmaceuticals (e.g. diclofenac) and nonylphenol due to their high K_{OW} (4–6). Besides, neither the coagulant dose nor operation temperature influenced the removal of pesticides significantly (Thuy *et al*., 2008). Although there are a few differences among coagulants types at varying doses, Suárez *et al*. (2009) reported that the addition of 25 mg/L $FeCl_3$ achieved optimal results in most cases. Huerta-Fontela *et al*. (2011) demonstrated that aluminium sulfate was potentin eliminating some hydrophobic pharmaceutical compounds. Composition of wastewater can exert either synergistic or antagonistic effects on micropollutant removal during coagulation-flocculation treatment. For example, high-fat content in water source was reported to improve the removal of hydrophobic compounds (Suárez *et al*., 2009). Dissolved humic acid could also improve the elimination of some pharmaceutical compounds, such as diclofenac, ibuprofen and bezafibrate (Vieno *et al*., 2006). On the contrary, the presence of dissolved organic matters

(DOM), especially low-molecular-weight fractions, can possibly inhibit micropollutant removal due to the preferential removal of DOM through coagulation. Negatively charged DOM could react with positively charged aluminium hydrolysis species, leading to a less amount of coagulant available for the elimination of the compounds (Choi *et al*., 2008). In addition, the performance of coagulation-flocculation processes can be also controlled by several operating conditions including mixing conditions,pH, alkalinity, temperature as well as the presence of divalent cations and concentrations of destabilizing anions (e.g. bicarbonate, chloride, and sulfate) (Alexander *et al*., 2012).

2.5.2 Activated carbon adsorption

Adsorption by activated carbons (ACs) is commonly employed for controlling taste and odour in drinking water. This technique has also great potential for the treatment of secondary effluent and has proved to be more effective in removing micropollutants in comparison with the coagulation-flocculation process (Choi *et al*., 2008). Both powdered activated carbon (PAC) and granular activated carbon (GAC) have been widely used in adsorption processes, which can be affected by the properties of both adsorbate (KOW, pKa, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups) and adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content) (Kovalova *et al*., 2013).

2.5.2.1 Powdered activated carbon (PAC)

PAC has been considered as a potent adsorbent for treatingpersistent/non-biodegradable organic compounds. An advantage ofusing PAC lies in its capacity to provide fresh carbon continuously or can be used seasonally or occasionally when risk of trace organics is

present at a high level (Snyder *et al*., 2007). Kovalova *et al.* (2013) investigated the elimination of micropollutants from an MBR-treated hospital effluent using PAC treatment at a retention time of two days. With PAC doses of 8, 23 and 43 mg/L and retention time of 2 days, the PAC reactor effectively eliminated most of the micropollutants (pharmaceuticals, metabolites and industrial chemicals). The reduction of total load of selected pharmaceuticals and metabolites was around 86%. Batch tests performed by Hernández-Leal*et al.* (2011) also showed marked removal (>94%) of various micropollutants (personal care products, bisphenol A and nonylphenol) during PAC treatment with initial compound concentrations of 100–1600 μg/L at a dose of 1.25 g/L and a contact time of 5 min.PAC addition in activated sludge tank or post-treatment configurations is a major application of PAC in the full-scale municipal WWTPs.

A study was carried out to assess the efficiency of micropollutant removal by addition of PAC in different flow schemes in municipal wastewater treatment (Boehler *et al*., 2012). It was found that counter-current use of PAC by recycling waste PAC from post-treatment tank to biological treatment tank could improve micropollutant removal by 10 to 50% incomparison with the application without recycling.

PAC addition in WWTPs was shown to be able to reduce micropollutant levels by more than 80%. The PAC dosage for adequate treatment of secondary effluent with dissolved organic carbon (DOC) of 5–10 mg/L was 10–20 mg/L, while a higher amount (30–40 g/m^3 influent) was required to achieve similar results if direct PAC addition was employed in biology tank. The performance of PAC in eliminating micropollutants depends upon PAC dose and contact time, the molecular structure and behaviour of the targeted compound, as well as the water/wastewater composition (Boehler *et al*., 2012; Snyder *et al*., 2007). Either

higher dose or longer contact time can probably result in greater removal of micropollutants.

Westerhoff *et al*. (2005) showed that micropollutant removal was improved with higher PAC dosages (20 mg/L) and independent of the initialcompound concentrations. Water/wastewater composition also affects the adsorption of micropollutants. The sorption efficiency of PAC could be limited as the DOC content increases (Boehler *et al*., 2012). Irrespective ofthe influence of other contaminants in wastewater, the efficacy of applying PAC to wastewater for micropollutant removal is comparable with that of ozonation. Thus, PAC addition appears a promising method for upgrading municipal WWTPs for improved micropollutant removal (Bolong *et al.*, 2009).

2.5.2.2 Granular activated carbon (GAC)

Rossner *et al*. (2009) opined that GAC dosage typically applied to taste and odour control in drinking water (b10 mg/L) was capable to enhance removal for most of the various compounds in a lake water. Hernández-Leal *et al*. (2011) showed the effectiveness of GAC in treating two wastewaters: (1) spiked (0.1–10 μg/L) aerobic effluent in a GAC column operated at low flow and (2) aerobic effluent with real concentrations (40 ng/L to 7.9 μg/L) of micropollutants in a GACcolumn. In the first instance, removals for all the compounds were generallyhigh (>67%), particularly for ethyl-, propyl- and butylparaben, triclosanand caffeine (>90%). In the second instance, most compounds were also efficiently eliminated. Specifically, the removal efficiency ranged from 50% (tonalide and nonylphenol) to more than 90% (galaxolide).

A full-scale granular activated carbon plant treating a WWTP effluent was assessed in terms of the removal efficiency of steroidal estrogens and pharmaceuticals (Grover *et al*., 2011). Reasonable removals of steroidal estrogens from sewage effluent were observed during the GAC tertiary treatment. By comparison, the reduction of pharmaceutical concentrations was more variable (Luo *et al*., 2013) For example, higher removals (84–99%) were observed for mebeverine, indomethacine, and diclofenac, while some compounds (e.g. carbamazepine and propranolol) displayed much fewerremovals (17–23%). In spite of the efficient treatment of sewage effluent, GAC-based removal technology should be carefully operated, as the efficiency will decrease over time due to the saturation of the adsorption site. Similar to PAC, the contact time is a major factor that affects the degree of adsorption. Short contact time is likely to lead to significantly lowered adsorption efficiency (Luo *et al*., 2014). As the removal of the trace contaminants depends largely upon particle–contaminant interactions, the competition for adsorption sites and/or pore blocking (by particle solids) can limitthe removal efficiency of activated carbon (Bolong *et al*., 2009). Snyder *et al*. (2007) suggested that a steam-treated GAC could be employed to overcome the setbacks of GAC due to its greater absorption capacity. Regular regeneration of GAC also seemed of vital importance to maintain minimal breakthrough of micropollutants. Furthermore, pore shape/size and volumes of activated carbons, carbon type, surface charge of compounds and operation year were noted to have influence on the removal performances (Choi *et al*., 2008; Rossner *et al*., 2009): first, a broader micropore size distribution of the GAC led to more efficient adsorption of micropollutants with different shapes and sizes; second, the pore volume was more important to adsorption capacity than specific area and larger pore volume was commonly associated with greater removal efficiency; third, negatively charged micropollutants were likely to be poorly

adsorbed by the negatively charged carbon and well adsorbed by the positively charged carbon; and fourth, adsorption capacity reduced with operation year.

GAC and PAC appear to be prospective methods for micropollutant removal. In general, efficient removal is potentially achievable when the compounds have non-polar characteristics as well as matching pore size/shape requirements (Rossner *et al*., 2009; Verlicchi *et al*., 2010). However, activated carbon efficacy could be remarkably lowered by the presence of natural organic matter (NOM) which competes for binding sides, thereby resulting in blocked pores. Besides, PAC dose, GAC regeneration, as well as contact time, play key roles in efficient removal of micropollutants.

2.5.3 Ozonation and advanced oxidation processes (AOPs)

Due to the refractory nature of some micropollutants, conventionalphysicochemical and biological treatments are not able to adequately eliminate them (Luo *et al*., 2014). To surmount this inadequacy, ozonation and AOPs can be considered. Ozonation and AOPsare efficient redox technologies which demonstrate some superiority over conventional treatments, such as high degradation rates and non-selectivity (Luo *et al*., 2014). Furthermore, these processes have disinfecting effects, which are essential for reuse applications that involve direct human contact, for example, household reuse applications (Hernández-Leal *et al*., 2011).

Ozone can breakdown contaminants directly and indirectly (mainly via the formation of stronger and less selective oxidizing agent (•OH) into harmless compounds. Some pharmaceutical compounds are susceptible to both ozone and AOPs (e.g., naproxen and carbamazepine), whereas some are only subject to OH (e.g. atrazine and meprobamate) and

some are resistant to both forms of oxidation (e.g. TCEP and TCPP) (Gerrity *et al*., 2011). The generation of •OH can be promoted with the presence of H_2O_2, Fenton reagent and ultraviolet.

Ozonation is an attractive technique to considerably decrease the micropollutant load of full-scale WWTPs (Hollender *et al*., 2009). Hernández-Leal *et al*. (2011) evaluatedthe efficiency of ozonation for the removal of a wide range of micropollutants (UV-filter, fragrance, biocide and surfactant) from biologically treated greywater. In general, all the compounds were significantly removed (>79%) from the biologically treated effluent at an applied ozone dose of 15 mg/L. In another study, low ozone dose of 5 mg/L also showed high removal efficacyfor most of the targeted micropollutants (Sui *et al*., 2010). The concentrations of carbamazepine, diclofenac, indomethacin, sulpiride and trimethoprim were considerably reduced by more than 95%. The reductions of DEET and metoprolol were moderate. However, bezafibrate was very resistant to ozonation and was removed by only 14%.

A study conducted by Gerrity *et al*. (2011) focused on the application of O_3/H_2O_2 for removing a host of micropollutants (PPCPs and steroid hormones) during water reclamation. The process showed reasonableremoval efficiency (>90%) for almost all of the target contaminants, except TCEP (13%), TCPP (26%), atrazine (69%), meprobamate (80%), and ibuprofen (83%). They indicated that micropollutants which exhibited the highest levels of oxidation were characterized by high ozone and •OH rate constants associated with their electron-rich moieties (e.g., phenols, anilines, olefins and activated aromatic) (Luo *et al*., 2014).

Although the formation of •OH was enhanced under alkaline conditions, Zhang *et al*.(2012) reported that low pH was beneficial for EDCs removal by ozone when treating synthetic secondary effluent. This is because ozone wasless reactive to the inorganic and organic matters (non-target compounds) in the synthetic secondary effluent as compared to •OH (generated at high pH) and a great amount of O_3 could thereby be preserved for the reactions with target compounds.

2.5.4. Membrane processes

The retention of pharmaceutical compounds in membrane processes can generally be achieved by size exclusion, adsorption onto membrane, and charge repulsion. These removal mechanisms largely depend on a number of factors, such as membrane process type, membrane characteristics, operating conditions, specific pharmaceutical characteristics and membrane fouling (Schäfer *et al*., 2011). Although microfiltration (MF) and ultrafiltration (UF) have been provenprocesses that efficiently eliminate turbidity, pharmaceuticals are generally poorly removed during UF and MF, as the membrane pore sizes aremuch larger than the molecular sizes of pharmaceutical compounds. However, they can be removed via adsorption on to membrane polymers, as well as interaction with NOM in wastewater.

Jermann *et al*. (2009) examined the fate of ibuprofen and estradiol during a UF process and the effects of fouling by NOM. Without NOM, UF with hydrophilic membrane showed insignificant removal for ibuprofen and low (8%) removal for estradiol, while hydrophobic membrane retained a much larger amount of estradiol (up to 80%) and ibuprofen (up to 25%). The higher retention of estradiol was due to the higher Carbon–Water Partitioning

Coefficient (Koc) value of the compound. As for the effect of NOM, NOM substances of high molecular weight such as alginate and Aldrich humic acid showed a greater effect than the lower molecular weight Nordic aquatic humic acid on improvingthe removal of pharmaceutical compounds.

Due to the low removal efficiency, MF or UF alone is not feasible for theirremoval. Hence, the combination of MF or UF with other processes (e.g. NF or RO) is essential for enhanced elimination of different pharmaceuticals. Garcia *et al*. (2013) combined MF with RO to remove micropollutants for municipal wastewater reuse. MF was observed to be able to reduce the concentrations of some compounds, such as DEHP, by more than 50%. With the incorporation of RO, the removal efficiency was significantly enhanced, ranging from 65% to 90% for most micropollutants (except ibuprofen and nonylphenol).

2.5.5 Membrane bioreactor

Membrane bioreactor (MBR) process combine activated sludge biological treatment and membrane filtration (MF and UF). MBRs possess the following advantages over conventional wastewater treatment in the following aspects (Ngo *et al*., 2012) such as high effluent quality, excellent microbial separation ability, absolute control of SRTs and HRTs, high biomass content and less sludge bulking problem, low-rate sludge production, small footprint and limited space requirement, and possibilities for a flexible and phased extension of existing wastewater treatment plants (WWTPs).

MBRs are able to effectively remove a wide spectrum of micropollutants including compounds that are resistant to activated sludge processes (Radjenovic *et al*., 2009). This is because of the following: first, they are able to retain sludge to which many compounds

have adhered; second,the membrane surface can also intercept the compounds; and third,the longer SRT in MBRs may promote microbial degradation of the compounds (Spring *et al*., 2007). The removal of micropollutants in MBR can be affected byanumberof factors, such as sludge age and concentration, existence of anoxic and anaerobic compartments, the composition of the wastewater, operating temperatures, pH and conductivity (Kovalova *et al*., 2012).

Trinh *et al*. (2012) investigated the micropollutant removal efficiency of a full-scale MBR. High elimination(>90%) was found for most of the micropollutants. Nevertheless, some compounds were incompletely removed (24–68%), including amitriptyline, carbamazepine, diazepam, diclofenac, fluoxetine,gemfibrozil,omeprazole, sulfamethoxazoleandtrimethoprim. Hence, these compounds were considered as potential indicators for evaluating micropollutant removal using MBR processes.

2.5.6. Attached growth treatment processes

Attached growth technology is a promising alternative to activatedsludge processes for wastewater treatment which involves attachedgrowth on inert carriers either fixed or mobilized in the suspension of thereactor (Luo *et al*., 2014). The attached growth processes offer the following advantagesover activated sludge processes in wastewater treatment (Guo *et al*.,2012): better oxygen transfer, high nitrification rate and higher biomass concentrations; more effective in organicc removal, and canapply for high organic loading rates at relatively shorter HRT;allowing the development of microorganisms with relatively lowspecific growth rates (e.g., methanogens); less subject to variable orintermittent

loadings; small reactor size and lower space requirement; and lower operational costs (e.g. fixed-bed biofilm processessuch as trickling filters and rotating biological contactors).

The attached growth systems can be grouped into two majorcategories: fixed-bed bioreactors and moving bed bioreactors. Biofiltration seems a compelling biological technique formicropollutant removal (Reungoat *et al*., 2011). Commonly used systems in water and wastewater treatment include trickling filter, sandfiltration and biological activated carbon (BAC). A BAC filter is typicallycomposed of a fixed bed of GAC serving as the carrier for bacterial adhesion and growth.

Reungoat *et al*. (2011) examined and compared theperformance of biofilters with two media, activated carbon and sand,during long-term operation. The results demonstrated that BAC had agreat potential for PPCP (e.g. diclofenac, carbamazepine, sulfamethoxazole and gemfibrozil) removal (>90%) and reduction of the potentialrisk of environmental and/or human health impact. On the otherhand, sand filters could only achieve limited elimination for PPCPs. Dissolved oxygen was the main factor affecting the performance of BAC filters, while empty-bed contact time (from 30 min to 120 min) did notresult in considerable variation in the removals of compounds. In addition, long-term observation indicated that the main mechanism for organic matter and PPCP removal in biofiltration was biodegradationrather than adsorption.

Another biofilter, namely sequencing batchbiofilter granular reactor (SBBGR), was investigated by Balest *et al*.(2008) for removing several selected EDCs. The results showed thatSBBGR achieved much higher removal efficiency for EDCs removalthan the conventional activated sludge process in a municipal WWTP.The removal efficiencies for

bisphenol A, estrone, estradiol and 4-tertoctylphenol were 91.8%, 62.2%, 68% and 77.9% for the demonstrativeSBBGR system and 71.3%, 56.4% 36.3% and 64.6% for the conventionalactivated sludge process of the municipal WWTP, respectively. The excellent performance of the SBBGR was attributed to the very high sludgeage (about 160 days). Due to the excellent performance, biofiltrationwas suggested as an efficient treatment method that could be employedin advanced treatment processes for reducing the impact of the effluentdischarge into the environment and/or providing water of higher quality for recycling.

Falås *et al*. (2012) conducted a set of batch experiments to evaluatethe effectiveness of a hybrid moving bed biofilm-activated sludge process for the removal of various micropollutants. It was indicated thatthe presence of carriers could enhance the overall biological eliminationof some compounds. For example, diclofenac, clofibric acid andmefenamic acid were not eliminated in the activated sludge reactors,while the carrier reactors showed more obvious and rapid removals(at least 60% after 24 h) of the three compounds. In another study, amoving bed biofilm system was investigated in terms of the removal efficiency for bisphenol A, oseltamivir and atrazine from wastewaterusing carriers made from existing bioplastic-based products (Accinelli*et al.*, 2012). During the experiments with control wastewater samples,mineralization rates for bisphenol A, oseltamivir and atrazine wererelatively low, accounting for only 18%, 7% and 3.5% of the initial concentrations, respectively. By contrast, the addition of incubated carriers enhanced the removals of bisphenol A, oseltamivir and atrazine by 34%,49% and 66%, respectively.

2.6 Response Surface Methodology (RSM)

Response surface methodologies are multivariate techniques that mathematically/statistically fit the experimental domain studied in the theoretical design through a response function (Myers, 1971; Box *et al.*, 1978). This method is based on the fit of mathematical models (linear, square, polynomial functions) to the experimental results or responses generated from the designed experiment and validation of the model obtained through statistical techniques. The major aim of this method is to vary all significant factors at a time and then fit the experimental data to a mathematical model (Krowiak *et al.*, 2014). Thus, the number of experimental runs in RSM is less than the conventional methods.

According to Krowiak *et al.*(2014), Optimization through RSM approach can be divided into six stages as follows:

i. Selection of independent variables and possible responses
ii. Selection of the experimental design strategy
iii. Performing the experiments and obtaining the results
iv. Fitting the model equation to the experimental data
v. Obtaining response graphs and verification of the model (ANOVA), and
vi. Determination of optimal conditions.

The two most common designs commonly employed in response surface modelling are central composite and Box-Behnken designs (Grady and Kenneth, 2006).

2.6.1 Central Composite Design (CCD)

CCD comprises of a 2^kfactorial design, which provides data for approximating the first-order effects for each factor and interactions between the factors, and a "star" design

consisting of $2k + 1$ points, which provides data for estimating second-order effect (David, 2000). The star points represent new boundary values (low and high) for each factor in the design (Grady and Kenneth, 2006). Where k is the number of factors considered during the course of the experiment.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of Study Area

This study was conducted in Zaria, Kaduna State, Nigeria. Zaria is located on latitude 11° 30 and longitude 7°50 and is about 686 m above sea level. It falls within the tropical savannah climate, according to Koppen's world climate classification. It lies in the natural vegetation of the Northern Guinea Savannah, some 80 km North of Kaduna town, along the major high way from Kaduna to Kano State. Zaria is blessed with abundant water resource both ground and surface (Yusuf *et al*., 2007).

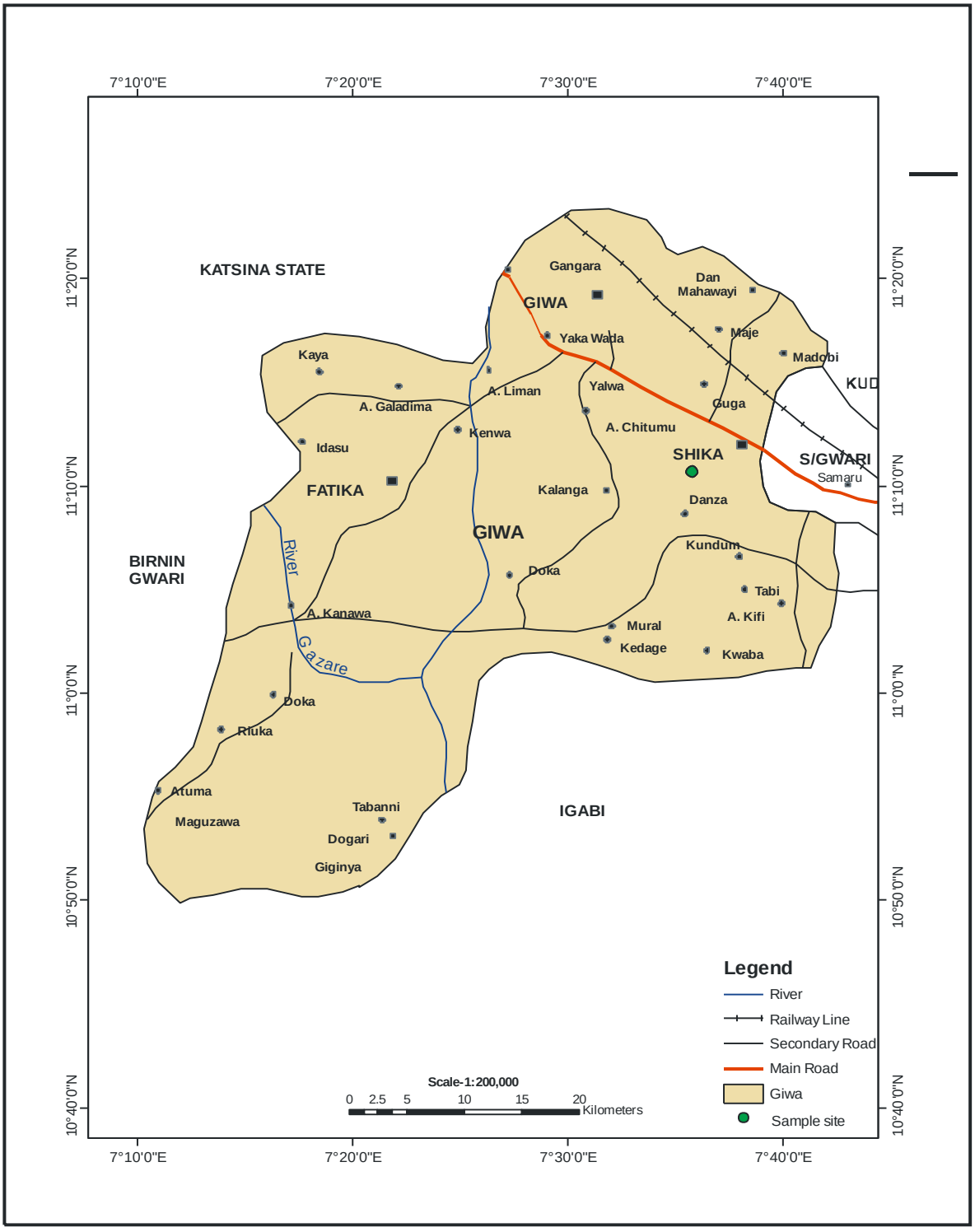


Figure 3.1: The Map of Giwa Local Government Area Showing the Sample Area

3.2 Materials

3.2.1 Chemicals and reagents

The following chemicals/reagents were employed during the course of this research work; they were used as supplied without further purification:

a. Acetaminophen, 99.8% purity.
b. Amoxicillin, 86.6% purity.
c. Ibuprofen, 98% purity.
d. H_3PO_4, 99% purity by BDH, England.
e. Distilled water
f. Ultra-pure water
g. 0.1M HCl
h. 0.1M NaOH
i. 0.1M Acetic acid
j. 50% HNO_3

3.2.2 Equipment and apparatus

The following equipment were employed during the course of this research work; they were used as supplied and calibration was carried out where necessary:

a. Shaking water bath (SBS40, UK)
b. pH meter (HI 9813-5, Romania)
c. Sample bottles
d. Volumetric flasks
e. Pipette

f. UV Spectrophotometer (Agilent Technologies Cary 300 Series, USA)

g. High-Performance Liquid Chromatography (HPLC)

h. Hydrophobic-Lipophilic Balance (HLB) cartridges

i. FTIR spectrophotometer (Agilent Technologies Cary 630 Series, USA)

j. Mortar and pestle

k. Oven (by Gallenkamp, England)

l. Muffle furnace (by Carbolite, Sheffield, England)

m. Scanning Electron Microscope (Quanta Scanning Electron Microscope FEI Quanta 250).

n. BET analyser (Nova 4200e USA)

3.3 Sample Collection and Preparation

Jatrophacurcas seedswere obtained from the National Research Institute for Chemical Technology (NARICT), Zaria. Wastewater samples were collected from the Ahmadu Bello University Teaching Hospital Wastewater Treatment Plant Shika. A grab sampling technique was used to collect the samples from a depth of 1-2 cm from the water surface. Samples were collected in clean 2.5L amber bottles. A 1ml aliquot of 50% nitric acid was added to each of the composite sample to prevent microbial degradation. The sample was taken to the laboratory for extraction following the method described by Hischerova *et al.*(2003).

3.4 Extraction of Pharmaceutical Compounds fromthe Hospital WastewaterSample

The sample was filtered using the Whatman filter paper (125mm in diameter) and the target analytes were extractedusing the methods reported by Matongo *et al*. (2015) after

pHoptimization in order to improve the recovery of the target analyte.Solid Phase Extraction (SPE) cartridges were used to achieve simultaneous extraction of the target analytes due to its versatility. The optimized extraction method that was used is briefly described as follows: The SPE cartridge was conditioned with 5ml methanol and equilibrated with 5ml of water and adjusted to a pH of 4.0 with 0.1M acetic acid. The sample (300ml) wasthen loaded into the cartridge and eluted. Afterwards,the cartridgewas driedat 25°C for 30 minutes and analytes adsorbedwere eluted with 10ml of methanol followed by 5ml of acetone. It was evaporated to dryness under vacuum and reconstituted with 1 ml of methanol.

3.5 High-Performance Liquid Chromatography (HPLC) Determination of ExtractedPharmaceutical Compounds

Reference standards (USP) of acetaminophen, ibuprofen, and amoxicillinwere used in this study. All reagents used for HPLC analysis were of HPLC grade. Ultra-pure water using Elix Millipore water system was used in the preparation of all the standards.The determination of the selected pharmaceutical compounds was performed using the HPLCMerck Hitachi Elite LaChrom L-2200 Series. L1column was used for separation and quantification of the target analytes and the UV detector was used.The method was validated by plotting a calibration plot for each drug within the concentration range of 0.0025-0.025 mg/ml of the reference standard using the mean values of peak area against concentration. Linear regression equation, coefficient of regression (r^2) and standard deviation at intercept of y-axis were computed using Microsoft Office Excel 2019 (Appendices I-III)

3.5.1 Chromatographic conditions for Acetaminophen

Mobile Phase: Methanol and water (1:3)

Column: (30 cm × 3.9 mm in diameter, 5 µm particle size)

Flow rate: 1.5mL/min

Detector: UV

Maximum wavelength: 243nm

3.5.2 Chromatographic conditions for Amoxicillin

Mobile Phase: Acetonitrile and phosphate buffer (1:24)

Column: (25 cm × 4 mm in diameter, 5 µm particle size)

Flow rate: 1.5mL/min

Detector: UV

Maximum wavelength: 239nm

3.5.3 Chromatographic conditions for Ibuprofen

Mobile Phase: Orthophosphoric acid, water and methanol (300:247:750)

Column: (25 cm × 4.6 mm in diameter, 5 µm particle size)

Flow rate: 1.5mL/min

Detector: UV

Maximum wavelength: 221nm

3.6 *Jatrophacurcas* Sample Preparation

The *Jatropha*seeds collected were crushed using a mechanical press to remove the oil. The cake obtained after the extraction was sun-dried for three days to remove moisture according to the method described by Itodo *et al.* (2009). The sundried sample was properly washed with distilled water to remove dust and water-soluble impurities. The sample was allowed to drain off excess water accumulated during washing. Thereafter, the

sample was introduced into a thermostatic laboratory oven set at 105ºC for 24 hours. The dried sample were gently crushed using a laboratory mortar and pestle followed by sieving with a < 400µm aperture sieve. The sieved sample was stored in airtight containers for further use.

3.6.1 Carbonization of *Jatropha* waste cake

The prepared *Jatropha*curcas samplewas carbonized using the method described by Gimba *et al* (2004). About 50g of the *Jatropha* waste cake was placed in large-sized ceramic crucibles and carbonized at 400 ºC in a mufflefurnace. The carbonized samples were allowed to cool in desiccators prior to activation.

3.6.2 Chemical activation of the carbon

Chemical activation of the carbonized samplewas done using 85 w/v H_3PO_4 as a dehydrating agent.The carbonized sample (50 g)was mixed withH_3PO_4. The impregnation ratio defined by the weight of the impregnant (H_3PO_4) to the precursor was 1:1. Stirring was used to ensure the access of the acid to the interior of the precursor. The pyrolysis of the impregnated material was conducted in a regulated furnace at temperatures between 350ºC and 650ºC while the adsorption time was maintained at 2 hours.After cooling down to room temperature, the prepared adsorbent was thoroughly washed with hot distilled water until a pH of 7 is obtained. The prepared adsorbent was then dried at 105ºC overnight, ground and stored in the hermetic bottle for subsequent analyses.

3.7 Characterization of Prepared Adsorbent

3.7.1 Specific Surface Area

The Brunauer–Emett–Teller (BET) surface area was measured from N_2 sorption isotherm at 77 K using a Micrometrics Tristar II. The samples were degassed under flowing nitrogen at 250 °C for 4 hours using the Smart Prep™ 065. The degassing unit removes adsorbed contaminants from the surface and pores of a sample in preparation for analysis. The sample tube in the analysis port was again degassed before the Dewar containing liquid nitrogen was automatically elevated upwards to submerge the sample tube. A predetermined pressure of nitrogen was bled into the manifold above the analysis port. The sample analysis port valve was then opened, exposing the sample to nitrogen. The quantity of adsorbed nitrogen was determined by the difference in the recorded pressure. The sample analysis port was then closed and the manifold filled with a slightly higher pressure of nitrogen before re-exposure to the sample followed by calculation of the next value. Anisotherm was generated and the surface area of the sample was then calculated from the isotherm using the Brunauer–Emett–Teller (BET) equation and N_2 cross-sectional area of $0.162nm^2$. The analysis was carried out at the Federal University of Technology, Minna, Niger State, Nigeria.

3.7.2 Morphology analysis

The morphology of the activated carbon samples was analyzed by SEM analysis. Minimal preparation included acquisition of the sample and placing the sample on a clean carbon strap that was attached on the sample holder, which fit into the SEM chamber and some accommodation to prevent charge build-up and the sample from making a contact with the

detector. SEM was viewed using Quanta Scanning Electron Microscope FEI Quanta 250 at the Umaru Musa Yar'adua University, Katsina, Katsina State, Nigeria.

3.7.3 Fourier Transform Infra-Red (FTIR) spectroscopy Analysis

The functional groups and structure of the sample (*Jatropha* waste cake) and the adsorbent prepared in the optimal conditions were studied using FTIR spectroscopy.The FT-IR spectra of the raw and modified jatropha samples were recorded on a Fourier Transform Infrared Spectrometer (Agilent Technologies Cary 630) at the Multi-User Laboratory, Ahmadu Bello University, Zaria, Nigeria. The sample was mixed with Potassium bromide (KBr) and then ground to a homogeneous blend and compressed to give a small transparent disc of 13 mm diameter. The disc containing the sample was then placed in the infrared spectrometer and the spectrum of the samples was collected. There were 20 scans collected for each measurement over the spectral range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were presented without baseline correction or normalization.

3.8 Preparation of Stock Solution of the Pharmaceutical Compounds

3.8.1 Acetaminophen stock preparation

Stock solution of 1 mg/mL was prepared by dissolving 250 mg of acetaminophen powder of high purity in a 250 mL volumetric flask and made up to volume. A 25 mL aliquot of the solution was further diluted to 1000 mL to give the concentration of 25 mg/L. This was repeated with 20, 15, 10 and 5 mL aliquots to give concentrations of 20, 15, 10, and 5 mg/L respectively. The absorbance of each resulting solution was read at a maximum wavelength of 243 nm using the UV spectrophotometer (Agilent Technologies Cary 300 Series). This was used in preparing the calibration plot for acetaminophen (Appendix IV).

3.8.1.1 Acetaminophen Sample preparation

The average weight of 10 tablets was obtained using a weighing balance. The tablets were crushed into powder using a tablet miller. Powder quantity equivalent to250 mg acetaminophen was dissolved in a 250 mL volumetric flask and made up to volume. The solution was filtered with a Whatman filter paper and25 mL aliquot of the solution was further diluted to 1000 mL to give a 25 mg/L solution.This was repeated with 20, 15, 10 and 5 mL aliquots to give concentrations of 20, 15, 10, and 5 mg/L respectively andthe absorbance of each resulting solution was read at 243 nm using the UV spectrophotometer (Agilent Technologies Cary 300 Series). This was used for adsorption studies of acetaminophen.

3.8.2 Amoxicillin stockpreparation

Stock solution of 1mg/mL was prepared by dissolving 250 mg of amoxicillin powder of high purity in a 250 mL volumetric flask and made up to volume. A 25 mL aliquot of the solution was further diluted to 1000 mL to give the desired concentrationThis was repeated with 20, 15, 10 and 5 mL aliquots to give concentrations of 20, 15, 10, and 5 mg/L respectively. The absorbance of the resulting solution was read at a maximum wavelength of 239 nmusing the UV spectrophotometer (Agilent Technologies Cary 300 Series). This was used in preparing the calibration plot for amoxicillin (Appendix V).

3.8.2.1 Amoxicillin sample preparation

The average weight of 10 tablets was obtained using a weighing balance. The tablets was crushed into powders using a tablet miller. Powder quantity equivalent to100 mg amoxicillin was dissolved in a 100 mL volumetric flask and made up to volume. The

solution was filtered with a Whatman filter paper and25 mL aliquot of the solution was further diluted to 1000 mL to give a 25 mg/L solution. This was repeated with 20, 15, 10 and 5 mL aliquots to give concentrations of 20, 15, 10, and 5 mg/L respectivelyThe absorbance of the resulting solution was read at a maximum wavelength of 239 nmusing the UV spectrophotometer (Agilent Technologies Cary 300 Series). This was used for adsorption studies of amoxicillin.

3.8.3 Ibuprofen stock preparation

A total of 1 mg/mL stock solution was prepared by dissolving 100 mg of ibuprofen powder in a 100 mL volumetric flask and made up to volume.A 25 mL aliquot of the solution was further be diluted to 1000 mL to give the desired concentration.This was repeated with 20, 15, 10 and 5 mL aliquots to give concentrations of 20, 15, 10, and 5 mg/L respectively The absorbance of the resulting solution was read at a maximum wavelength of 221 nmusing the UV spectrophotometer (Agilent Technologies Cary 300 Series). This was used in preparing the calibration plot for ibuprofen (Appendix VI).

3.8.3.1Ibuprofen sample preparation

The averageweight of 10 tablets was obtained using a weighing balance. The tablets was crushed into powders using a tablet miller. Powder quantity equivalent to100 mg ibuprofen was dissolved in a 100 mL volumetric flask and made up to volume. The solution was filtered with a Whatman filter paper and25 mL aliquot of the solution was further diluted to 1000 mL to give a 25 mg/L solution.This was repeated with 20, 15, 10 and 5 mL aliquots to give concentrations of 20, 15, 10, and 5 mg/L respectively The absorbance of the resulting solution was read at 221 nmusing the UV spectrophotometer (Agilent Technologies Cary 300 Series). This was used for adsorption studies of ibuprofen.

3.9 Adsorption Studies

An adsorption experiment was performed to measure the adsorption of each pharmaceutical compound (acetaminophen, ibuprofen and amoxicillin) on commercial activated carbon (CAC) and *Jatropha*activated carbon (JAC) from aqueous solution using the batch adsorption experiment. Four adsorption parameters namely contact time, concentration, pH and adsorbent dosage were studied. The experimental matrix obtained from the design of the experiment is given in Table 3.1. Varying contact time, concentration, pH and adsorbent dosage were used as shown in the experimental matrix. A mechanical shaker was used to agitate the solution at different contact times. The resulting solution was filtered through a 0.45 μm Whatman filter paper. The filtrate solution remaining after the adsorption process and the initial solution before the adsorption process were analyzed using a UV spectrophotometer (Agilent Technologies Cary 300 Series).The study was done in triplicate and separate controls containing commercial adsorbent were prepared using the same method.

The adsorption loading, q (mg/g) represents the adsorbate uptake and was calculated from the difference in adsorbate concentration in the aqueous phase before and after adsorption, as per following equation:

$$q = \frac{V(C_i - C_f)}{W} \qquad 3.1$$

where q is the adsorption loading, V is the volume of adsorbate in solution (L), C_i and C_f are the initial concentration of adsorbate in solution (mg/L) and the final concentration of adsorbate in solution (mg/L) (after 120 minutes) respectively, and W is the mass of *Jatropha* activated carbon (g).

The percentage removal of the pharmaceutical compounds was calculated using the equation below.

$$\text{removal}\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad 3.2$$

Where C_i and C_f are the initial concentration of the adsorbate in solution (mg/L) and the final concentration of adsorbate in solution (mg/L) (after 120 minutes) respectively.

3.10 Statistical Analysis

The statistical analysis was done using the Design-Expert software version 7.0 (Stat-Ease, Inc., Minneapolis, MN 55413, USA). The Central Composite Design which is a subset of the Response Surface Methodology (RSM) was used in the design of this experiment.

Table 3. 1: Experimental matrix

Run	Factor 1 A:CT	Factor 2 B:C	Factor 3 C:AD	Factor 4 D:pH
1	70.00	5.00	0.60	6.00
2	20.00	25.00	1.00	10.00
3	120.00	15.00	0.60	6.00
4	20.00	5.00	0.20	10.00
5	120.00	25.00	0.20	10.00
6	70.00	15.00	0.60	6.00
7	70.00	15.00	0.60	2.00
8	120.00	5.00	1.00	2.00
9	70.00	15.00	0.60	6.00
10	20.00	15.00	0.60	6.00
11	70.00	15.00	0.60	10.00
12	120.00	5.00	1.00	10.00
13	120.00	25.00	0.20	2.00
14	70.00	15.00	0.60	6.00
15	120.00	5.00	0.20	10.00
16	20.00	5.00	1.00	10.00
17	120.00	25.00	1.00	10.00
18	20.00	5.00	0.20	2.00
19	20.00	25.00	0.20	10.00
20	20.00	25.00	1.00	2.00
21	70.00	15.00	1.00	6.00
22	120.00	25.00	1.00	2.00
23	20.00	25.00	0.20	2.00
24	70.00	15.00	0.60	6.00
25	70.00	15.00	0.20	6.00
26	70.00	25.00	0.60	6.00
27	70.00	15.00	0.60	6.00
28	20.00	5.00	1.00	2.00
29	120.00	5.00	0.20	2.00
30	70.00	15.00	0.60	6.00

Key*:* CT-Contact time (mins), C-Concentration (mg/L) and AD-Adsorbent dosage (g)

CHAPTER FOUR

RESULTS

4.1 Detection and Quantification of the Pharmaceutical Compounds in the Hospital Wastewater

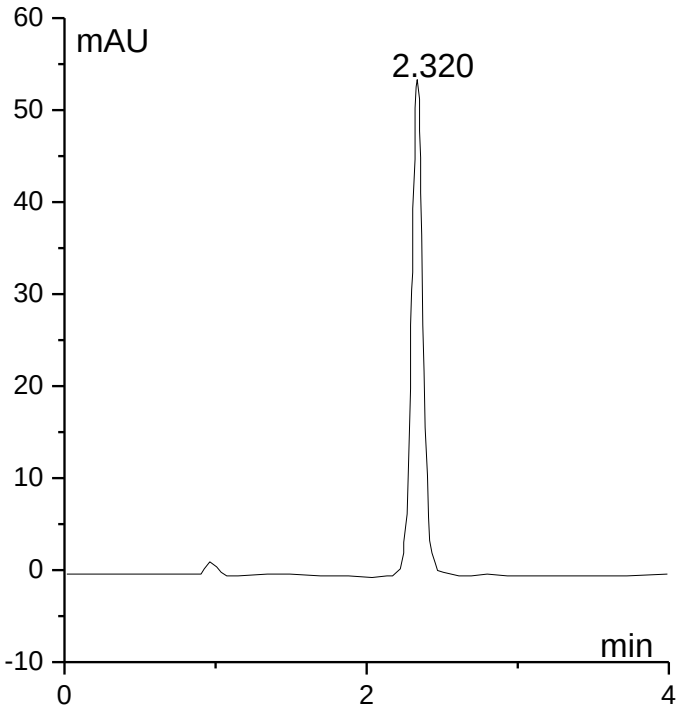
The high-performance liquid chromatography (HPLC) chromatograms of the pure standard acetaminophen, amoxicillin and ibuprofen and their detection in the hospital wastewater sample are shown in figures 4.1–4.6 respectively. Table 4.1 gives the concentration of the pharmaceutical compounds found in the hospital wastewater. The concentration was calculated using the calibration equation on the calibration plots of each compound. Acetaminophen was found to have a concentration of 34.31 µg/L; amoxicillin had a concentration of 8066 µg/L and ibuprofen had a concentration of 165.50 µg/L.

4.2 The Brunauer Emett Teller (BET) Surface Area and Pore Characterization of the prepared Activated Carbon

The BET surface area, pore-volume, pore diameter and coefficient of regression (r^2) of the *Jatropha* carbon activated with H_3PO_4 are presented in Table 4.2. The BET surface area (S_{BET}) was found to be 868 m^2g^{-1}, pore volume was observed to be 0.4866 cm^3g^{-1}, the pore diameter was found to be 2.128 nm and thecoefficient of regression (r^2) was 0.9960. The results were linearly regressed using the BET equation.

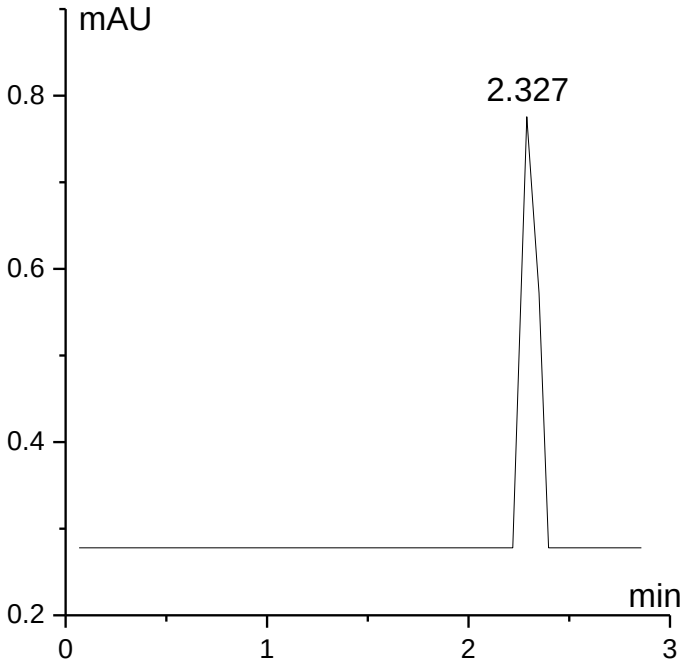
4.3 Scanning Electron Microscope (SEM)

The micrographs of the transverse section of the *Jatropha* activated carbons are presented in Plates 4.1 – 4.3.



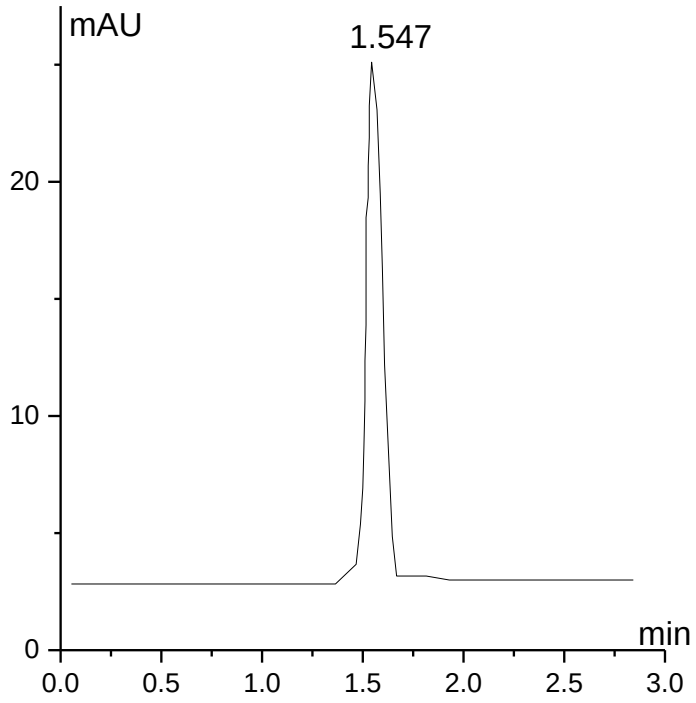
Key: mAU- milli Absorbance Units

Figure 4. 1: HPLC Chromatogram of Acetaminophen Standard



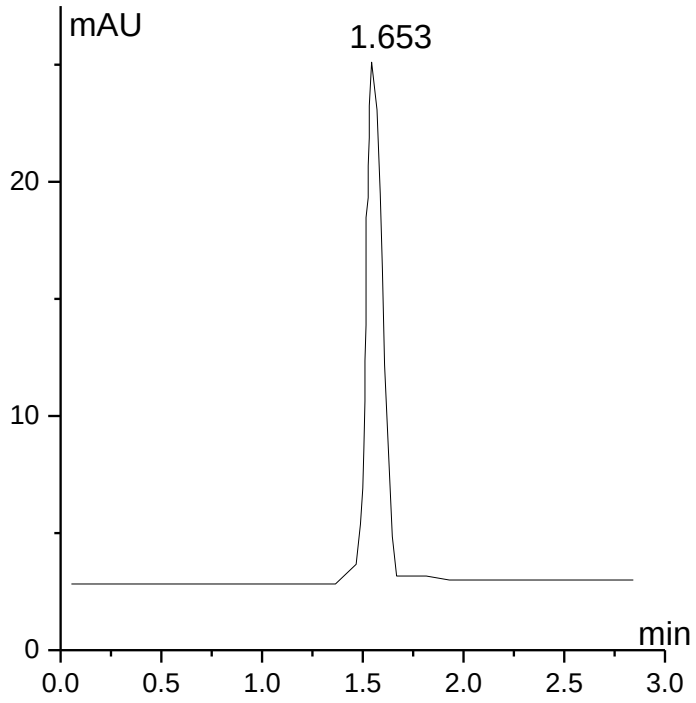
Key: mAU- milli Absorbance Units

Figure 4. 2: HPLC Chromatogram of Acetaminophen in the Wastewater



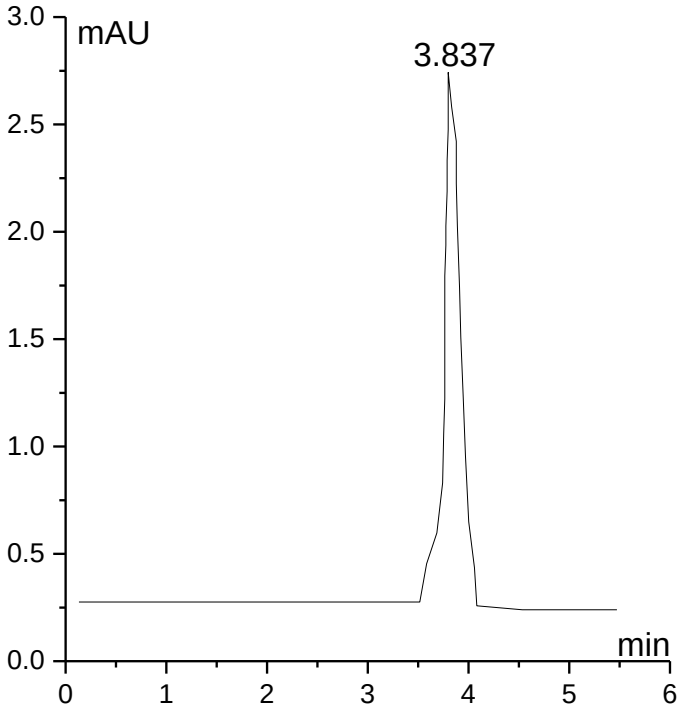
Key: mAU- milli Absorbance Units

Figure 4. 3: HPLC Chromatogram of Amoxicillin Standard



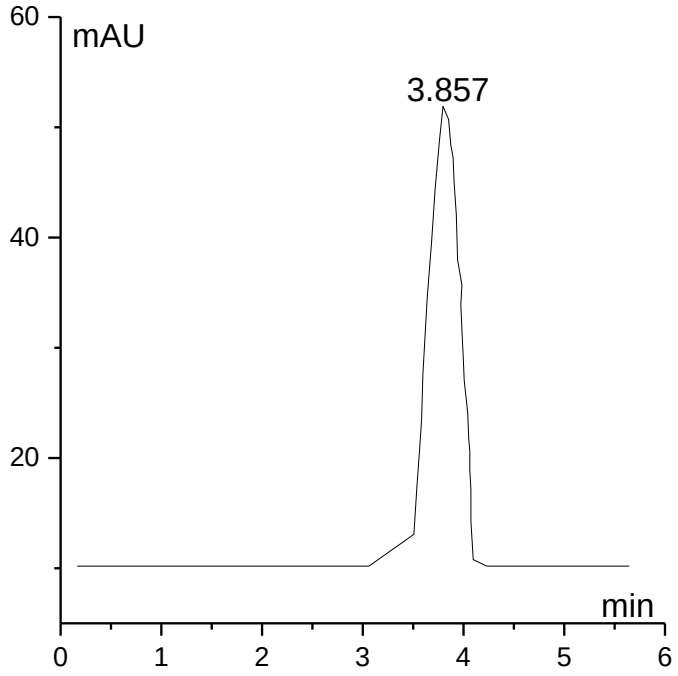
Key: mAU- milli Absorbance Units

Figure 4. 4: HPLC Chromatogram of Amoxicillin in the Wastewater



Key: mAU- milli Absorbance Units

Figure 4. 5: HPLC Chromatogram of Ibuprofen Standard



Key: mAU- milli Absorbance Units

Figure 4. 6: HPLC Chromatogram of Ibuprofen in the Wastewater

Table 4. 1: Pharmaceutical Compounds Identified in the Wastewater

Analyte	Concentration (µg/L)	Retention Time (min)	r^2
Acetaminophen	34.00±0.72	2.327	0.9997
Amoxicillin	8066.00±48.10	1.653	0.9939
Ibuprofen	165.50±2.12	3.857	0.9770

Table 4. 2: Textural Characteristics of the Prepared*Jatropha* Activated Carbon (JAC)

Parameter	Value
S_{BET}[a](m^2g^{-1})	868
Pore volume(cm^3g^{-1})	0.4866
Average pore diameter(nm)	2.128
R^2	0.9960

[a] *Specific surface area (multipoint BET method)*

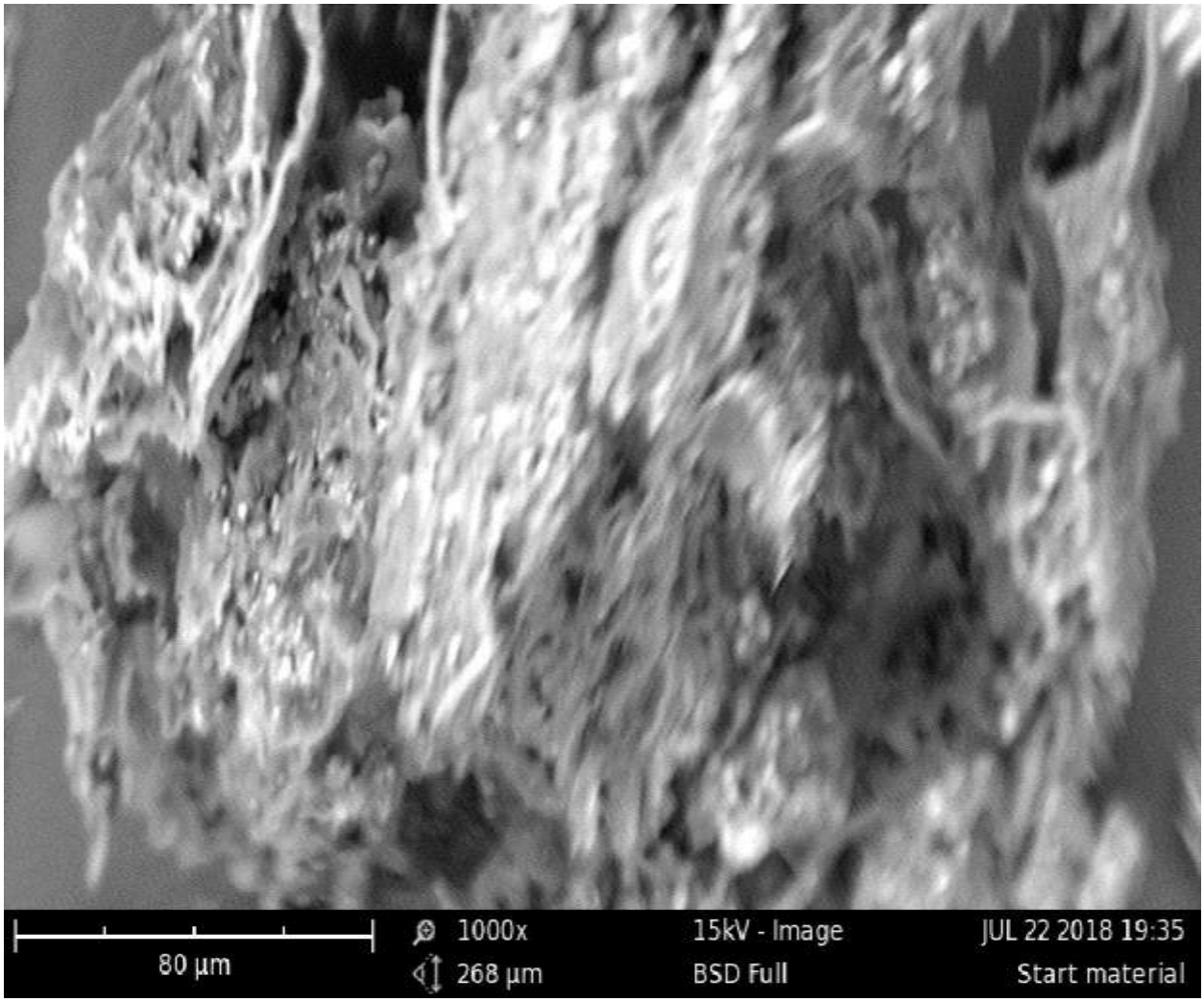


Plate 4. 1: SEM Micrograph of *Jatropha* Waste Cake

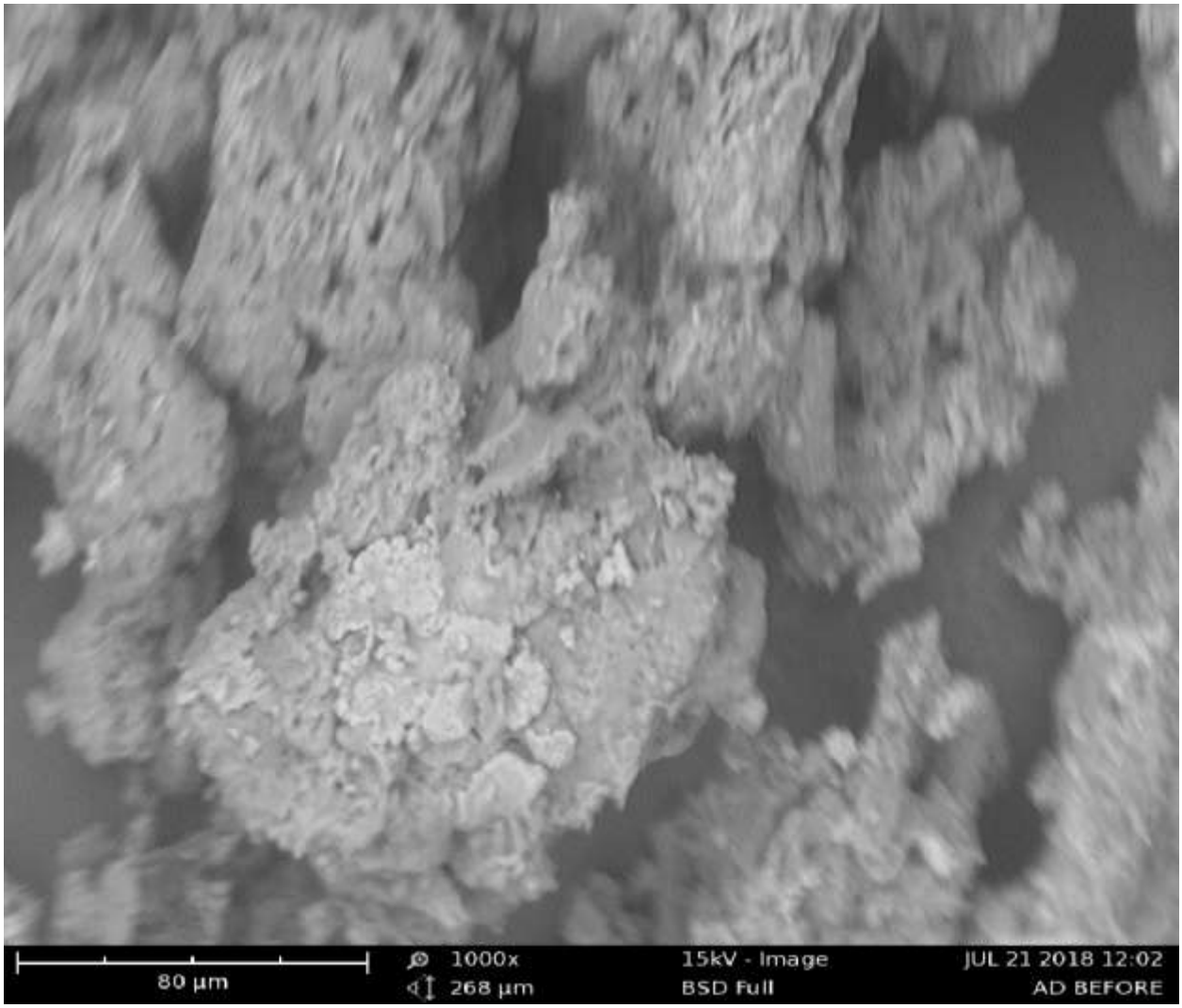


Plate 4. 2: SEM micrograph of prepared *Jatropha* activated carbon

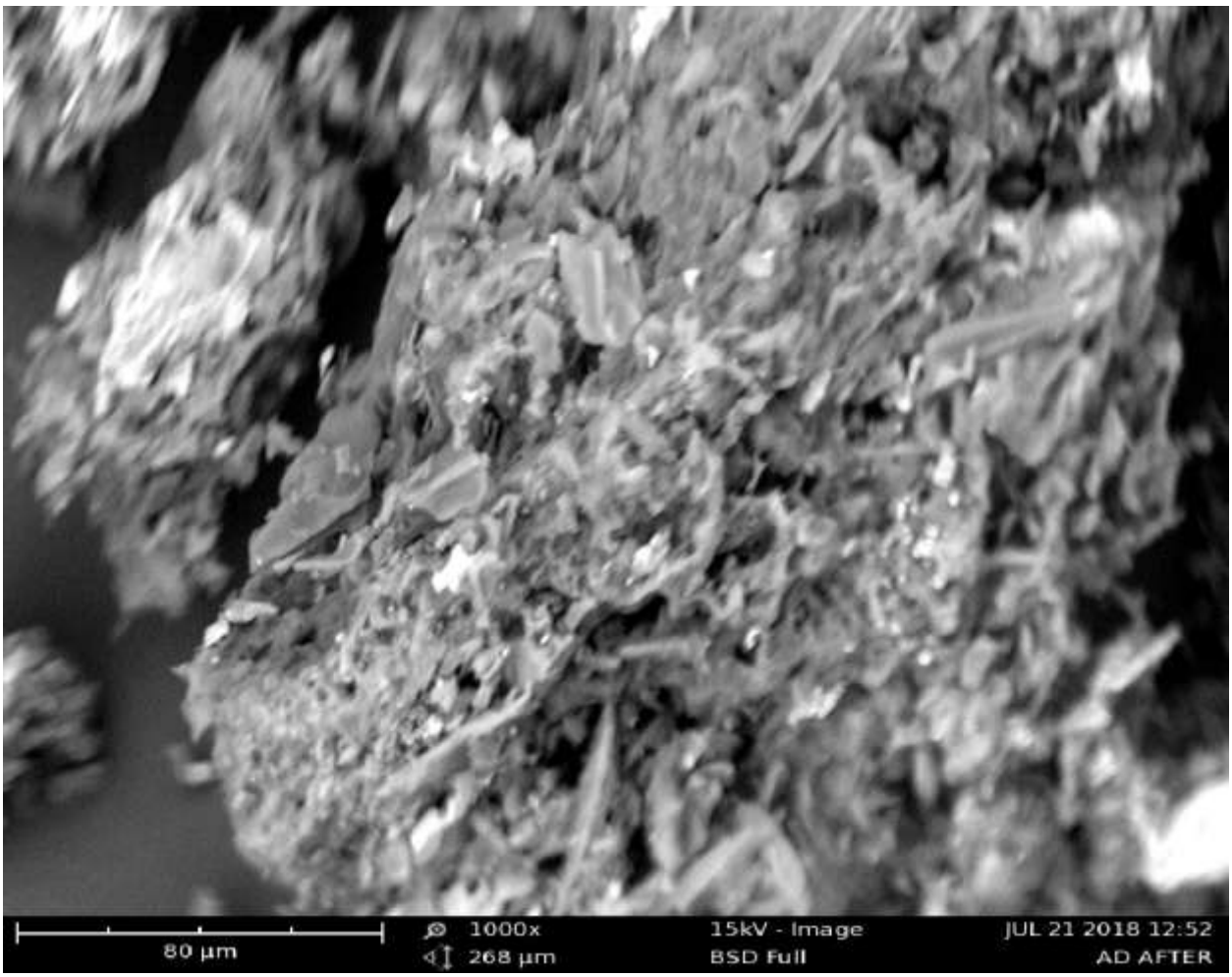


Plate 4. 3: SEM Micrograph of *Jatropha* Activated Carbon after Adsorption

4.4 Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra of the *Jatropha* cake and *Jatropha*activated carbons are shown in Figures 4.7 and 4.8 respectively. The major bands observed for the jatropha cake werebetween 3000 – 3300 cm^{-1}, 2800 – 2900 cm^{-1}, 1400 – 1700 cm^{-1} and 1000 -1300 cm^{-1} while that observed for the prepared activated carbon were at 3463 cm^{-1}, 2700-2100 cm^{-1}, 1625 cm^{-1}, 1208 cm^{-1}, 1080 cm^{-1} and less than 1000 cm^{-1}. The band frequencies and their assignments for the *Jatropha* cake and *Jatropha* activated carbon over the range of 1000 – 3500 cm^{-1} are presented in Tables 4.3 and 4.4.

4.5 Adsorption Studies

The design matrix incorporating the adsorption parameters and the responses which are the percentage removal of acetaminophen by commercial activated carbon (CAC) and *Jatropha* activated carbon (JAC) respectively are shown in Table 4.5. The removal percentage of acetaminophen ranged from 99.84 – 99.98 % with CAC and 99.28 – 99.98 % with JAC respectively.

The model summary statistics for the response using commercial activated carbon (CAC) is shown in Table 4.6. The statistical parameters obtained from the analysis of variance (ANOVA) are given in Table 4.7. The values of R^2 , adjusted R^2 ,predictedR^2, correlation of variance (C.V) and adequate precision were found to be 0.8800, 0.7680, 0.2423, 0.020 and 10.910 respectively.The final empirical model equation for the percentage removal of acetaminophen using commercial activated carbon (CAC) is given as equation 4.1 (CAC = 99.95 – 6.667E-003A + 0.041B – 1.667E-003C + 3.889E-003D + 0.014AB + 1.250E-003AC- 6.250E-003AD + 8.750E-003BC + 1.250E-003BD – 8.750E-003CD - 9.825E-003A^2+1.754E-004B^2 + 5.175E-003C^2 – 0.025D^2).

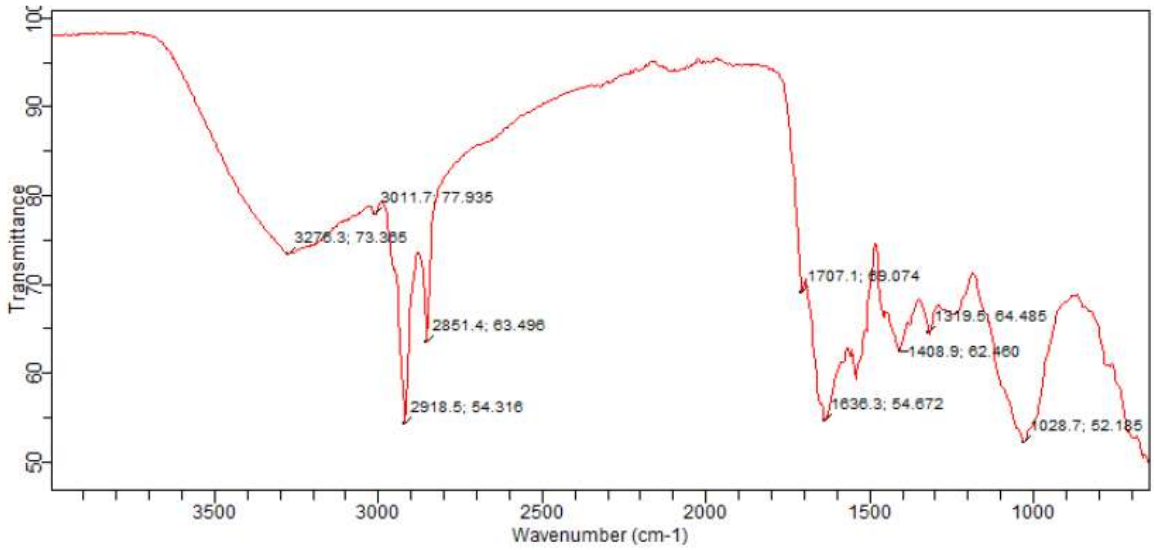


Figure 4.7: FTIR Spectrum of *Jatropha*Waste Cake

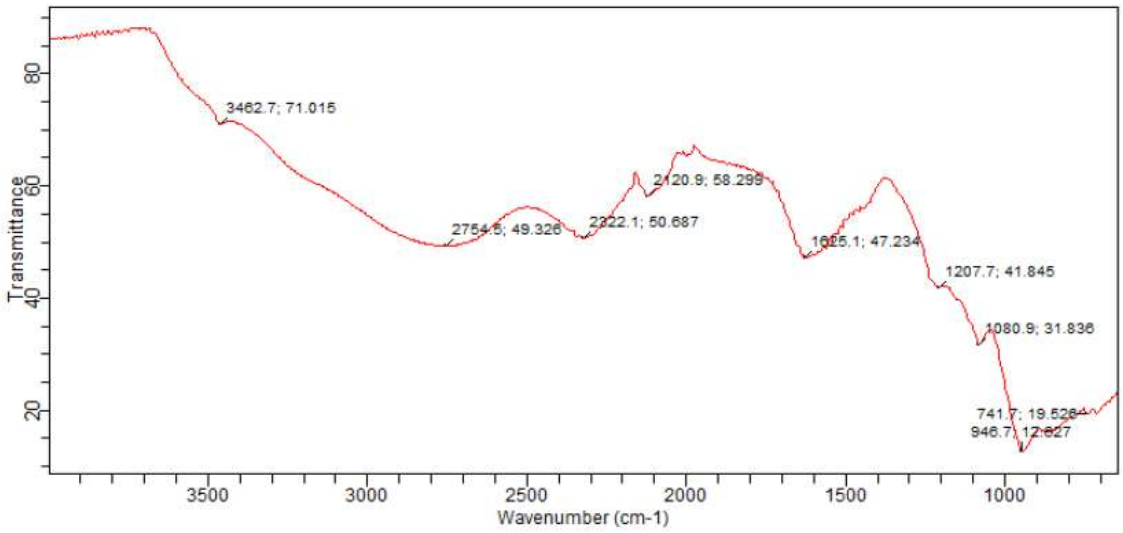


Figure 4.8: FTIR Spectrum of *Jatropha* Activated Carbon

Table 4. 3: FTIR Table of Assignment for the *Jatropha* Waste Cake

Wavenumber (cm^{-1})	Functional Group	Assignment
3276.3	O-H Stretch	Hydroxyl group
2918.5-2851.4	C=O	Carbonyl
1707.1	C=O Stretch	Carboxylic acids and esters
1636.3	C=O	Amide
1408.9-1319.5	C=O	Carboxylate group
1028.7	Si-O-Si	Organic siloxane

Table 4. 4: FTIR Table of Assignment for the *Jatropha* Activated Carbon

Frequency (cm^{-1})	Functional Group	Assignment
3462.7	O-H Stretch	Hydroxyl group
2754.5-2322.1	C=O	Carbonyl
2120.9	C≡C	Terminal alkyne
1625.1	C=O	Conjugated ketone
1207.7	P-O-C	Phosphates
1080.9	Si-O-C	Organic siloxane or silicone
946.7	PO_4^{3-}	Phosphates

The adequacy of the model was further estimated using the diagnostic plots as shown in figures 4.9 – 4.10.The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) are shown in three-dimensional response plots in figures 4.11-4.12.

Table 4.8 show the model summary statistics for the response using*Jatropha* activated carbon (JAC) while Table 4.9 gave the statistical parameters obtained from the analysis of variance (ANOVA). The values of R^2, adjusted R^2,predictedR^2, correlation of variance (C.V) and adequate precision were found to be 0.5887, 0.3722, -1.6867, 0.010 and 8.551 respectively.

The final empirical model equation for the percentage removal of acetaminophen using *Jatropha* activated carbon (JAC) is given in equation 4.2 (JAC = 99.92 + 0.026A + 0.064B + 0.032C + 0.033D – 0.040AB – 0.034AC – 0.042AD – 0.025BC – 0.049BD – 0.040CD).

The adequacy of the model was further estimated using the diagnostic plots as shown in Figures 4.13 – 4.14 while Figures 4.15-4.16 showed the effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) in three-dimensional response plots.

Figure 4.17 showed the ramp function graphs of the optimization of the adsorption of acetaminophen.

The design matrix incorporating the adsorption parameters and the responses which are the percentage removal of amoxicillin by commercial activated carbon (CAC) and *Jatropha* activated carbon (JAC) respectively are shown in Table 4.10. The removal percentage of amoxicillin ranged from 99.60 – 99.96 % with CAC and 99.50 – 99.96 % with JAC respectively.

Table 4. 5: Experimental matrix for Acetaminophen Adsorption

Run	Factor 1 A:CT	Factor 2 B:C	Factor 3 C:AD	Factor 4 D:pH	Response CAC (%)	Response JAC (%)
1	70.00	5.00	0.60	6.00	99.92	99.91
2	20.00	25.00	1.00	10.00	99.97	99.97
3	120.00	15.00	0.60	6.00	99.94	99.96
4	20.00	5.00	0.20	10.00	99.96	99.96
5	120.00	25.00	0.20	10.00	99.97	99.89
6	70.00	15.00	0.60	6.00	99.96	99.96
7	70.00	15.00	0.60	2.00	99.89	99.96
8	120.00	5.00	1.00	2.00	99.87	99.87
9	70.00	15.00	0.60	6.00	99.96	99.96
10	20.00	15.00	0.60	6.00	99.94	99.95
11	70.00	15.00	0.60	10.00	99.96	99.96
12	120.00	5.00	1.00	10.00	99.84	99.89
13	120.00	25.00	0.20	2.00	99.97	99.97
14	70.00	15.00	0.60	6.00	99.96	99.96
15	120.00	5.00	0.20	10.00	99.86	99.92
16	20.00	5.00	1.00	10.00	99.87	99.88
17	120.00	25.00	1.00	10.00	99.98	99.97
18	20.00	5.00	0.20	2.00	99.88	99.28
19	20.00	25.00	0.20	10.00	99.96	99.97
20	20.00	25.00	1.00	2.00	99.97	99.98
21	70.00	15.00	1.00	6.00	99.96	99.96
22	120.00	25.00	1.00	2.00	99.98	99.97
23	20.00	25.00	0.20	2.00	99.95	99.97
24	70.00	15.00	0.60	6.00	99.96	99.96
25	70.00	15.00	0.20	6.00	99.95	99.97
26	70.00	25.00	0.60	6.00	99.98	99.98
27	70.00	15.00	0.60	6.00	99.96	99.96
28	20.00	5.00	1.00	2.00	99.91	99.91
29	120.00	5.00	0.20	2.00	99.88	99.90
30	70.00	15.00	0.60	6.00	99.96	99.96

The model summary statistics for the response using commercial activated carbon (CAC)are shown in Table 4.11. The statistical parameters obtained from the analysis of variance (ANOVA) are given in Table 4.12. The values of R^2, adjusted R^2,predictedR^2, correlation of variance (C.V) and adequate precision were found to be 0.6627, 0.4851, -1.2015, 0.18 and 9.932 respectively.

The final empirical model equation for the percentage removal of amoxicillin using commercial activated carbon (CAC) is given in equation 4.3 (CAC =99.78 - 0.065A + 0.17B - 0.072C + 0.047D + 0.065AB - 0.045AC + 0.086AD + 0.091BC -0.032BD + 0.078CD).

The adequacy of the model was further estimated using the diagnostic plots as shown in Figures 4.18 – 4.19. The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) are shown in three-dimensional response plots in Figures 4.20-4.21.

The modelsummary statistics for the response using *Jatropha* activated carbon (JAC) are shown in Table 4.13 and the statistical parameters obtained from theanalysis of variance (ANOVA) were given in Table 4.14. The values of R^2, adjusted R^2,predictedR^2, correlation of variance (C.V) and adequate precision were found to be 0.9538, 0.9106, 0.6804, 0.038 and 16.340 respectively.

The final empirical model equation for the percentage removal of amoxicillin using *Jatropha* activated carbon (JAC) is given as equation 4.4 (JAC = 99.90 – 0.012A + 0.12B – 0.051C + 0.020D + 0.039AB + 0.023AC + 0.015AD + 0.028BC – 0.017BD – 1.250E-003CD + 0.010A^2 0.075B^2– 0.045C^2 – 9.649E-003D^2).

The adequacy of the model was further estimated using the diagnostic plots as shown in Figures 4.22 – 4.23 while Figures 4.24 - 4.25 present the effect of the interractions of the

adsorption factors (contact time, concentration, adsorbent dosage and pH) in three-dimensional response plots.

The ramp function graphs of the optimization of the adsorption of amoxicillin are presented in Figure 4.26.

Table 4.15 presents the design matrix incorporating the adsorption parameters and the responses which are the percentage removal of ibuprofen by commercial activated carbon (CAC) and *Jatropha* activated carbon (JAC) respectively. The removal percentage of ibuprofen ranged from 99.14–99.99 % with CAC and 99.34–99.99 % with JAC.

Tables 4.16 present the model summary statistics for the response using commercial activated carbon (CAC). The statistical parameters analysis of variance (ANOVA) is given in Table 4.17. The values of R^2 , adjusted R^2 ,predictedR^2, and correlation of variance (C.V) were found to be 0.5867, 0.3691, -1.5200, and 0.34 respectively. The final empirical model equation for the percentage removal of ibuprofen using commercial activated carbon (CAC) is given as equation 4.5(CAC = 99.71 + 0.036A + 0.30B - 0.13C - 0.11D - 0.029AB - 0.095AC - 0.16AD + 0.10BC + 0.085 BD + 0.11CD).

The adequacy of the model is illustrated using the diagnostic plots as shown in Figures 4.27 – 4.28. The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) are shown in three-dimensional response plots in Figure 4.29 - 4.30.

The model summary statistics for the response using *Jatropha* activated carbon (JAC) are shown in Table 4.18. The statistical parameters obtained from the analysis of variance (ANOVA) is given in Table 19. The values of R^2, adjusted R^2,predictedR^2, and correlation of variance (C.V) were found to be 0.5993, 0.3884, -1.3820, and 0.28 respectively.

Table 4.6: Model Summary Statistics (CAC)

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	0.027	0.6361	0.5779	0.4329	0.028	
2FI	0.025	0.7602	0.6339	0.0793	0.046	
Quadratic	0.020	0.8800	0.7680	0.2423	0.038	Suggested
Cubic	0.012	0.9800	0.9170	-3.0005	0.20	Aliased

Table 4.7: Statistical Parameters Obtained from Analysis of Variance of the Models for Acetaminophen Adsorption Using CAC

Parameter	CAC (%)
Standard deviation (S.D)	0.020
Mean	99.94
Coefficient of variance (C.V)%	0.020
PRESS	0.038
R^2	0.8800
Adjusted R^2	0.7680
Predicted R^2	0.2423
Adequate Precision	10.910

$$CAC = 99.95 - 6.667E\text{-}003A + 0.041B - 1.667E\text{-}003C + 3.889E\text{-}003D + 0.014AB + 1.250E\text{-}003AC - 6.250E\text{-}003AD + 8.750E\text{-}003BC + 1.250E\text{-}003BD - 8.750E\text{-}003CD - 9.825E\text{-}003A^2 + 1.754E\text{-}004B^2 + 5.175E\text{-}003C^2 - 0.025D^2 \quad 4.1$$

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interaction effects of the factors. A^2, B^2, C^2, and D^2 are the square effects of the factors.

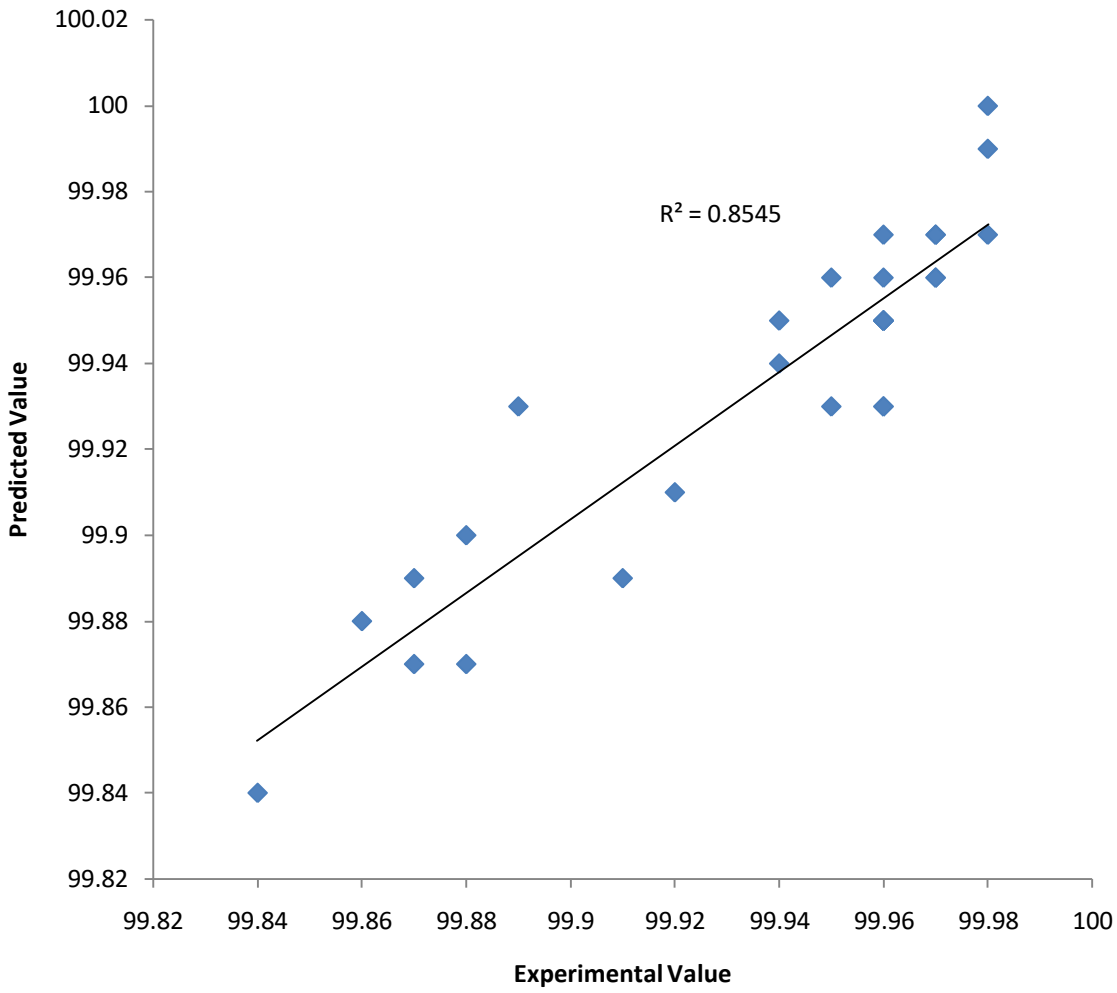


Figure 4.9: Diagnostic Plot of the RelationshipBetween Predicted and Experimental (Actual) Data for Acetaminophen Adsorption Using Commercial Activated Carbon (CAC)

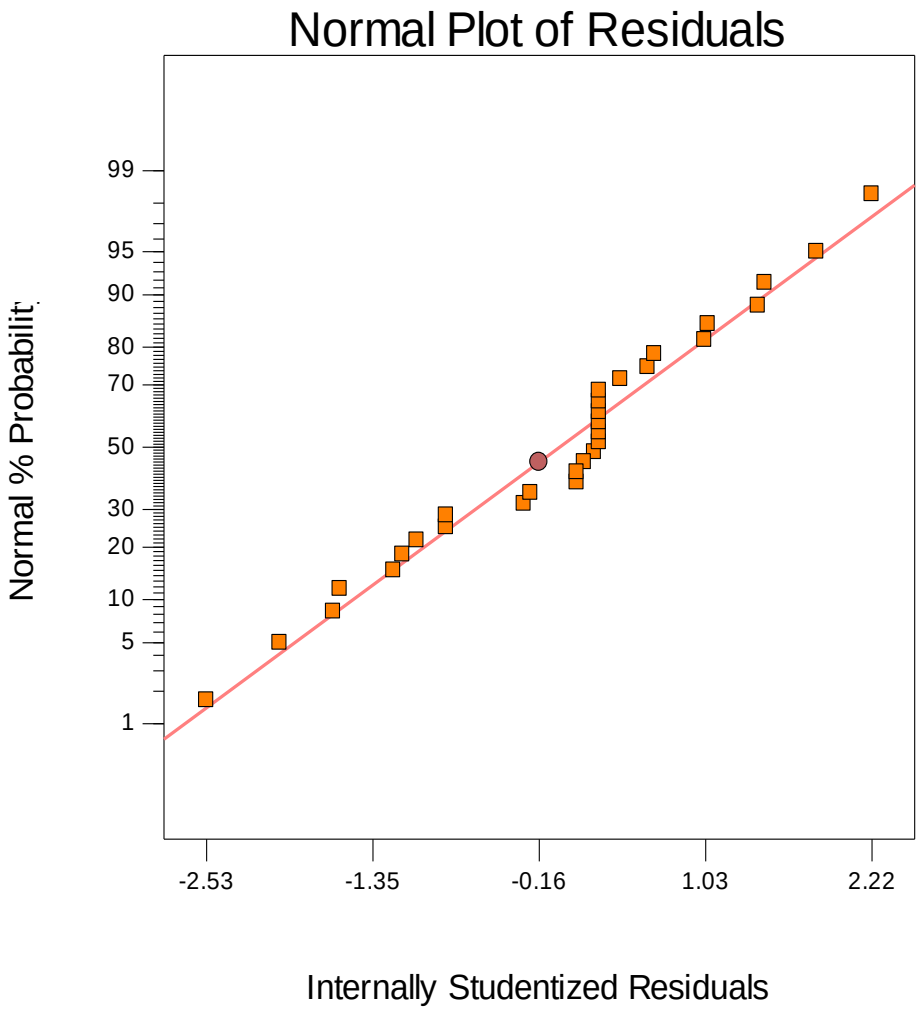


Figure 4.10:Diagnostic Plot of the Relationship Between Studentized Residuals and Normal Percentage Probability for Acetaminophen Adsorption Using Commercial Activated Carbon (CAC)

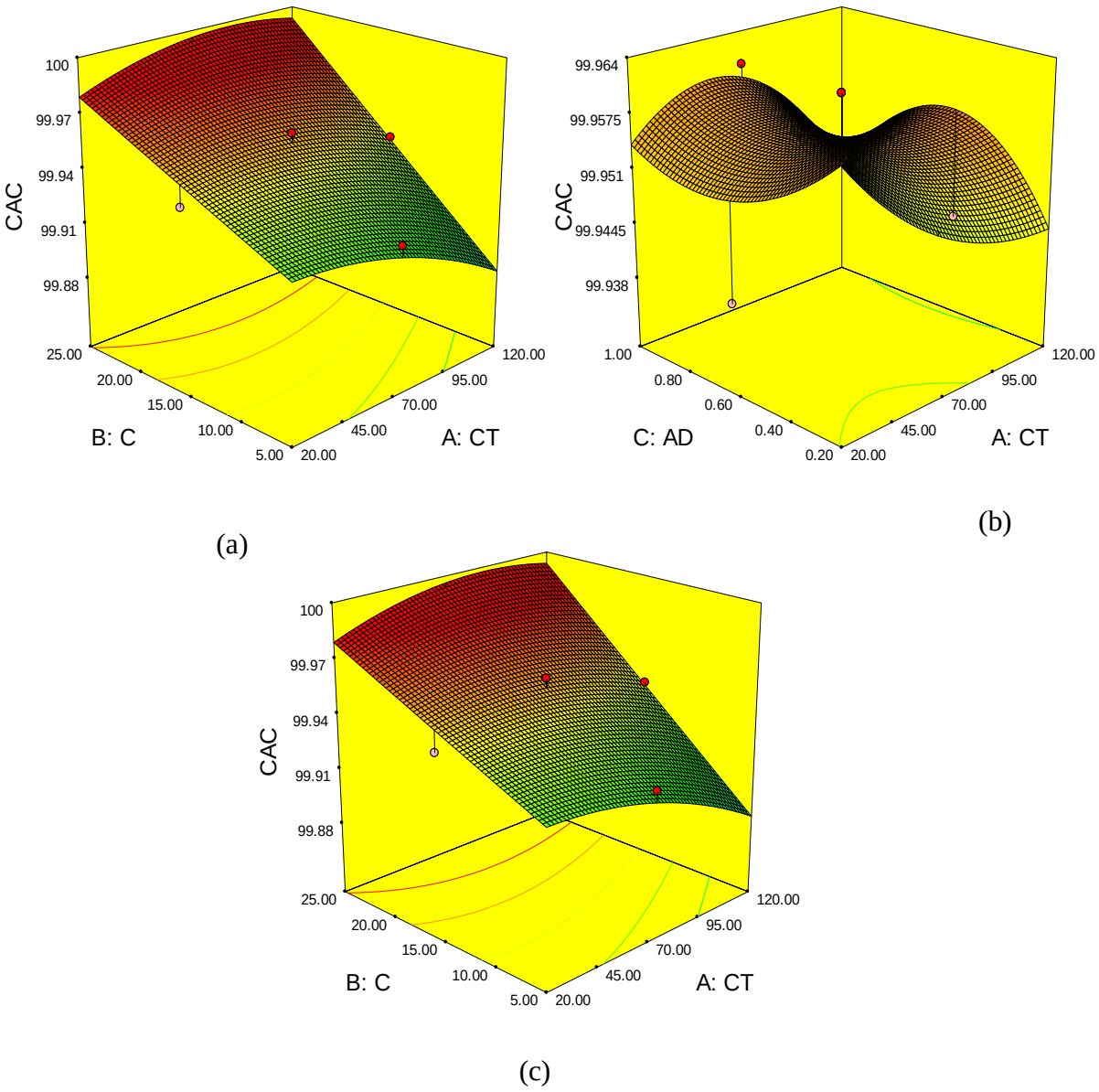


Figure 4.11: Response Surface Plot of the Effectsof (a) Concentration(mg/L) and Contact Time (min), (b) Adsorbent Dosage(g) and Contact Time (min) and (c) pH and Contact Time (min) on Acetaminophen Adsorption Using Commercial Activated Carbon (CAC)

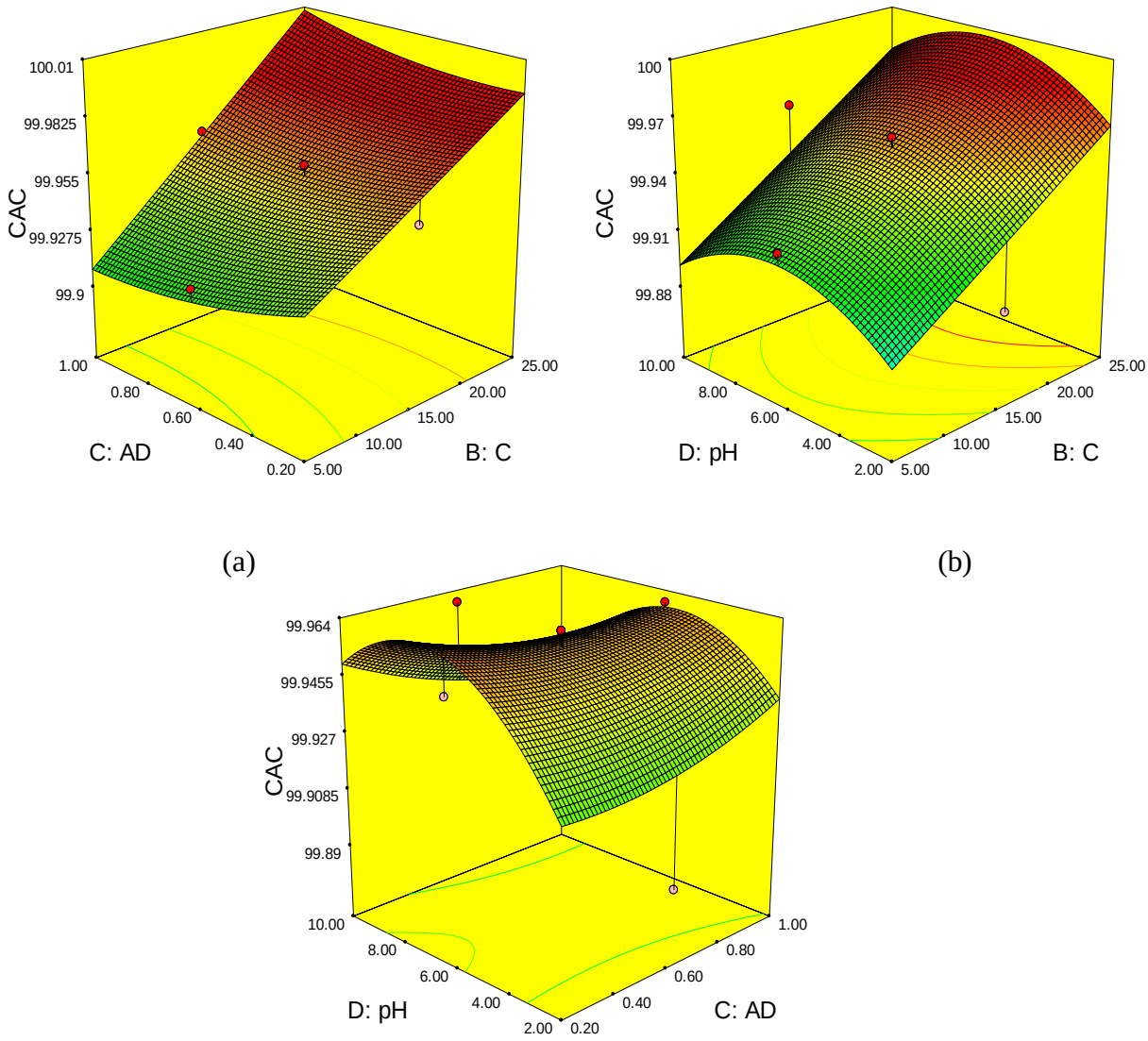


Figure 4.12: Response Surface Plot for the Effects (a) of Adsorbent Dosage (g) and Concentration (mg/l), (b)pH and Concentration (mg/l) and (c) pH and Adsorbent Dosage (g) on Acetaminophen Adsorption Using Commercial Activated Carbon (CAC)

Table 4.8:Model Summary Statistics (JAC)

Source	Std.Dev	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.12	0.2698	0.1529	-0.2835	0.59	
2FI	0.100	0.5887	0.3722	-1.6867	1.23	Suggested
Quadratic	0.10	0.6550	0.3330	-1.8729	1.32	
Cubic	0.059	0.9460	0.7764	-12.1354	6.03	Aliased

Table 4.9:Statistical Parameters Obtained from Analysis Of Variance of the Model for Acetaminophen Adsorption Using JAC

Parameter	JAC (%)
Standard deviation (SD)	0.010
Mean	99.92
Correlation of variance (C.V)%	0.010
PRESS	1.23
R^2	0.5887
Adjusted R^2	0.3722
Predicted R^2	-1.6867
Adequate Precision	8.551

$$JAC = 99.92 + 0.026A + 0.064B + 0.032C + 0.033D - 0.040AB - 0.034AC - 0.042AD - 0.025BC - 0.049BD - 0.040CD \quad 4.2$$

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors.

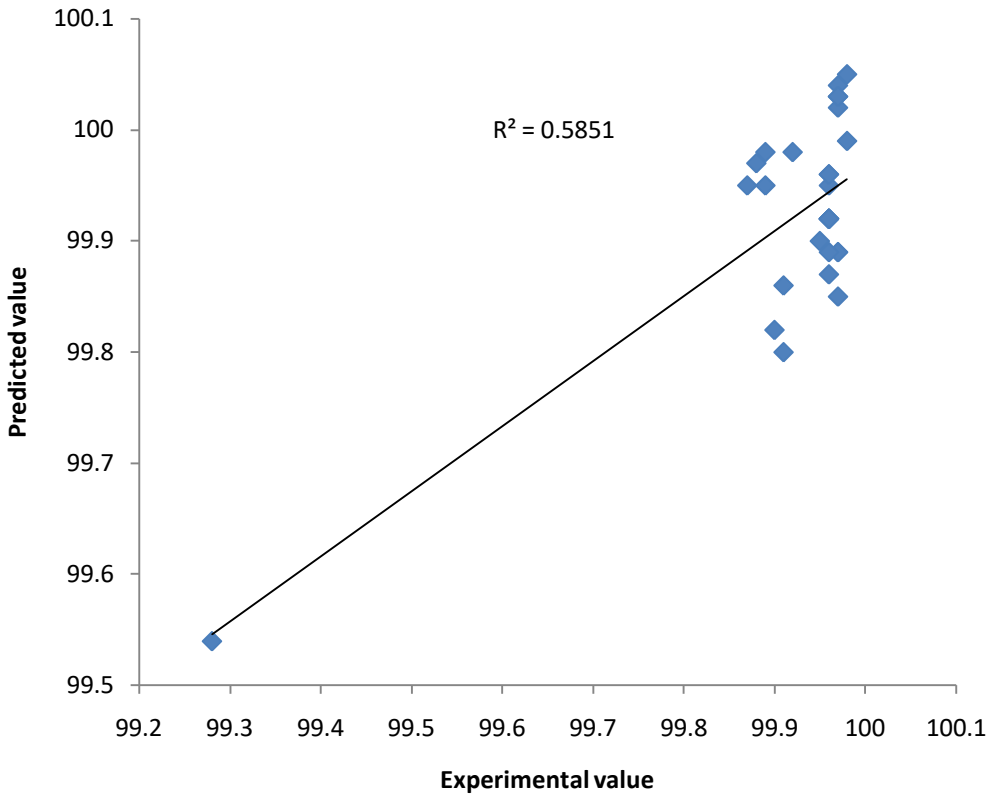


Figure 4.13:Diagnostic Plot of theRelationship Between Predicted and Experimental (Actual) Data of Acetaminophen Adsorption Using *Jatropha* Activated Carbon (JAC)

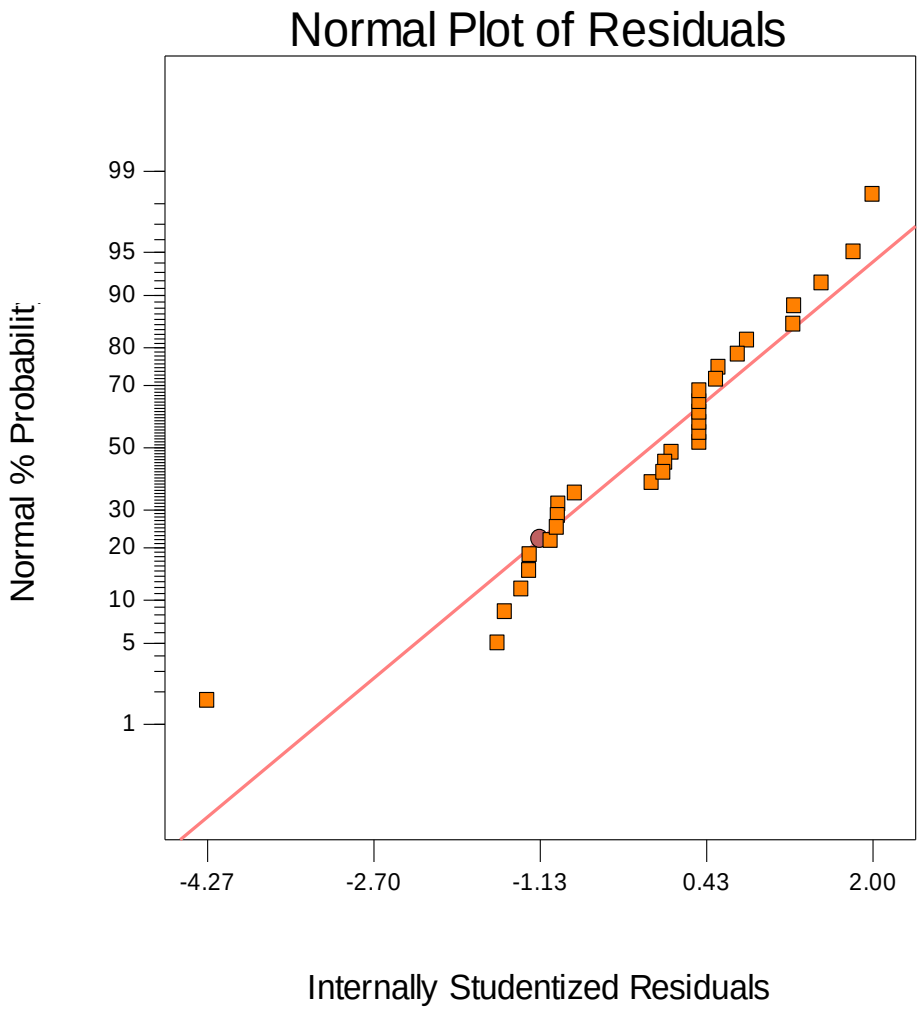


Figure 4.14:Diagnostic Plot of the Relationship Between Studentized Residuals and Normal Percentage Probability of Acetaminophen Adsorption Using *Jatropha* Activated Carbon (JAC)

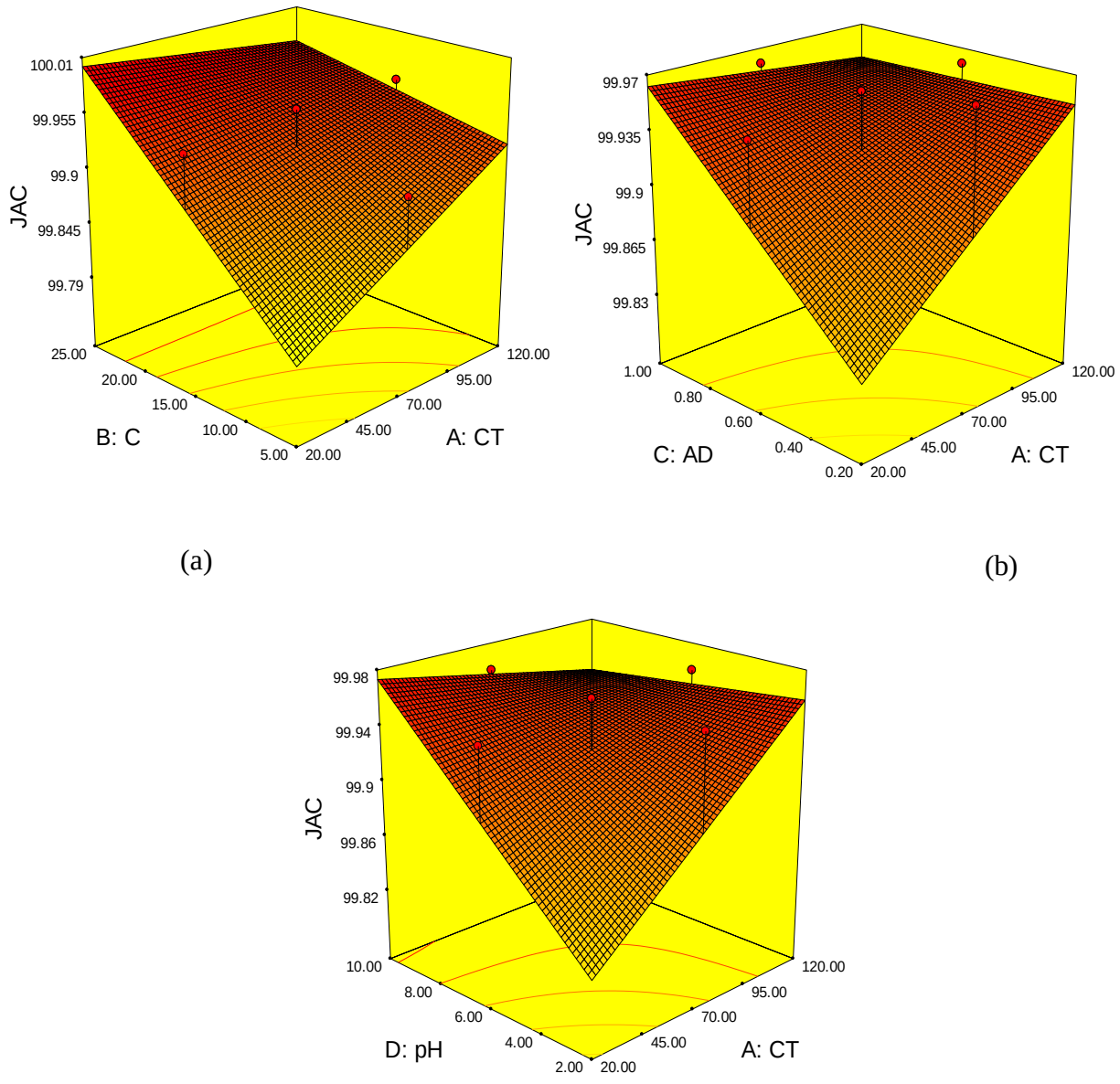


Figure 4.15:Response Surface Plot of the Effects of (a)Concentration(mg/l) and Contact Time (min), (b)Adsorbent Dosage (g) and Contact Time (min) and (c) pH and Contact Time (min) on Acetaminophen Adsorption Using *Jatropha* Activated Carbon (JAC)

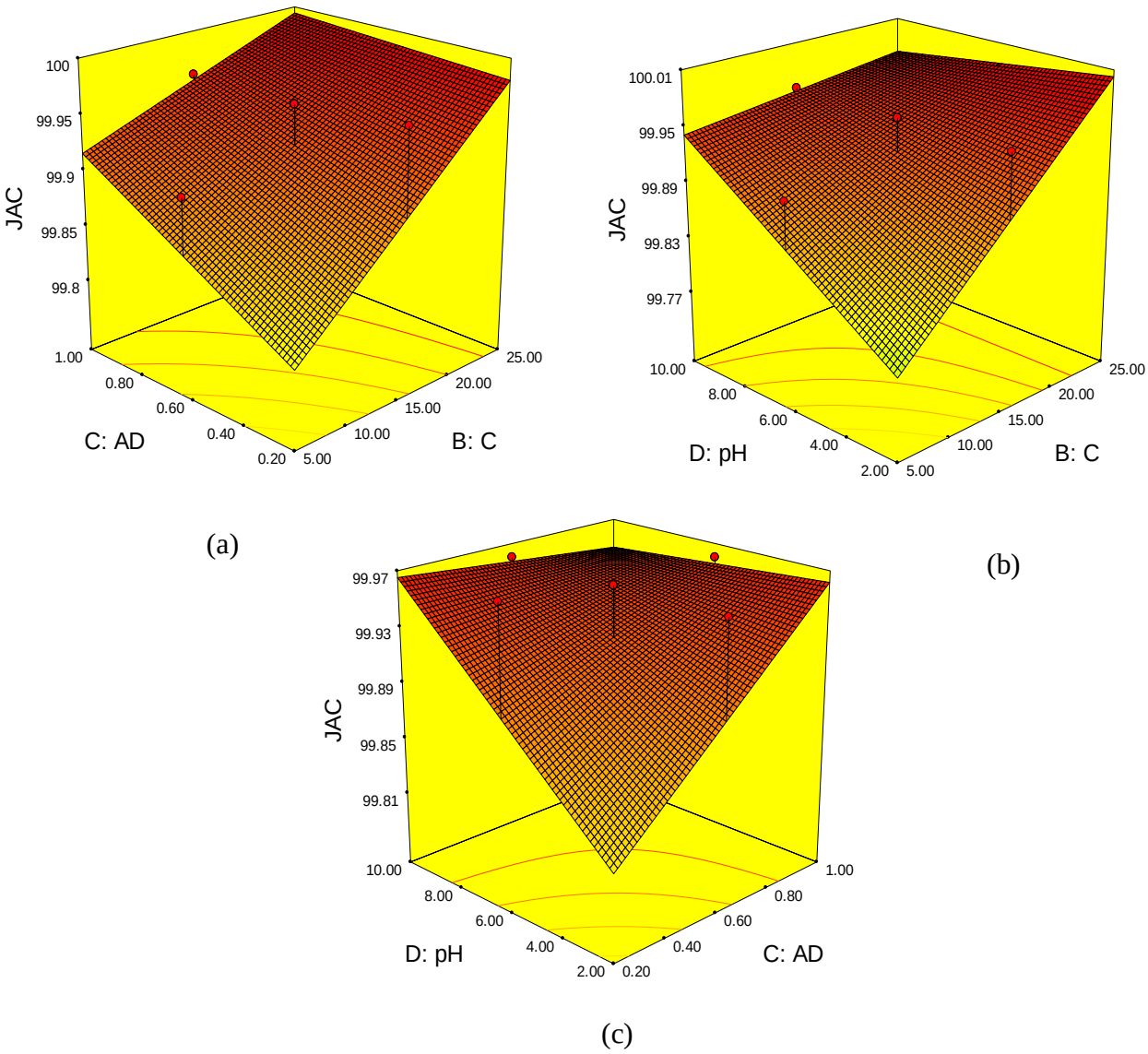


Figure 4.16:ResponseSurface Plot of the Effectsof (a) Adsorbent Dosage (g) and Concentration (mg/L), (b)pH and Concentration (mg/L) and (c)pH and Adsorbent Dosage (g) on Acetaminophen Adsorption Using *Jatropha*Activated Carbon (JAC)

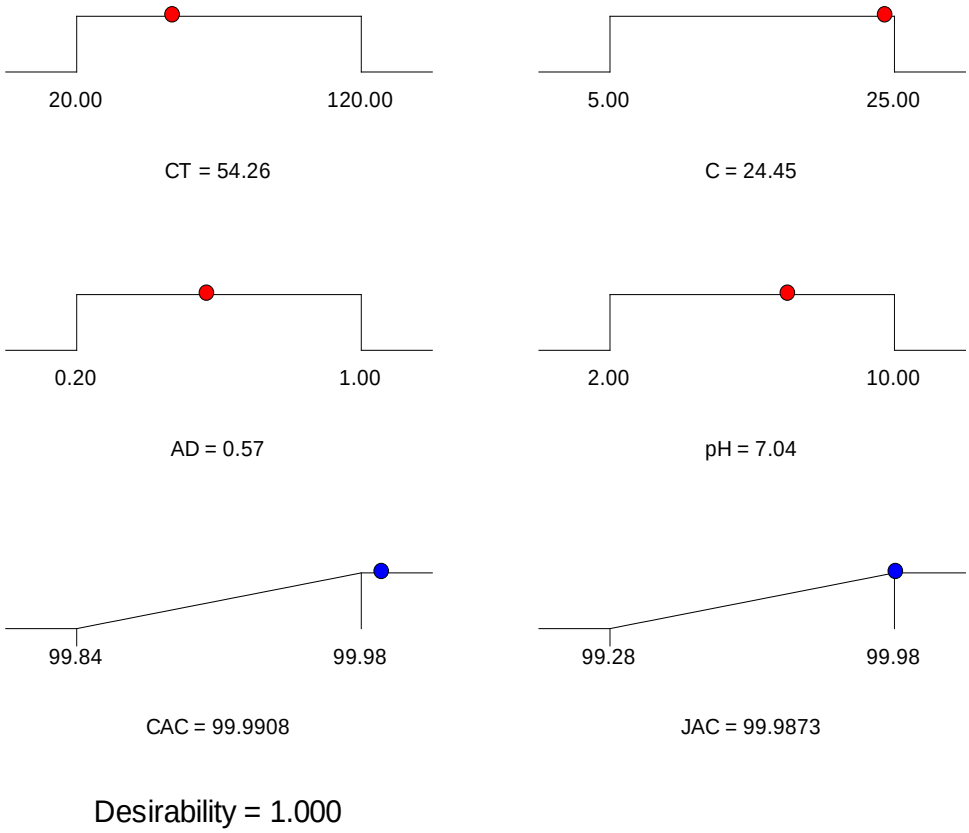


Figure 4.17: Ramp Function Graphs of the Optimization of the Adsorption of Acetaminophen

Table 4.10: Experimental matrix for Amoxicillin Adsorption

Run	Factor 1 A: CT	Factor 2 B: C	Factor 3 C: AD	Factor 4 D: pH	Response CAC (%)	Response JAC (%)
1	70.00	5.00	0.60	6.00	99.64	99.74
2	20.00	25.00	1.00	10.00	99.93	99.79
3	120.00	15.00	0.60	6.00	99.88	99.92
4	20.00	5.00	0.20	10.00	99.69	99.80
5	120.00	25.00	0.20	10.00	99.94	99.96
6	70.00	15.00	0.60	6.00	99.82	99.90
7	70.00	15.00	0.60	2.00	99.69	99.86
8	120.00	5.00	1.00	2.00	98.60	99.50
9	70.00	15.00	0.60	6.00	99.82	99.90
10	20.00	15.00	0.60	6.00	99.91	99.90
11	70.00	15.00	0.60	10.00	99.92	99.92
12	120.00	5.00	1.00	10.00	99.76	99.60
13	120.00	25.00	0.20	2.00	99.88	99.92
14	70.00	15.00	0.60	6.00	99.82	99.90
15	120.00	5.00	0.20	10.00	99.58	99.72
16	20.00	5.00	1.00	10.00	99.52	99.66
17	120.00	25.00	1.00	10.00	99.90	99.92
18	20.00	5.00	0.20	2.00	99.90	99.85
19	20.00	25.00	0.20	10.00	99.92	99.95
20	20.00	25.00	1.00	2.00	99.96	99.88
21	70.00	15.00	1.00	6.00	99.85	99.85
22	120.00	25.00	1.00	2.00	99.92	99.91
23	20.00	25.00	0.20	2.00	99.88	99.90
24	70.00	15.00	0.60	6.00	99.82	99.90
25	70.00	15.00	0.20	6.00	99.86	99.86
26	70.00	25.00	0.60	6.00	99.87	99.91
27	70.00	15.00	0.60	6.00	99.82	99.90
28	20.00	5.00	1.00	2.00	99.70	99.54
29	120.00	5.00	0.20	2.00	99.78	99.60
30	70.00	15.00	0.60	6.00	99.82	99.90

Table 4.11:Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.21	0.4023	0.3066	-0.0515	1.88	
2FI	0.18	0.6627	0.4851	-1.2015	3.93	Suggested
Quadratic	0.19	0.7021	0.4241	-1.4678	4.41	
Cubic	0.13	0.9353	0.7321	-14.7517	28.14	Aliased

Table 4.12: Statistical Parameters Obtained from Analysis of Variance for the Model for Amoxicillin Adsorption Using CAC

Parameter	CAC (%)
Standard deviation (SD)	0.18
Mean	99.78
Correlation of variance (C.V)%	0.18
PRESS	3.93
R^2	0.6627
Adjusted R^2	0.4851
Predicted R^2	-1.2015
Adequate Precision	9.932

$$CAC = 99.78 - 0.065A + 0.17B - 0.072C + 0.047D + 0.065AB - 0.045AC + 0.086AD + 0.091BC - 0.032BD + 0.078CD \quad (4.3)$$

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interaction effects of the factors.

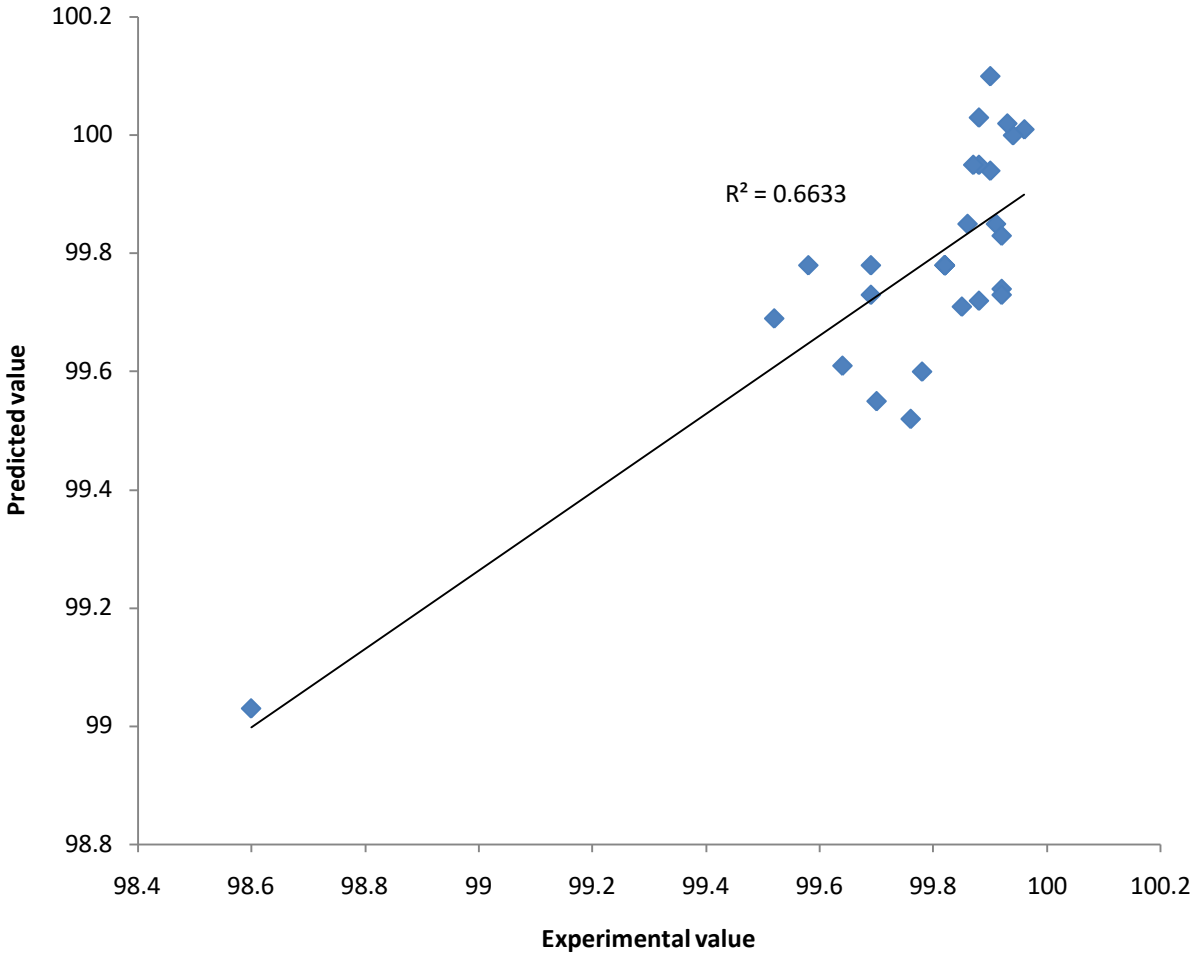


Figure 4.18:Diagnostic Plot of the Relationship Between Predicted and Experimental (actual) Data for Amoxicillin Adsorption Using Commercial Activated Carbon (CAC)

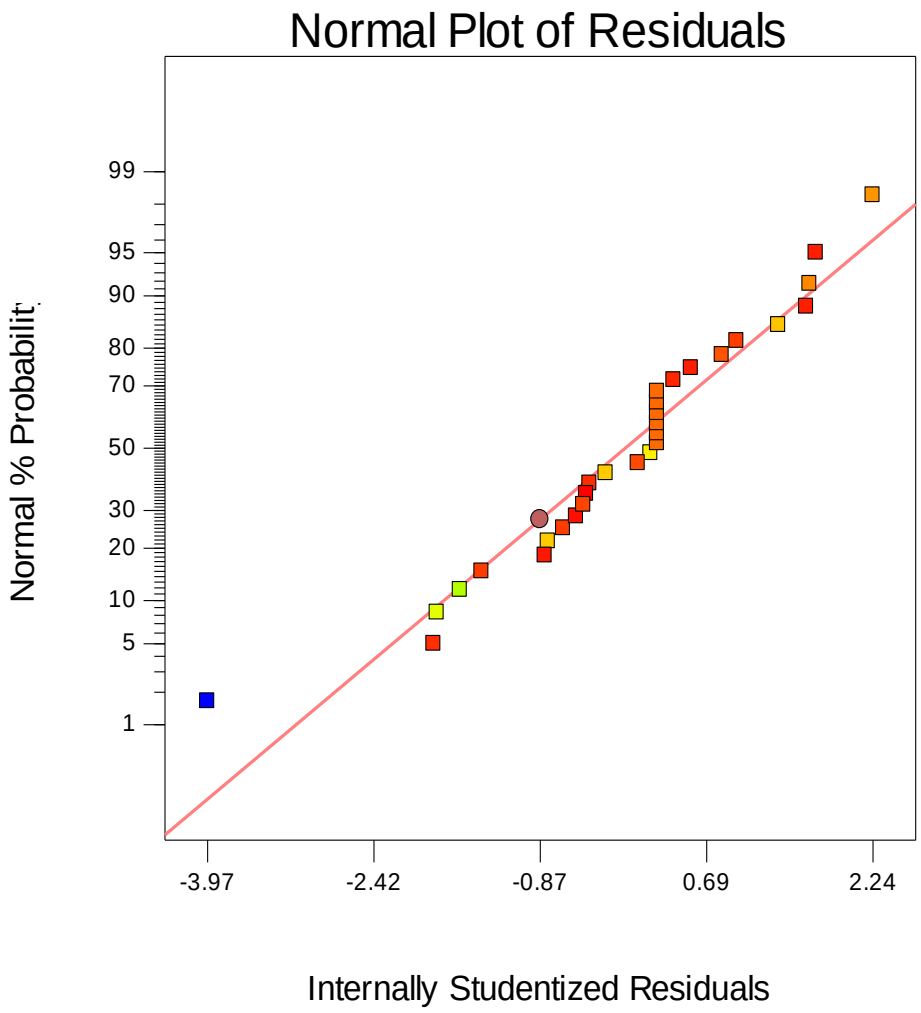


Figure 4.19:Diagnostic Plot of the Relationship between Studentized Residuals and Normal Percentage Probability for Amoxicillin Adsorption Using Commercial Activated Carbon (CAC)

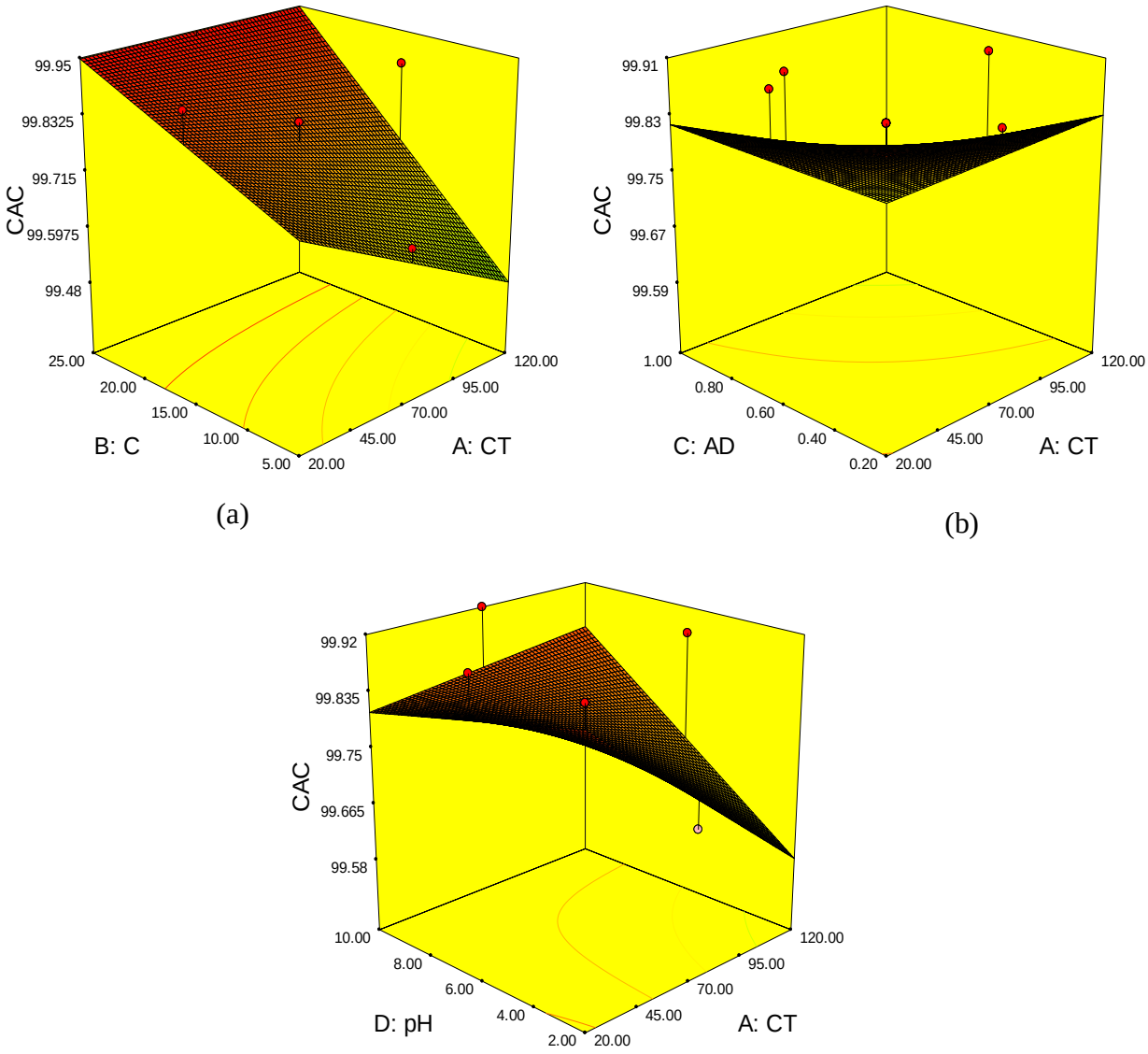


Figure 4.20:Response Surface Plot of the Effectsof (a) Concentration (mg/L) and Contact Time (min),(b)Adsorbent Dosage (g) and Contact Time (minutes) and (c) pH and Contact Time (minutes) on Amoxicillin Adsorption Using Commercial Activated Carbon (CAC)

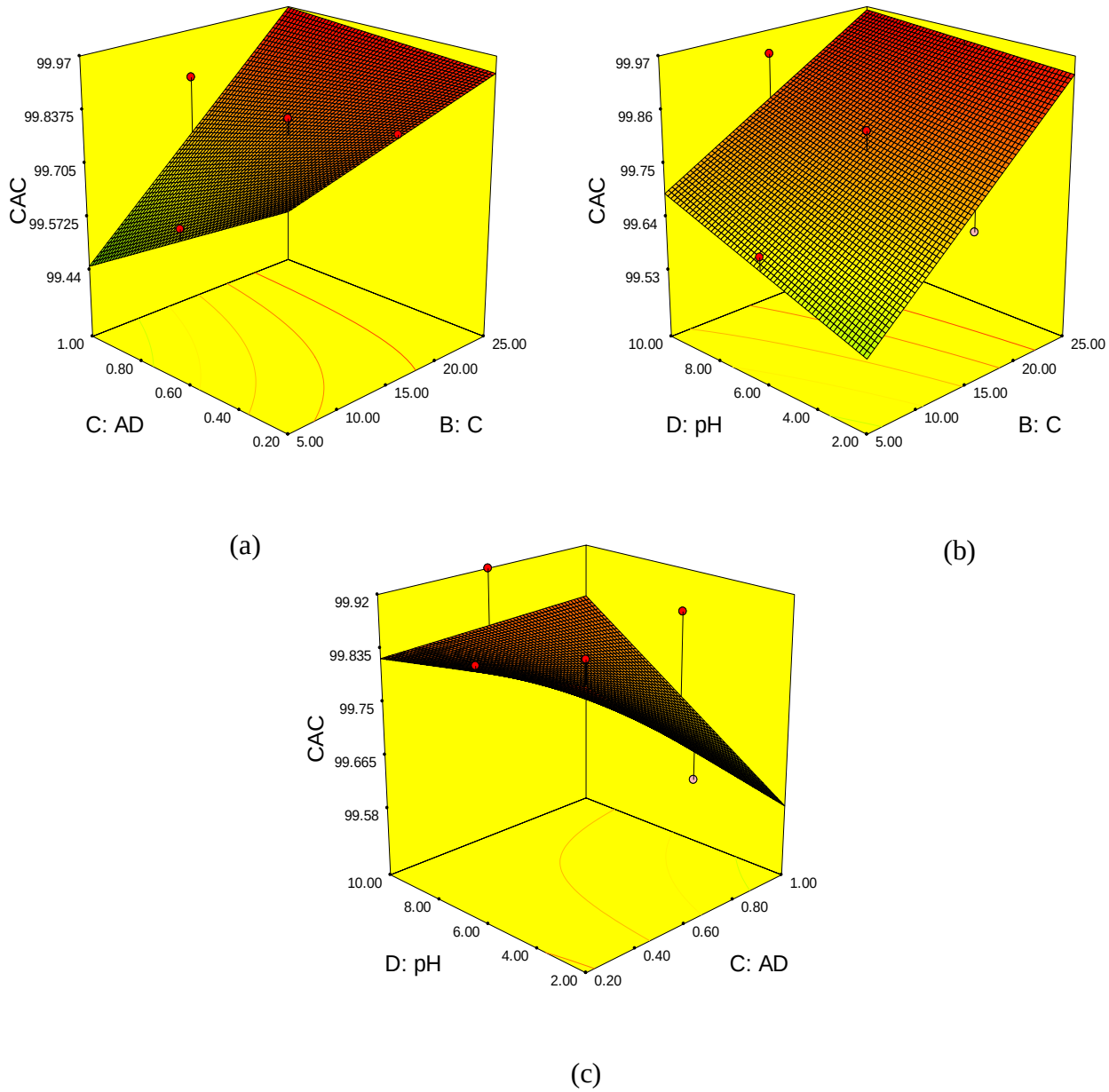


Figure 4.21:Response Surface Plot of the Effectsof (a) Adsorbent Dosage (g) and Concentration (mg/l),(b)pH and Concentration (mg/l) and (c) pH and Adsorbent Dosage (g) on Amoxicillin Adsorption Using Commercial Activated Carbon (CAC)

Table 4.13:Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.081	0.6536	0.5982	0.4604	0.25	
2FI	0.076	0.7656	0.6422	0.0741	0.44	
Quadratic	0.038	0.9538	0.9106	0.6804	0.15	Suggested
Cubic	0.028	0.9881	0.9505	-1.9520	1.39	Aliased

Table 4.14:Statistical Parameters Obtained from Analysis of Variance for the Model for Amoxicillin Adsorption UsingJAC

Parameter	JAC (%)
Standard deviation (SD)	0.038
Mean	99.83
Correlation of variance (CV) %	0.038
PRESS	0.15
R^2	0.9538
Adjusted R^2	0.9106
Predicted R^2	0.6804
Adequate Precision	16.340

$$JAC = 99.90 - 0.012A + 0.12B - 0.051C + 0.020D + 0.039AB + 0.023AC + 0.015AD + 0.028BC - 0.017BD - 1.250E\text{-}003CD + 0.010A^2 - 0.075B^2 - 0.045C^2 - 9.649E\text{-}003D^2 \quad 4.4$$

Note: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interaction effects of the factors. A^2, B^2, C^2, and D^2 are the square effects of the factors.

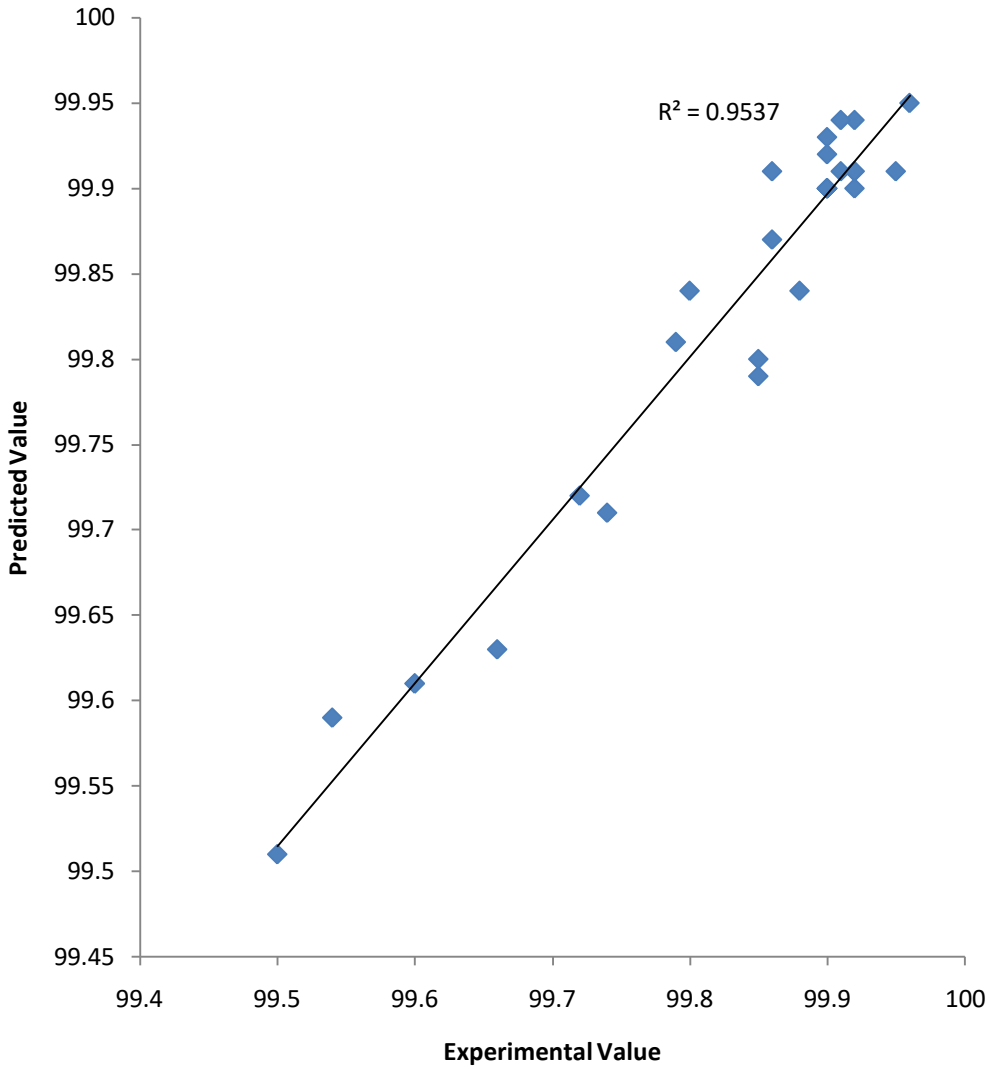


Figure 4.22:Diagnostic Plot of the Relationship between Predicted and Experimental (actual) Data for Amoxicillin Adsorption Using *Jatropha* Activated Carbon (JAC)

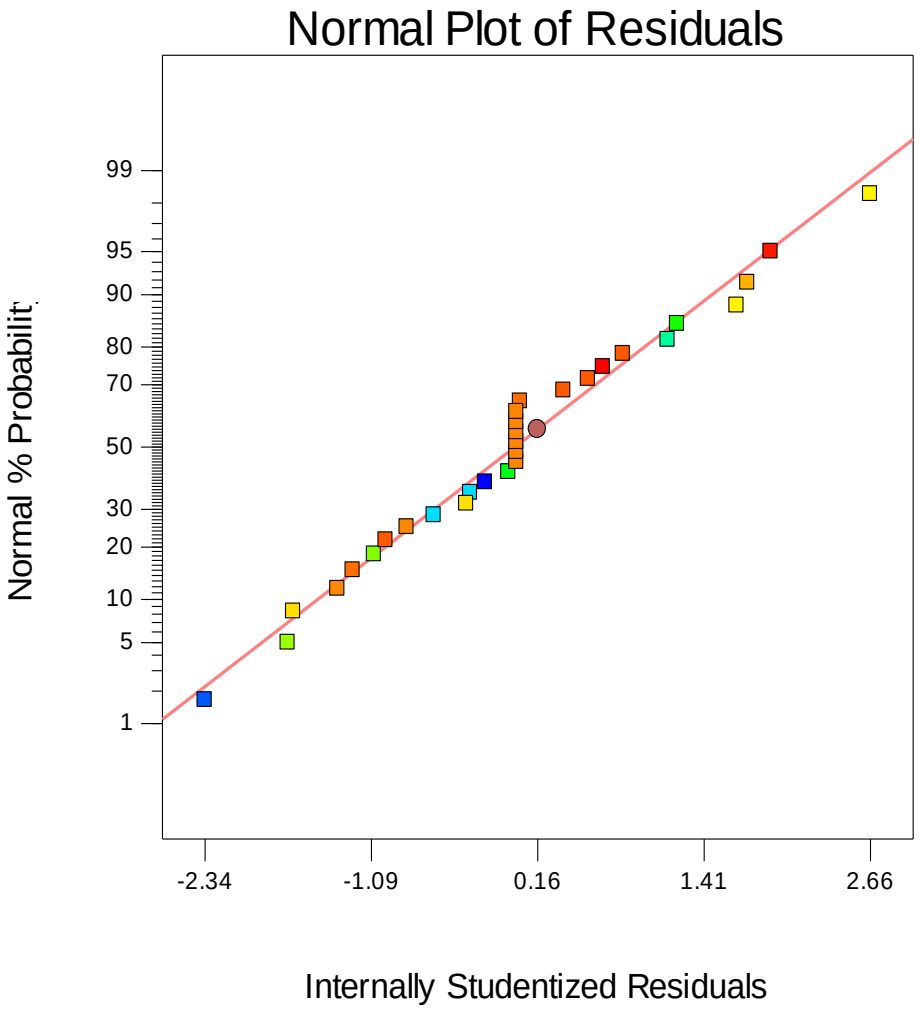


Figure 4.23:Diagnostic Plot of theRelationship between Studentized Residuals and Normal Percentage Probability for Amoxicillin Adsorption Using *Jatropha* Activated Carbon (JAC)

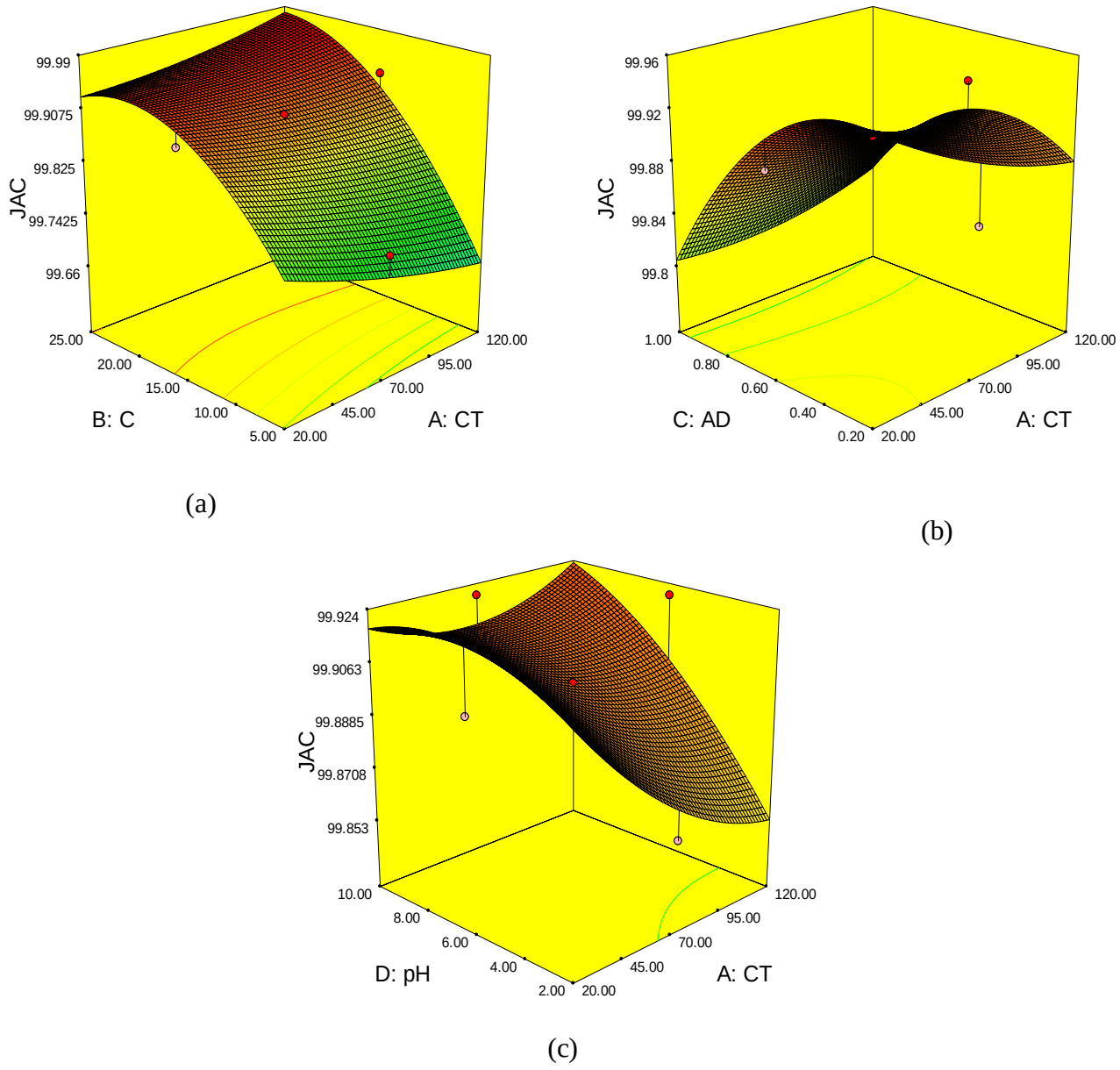


Figure 4.24:Response Surface Plot for the Effects of (a) Concentration (mg/l) and Contact Time (minutes),(b)Adsorbent Dosage (g) and Contact Time (minutes) and (c)pH and Contact Time (minutes) on Amoxicillin Adsorption Using *Jatropha* Activated Carbon (JAC)

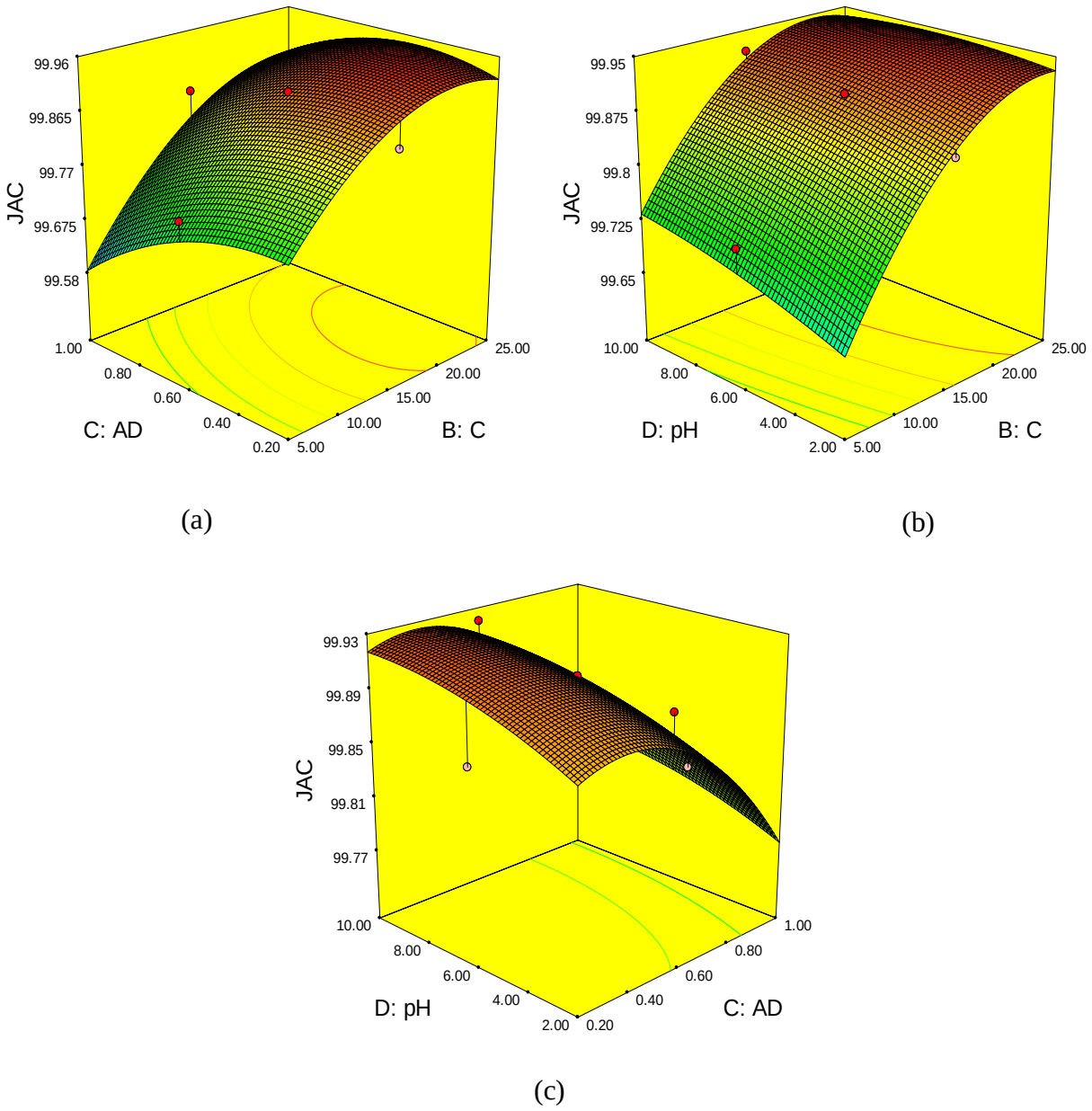


Figure 4.25:Response Surface Plot of the Effectsof (a) Adsorbent Dosage (g) and Concentration (mg/l), (b) pH and Concentration (mg/l) and (c)pH and Adsorbent Dosage (g)on Amoxicillin Adsorption Using *Jatropha* Activated Carbon (JAC)

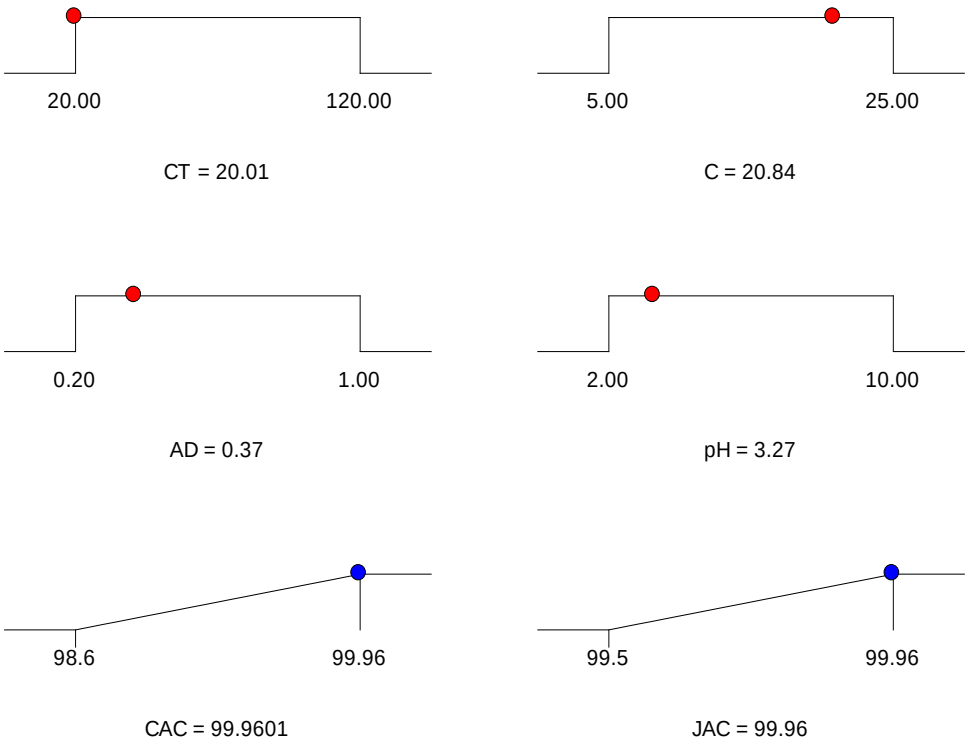


Figure 4.26:Ramp Function Graphs of the Optimization of the Adsorption of Amoxicillin

The final empirical model equation for the percentage removal of ibuprofen using *Jatropha* activated carbon (JAC) is given in equation 4.6 (JAC = 99.71 + 0.10A + 0.27B + 0.024C - 0.046D - 0.13AB - 0.012AC + 0.058AD - 0.031BC + 0.056BD + 0.14CD). The adequacy of the model was further estimated using the diagnostic plots as shown in figures 4.31 – 4.32. The effect of the interractions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) are shown in three-dimensional response plots in Figure 4.33 - 4.34. Figure 4.35 showed the ramp function graph of the optimization of the adsorption of ibuprofen.

Table 4.15:Experimental Matrix for Ibuprofen Adsorption

Run	Factor 1 A:CT	Factor 2 B:C	Factor 3 C: AD	Factor 4 D: pH	Response CAC (%)	Response JAC (%)
1	70.00	5.00	0.60	6.00	99.66	99.40
2	20.00	25.00	1.00	10.00	99.72	99.99
3	120.00	15.00	0.60	6.00	99.91	99.98
4	20.00	5.00	0.20	10.00	99.28	98.34
5	120.00	25.00	0.20	10.00	99.98	99.97
6	70.00	15.00	0.60	6.00	99.87	99.95
7	70.00	15.00	0.60	2.00	99.81	99.89
8	120.00	5.00	1.00	2.00	99.81	99.76
9	70.00	15.00	0.60	6.00	99.87	99.95
10	20.00	15.00	0.60	6.00	99.88	99.94
11	70.00	15.00	0.60	10.00	99.87	99.93
12	120.00	5.00	1.00	10.00	98.72	99.68
13	120.00	25.00	0.20	2.00	99.91	99.94
14	70.00	15.00	0.60	6.00	99.87	99.95
15	120.00	5.00	0.20	10.00	98.80	99.64
16	20.00	5.00	1.00	10.00	99.42	99.60
17	120.00	25.00	1.00	10.00	99.87	99.94
18	20.00	5.00	0.20	2.00	99.94	99.88
19	20.00	25.00	0.20	10.00	99.93	99.94
20	20.00	25.00	1.00	2.00	99.98	99.99
21	70.00	15.00	1.00	6.00	99.79	99.94
22	120.00	25.00	1.00	2.00	99.93	99.90
23	20.00	25.00	0.20	2.00	99.98	99.99
24	70.00	15.00	0.60	6.00	99.87	99.95
25	70.00	15.00	0.20	6.00	99.94	99.97
26	70.00	25.00	0.60	6.00	99.82	99.97
27	70.00	15.00	0.60	6.00	99.87	99.95
28	20.00	5.00	1.00	2.00	98.14	98.90
29	120.00	5.00	0.20	2.00	99.99	99.60
30	70.00	15.00	0.60	6.00	99.87	99.95

Table 4.16:Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.36	0.3951	0.2983	-0.0383	5.60	Suggested
2FI	0.34	0.5867	0.3691	-1.5200	13.60	
Quadratic	0.34	0.6868	0.3944	-1.5581	13.81	
Cubic	0.18	0.9563	0.8188	-9.6815	57.64	Aliased

Table 4.17:Statistical Parameters Obtained from Analysis of Variance for the Model for Ibuprofen Adsorption Using CAC

Parameter	CAC
Standard deviation (SD)	0.34
Mean	99.71
Correlation variance (C.V)%	0.34
PRESS	13.60
R^2	0.5867
Adjusted R^2	0.3691
Predicted R^2	-1.5200
Adequate Precision	6.247

$$CAC = 99.71+0.036A + 0.30B - 0.13C - 0.11D - 0.029AB - 0.095AC - 0.16AD + 0.10BC + 0.085 BD + 0.11CD \quad 4.5$$

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interaction effects of the factors

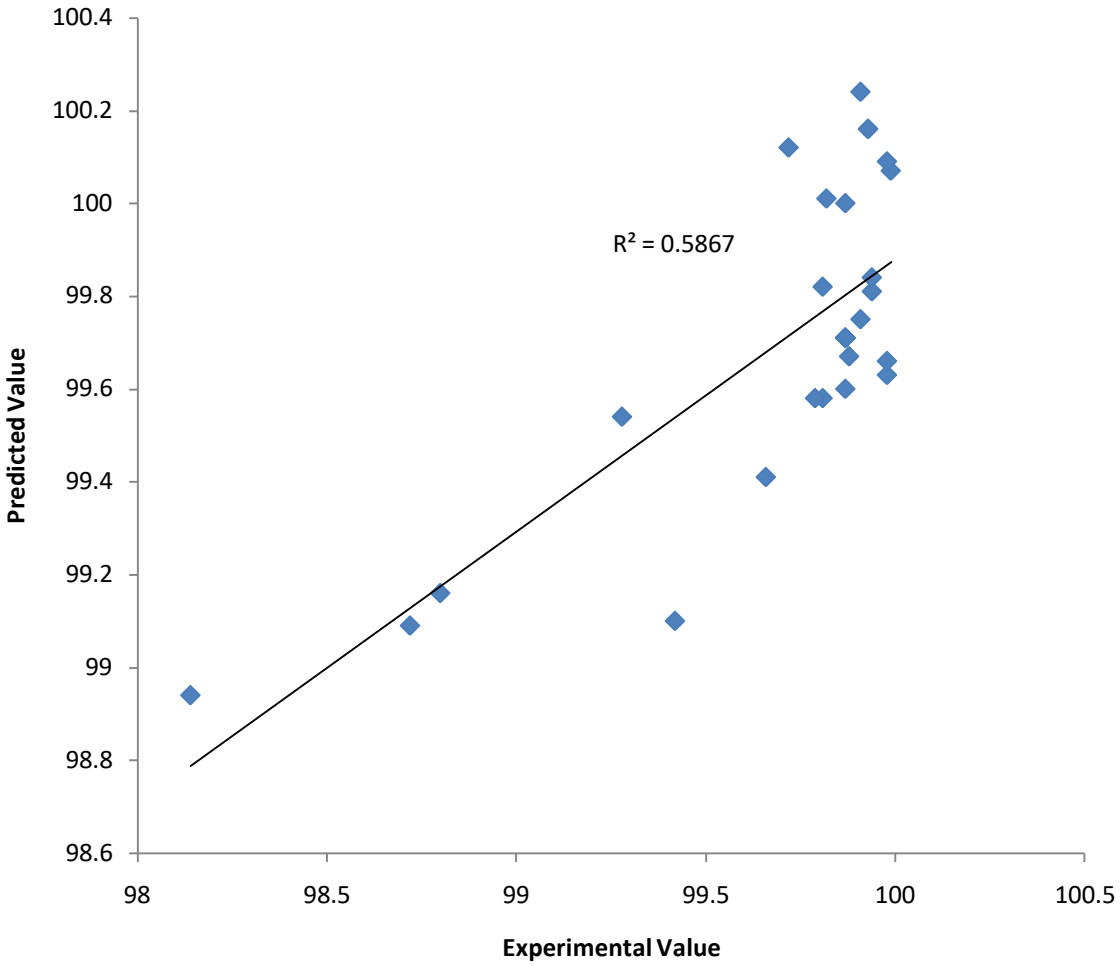


Figure 4.27:Diagnostic plot of theRelationship Between Predicted and Experimental (actual) Data for Ibuprofen Adsorption Using Commercial Activated Carbon (CAC)

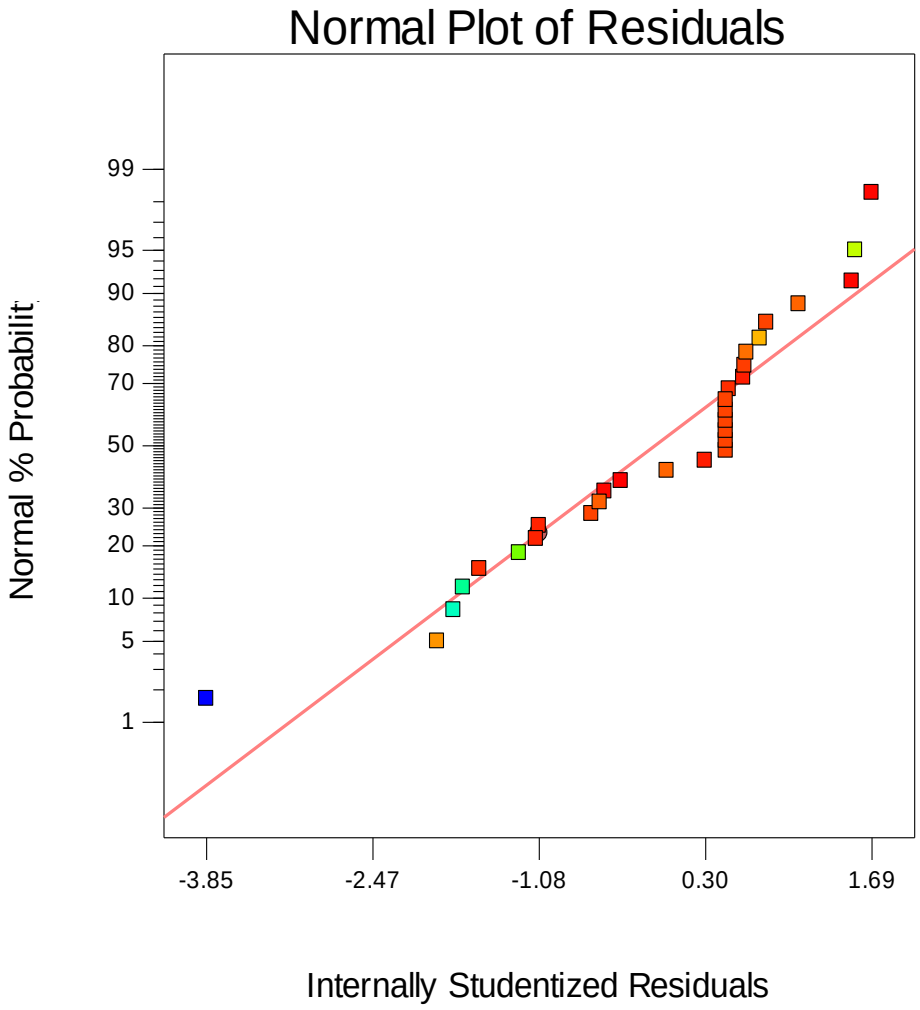

Normal Plot of Residuals
Normal % Probabilit
99
95
90
80
70
50
30
20
10
5
1
-3.85
-2.47
-1.08
0.30
1.69
Internally Studentized Residuals

Figure 4.28:Diagnostic Plot of theRelationship Between Studentized Residuals and Normal Percentage Probability for Ibuprofen Adsorption Using Commercial Activated Carbon (CAC)

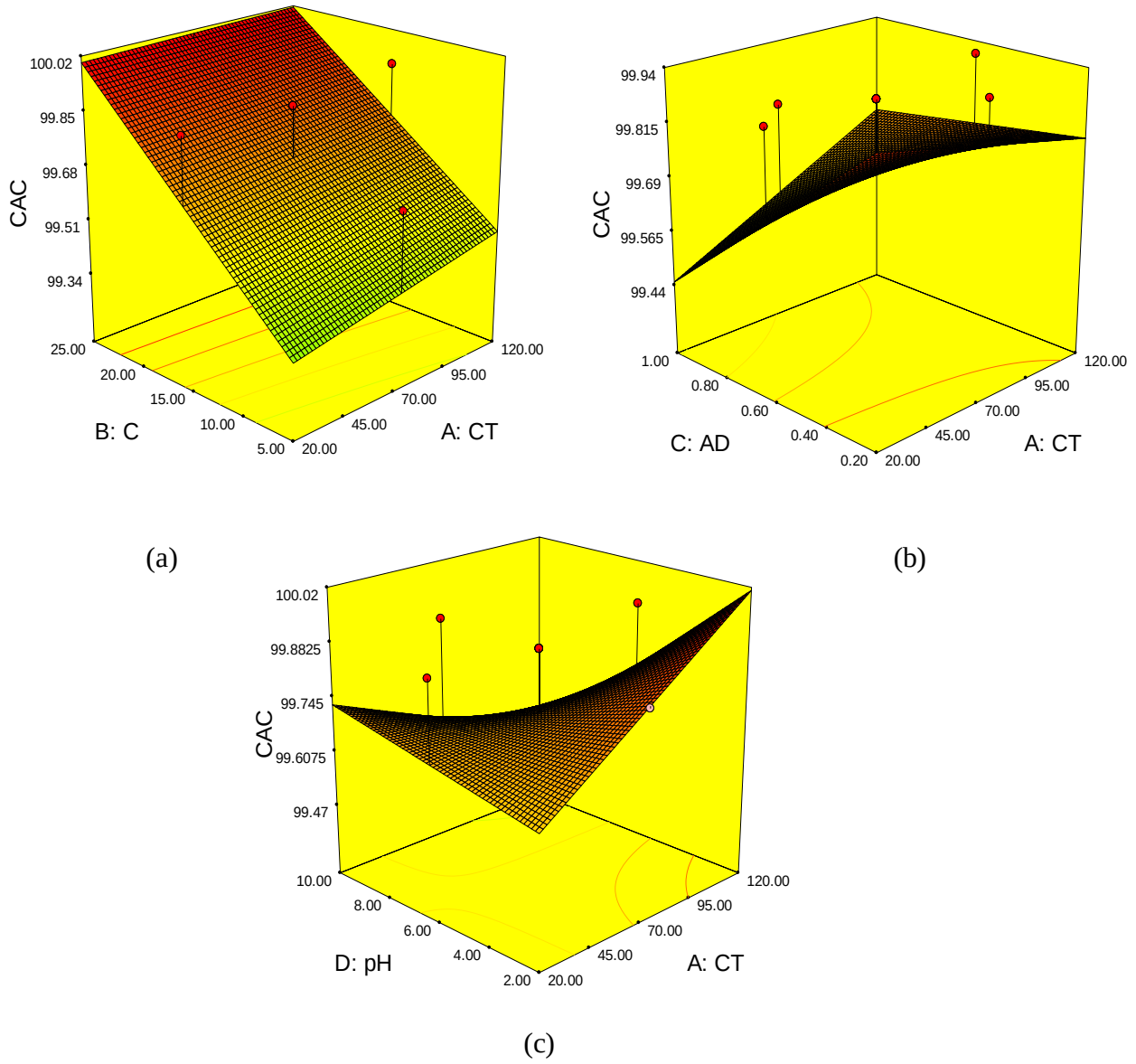


Figure 4.29:Response Surface Plot for the Effects of (a) Concentration (mg/l) and Contact Time (minutes), (b)Adsorbent Dosage (g) and Contact Time (minutes) and (c) pH and Contact Time (minutes) on Ibuprofen Adsorption Using Commercial Activated Carbon (CAC)

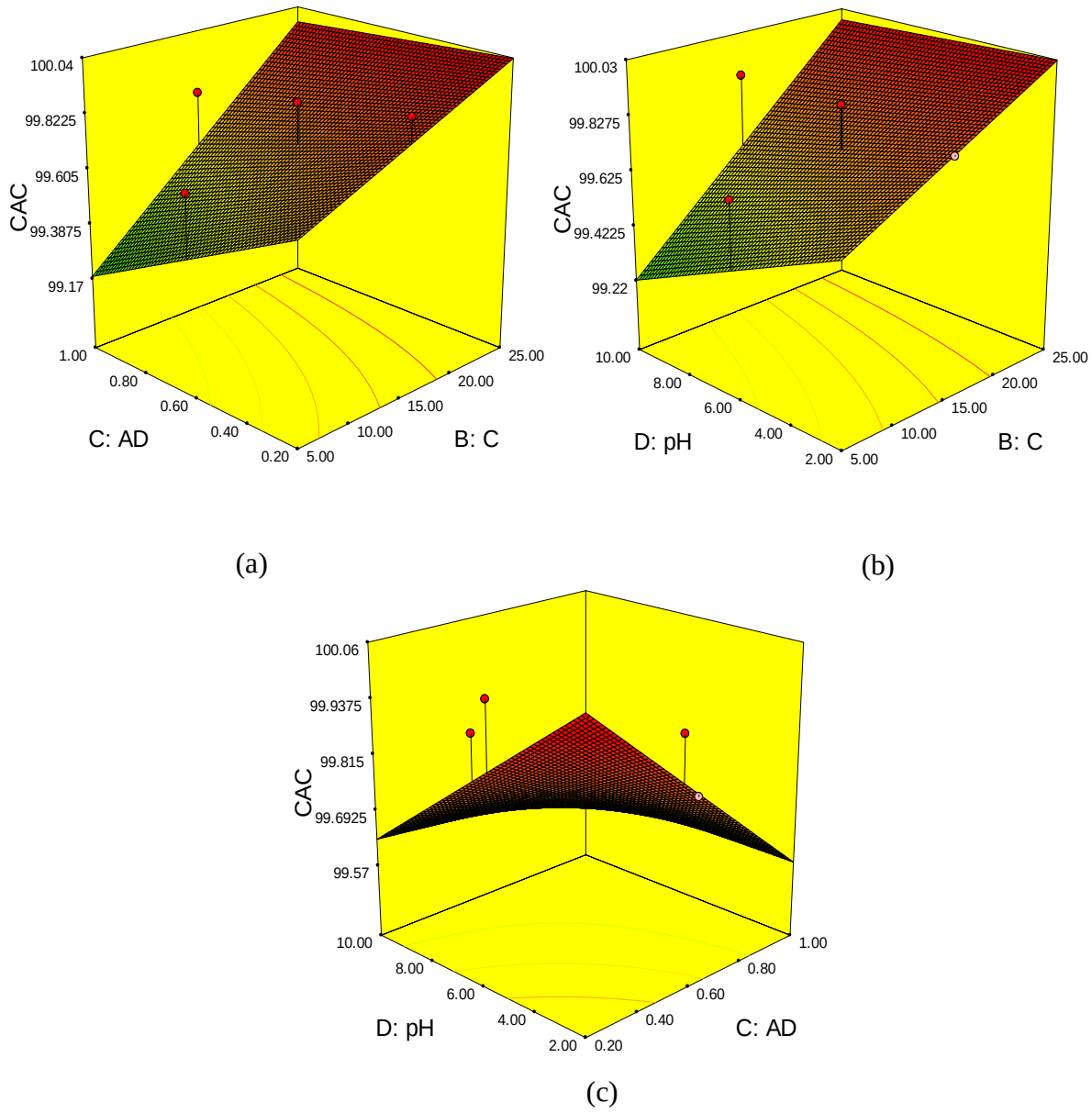


Figure 4.30:**Response Surface Plot for the Effects of (a) Adsorbent Dosage (g) and Concentration (mg/l), (b)pH and Concentration (mg/l) and (c) pH and Adsorbent Dosage (g) on Ibuprofen Adsorption Using Commercial Activated Carbon (CAC)**

Table 4.18: Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.30	0.4114	0.3172	-0.0030	3.73	Suggested
2FI	0.28	0.5993	0.3884	-1.3820	8.87	
Quadratic	0.26	0.7261	0.4705	-1.3147	8.63	
Cubic	0.22	0.9096	0.6254	-21.3471	83.21	Aliased

Table 4.19: Statistical Parameters Obtained from Analysis of Variance for the Model for Ibuprofen Adsorption Using JAC

Parameter	JAC
Standard deviation (SD)	0.28
Mean	99.79
Correlation of variance (C.V)%	0.28
PRESS	8.87
R^2	0.5993
Adjusted R^2	0.3884
Predicted R^2	-1.3820
Adequate precision	7.913

$$JAC = 99.71+0.10A+0.27B+0.024C-0.046D-0.13AB-0.012AC+0.058AD-0.031BC+0.056BD+0.14CD \quad 4.6$$

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interaction effects of the factors

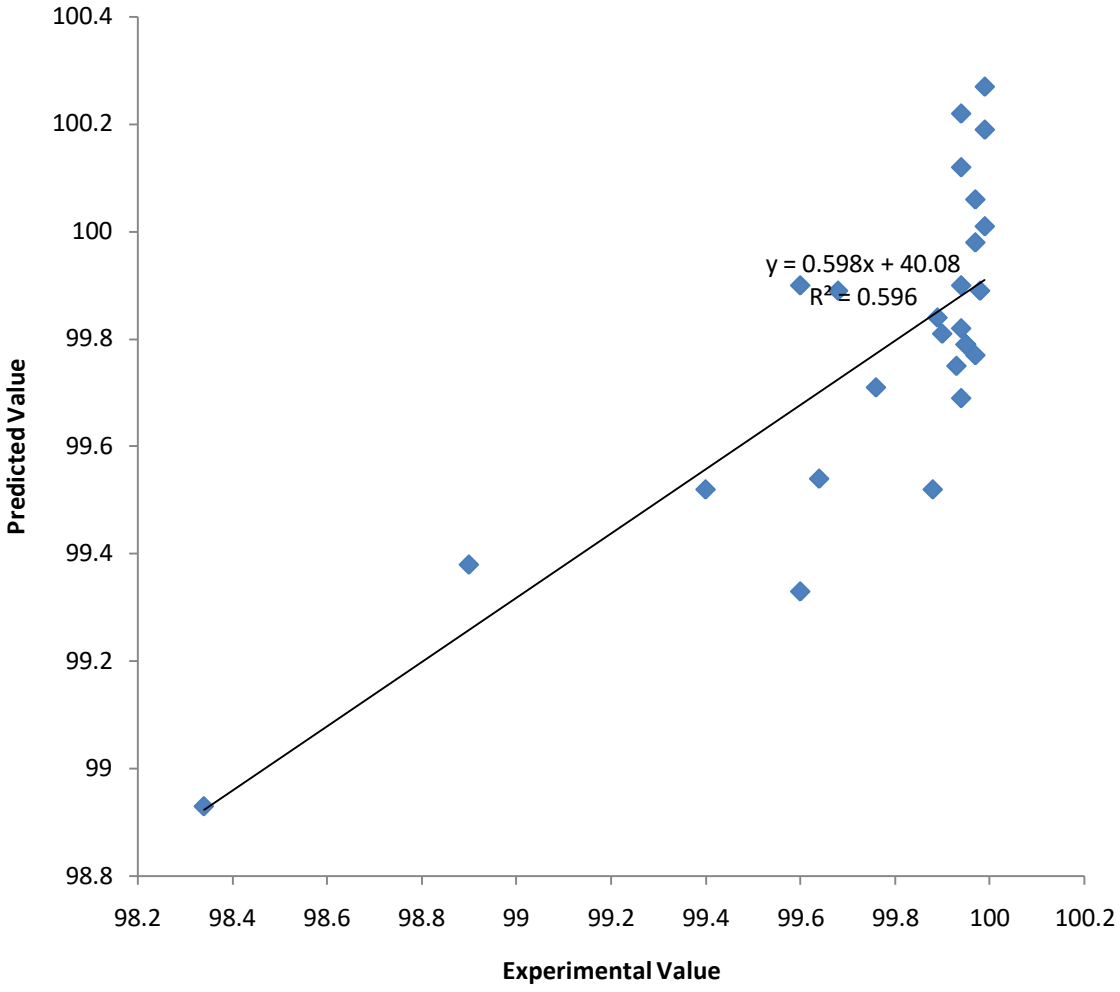


Figure 4.31:Diagnostic Plot of theRelationship Between Predicted and Experimental (Actual) Data for Ibuprofen Adsorption Using *Jatropha* Activated Carbon (JAC)

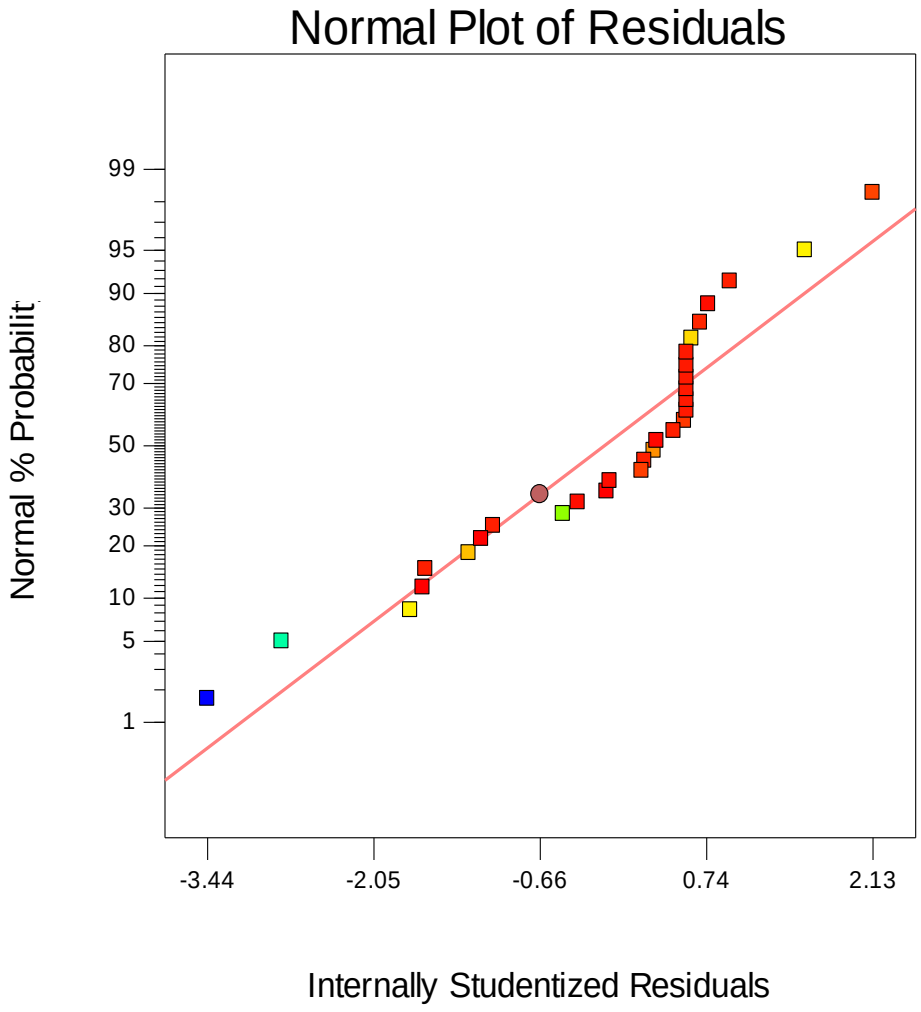


Figure 4.32:Diagnostic Plot of theRelationship Between Studentized Residuals and the Normal Percentage Probability for Ibuprofen Adsorption Using *Jatropha* Activated Carbon (JAC)

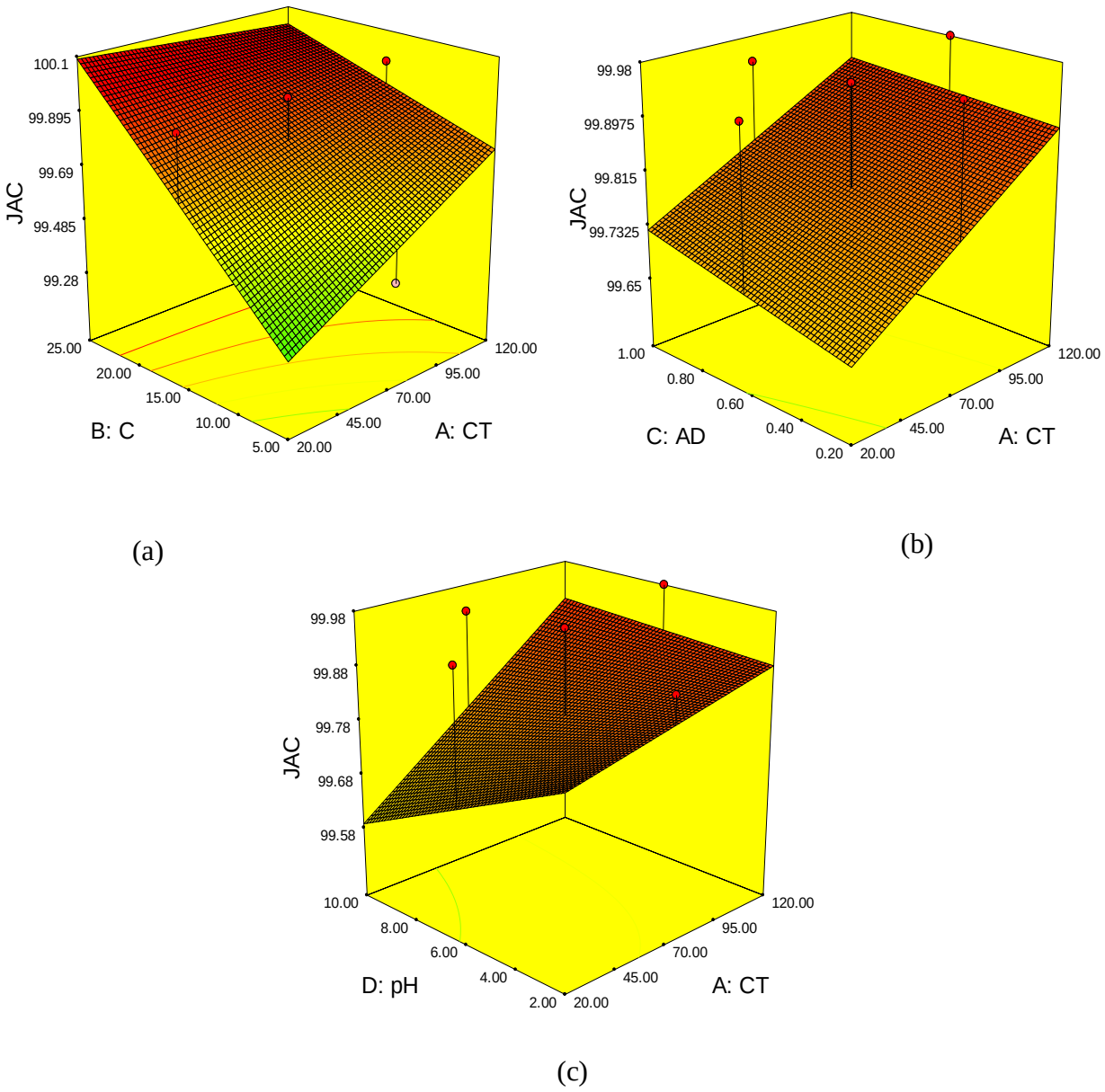


Figure 4.33:Response Surface Plot for the Effectsof (a) Concentration (mg/l) and Contact Time (minutes), (b)Adsorbent Dosage (g) and Contact Time (minutes) and pH and contact time (minutes) on Ibuprofen Adsorption Using *Jatropha*Activated Carbon (JAC)

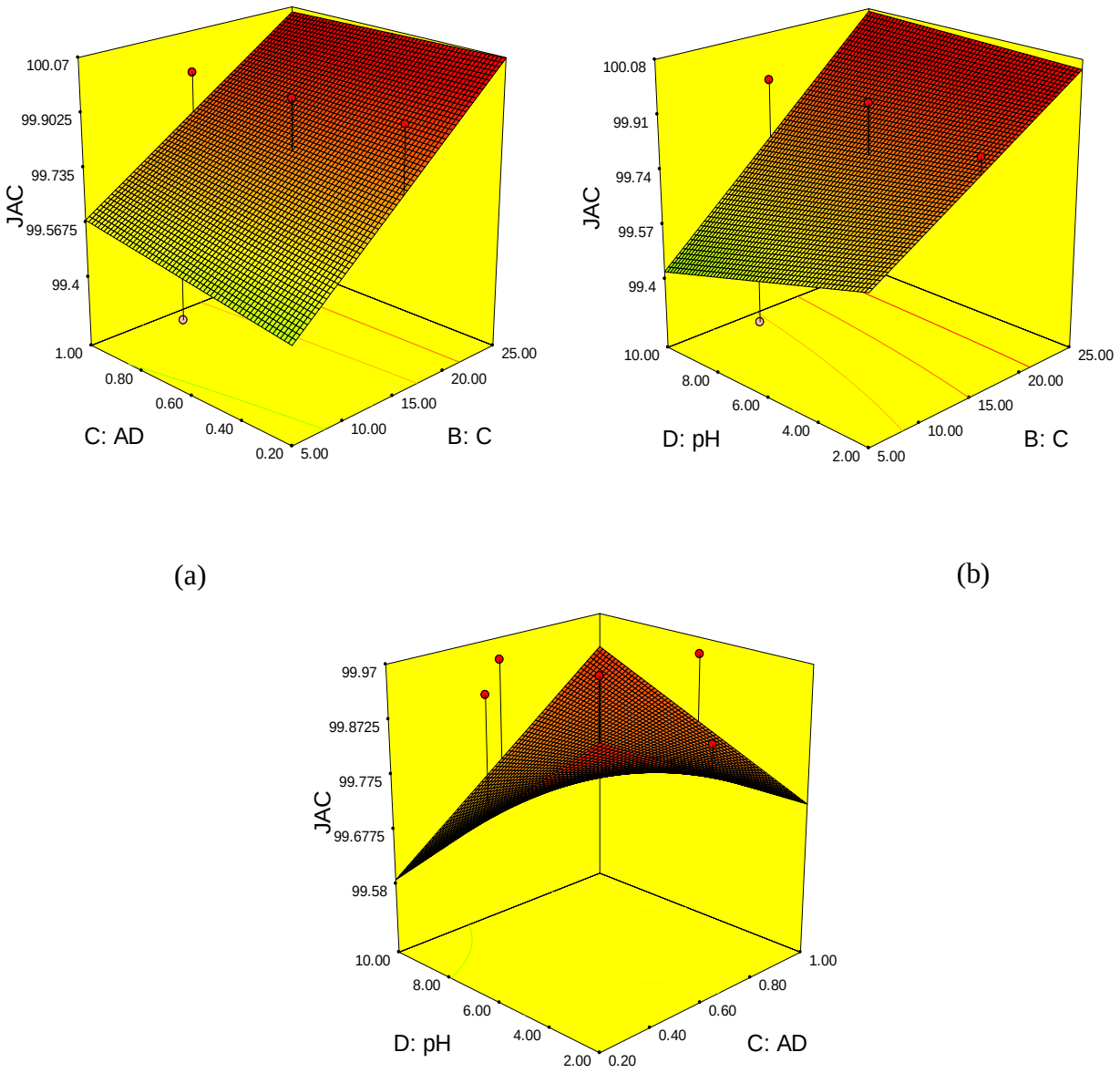


Figure 4.34: Response Surface Plot for the Effectsof (a) Adsorbent Dosage (g) and Concentration (mg/l), (b) pH and Contact Time (minutes) and (c) pH and Adsorbent Dosage (g) on Ibuprofen Adsorption Using *Jatropha* Activated Carbon (JAC)

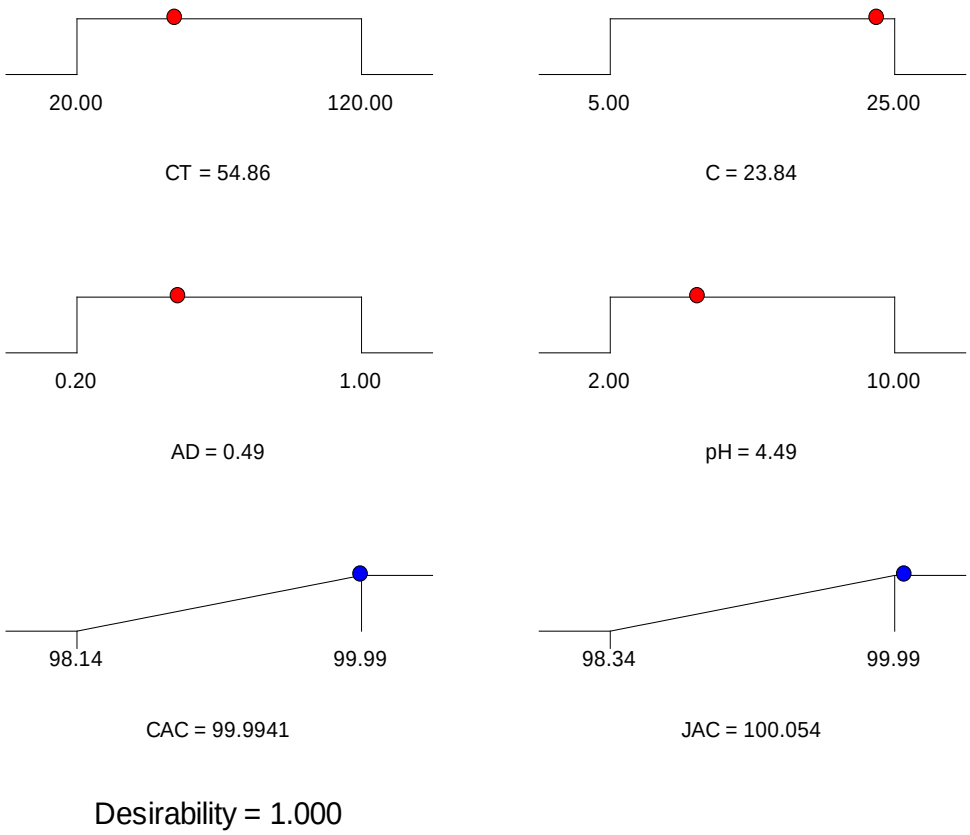


Figure 4.35:Ramp Function Graphs of the Optimization of the Adsorption of Ibuprofen

CHAPTER FIVE

DISCUSSION

5.1 Detection and Quantification of the Pharmaceutical Compounds in the Hospital Wastewater

Acetaminophen, ibuprofen and amoxicillin were detected in the hospital wastewater.Acetaminophen, amoxicillin and ibuprofen were identified because they were present in the hospital wastewater in their parent form. Most pharmaceutical compounds get transformed into other compounds within the wastewater and as such may not be identified as the parent compound (Kummerer, 2009).

Acetaminophen was found to have a concentration of 34.31µg/L in the hospital wastewater. This is higher than the concentration of 2.57µg/L obtained by Olaitan *et al*. (2014) in irrigation wells in a pharmaceutical industrial area in Sango Ota, Ogun State, Nigeria.Amoxicillin had a concentration of 8066 µg/L. It was the most abundant pharmaceutical residue observed in this study and its high presence could be an evidence of the high dependence of the people in the locality on amoxicillin.This observation is in line with reports from the literature that commonly detected pharmaceutical residues are dependent on social, cultural, technological and agricultural factors (Dehghani *et al.*, 2011; Agunbiade and Moodley, 2014).Ibuprofen had a concentration of 165.50 µg/L.

5.2 The BET Surface Area and Pore Characterization of the Prepared Activated Carbon

The textural characteristics of the prepared jatropha activated carbon (JAC) showed that the adsorbent has a large specific surface area (868 m^2g^{-1}) and the pore diameter was found to be 2.128 nm. The adsorbent prepared from *jatropha* waste was mainly mesoporous and it is favourable for the adsorption of large molecules like the studied drugs.

5.3 Scanning Electron Microscope (SEM)

Large pores in a honeycomb shape were clearly found on the surface of the *Jatropha*activated carbon. The well-developed pores had led to the large surface area and porous structure of the activated carbon (Ahmad and Hameed, 2009).Comparison of the precursor morphology with that of the prepared carbon showed substantial changes occasioned by phosphoric acid activation. The phosphoric acid incorporated into the interior of the precursor particle restricted the formation of tar as well as other liquids such as acetic acid and methanol, present in the raw *Jatropha* material, and inhibited the particle shrinkage or volume contraction during heat treatment as stated by Bansal and Goyal (2005). A distinguishing feature of the JAC micrograph that should be noted is the crack in the carbon matrix probably developed as aresult of thermal stress on the carbon matrix due to temperature changes in theactivation process(Bansal and Goyal, 2005). The crack contributes to the overall surface of the activated carbonwhich in turn increases its adsorption capacity (Bansal and Goyal, 2005).

5.4 Fourier Transform Infrared (FTIR) Analysis

Infrared spectroscopy was used to obtain information about the chemical structure and functional groups of the raw material and the prepared activated carbon. The FTIR spectrum of the *Jatropha*waste cakes is quite similar to those of other lignocellulosic materials such as neem waste, and olive-waste cake (Baccar *et al*., 2009;Alau, 2015). The bands located at 2918.5 and 2851.4cm^{-1} corresponds to the C=O vibrations in carbonates group. The band at 1707.1cm^{-1} is ascribed to carbonyl C=O groups in carboxylic acids and esters. The C=O vibrations in amides may have caused the emergence of the band at about

1639.3cm^{-1}, while the vibrations at 1408.9 and 1319.5cm^{-1} are assigned to the bands C=O in carboxylate groups. When comparing the two spectra (the *Jatropha* waste cake and the *Jatropha* activated carbon), some noticeable modifications took place in the wavenumber range of 3500–1000 cm^{-1}.These modifications make the spectrum of the *Jatropha*activated carbon lesscomplicated than that of the precursor.

Considering the spectrumof the *Jatropha* activatedcarbon, itwas observed that there was a decrease in intensity of the band corresponding to O-H groups (~3500 cm^{-1}) andthis may have resulted from the dehydration effect of H_3PO_4. Bands between 1408.9 and 1319.5 cm^{-1} which corresponds to the C=O disappeared which suggests that phosphoric acid activated carbon contains less C=O groups than the raw material. The decrease of the amount of carbonyl groups may be due to dehydration effect of H_3PO_4, resulting in the decomposition of these groups and subsequent release of their byproducts as volatile matter(Baccar, *et al.*, 2009).A disappearance of the weak band located between 3011 cm^{-1} and a shift of the C=O band from between 2918.5 and 2851.4 to 2754.5 and 2322.1 cm^{-1}were also observed.Thus, it can be inferred that the acid impregnation of the*Jatropha* waste cake followed by the pyrolysis step led to a more carbonaceousstructure due to the dehydration effect of H_3PO_4 andevolution of volatiles during pyrolysis. From the spectra of *Jatropha* activated carbon, it was noted that itcontains oxygenated surface functional groups such as hydroxyl, carbonyl and carboxyl (Sahira *et al.*, 2013).Oxygen containing surface functional groups plays important role in influencing the surface properties and adsorption behaviour of the sample (Bansal and Goyal, 2005). The nature of activating agents does not have much effect in the type of oxygenated surface functional groups (Sahira *et al.*, 2013).The FTIR analysis

suggests that phosphoric acid chemical activationled to the incorporation of a phosphorous in the structureof the obtained carbon(Baccar, *et al*., 2009).

5.5 Adsorption Studies

The percentage removal of acetaminophen by commercial activated carbon (CAC) and *Jatropha* activated carbon (JAC) ranged from 99.84 – 99.98% with CAC and 99.28 – 99.98% respectively. This percentage removal is higher than that reported this implies that the prepared activated carbon can favourably compete with the commercial activated carbon in the adsorption of acetaminophen.

The analysis of variance (ANOVA) was used to statistically evaluate the significance of the quadratic model and it was found that the regression was statistically significant at the F – value of 7.86. The correlation coefficient (R^2) was used to confirm the accuracy of the model.It describes the extent to which a model can estimate the experimental data and the adjusted R^2 measures the variation about the mean as explained by the model. It was found the values of R^2 and adjusted R^2 were close(0.8800 and 0.7680) respectively.

The Predicted R-Squared of 0.2423 is not as close to the Adjusted R^2 of 0.7680 as it should have normally been. This may indicate a large block effect. The adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable (Design Expert, 2005). The ratio of 10.910 obtained for this model indicates an adequate signal and the model can be used to navigate the design space and to find the optimal conditions for the adsorption process. A low value of the variation coefficient (CV = 0.020) shows the reliability of the experiments.Model term B (concentration) and AB (the interaction of contact time and concentration) were significant.

The final empirical model equation for the percentage removal of acetaminophen using commercial activated carbon (CAC) indicated that the equation variables showed synergistic and antagonistic effects on the process as informed by the positive and negative signs before the terms. The appearance of a single variable in a term signifies a uni-factor effect; two variables imply a double factor and a second-order term of variable expression indicates a quadratic effect.The experimental and predicted removal capacity plot (Figure 4.9)adequately captured the relationship between the adsorptionprocess variables to the response. The normal percentage probability plot (Figure 4.10) shows that there is neither any apparent problem with normality nor is response transformation required.

The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) were shown in three-dimensional response plots (Figures 4.11-4.12). The values on the axis are real values. The removal of acetaminophen increased with increasing the concentration from 5 to 25 mg/l, whereas removal increased with increase in contact time from 20 to 45 min but decreases as the contact time increases. This may have resulted from the saturation of the pores. Acetaminophen removal decreased with increase in adsorbent dosage. This can be as a result of the fact that the adsorption sites remain unsaturated during the adsorption reaction or the agglomeration of the adsorbent (Javanbakht and Ghoreishi, 2017).

The removal decreases with increase in contact time. The combined effect of pHand contact timeshowed that the removal increased with increase in pH from 2 to 7 and contact time from 20 to 80 min. The effect of adsorbent dosage and concentration on the acetaminophen adsorption showed that the removal decreases with increase in adsorbent dosage from 0.2-0.8g whereas it increased with increase in concentration from 5-25 mg/L. The combined

effect of concentration and pH on the adsorption process shows that removal increases with increase in concentrationand increase in pH from 2-7. However, removal decreases with an increase in pH from 7-10.The possible reason may be at lower solution pH, a successive deprotonation of positive charged groups on the adsorbent surface takes place and as a result the electrostatic force of repulsion acts between negatively charged adsorbent sites and acetaminophen (Mphahlele *et al*., 2015). The removal of acetaminophen is observed to increase with increase in pHand adsorbent dosage.

The model selection parameters for the response using *jatropha* activated carbon (JAC) showed that the 2FI model was suggested. The analysis of variance (ANOVA) indicated that the 2FI model was significant with an F –value of 2.72.It was found the values of R^2 and adjusted R^2 were 0.5887 and 0.3722 respectively. The Predicted R^2 was found to be -1.6867.A negative Predicted R^2implies that the overall mean is a better predictor of the response than the current model. Thus, the overall mean of 99.92% predicts the response better. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 8.551 obtained for this model indicates an adequate signal and the model can be used to navigate the design space and to find the optimal conditions of the adsorption process. A low value of the variation coefficient (CV = 0.010) showsthe reliability of the experiments. Model term B (concentration) was significant.

The final empirical model equation for the percentage removal of acetaminophen using jatropha activated carbon (JAC) showed that the model terms A, B, C and D (A-contact time, B-concentration, C-adsorbent dosage and D-pH) enhanced the adsorption process with concentration having the highest positive impact. The influence of the double factors of AB, AC, AD, BC, BD and CD delimited the adsorption process.

The experimental and predicted removal capacity plot (Figure 4.13) adequately captured the relationship between the adsorption process variables to the response. The normal percentage probability plot (Figure 4.14) showed that response transformation is not required.

The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) were shown in three-dimensional response plots (Figures 4.15-4.16). The combined effect of concentration and contact time showed that the removal of acetaminophen increased with the increase in concentration and contact time.The acetaminophen adsorption increases with the increasein time as more and more acetaminophen molecules get attached on the activated carbon surface which enables higher acetaminophen adsorption efficacy (Nugroho, 2010).This was also observed in the combined effect of adsorbent dosage and contact time, pH and contact time, adsorbent dosage and concentration, pH and concentration and pH and adsorbent dosage. The interaction of the factors all enhanced the removal of acetaminophen using jatropha activated carbon.

In the optimization of the adsorption of acetaminophen, the best local maximum was found to be at the contact time of 54.26 min, a concentration of 24.45 mg/L, an adsorbent dosage of 0.57g, a pH of 7.04, a removal of 99.9908% with CAC and 99.9873% with JAC and the desirability of 1. The desirability of 1 indicated that the estimated function may express the desired conditions and the experimental model (Design Expert, 2005).

The design matrix incorporating the adsorption parameters and the responses which are the percentage removal of amoxicillin by commercial activated carbon (CAC) and jatropha activated carbon (JAC) showed that the removal percentage of amoxicillin ranged from

99.60 – 99.96% with CAC and 99.50 – 99.96% with JAC respectively. It can be inferred from these results that the prepared activated carbon was suitable for adsorption studies of amoxicillin in the same way as the commercial adsorbents.

The two-factor interaction (2FI) model was suggested and the analysis of variance (ANOVA) showed that the 2FI model was significant with an F – value of 3.73. The 2FI model had an insignificant lack of fit. The values of R^2, adjusted R^2,predictedR^2, correlation of variance (C.V) and adequate precision were found to be 0.6627, 0.4851, -1.2015, 0.18 and 9.932 respectively.A negative Predicted R^2 (-1.2015) implies that the overall mean is a better predictor of the response than the current model.Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 9.932 obtained for this model indicates an adequate signal and the model can be used to navigatethe design space and to find the optimal conditions of the adsorption process. A low value of the variation coefficient (CV = 0.18) shows reliability and Model term B (concentration) was significant.

Furthermore, the final empirical model equation for the percentage removal of amoxicillin using commercial activated carbon (CAC) showed that model terms B and D (B-concentration and D-pH) enhanced the adsorption process with concentration having the highest positive impact while A and C (A-contact time and C-adsorbent dosage) delimited the process. However, the influence of the double factors of AB, AD, BC and CD enhanced the adsorption process while AC and BD delimited the process.

The experimental and predicted removal capacity plot (Figure 4.18) showed the relation between the adsorption process variables to the response. It was observed from the normal

percentage probability plot (Figure 4.19) that there is neither any apparent problem with normality nor is response transformation required.

The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) were given in three-dimensional response plots (Figures 4.20-4.21). The removal of amoxicillin was observed to increase as the interaction of concentration and contact time increase. This was also observed for the interaction of adsorbent dosage and contact time, pH and concentration. However, removal increased with increase in concentration and decreased with increase in contact time. It also increasedwith increase in pH and decreased with increase in adsorbent dosage. The removal increased with increase in pH but decrease with increase in adsorbent dosage. This revealed that removal is favoured at high pH and low adsorbent dosage.

The quadratic modelwas suggested and the analysis of variance (ANOVA) revealed that the model was significant with an F – value of 22.10.The correlation coefficient (R^2) was used to confirm the accuracy of the model.It described the extent to which a model can estimate the experimental data and the adjusted R^2 measured the variation about the mean as explained by the model. It was found the values of R^2 and adjusted R^2 were 0.9538 and 0.9106 respectively.The Predicted R^2 of 0.6804 is close to the Adjusted R-Squared of 0.9106 which indicated that the model was good.

Theadequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 16.340 obtained for this model indicated an adequate signal and the model was used to navigate the design space and to find the optimal conditions of the adsorption process. A low value of the variation coefficient (CV = 0.038) shows the reliability of the

experiments.The model terms B (concentration), C (adsorbent dosage), D (pH), AB (the interaction of contact time and concentration), AC (the interaction of contact time and adsorbent dosage), BC (the interaction of concentration and adsorbent dosage), and B^2 (square of concentration) were significant.

The final empirical model equation for the percentage removal of amoxicillin using jatropha activated carbon (JAC) revealed that model terms B and D (B-concentration and D-pH) enhanced the adsorption process with concentration having the highest positive impact while A (contact time) and C(adsorbent dosage) delimited the process. The influence of the double factors of AB, AC, AD and BC also enhanced the process while BD and CD delimited the adsorption process. The influence of the squared factor A^2 enhanced the process while B^2, C^2 and D^2delimited the process. The experimental and predicted removal capacity plot (Figure 4.22) showed the relation between the adsorption process variables to the response. It was observed from the normal percentage probability plot (Figure 4.23) that there is neither any apparent problem with normality nor is response transformation required.

The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) were depicted three-dimensional response plots (Figures 4.24-25). Removal increased with increase in concentration from 5-25 mg/L and decreased with increase in contact time from 20-120 minutes. Removal decreased with increase in adsorbent dosage and contact time from 0.20-1.0 g and 20-120 minutes respectively. Amoxicillin removal increased with increase in pH but decreased with increase in contact time. The removal increasedwith increase in adsorbent dosage from 0.20-0.60 g but the removal decreased withan increase from 0.60-1.0 g. However, amoxicillin removal

increased with increase in concentration from 5 to 25 mg/L. The interaction of pH and concentration revealed that the removal of amoxicillin increased with increase in pH and concentration. The interaction of pH and adsorbent dosage showedthat the removal increased with increase in pH and adsorbent dosage from 2-10 and 0.2-0.40 respectively. However, a decrease in the removal is observed at higher values of the adsorbent dosage.

In the optimization of the adsorption of amoxicillin, the best local maximum was found to be at the contact time of 20.01 minutes, a concentration of 20.84mg/L, an adsorbent dosage of 0.37g, a pH of 3.27, a removal of 99.96% with CAC and 99.96% with JAC and the desirability of 1. The desirability of 1 indicated that the estimated function may express the desired conditions and the experimental model.

The removal percentage of ibuprofen ranged from 99.14 – 99.99% with CAC and 99.34 – 99.99% with JAC respectively. The comparable yield between CAC and JAC implies that prepared adsorbent can be used for adsorption of ibuprofen as well as commercial adsorbents.

The linear model was suggested but was modified to the 2FI model using the software. The values of R^2, adjusted R^2,predictedR^2, and correlation of variance (C.V) were found to be 0.5867, 0.3691 and-1.5200. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 6.247 obtained for this model indicates an adequate signal and the model can be used to navigate the design space and to find the optimal conditions of the adsorption process. A low value of the variation coefficient (CV = 0.34) implied that the experiments were reliable.The model term B (concentration) was significant with an F value of 13.60.

The final empirical model equation for the percentage removal of ibuprofen using commercial activated carbon (CAC) revealed that model terms A (contact time), B (concentration), BC (interaction of concentration and adsorbent dosage), BD (interaction of concentration and pH) and CD (adsorbent dosage and pH) contributed positively to the adsorption process while C (adsorbent dosage), D (pH), AB (interaction of contact time and concentration), AC (interaction of contact time and adsorbent dosage) and AD (contact time and pH) were antagonistic to the process.Moreover,the model was further estimated using the diagnostic plots. The experimental and predicted removal capacity plot (Figure 4.27) showed the relation between the adsorption process variables to the response. It was observed from the normal percentage probability plot (Figure 4.28) that there is neither any apparent problem with normality nor is response transformation required.

The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH)are revealed in three-dimensional response plots (Figures 4.29-4.30). Ibuprofen removal increased with increase in concentration and contact time. It decreased with increase in adsorbent dosage and contact time. However, it increased with increase in pH and contact time. The removal decreased with increase in adsorbent dosage but increased with increase in concentration. It was also observed to decrease with increase in pH and increased with increase in concentration. It was noted again however that the removal decreased with an increase in pH and adsorbent dosage.

The linear model was suggested and it was modified to give the 2FI model. The values of R^2, adjusted R^2,predictedR^2, and correlation of variance (C.V) were found to be 0.5963, 0.3884, and -1.3820.The ratio of 7.913 obtained for this model indicates an adequate signal and the model can be used to navigate the design space and to find the optimal conditions

of the adsorption process. A low value of the variation coefficient (CV = 0.28%) revealed the reliability of the experiments.There was model term B (concentration) was significant with an F value of 16.50.

The final empirical model equation for the percentage removal of ibuprofen using jatropha activated carbon (JAC) showed that model terms A (contact time), B (concentration), C (adsorbent dosage) and AD (interaction of contact time and pH) influenced the process positively while D (pH), AB (interaction of contact time and concentration), AC (interaction of contact time and adsorbent dosage) and BC (interaction of concentration and adsorbent dosage) influenced the process negatively.

The adequacy of the model was further estimated using the diagnostic plots.The experimental and predicted removal capacity plot (Figure 4.31) showed the relation between the adsorption process variables to the response. It was observed from the normal percentage probability plot(Figure 4.32) that there is neither any apparent problem with normality nor is response transformation required.

The effect of the interactions of the adsorption factors (contact time, concentration, adsorbent dosage and pH) were shown in three-dimensional response plots (Figures 4.33-4.34). Ibuprofen removal increased with increase in concentration and contact time. It also increased with increase in adsorbent dosage and contact time. However, ibuprofen removal decreased with increase in pH but increased with increase in contact time. The removal increased with increase in adsorbent dosage and concentration. It was also observed to increase with increase in pH and concentration. It was noted again however that the removal decreased with an increase in pH and adsorbent dosage.

In optimization of the adsorption parameters for ibuprofen removal the best local maximum was found to be at the contact time of 54.86 minutes, a concentration of 23.84 mg/L, an adsorbent dosage of 0.49g, a pH of 4.49, a removal of 99.994% with CAC and 100% with JAC and the desirability of 1. The desirability of 1 indicated that the estimated function may express the desired conditions and the experimental model.

CHAPTER SIX

SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 Summary

Acetaminophen, amoxicillin and ibuprofen were successfully identified and quantified in the hospital wastewater.The *Jatropha* waste cake was successfully carbonized at 400°C and activated using H_3PO_4as the activating agent at 450°C.The BET surface area and pore diameter of the prepared jatropha activated carbon was found to be 868 m^2g^{-1} and 2.128 nm respectively. The SEM further confirmed the well-defined pore structure of the *Jatropha*activated carbon. The changes on the surface functional groups of the raw and activated jatropha carbons as shown by the FTIR results are evidence that the carbonization and activation process were successful.Four adsorption parameters (contact time, concentration, adsorbent dosage and pH) were optimized using the central composite design for the adsorption of acetaminophen, amoxicillin and ibuprofen from wastewater. The effectiveness and efficiency of the prepared jatropha carbons was proven in reducing the following drug residues in a single-component system: Acetaminophen (99.98%), amoxicillin (99.96%), and ibuprofen (100%). This was also compared with commercial activated carbon and the adsorption efficiency was found to be similar.

6.2 Conclusion

Three Pharmaceutical compounds, acetaminophen, amoxicillin and ibuprofen were identified and quantified in the hospital wastewater.*Jatropha* cake is a readily available bioresource material and can be classified as waste material. The carbonization of *Jatropha* cake and subsequent activation with phosphoric acid to produce jatropha activated carbon suitable for the treatment of hospital wastewaters was successful when compared with the raw sample. The *Jatropha* cake was carbonized to remove volatile organic matter and

subsequently activated with H_3PO_4 which is efficient and cost-effective. The results of the nitrogen gas adsorption analysis showed that the activation process produced high surface area materials with well-developed pores and volume. The surface areas and pore diameter of the *Jatropha* activated carbon was foundto be 868 m^2g^{-1} and 2.128 nm respectively.FTIR showed the changes on the surface functional groups between the *Jatropha* cakeand *Jatropha*activated carbons.There was a decrease in intensity of the band corresponding to O-H groups (~3500 cm^{-1}), bands between 1408.9 and 1319.5 cm^{-1} which corresponds to the C=O disappeared,and the disappearance of the weak band located between 3011 cm^{-1} and a shift of the C=O band from between 2918.5 and 2851.4 to 2754.5 and 2322.1 cm^{-1}were indications that the activation process was successful. The central composite design was used to optimize the effects of contact time, concentration, adsorbent dosage and pH on the adsorption process. This resulted in the successful adsorption ofacetaminophen (99.98%), amoxicillin (99.96%), and ibuprofen (100%). This was also compared with commercial activated carbon and the adsorption efficiency was found to be similar.

6.3 Recommendations

The following recommendations are made from the study of wastewater treatment using *Jatropha* activated carbon:

i. Further studies can be carried out to identify and quantify the transformation products of drug compounds in wastewater
ii. Further studies can be carried outusing *Jatropha* activated carbonto treat industrial and other municipal wastewater.
iii. Other activating agents and activating methods could be used to further prepare the *Jatropha* carbon to treat wastewater or other effluents.

iv. Studies on the synergy of *Jatropha* activated carbon and Titanium Dioxide for pharmaceutical adsorption can be undertaken.

v. Further studies on the removal of other pharmaceutical compounds in surface water and groundwater using *Jatropha*activated carbon can be undertaken.

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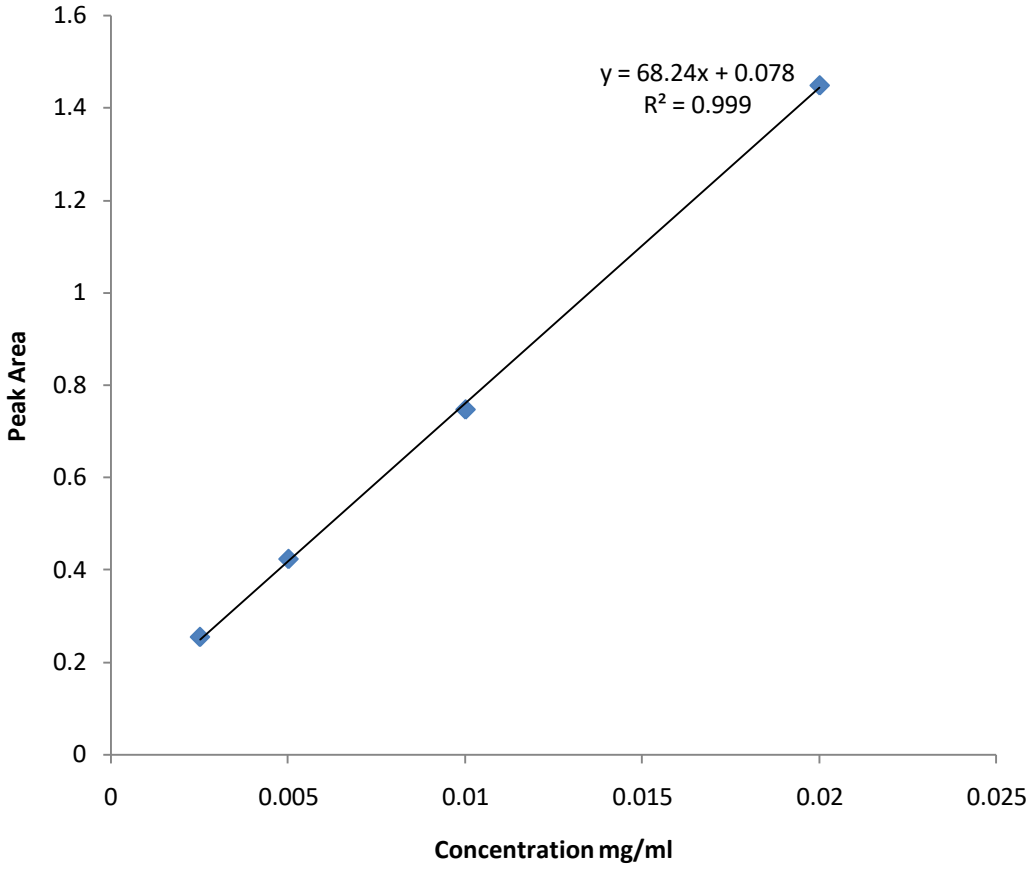
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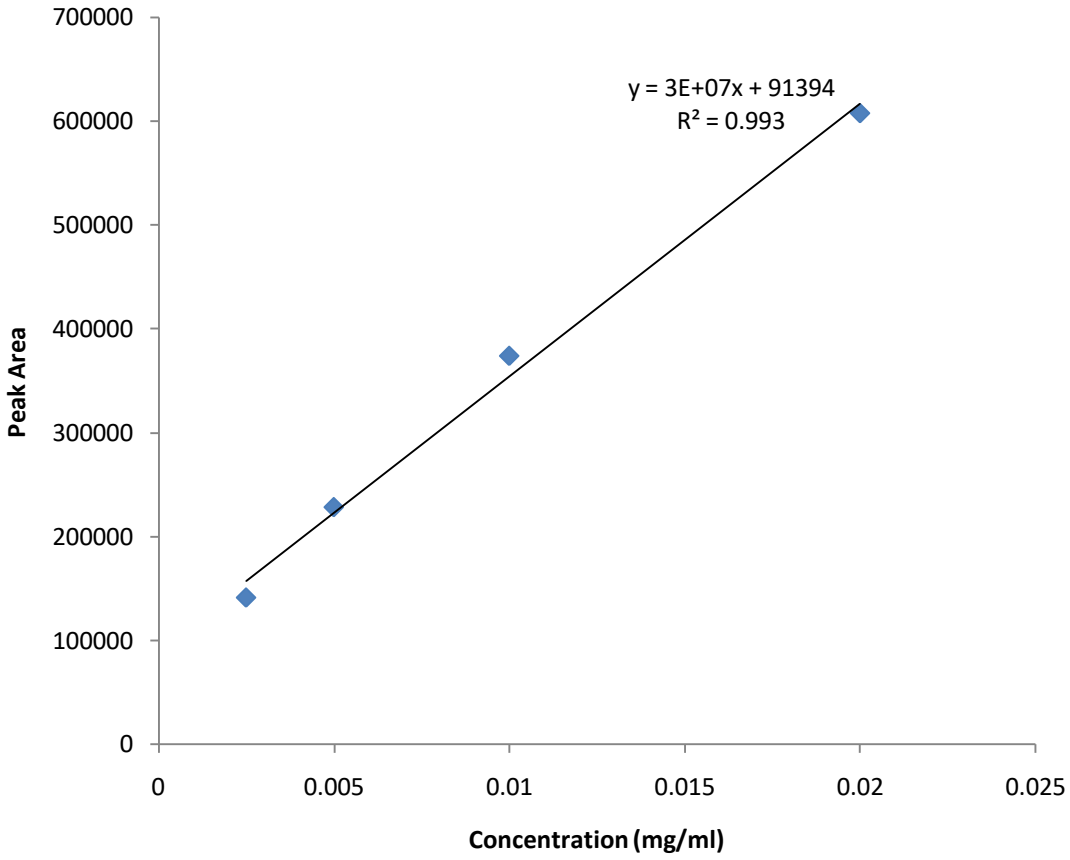
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APPENDICES

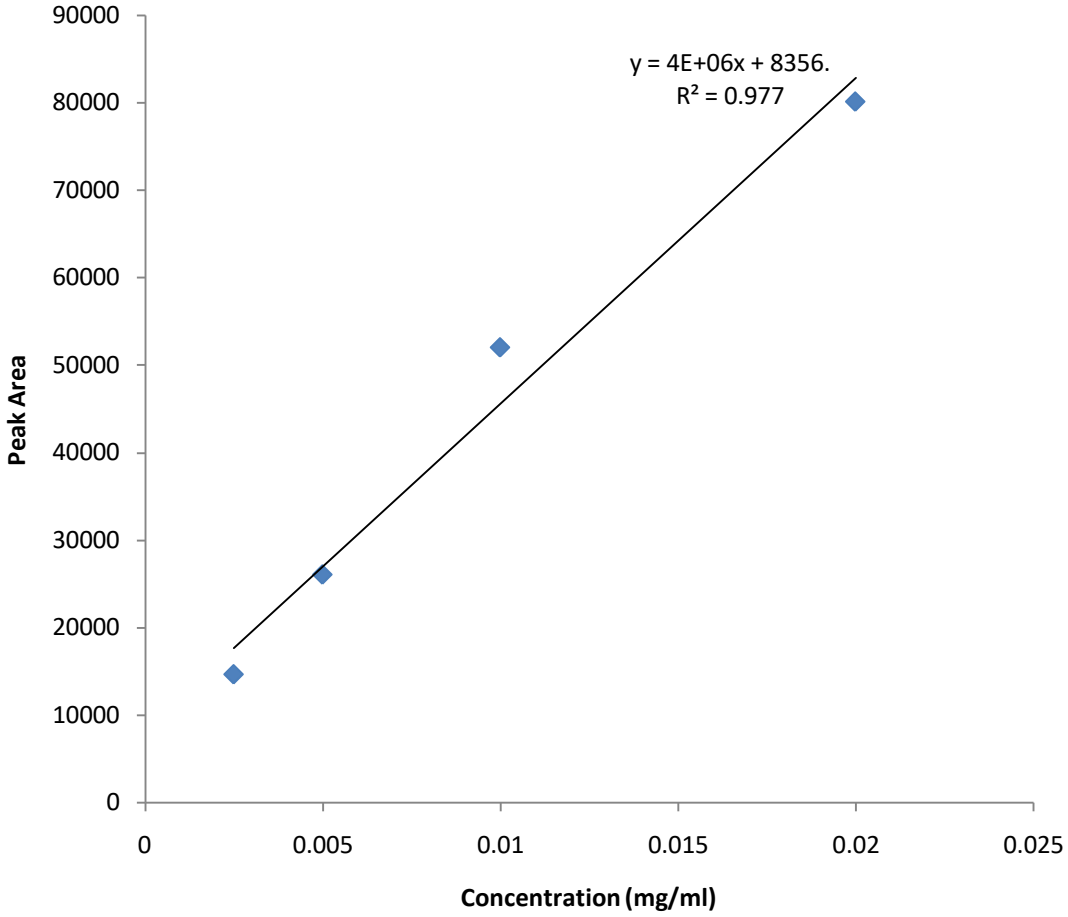
AppendixI: HPLCCalibration Plot of Acetaminophen Standard



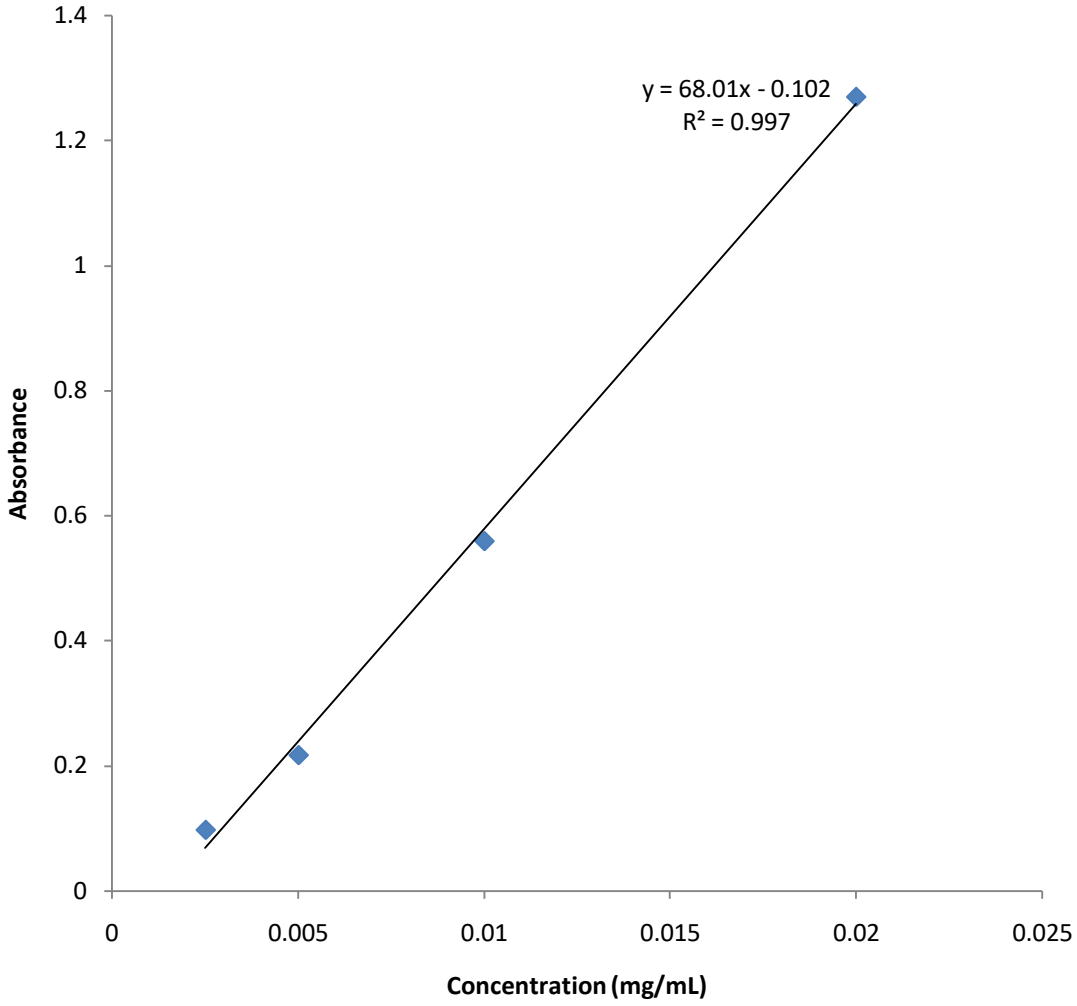
Appendix II:HPLCCalibration Plot of Amoxicillin Standard



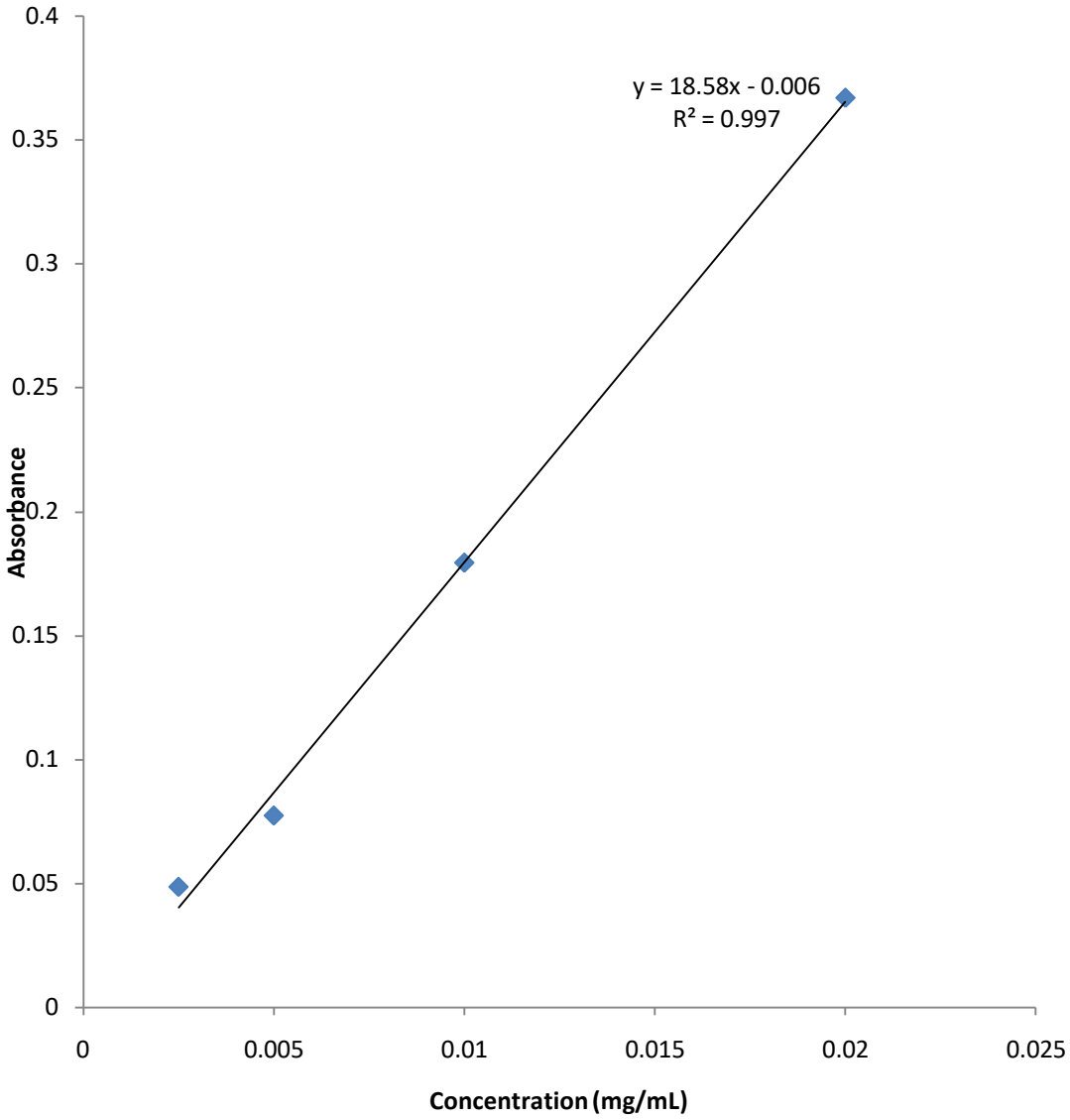
Appendix III:HPLC Calibration Plot of Ibuprofen Standard



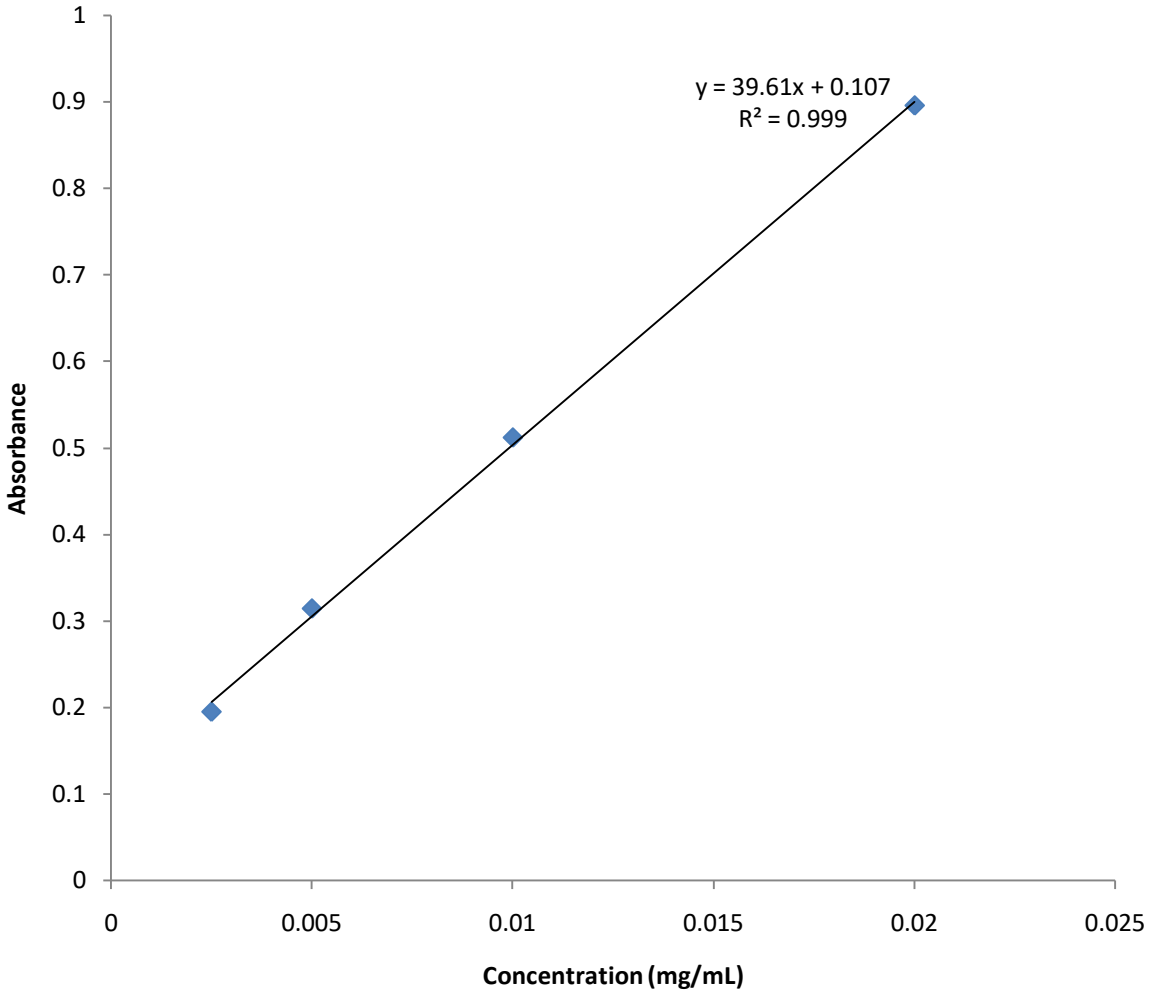
Appendix IV: UVCalibration Plot of Acetaminophen Standard



Appendix V: UVCalibration Plot of Amoxicillin Standard



Appendix VI: UVCalibration Plot of Ibuprofen Standard



Appendix VII: Analysis of Variance Table (ANOVA) of Acetaminophen Adsorption usingResponse Surface Quadratic Model (CAC)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.044	14	3.117E-003	7.86	0.0001	significant
A-CT	8.000E-004	1	8.000E-004	2.02	0.1760	
B-C	0.030	1	0.030	76.70	0.0001	significant
C-AD	5.000E-005	1	5.000E-005	0.13	0.7275	
D-pH	2.722E-004	1	2.722E-004	0.69	0.4204	
AB	3.025E-003	1	3.025E-003	7.63	0.0145	significant
AC	2.500E-005	1	2.500E-005	0.063	0.8052	
AD	6.250E-004	1	6.250E-004	1.58	0.2286	
BC	1.225E-003	1	1.225E-003	3.09	0.0992	
BD	2.500E-005	1	2.500E-005	0.063	0.8052	
CD	1.225E-003	1	1.225E-003	3.09	0.0992	
A^2	2.501E-004	1	2.501E-004	0.63	0.4395	
B^2	7.974E-008	1	7.974E-008	2.011E-004	0.9889	
C^2	6.940E-005	1	6.940E-005	0.17	0.6817	
D^2	1.597E-003	1	1.597E-003	4.03	0.0632	
Residual	5.949E-003	15	3.966E-004			
Lack of Fit	5.949E-003	10	5.949E-004			
Pure Error	0.000	5	0.000			
Cor Total	0.050	29				

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors. A^2, B^2, C^2, and D^2 are the square effects of the factors.

AppendixVIII: Analysis of Variance (ANOVA) of Acetaminophen Adsorption using Response Surface 2FI Model (JAC)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.27	10	0.027	2.72	0.0291	significant
A-CT	0.012	1	0.012	1.24	0.2802	
B-C	0.073	1	0.073	7.40	0.0136	significant
C-AD	0.018	1	0.018	1.82	0.1935	
D-pH	0.020	1	0.020	2.01	0.1721	
AB	0.026	1	0.026	2.58	0.1249	
AC	0.018	1	0.018	1.83	0.1915	
AD	0.029	1	0.029	2.91	0.1044	
BC	1.000E-002	1	1.000E-002	1.01	0.3283	
BD	0.038	1	0.038	3.83	0.0653	
CD	0.026	1	0.026	2.58	0.1249	
Residual	0.19	19	9.934E-003			
Lack of Fit	0.19	14	0.013			
Pure Error	0.000	5	0.000			
Cor Total	0.46	29				

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors.

AppendixIX: Analysis of Variance Table (ANOVA) for Amoxicillin Adsorption using Response Surface 2FI Model (CAC)

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob>F	
Model	1.18	10	0.12	3.73	0.0066	Significant
A-CT	0.076	1	0.076	2.40	0.1380	
B-C	0.51	1	0.51	16.08	0.0007	Significant
C-AD	0.092	1	0.092	2.91	0.1041	
D-pH	0.040	1	0.040	1.27	0.2746	
AB	0.068	1	0.068	2.13	0.1607	
AC	0.032	1	0.032	1.02	0.3249	
AD	0.12	1	0.12	3.75	0.0677	
BC	0.13	1	0.13	4.20	0.0545	
BD	0.017	1	0.017	0.53	0.4743	
CD	0.096	1	0.096	3.03	0.0979	
Residual	0.60	19	0.032			
Lack of Fit	0.60	14	0.043			
Pure Error	0.000	5	0.000			
Cor Total	1.79	29				

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors.

AppendixX: Analysis of Variance Table (ANOVA) for Amoxicillin Adsorption usingResponse Surface Quadratic Model (JAC)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.45	14	0.45	22.10	0.0001	Significant
A-CT	2.689E-004	1	2.689E-004	1.85	0.1937	
B-C	0.25	1	0.25	173.58	0.0001	Significant
C-AD	0.046	1	0.046	31.68	0.0001	Significant
D-pH	7.200E-003	1	7.200E-003	4.96	0.0417	Significant
AB	0.024	1	0.024	16.55	0.0010	Significant
AC	8.100E-003	1	8.100E-003	5.58	0.0321	Significant
AD	3.600E-003	1	3.600E-003	2.48	0.1362	
BC	0.012	1	0.012	8.33	0.0113	Significant
BD	4.900E-003	1	4.900E-003	3.37	0.0861	
CD	2.500E-005	1	2.500E-005	0.017	0.8974	
A^2	2.776E-004	1	2.776E-004	0.19	0.6682	
B^2	0.014	1	0.014	9.94	0.0066	Significant
C^2	5.165E-003	1	5.165E-003	3.56	0.0788	
D^2	2.412E-004	1	2.412E-004	0.17	0.6893	
Residual	0.022	15	1.452E-003			
Lack of Fit	0.022	10	2.178E-003			
Pure Error	0.000	5	0.000			
Cor Total	0.47	29				

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors. A^2, B^2, C^2, and D^2 are the square effects of the factors.

AppendixXI: Analysis of variance (ANOVA) for Ibuprofen Adsorption using Response Surface 2FI Model (CAC)

Source	Sum of Squares		df	Mean Square	F Value	p-value Prob > F	
Model	3.17	10	0.32	2.70	0.0301	significant	
A-CT	0.023		1	0.023	0.20	0.6598	
B-C	1.60		1	1.60	13.60	0.0016	significant
C-AD	0.31		1	0.31	2.66	0.1195	
D-pH	0.20		1	0.20	1.71	0.2068	
AB	0.013		1	0.013	0.11	0.7408	
AC	0.14		1	0.14	1.23	0.2812	
AD	0.42		1	0.42	3.54	0.0752	
BC	0.16		1	0.16	1.40	0.2518	
BD	0.12		1	0.12	0.98	0.3335	
CD	0.18		1	0.18	1.54	0.2299	
Residual	2.23		19	0.12			
Lack of Fit	2.23		14	0.16			
Pure Error	0.000		5	0.000			
Cor Total	5.40		29				

Note: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors.

AppendixXII: Analysis of Variance (ANOVA) for Ibuprofen Adsorption using Response Surface 2FI Model (JAC)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2.23	10	0.22	2.84	0.0241	significant
A-CT	0.19	1	0.19	2.40	0.1382	
B-C	1.30	1	1.30	16.50	0.0007	significant
C-AD	0.010	1	0.010	0.13	0.7216	
D-pH	0.037	1	0.037	0.48	0.4987	
AB	0.28	1	0.28	3.58	0.0739	
AC	2500E-0031	2500E-003	0.032	0.8603		
AD	0.053	1	0.053	0.67	0.4220	
BC	0.016	1	0.016	0.20	0.6606	
BD	0.051	1	0.051	0.64	0.4320	
CD	0.30	1	0.30	3.78	0.0667	
Residual	1.49	19	0.079			
Lack of Fit	1.49	14	0.11			
Pure Error	0.000	5	0.000			
Cor Total	3.72	29				

Key: CT-Contact time (mins), C-Concentration (mg/L), AD-Adsorbent dosage (g) and D-pH. The adsorption factors are coded A, B, C and D. AB, AC, AD, BC, BD, and CD are the interraction effects of the factors.