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REMOVAL OF ACTIVE PHARMACEUTICAL INGREDIENTS FROM PHARMACEUTICAL WASTEWATER USING ORGANIC ACID MODIFIED PLANTAIN PEELS.

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ABSTRACT: This review focused on the isotherm modeling of the removal of lead and metallic contaminants from pharmaceutical wastewater using activated oil palm empty fruit bunch. The heavy metals in pharmaceutical wastewater sample were revealed by the Atomic Absorption Spectrometry analysis, which proved that lead and cadmium metals are the most dangerous metals in the sample under analysis because they exceed the acceptable limitsgiven by World Health Organization. The nutritional value of the raw and activated oil palm bunch, revealed through proximate analysis, indicated an increase in adsorbent properties after chemical activation. The surface morphological analysis of the raw and activated samples revealed considerable increment in the number of the vacant pores for effective adsorption after acid treatment while the Fourier Transform Infrared Spectrometer analysis also indicated an increase in void spaces after activation due to the disappearance of certain functional groups. Kinetic, thermodynamic and isotherm modelling of lead and cadmium removal by adsorption were done using standard equations. Langmuir model closely followed by Temkin model were the most fitting models for the adsorption experiment. Pseudo-second order kinetic model is the most suitable kinetic model while the results from the thermodynamic analysis, such as change in enthalpy, change in entropy and standard Gibb's free energy showed that the process is notspontaneous. The adsorption was carried out in batches to determine the effects of stirring time, temperature and dosage of the activated palm bunch on the removal of lead and cadmium ions.These process conditions were optimized with central composite design of response surface methodology with the aid of a design expert (version 13). The response was removal efficiency while the suggested model was quadratic. The predicted adsorbent removal efficiencies for lead and cadmium are 89.234% and 73.318% respectively at 69.150mins, 345.155°C and 0.266g adsorbent dosage. This was validated by carrying out the metal removal at the suggested conditions to obtain actual adsorbent removal efficiencies of87.82% and 72.51% for lead and cadmium respectively.Thus, activated oil palm bunch is economically viable and practically proven biomass waste for pharmaceutical wastewater treatment.

KEYWORDS: Residual gases, Pollution, Wastewater Treatment, Modelling, Enthalpy

1. INTRODUCTION

Advancement in technology and industrialization is the major cause of environmental pollution. Air pollution and water pollution are among the commonest environmental pollution, however, while air pollution are mainly due to industrial activities involving the release of flue gases and residual gases, water pollution are mainly due to industrial activities leading to unruly discharge of industrial effluents and wastewaters into the different natural water bodies. In reality, it is not only industrial activities that pollute our water streams, domestic activities also play a role in water contamination, though industrial operations are the major culprits. According to Loredo-Cancino et al.(2016), the industries guilty of releasing large amount of wastewater into the environment include pharmaceutical industry,

food processing industry, petroleum industry, plastic, fertilizer production industries, steel, coal and mining industries. Anyakora et al. (2011) noted that pharmaceutical companies of the major sources of solid wastes and effluents in the environment due to high increase in global demand of drug. Also, 50% of pharmaceutical wastewaters are discharged without any recommended practice (Osaigbovo and Orhue, 2006). Recently, pharmaceutical products are used for the prevention and curing of livestock and fish diseases in livestock rearing and aquaculture and has led to a high increase in its production (Justyna et al., 2019; Wang & Wang, 2016). The fact that pharmaceutical products are everywhere is the reason for the persistence of their pollutants (Noelia, 2011). Lee et al. (2017) opined that pharmaceutical discharges are high toxic emerging pollutants. They contain complex compounds which are highly carcinogenic and less biodegradable (Qin et al., 2015; Kantar et al., 2019). As a result, pharmaceutical wastewater could be very complex and lead to serious health hazards (Pal, 2018; Guo et al., 2017). Pharmaceuticals effluents are known to have high concentration of antibiotic resistant bacterial and organic compounds (Hou et al., 2019; Priya& Philip, 2013).

The ingredients used during the production of pharmaceutical products may be classified into active, inactive, additive or preservative. Active pharmaceutical ingredients (APIs) could be described as the potent substance in the pharmaceutical product or drug charged with performing the primary function of the drug. Examples include acetaminophen (paracetamol), Ibuprofen, Amoxicillin and Salbutamol (Comerton et al., 2009).There has been a number of publications that identified many chemical constituents in pharmaceutical wastewaters as well as their hazardous effects (Larson et al., 2007; Idris et al., 2013). Thus active pharmaceutical ingredients are the major causes of water pollution (Hemine et al., 2020). They must therefore be removed from pharmaceutical wastewater before discharge to avert the catastrophic effects they may cause human and lower organisms' lives. Recently, focus has been shifted on wastewater treatment by adsorption, especially in the developing countries like Nigeria, because of abundance of agricultural wastes, which in most cases have no other economic values rather they even pose serious environment threats since there is no efficient means of disposing them. Moreover, adsorption has numerous benefits over other conventional methods. Varieties of biomass adsorbents have been used in remediation of wastewater. According to Mohan et al. (2014), factors to consider when choosing materials include nature of water contamination, amount of contaminants and the adsorbent removal capacity. This review will concern itself with the use of plantain peel in removing Amoxicillin and Ibuprofen from pharmaceutical wastewater.The choice of plantain peel as one of the adsorbent in this work could also be traced to the fact that it is one of the readily available and abundant waste in Nigeria, which is easily obtainable from dump sites and local farmers. Oluyemi et al (2009) observed that plantain is a better source of activated carbon than bones and woody materials in terms of production cost and time convenience.

II. Historical Background

There are two main factors affecting water quality: natural and man-made factors. Natural conditions affecting surface water bodies include rainfall, soil particles, dissolved solids such as ions coming from the dissolution of rocks and so many other natural factors that have the capacity of mixing and dissolving in the water bodies, rendering it impure for certain special purposes. Man-made factors are the interferences due to all forms of human activities. This means that water quality is affected by the manner in which human beings occupy and use lands. Pharmaceutical industries like plastic, petroleum, rubber, fertilizer production, steel, coal and mining industries generate huge amount of wastes that litter and make the environment unsafe (Loredo-Cancino et al., 2016). The products from pharmaceutical industries are humongous because pharmaceuticals are used in every facet of life, such as livestock rearing and aquaculture for cure and prevention of diseases in fishes (Noelia, 2011; Wang and Wang, 2016; Justyna et al., 2019). Drugs could be manufactured with chemicals, grouped into active, inactive, additive or preservative. Some examples of pharmaceutical active ingredients are Amoxicillin, Salbutamol, Ibuprofen, Acetaminophen (Paracetamol) (Comerton et al., 2009). Though active pharmaceutical ingredients are the most important substance charged with the major function of a given drug, they are still considered as the main cause of pollution when the pharmaceutical wastewater is released into the environment (Hemine et al., 2020). The effects of these pharmaceutical pollutants depend on the processing technology, nature of chemicals used during the production, size and characteristics of wastewater. Chang et al. (2015) has opined that pharmaceutical wastewater forms what is called 'emerging organic contaminants,' whose release into our environment are due to the making of new products, disposal of by-products or unused products and also from excreta.

2.2 Plantain Peel

Plantain is a plant grown majorly in the tropical region. Because of its high fibre content, it can be used to lower cholesterol, constipation and aids prevention of colon cancer. Moreover, Ng and Fong (2000) said that plantain has the ability to prevent high blood pressure and muscle cramp because it is rich in potassium. Various parts of the plant such as the leaves, root, fruit stalk, bract and fruit have been used for medicinal and domestic purposes. The fruit is consumed as food, the leaf juice is used in the treatment of fresh wounds, cuts and insect bites while the plantain waste (peel) could be used as an adsorbent and as raw materials for animal feed production because it is rich in crude fibre, carbohydrates and ash. Plantain peels are by-products of the plantain processing industry, which are normally dumped in landfills, rivers or unregulated grounds (Osma et al., 2007). The peel of the fruit is discarded as waste after the inner fleshy portion has been eaten, thereby constituting a menace to the environment, especially where its consumption is common. In Nigeria, plantain peel is an abundant waste because of the high consumption of plantain. Oluyemi et al (2009) observed that proximate and mineral compositions of plantain makes it a better source of activated carbon than bones and woody materials in terms of production cost and time convenience.

2.3 Active Pharmaceutical Ingredients

Chemicals which are used due to biological activities are known as pharmaceuticals. They are of immesnse importance because they improve both our standard of lives and state of health. Pharmaceuticals are made up of substances classified as active pharmaceutical ingredients, excipients and additives alongside other inorganic salts and organic chemicals, such as sugars, pigments and dyes. It is already an established fact that pharmaceuticals are manufactured and consumed in large quantities due to their usefulness. Pe´rez (2013) said that Latin America produces at least 3% of the global pharmaceuticals. This means that the consumption of active pharmaceutical ingredients by the world populace is enormous because every drug is made up of an API. By definition, Active pharmaceutical ingredients (APIs) are the active substances in a pharmaceutical drug that produce the required effect on the body to treat a condition. They are the biological active substances in pharmaceutical drugs, responsible for their potency. APIs are produced by processing chemical compounds. APIs enshrines large number of tiny molecules in drugs with typical differences in physical, chemical and biological features. Thus little adjustments in its chemical nature could affect its effect on the environment (Cunningham, 2008).

APIs are broadly classified into– synthetic and natural. Synthetic APIs are further classified into innovative and generic synthetic APIs, based on the type of synthesis used. Synthetic chemical APIs, also known as small molecules, constitute a large part of the pharmaceutical market, with many small molecule drugs commercially available in the market while Natural APIs are used in making biologics, which are increasingly becoming the top-selling drugs in the market. Despite the growing demand, biologics are currently significantly fewer in number compared to small molecule drugs.

APIs are also grouped into soluble and insoluble ingredients based on their solubility.

The APIs, their metabolites and conjugates from the manufactured pharmaceutical drugs and its discarded material and human wastes, urine or faeces inclusive, easily enter our land and water environments (Kleywegt et al., 2019). According to Caldwell et al. (2016), the continuous production of pharmaceuticals heightens global pollution due to the accumulation of large number of API in the pharmaceutical wastewaters. Effluents from hospitals, industries, domestic and veterinary sources contain pharmaceuticals which eventually reach treatment plants or rivers and in most cases without pre-treatment (Araujo and McNair, 2007). The risks posed to humans from pharmaceuticals in the environment seem to concern environmental hygiene rather than toxicology and pharmacology (Jones et al., 2004). However, there are some exceptions: Endocrine-active compounds and hormones may interfere with sexual development in humans, as they are highly active compounds that interact with hormone systems (Hannah et al., 2009; Lange et al., 2001; Kidd et al., 2007; Caldwell et al., 2008). Data concerning the effects of the active substances on organisms in the aquatic and terrestrial environments is increasing but still too little. Effects on fish, daphnia, algae, and bacteria have been demonstrated using low concentrations in long-term tests (Fenk et al., 2006; Yamashita et al., 2006).

Ibuprofen and Amoxicillin are among the commonest non-steroidal anti-inflammatory drugs (NSAIDs) and antibiotics for killing pain and treating bacterial infections respectively. Using Mexico as a case study, study have shown that in Mexico, there is almost no restriction in purchasing ibuprofen since it has lesser side effect than amoxicillin (Dresser et al., 2008). Also in Mexico, ibuprofen is among the essential drug list (CSG, 2014). However, amoxicillin is one of the most widely administered antibiotics as well (Vargas-Jime´nez et al., 2011). There are many traces of amoxicillin and ibuprofen particles in freshwaters and effluents from many sewage treatment plants in many nations (Andreozzi et al., 2004; Brun et al., 2006; Gomez et al., 2007; Kim et al., 2007).

2.4 Industrial Wastewater Treatment

It is an industrial requirement to treat and reuse the wastewater after removal of the contaminants in order to combat water pollution and problems of scarcity of pure water. Treatment technologies which have been used in literature include coagulation, flocculation, sedimentation, adsorption, amongst others (Yasmin et al., 2015; Krishnarao, et al., 2001). Treatments using advanced technologies like membrane bioreactor and advanced oxidations have also been reported in literatures (Alau et al., 2010; Papita, 2010; Shaobin et al., 2005).

Industrial wastewater treatment covers the mechanisms and processes used to treat wastewater that is produced as a by-product of industrial or commercial activities. After, treatment, the treated industrial wastewater (or effluent) may be reused or released to a sanitary sewer or to surface water in the environment. Most industries produce some wastewater although recent trends in the developed world have been to minimize such production or recycle such wastewater within the production process.

2.5 Adsorption Processes and Isotherm Models

Adsorption is a reversible process in which liquid or gaseous molecules are concentrated on the surface by chemical or physical forces or both.

2.5.1. Types of Adsorption Processes

The major processes of adsorption are:

Chemisorption: This is a term used for chemical adsorption; it is also known as specific adsorption. It is only applicable to the monolayer coverage of the substrate. The bonding force associated is much stronger and the heat energy given off during the process is much bigger than that in physisorption. For the chemisorbed molecule to react with the molecular kind, they require an amount of energy which may be significantly lower than that needed when the two kinds react directly in the gaseous state.

Physisorption: It is also known as non-specific adsorption. It results from long range weak vander-waal's forces between adsorbates and adsorbents. The energy evolved when a particle is physisorbed is in the similar order of magnitude as the enthalpy of condensation. The enthalpy of physisorption can be determined by monitoring the increase in temperature of a sample of known heat capacity. The adsorption process is irreversible, exothermic and gives off heat based on the magnitude of the force of attraction. Physisorption is always directly proportional to the amount of available solid surface.

Desorption: desorption is the release of one substance from another, either from the surface or through the surface. It may occur when an equilibrium state is changed.

2.5.2 Adsorption Isotherms

Adsorption isotherms provide basic information on the nature of interaction between the inhibitor and the metal through applying some adsorption isotherm models. Holistically, adsorption isotherms showcase two categories of adsorptio n namely; (i) reversible (comprising of physical adsorption and weak chemical adsorption) and (ii) irreversible (actively chemisorbed) (Al-Anber and Al-Anber, 2008; Al – Anber, 2007).

Occasionally, both physical adsorption and chemical adsorption may occur simultaneously or adversely, a film of molecule may undergo physisorption above an elemental chemisorbed film (Denizli et al., 2000).

2.5.2.1 Langmuir Model

Langmuir adsorption isotherm describes the quantitative formation of a monolayer adsorbate on the outer surface of the adsorbent. It is the most suitable for physical and chemical adsorption where there is no interaction between the adsorbate and adsorbent. Thereby, the Langmuir may represent the equilibrium distribution of metal ions between the solid and liquid phases. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \left(\frac{Q_0 K_L C_e}{1+K_L C_e}\right) \qquad (2.1)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation 2.11 into linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \qquad (2.2)$$

Where: C_e= the equilibrium concentration of adsorbate (mgL^{-1})

q_e= the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Q_o = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg).

2.5.2.2 Freundlich Model:

This is commonly used to describe the adsorption characteristics for the heterogeneous surface. The empirical equation proposed by Freundlich is given by:

$$Q_e = K_f C_e^{1/n} \qquad (2.3)$$

Where K_f = Freundlich isotherm constant (mg/g)

n = adsorption intensity;

C_e = the equilibrium concentration of adsorbate (mg/L)

Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation 2.36, we have:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \qquad (2.4)$$

The constant $K_f$is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process (Voudrias et.al, 2002). However$K_f$and *n* are parameters characteristic of the sorbent-sorbatesystem, which must be determined by data fitting, and where linear regression is generally used to determine the parameters of kinetic and isotherm models (Guadalupe, 2008). However, when n = 1, the relation becomes a linear adsorption isotherm. There is a favorable sorption process when the values of n lies in between one and ten (Goldberg, 2005).

2.5.2.3Temkin Model:

This model suggests that the heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with the surface coverage. The equation according to Temkin's model is written as:

$q_e = B\ln K_T + B\ln C_e$(2.5)

$$\text{Where } B = \frac{RT}{b} \qquad (2.6)$$

Where K_T(L/mol) is Temkin binding constant at equilibrium relating to the maximum binding energy.

2.5.2.4Dubinin-Radushkevich Model:

This model is typically used to differentiate physical and chemical adsorption according to the mean free energy.

$$\ln q_e = \ln q_n - \beta\varepsilon^2 \qquad (2.7)$$

Where β is a coefficient related to the mean free energy of adsorption per mol of the metal ion (mol^2/J^2), $q_n$is the theoretical saturation capacity (mg/g) and ε is the Polanyi potential mathematically explained as:

$\varepsilon = RT\ln(1 + \frac{1}{Ce})$. Ce and qe are the metal equilibrium concentration (mg/l) and equilibrium adsorption capacity (mg/g).

2.6 Importance of water in pharmaceutical industries

Several solvents are employed as vehicles in the pharmaceutical manufacturing process to dissolve gaseous, solid, or viscous reactants, products, and impurities. They are used in the chemical synthesis process to dissolve reactants in a homogeneous phase to overcome mass and heat transfer effects. Some solvents are
used to control the reaction temperature. A variety of pollutants released during the manufacture of pharmaceutical products are the reaction and purification solvents (perez et al, 2012; Gani et al., 2008). These include benzene, phenol, toluene, halogenated solvents, and cyanide. Although EPA has banned or put restriction on use of some 23 solvents including some VOCs and chlorinated solvents, some are still used by the pharmaceutical industry since the relevant drugs cannot be manufactured by using other solvents. The major nonconventional solvents used in industry are methanol, ethanol, isopropanol, acetone, and ethyl acetate. Also, many hetero-aromatics such as pyridine contribute to this list as they are inert in the reaction process. Many industries have their solvents recovery systems for purification of contaminated solvents consisting of distillation columns and solvent−solvent evaporation systems in which a second solvent is used to separate impurities (Zhang et al., 2003). These operations result in aqueous wastewaters being fully or partially saturated with residual solvents.

2.6.1 Characteristics of pharmaceutical wastewater

In general, the composition of pharmaceutical wastewater is complex, which has high concentration of organic matter, microbial toxicity and high salt. In addition, most of pharmaceutical productions are done in batches, and there are different raw materials and production process, which causes huge varieties in different wastewater constituents.

Different kinds of pharmaceutical wastewater have different characteristics. Biopharmaceutical wastewater is characterized as strong fluctuation in quantity, high suspended solid concentration, high sulfate concentration, complicated composition and biological toxicity. Chemical pharmacy is lack of nutrition, hard to biodegrade and toxicity to microbiology and it also has high salt content. The characteristics of the wastewater of Chinese patent medicine is containing sugar, glycosides, organic pigment, anthraquinone, tannins, Alkali content, cellulose, lignin and other organic matter (Yu, 2013).

2.6.2 Pharmaceutical Wastewater Treatment

There are variations in composition, quality and quantity of wastewaters generated from pharmaceutical industries, depending on the season, time, raw materials, location and processes used during production of many drugs. Hence it is very difficult to specify a particular treatment system for such a diversified pharmaceutical industry. Many alternative treatment processes are available to deal with the wide array of waste produced from this industry, but they are specific to the type of industry and associated wastes. However, the analysis of published information in the public domain shows that the six general approaches are employed to treat pharmaceutical wastewaters are (1) recovery of individual APIs or drugs which are likely to be present in wash waters and solvents, (2) physical−chemical treatment by sedimentation or floatation, (3) aerobic/anaerobic biological treatment in membrane bioreactors or bio-aeration, (4) inactivation of active substances by UV oxidation in conjunction with O3 or H2O2, (5) sterilization and decontamination of infectious and bioactive substances from biotechnology and (6) new hybrid technologies specific to the pharmaceutical industry. The treatment methods may be classified into two:

2.6.2.1 Recovery Processes

Pretreatment and recovery of various useful byproducts, such as solvents, acids, heavy metals and various important API's, which find their way into the waste streams comprise a very important waste control strategy for pharmaceutical plants. In the fermentation plants, the mycelia, the solvents exhibit very high BOD strength, and also some of the solvents are not biologically degradable. Recovery of the pharmaceutical substances can reduce or even eliminate waste disposal costs of the primary unit process and raw water requirements of the secondary unit process, quickly offsetting waste-treatment operational costs and improving the economics of the process. The recovered waste stream can be used elsewhere in the process, and the water could be used for boiler feed or cooling towers and other operations thereby reducing consumption of precious raw water and drastically reducing operating costs. Certain pharmaceuticals are recovered using membrane technology. Nano-filtration is a membrane separation process, which has been widely used in aqueous systems such as the concentration of antibiotic aqueous solutions (Sun et al., 2000; Zhang et al., 2003). Nanofiltration can be useful in recovering more than 80% of the complex waste stream. The ultrafiltration process has also been effectively used for the recovery of organic compounds from several synthetic media resulting from fermentation process wastewater. It was used in the recovery of protease from spent fermentation broth (Bezawada et al., 2011).

2.6.2.2 Treatment of Wastewater from Dilute Streams

The dilute streams from the manufacturing units are mainly treated by biological treatment methods as they convert most of the waste into gases and sludge can be disposed of harmlessly. Available treatments include the activated sludge process, trickling filtration, the powdered-carbon-fed activated sludge process and the anaerobic hybrid reactor. Apart from the foregoing conventional treatment processes there are several other processes, such as oxidation processes, membrane techniques, and advanced oxidation processes (Deegan et al., 2011).

The treatment processes can be divided into the following four categories and subcategories as follows:

(1) Biological treatment process: This is divided into aerobic and anaerobic treatment.

(2) Advanced treatments: These include membrane technology, activated carbon and membrane distillation.

(3) Advanced oxidation processes: These are ozone/hydrogen peroxide treatment, Fenton oxidation, photo-catalysis, electrochemical oxidation/degradation, ultrasound irradiation and wet air oxidation

(4) Hybrid technologies: This is an advanced technology removes completely the pharmaceutical contaminants by combining at least one conventional method with membrane separation process.

2.7 Analytical Techniques

2.7.1 Scanning electron microscopy (SEM): This is also known as SEM analysis or SEM technique. It can be regarded as an effective method in analysis of organic and inorganic materials on a nanometer to micrometer (μm) scale. SEM works at a high magnification reaches to 300,000x and even 1000000 (in some modern models) in producing images very precisely of wide range of materials. SEM is a tool at which invisible worlds of microspace and nanospace can be seen. Details and complexity that is inaccessible by light microscopy can be revealed by SEM.

2.7.2 Fourier Transform Infrared Spectroscopy: The term FTIR originates from the fact that a Fourier transform (mathematical process) is required to convert the raw data into the actual spectrum. An FTIR spectrometer simultaneously collects high-spectral solution over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelength at a time. FTIR has wide range of application, such as analysis of small molecules and tissues or cells. It is used for the mapping of cellular components (carbohydrates, lipids, proteins) to identify abnormal cells (Levin and Bhargava 2005; Petibois and De´le´ris 2006).

2.8 Optimization

Data (2011) defined optimization as the basic tool or technique which considers a set of conditions before it establishes the most probable result. In other words, in every optimization analysis, there is an objective function, which poses the challenge or problem to be solved, and there are also affecting variables and constraints. Here, the analysis of the effects of these independent or basic variables will be achieved using design of experiment (DOE) and analysis of variance (ANOVA) while the optimization studies was achieved using full factorial central composite rotatable design (CCRD) of response surface methodology (RSM). CCD is a basic tool in RSM (Sankha, 2021), which is preferred over other RSM techniques because of the accuracy and conciseness of its results. RSM is chosen over other optimization techniques because of its robust strength in handling many factors at the same time, given the best result by providing information on effects of the individual and interaction of the process variables at a decreased number of experimental runs (Uzoh et al., 2013). RSM, as a specialized technique, aims at establishing how the response(s) [dependent factor(s)] is affected by the basic factors (process conditions or parameters). The basic goal of RSM is to use the experimental outcomes or results to develop a statistical model for the particular system or process under study (Ugwele et al., 2020; Christian et al., 2019; Okpe et al., 2018). By definition, RSM is a system of numerical and standard techniques for developing empirical models. As already stated, it is used to create, improve and optimize a given process (Myers and Montgomery, 2002). RSM is primarily aimed at developing the numerical model of a given system based on experimental results. RSM was developed to model responses. Later, it migrated into the modeling of experiments. Errors are assumed to be random in RSM. Thus, RSM uses regression analysis to relate the properties of items (Adeyanju et al., 2016).

Design of Experiment (DOE)

DOE is one of the basic concepts in RSM. It facilitates systematic, efficient, cost effective planning and analysis of experimental studies (Montgomery, 2004).

These procedures were developed initially for the fitting of models of physical experiment, but could also be useful in experiments involving numerical values. An experiment could be described as a number of tests, known as runs. Here, changes are affected in the input parameters so as to identify the reasons behind the changes in the output parameters, called response.

Designed experiments can find and identify how different variables interact and affect the overall performance. Non-linear relationships exhibited by the factors are easier to identify when DoE is implemented.

There are three classic multi-level design groups:

Central Composite Designs

Face-Centered Cubic Design and

Box-Behnken design.

2.9 Reaction Kinetics

Chemical kinetics, also known as reaction kinetics, is the science of all processes involving chemical reaction (Gorban et al., 2015). Adsorption kinetics depends on the adsorbate–adsorbent interaction and system condition and has been investigated for their suitability for application in water pollution control. Two vital evaluation elements for an adsorption process operation unit are the mechanism and the reaction rate. Solute uptake rate determines the residence time required for completing the adsorption reaction and can be enumerated from kinetic analysis. Numerous attempts were made in formulating a general expression to describe the kinetics of adsorption on solid surfaces for the liquid–solid adsorption system (Ho 2004). The adsorption rate is an important factor for a better choice of material to be used as an adsorbent; where the adsorbent should have a large adsorption capacity and a fast adsorption rate.

2.9.1 Theories of adsorption kinetics

Most of adsorption studies used pseudo-first-order and pseudo-second-order models to study the adsorption kinetics (Salleh et al. 2011).

In this work, the theories of adsorption kinetics are discussed under the following models:

1. 1st order model
2. Pseudo-first order model
3. 2nd order model
4. Pseudo-second order model
5. Elovich model.
6. Intra-particle diffusion model

2.9.1.1 First order model

A simplified first order rate equation used in representing it is as follows:

$$C_t = C_o e^{-kit} \qquad (2.8)$$

Equation 2.5 can be linearized to obtain equation 2.20.

$$\text{Log}C_t = \frac{K1}{2.303}(t) + \log C_o \qquad (2.9)$$

C_t and C_o = solute concentration in (mg/l) at anytime time, t(s) and initial concentration in (mg/l) respectively, K_1 = first order rates constant (min^{-1}).

Hence, assuming first order kinetics is possible in the system, a plot of $\log C_t$ versus t of Equation (2.6) will give a linear graph of slope s, from which the constant Ki and initial concentration C_o can be calculated using the relations $K_1/2.303$ and log C_o as slope and intercept respectively.

2.9.1.2 Pseudo-first order model

The first order rate equation was deduced to describe the kinetic process of a liquid – solid phase adsorption of oxalic acid and malonic acid onto charcoal. This is assumed to be the earliest model with regards to the adsorption rate based on the adsorption capacity.

$$\frac{dq}{dt} = K_{pl}(q_e - q_t) \qquad (2.10)$$

Integrating eqn 2.21 using boundary conditions: $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, will yield

$$\ln q_e - \ln(q_e - q_t) = K_{p1}t \qquad (2.11)$$

Rearranging the equation, it will give

$$\log(q_e - q_t) = \log q_e - \frac{kpl}{2.303}(t) \qquad (2.12)$$

If the Lagergren's first order kinetics works in the system, then a plot of log ($q_e - q_t$) against (t) will yield in a linear graph with $\frac{Kp1}{2.303}$ as gradient and log q_e as intercept. In order to differentiate the kinetic equations based on the adsorption capacity from solution concentration, Lagergren's first order rate has been called pseudo-first order.

2.9.1.3 Second order model

The equation in solution systems is represented as follows:

$$\frac{dc_t}{dt} = k_2 C_t^2 \qquad (2.13)$$

Integrating equation (2.24), with the boundary conditions $C_t = 0$ at $t = 0$ and $C_t = C_t$ at $t = t$. It will give

$$\frac{l}{C_t} = k_2 t + \frac{1}{C_0} \qquad (2.14)$$

Where C_0 and C_t (mg/l) are the equilibrium concentration of solute and concentration at any time t, K_2 is the rate constant of second order model.

2.9.1.4 Pseudo-second-order model

Ho and Mckays (1999) explained the kinetic process of the adsorption of divalent metal ions onto peat. The driving force, (q_e - q_t) is proportional to the available fraction of active sites. Then, it yields;

$$\frac{dq_t}{dt} = K_{p2}(q_e - q_t)^2 \qquad (2.15)$$

re-arranging equation 2.26,

$$dq_t(q_e - q_t)^2 = K_{p2}dt \qquad (2.16)$$

Integrating equation 2.27 with boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$at $t = t$, it yields;

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_{p2}t \qquad (2.17)$$

Re-arranging equation 2.28 we will get

$$t/q_t = 1/K_{p2}q_e^2 + 1/q_e(t) \qquad (2.18)$$

Similarly, Ho's second-order rate equation has been called pseudo- second order rate equation to differentiate kinetic equations based on adsorption capacity from concentration. The pseudo second order kinetics model has been successfully used in several bio-sorption systems.

2.9.1.5 Elovich Model

This was developed by Zeldovich in 1934 to explain the rate of adsorption of carbon (ii) oxide (CO) on manganese dioxide. This is called the Elovich equation.

The equation is given below;

$$\frac{dq_t}{dt} = \alpha e^{-\beta qt} \qquad (2.19)$$

Where q_t = amount of gas adsorbed at time (t).

t, α and β = the adsorption constant (g/mg) during experiment.

The equation shows that the rate decreases exponentially with rise in the quantity of gas being adsorbed. To simplify the elovich equation, Chien and Clayton, (1980) assumed αβ >> t and by applying boundary condition at $q_t = 0$ at t=0 and $q_t = q_t$ at t=t, the equations becomes;

$$q_t = 1/\beta \ln(\alpha\beta) = 1/\beta \ln(t) \qquad (2.20)$$

A plot of q_t versus lnt will give a linear relationship with $1/\beta$ as slope and $1/\beta \ln(\alpha\beta)$ as slope and intercept respectively.

2.9.1.6 Intra–particle diffusion model

$$q_t = K_{id}t^{1/2} \qquad (2.21)$$

In 1962, Weber Moris was the first to that in most adsorption processes, solute uptake varies directly as $t^{1/2}$ instead of with the constant time, t.

The logarithm form of the above equation is

$$\log q_t = \log K_{id} + 0.5 \log t \qquad (2.22)$$

Where K_{id} = intra-particle diffusion rate constant. From equation (2.22), when log q_t is plotted against 0.5 log t, it will give a straight line with a positive intercept of log K_{id}.

III. MATERIALS AND METHODS

The materials for this experiment include plantain peel, sourced from Ugwogonike in Abakpanike Enugu east local government area, Enugu State. Pharmaceutical wastewater, collected with a 10litres sterile gallon directly from the drug production company in Enugu state, Nigeria. The sample was stored in a refrigerator at 3-8°C before analysis.

3.1.1 Reagents and Chemicals

The reagents include deionized water, normal hexane,wijs reagent, magnesium acetate, sodium hydroxide, acetic acid. All the reagents are of the highest quality.

3.1.2 Instruments and Equipment

The various equipment used are electric grinder, electromagnetic sieve shaker (Model BA 200N), electronic digital weighing balance (Model PA 213), desiccator, muffle furnace (M1024), stainless steel beaker, hot plates, Brush, crucible, 20x150mm test tube, 1000ml Erlenmeyer flask, reflux condenser, 250 ml Erlenmeyer flask, pH meter (Hanna M921),Oven (Techmel M228 USA), petri-dish, oven, 100ml conical flask, heating mantles, magnetic stirrer, refrigerator, gallon, water bath, Atomic absorption spectrophotometer (Model FS240AA) and FTIR Spectroscopy (Model: M530).

3.2 Methods

3.2.1 Preparation, carbonization andactivation of plantain peel

The samples were cleaned with deionized water and dried at 110 °C for 48 h to reduce the moisture content. The dried samples were then crushed and sieved to a size range of 1–1.5mm. Subsequently, the samples were carbonized in a muffle furnace at temperature of 550°C at the rate of 20 °C/min and held for 2 h. After carbonization, these samples were mixed with acetic acid (20%) in a stainless steel beaker in the weight ratio of 1:3. The mixture was stirred in a hot plate at 100^0C for 1hr. Water was evaporated at 130°C for 4hrs, after which the dried mixture was heated at a rate of 10 °C/min to 800°C, and kept at this temperature for one and half hour. The products were cooled to room temperature and washed with deionized water until the pH of the washing solution became neutral

3.2.2 Characterization of the Raw and Activated plantain peel

3.2.2.1 Moisture content: This was determined according AOAC (1990) standard.A petri-dish was washed, dried in the oven and weighed, after which 1g of the sample was weighed into petri-dish. The petri-dish containing the sample was weighed w_1.The petri-dish and sample were oven dried at 105^0C for 2hr and weighed (w_2). The drying procedure was continuously repeated until a steady weight was obtained.

$$\%\text{moisture content} = \frac{W1-W2}{\text{weight of sample}}\ x\ 100\% \qquad (3.1)$$

Where w_1 = weight of petri-dish and sample before drying
w_2 = weigh of petri-dish and sample after drying.

3.2.2.2 Ash content

The ash is the leftover residue, which is generally composed of inorganic substances. The ash content was determined by weighing 2g of the sample in a crucible (w_1). The sample is spread with a brush. Then the crucible is kept inside a muffle furnace and the temperature is gradually raised upto 800°C. At 800°C the temperature is kept constant and the incineration of sample is completed by heating the sample for an hour at that temperature. After incineration, the crucible is allowed to cool and transferred to a desiccator. After cooling, the crucible is re-weighed (w_2). The percentageash content is expressed as:

$$\text{Ash content} = \frac{W2-W1}{\text{weight of sample}}\ x\ 100\% \qquad (3.2)$$

3.2.2.3 Volatile matter

Here 2g of sample is taken in a silica crucible with a porous silica cover. The weight of the silica crucible and sample is w_1. The cover is used to avoid oxidation. The sample is then heated for 7 minutes at a constant temperature of 825°C inside a furnace. After heating, the crucible is cooled and transferred to a desiccator. After few minutes, the silica crucible is re-weighed (w_2). The difference between w_1 and w_2 gives the amount of apparent volatile matter in the sample.

$$\text{Apparent volatile matter} = \frac{W2-W1}{\text{weight of sample}}\ x\ 100\% \qquad (3.3)$$

Actual volatile mater = Apparent volatile matter – moisture content

3.2.2.4 Fixed carbon:

This is the carbon content in a sample which is in a free state (uncombined with any element). This is calculated as follows:

Fixed carbon% = 100 - (moisture% + ash% + %volatile matter)(3.4)

3.2.2.5 Lignin content

The procedure according to Crampton and Mayrand (1978) was used to measure the Lignin content as follows: 1g of sample weighed w_1 (initial sample weight), was placed in a 20 x 150mm test tube. 15ml of 72% was added and stirred for 1minute until the sample is thoroughly wetted. The sample was transferred to a 1000ml Erlenmeyer flask and dilute to 500ml of deionized water. The flask, placed on the heating manifold, was boiled gently and refluxed for 4 hours in the reflux condenser. At the end of 4 hours, the condenser was rinsed with a small amount of deionized water before disassembling reflux apparatus.

The hydrolyzed solution was placed on the crucibles. The weight of collected filtrate was measured. The crucible and contents were dried at 105^0C for 2 hours, after which it was cooled in the desiccators and recorded as w_2. The crucible and contents were placed on the muffle furnace and ignited at 575^0C for a minimum of 3 hours, or until all the carbon is eliminated; and then cooled in the desiccator and weighed as w_3

$$\% \text{ lignin} = \frac{W2 - W3}{W1 - \frac{total\ solid}{100}}\ x\ 100\% \qquad (3.5)$$

Note: total solid = 100 – moisture content

3.2.2.6 Determination of Iodine content

The sample is weighed in into a 250 ml Erlenmeyer flask and 20 ml of glacial acetic acid is added. Thereafter, 25 ml of Wijs reagent and 10 ml of the magnesium acetate catalyst were added. The Erlenmeyer flask is closed with the stopper and kept dark for 8 to 10 minutes. At the end of the reaction duration, 10 ml of the Potassium iodide solution is added. The sample is diluted with 100 ml of deionized water and the excess of iodine is back titrated with $Na_2S_2O_3$-Lösung (0.1 mol/L). A Blank value is measured.

$$\text{Iodine value} = \frac{(blank - titre)x\ 1.269}{\text{weight of sample}} \qquad (3.6)$$

Blank value = 27.7

3.2.2.7 Determination of pH

10g of the sample was weighed and placed in a beaker, after which 100ml of water was added. The whole solution was stirred thoroughly and allowed to stand for 1hr. Then the pH was read with a pH meter.

3.2.3 FTIR Analysis of the Raw and Activated Oil Palm Empty Fruit Bunch

Buck scientific M530 USA FTIR was used for the analysis. This instrument was equipped with a detector of deuteratedtriglycinesulphate and beam splitter of potassium bromide. The software of the Gram A1 was used to obtain the spectra and to manipulate them. An approximately of 1.0g of the plantain peel samples (raw and activated) and 0.5ml of nujol were mixed properly and placed on the salt pellet. During measurement, FTIR spectra was obtained at frequency regions of 4000–600cm^{-1} and co-added at 32 scans and at 4cm^{-1} resolution. FTIR spectra were displayed as transmitter values.

3.2.4 SEM Analysis of the Raw and Activated Oil Palm Empty Fruit Bunch

The scanning electron microscopy (SEM) was performed to examine the physical structure change of samples using SEM model PhenomProX,by phenomWorld Einhoven, Netherlands. The sample, placed on double adhesive which was on a sample stub, was coated sputter coater by quorum technologies model Q150R,with 5nm of gold. Thereafter it was taken to the chamber of SEM machine where it was viewed via NaVCaM for focusing and little adjustment, it was then transferred to SEM mode, was focused and brightness contrasting was automatically adjusted, afterward the morphologies of different magnification was store in a USB stick.

3.2.5 AAS Instrumentation Analysis of the Pharmaceutical wastewater

AAS instrument was used to analyse the active pharmaceutical ingredients in the pharmaceutical wastewater. At wavelength of 239.5ηm and 261.60ηm, Amoxicillin and Ibuprofen were discovered respectively among other tiny active molecules.

3.3 Adsorption Studies

The adsorption experiments were carried out in different batches by mixing 50ml of pharmaceutical wastewater with 0.1g of activated sample in a 100ml conical flask. The solution mixture was agitated at very high speed. The adsorbent particles were filtered off from the solution mixture, after which the filtrate was analyzed using AAS equipment to determine the concentration of the target the APIs present. The adsorption capacity and removal efficiency of the activated plantain peel will be calculated using equations 3.7 and 3.10.

3.3.1 Adsorption Capacity and Removal Efficiency

The adsorption capacity was calculated using the mass balance equation (Gunay et al., 2007):

$$Q = \frac{V}{m}(Co - Ce) \quad (3.7)$$

Where Q = adsorption capacity in mg/g; V = volume of the solution in ml; m = mass of the adsorbent in g, Co and Ce = initial and equilibrium concentration each API. Thus after an instantaneous time, t, the adsorption capacity can be calculated as:

$$Q = \frac{V}{m}(Co - Ct) \quad (3.8)$$

Where Ct = API concentration at that time. Other parameters have their usual meaning.

The removal efficiency of the metal is the percentage ratio of the amount of API removed to the API originally present.

$$\text{Removal efficiency (Re)} = \frac{\text{API removed}}{\text{initial API present}}\ x\ 100\% \quad (3.9)$$

That is: $$\text{Removal efficiency (Re)} = \frac{Co - Ct}{Co}\ x\ 100\% \quad (3.10)$$

Table 3.1: Experimental Design

Factors	Symbols	Unit	-1	0	1
Time	A	Mins	100	200	300
Temperature	B	°C	30	50	70
Dosage	C	G	0.04	0.12	0.2

Table 3.2: Design Matrix

Runs	Time (mins)	Temp (°C)	Dosage (g)	Type of API
1	200	50	0.12	Am
2	200	50	0.12	Ib
3	200	50	0.12	Am
4	100	70	0.2	Am
5	300	30	0.2	Am
6	200	83.6358	0.12	Am
7	100	30	0.2	Ib
8	200	50	0.12	Am
9	200	16.3642	0.12	Am
10	368.179	50	0.12	Am
11	100	70	0.2	Ib
12	200	50	0.12	Ib
13	300	70	0.2	Ib
14	200	50	0.12	Ib
15	200	50	0.254543	Am
16	200	50	-0.0145432	Am
17	200	50	0.12	Ib
18	200	50	0.12	Am
19	200	50	0.12	Ib
20	100	30	0.04	Ib
21	100	70	0.04	Ib
22	368.179	50	0.12	Ib

23	100	30	0.2	Am
24	200	50	0.12	Am
25	200	50	0.12	Ib
26	200	16.3642	0.12	Ib
27	200	50	-0.0145432	Ib
28	300	70	0.2	Am
29	200	50	0.12	Am
30	200	50	0.12	Am
31	300	30	0.2	Ib
32	300	70	0.04	Am
33	200	50	0.12	Ib
34	200	50	0.12	Am
35	31.821	50	0.12	Am
36	100	70	0.04	Am
37	200	50	0.254543	Ib
38	300	30	0.04	Am
39	200	83.6358	0.12	Ib
40	200	50	0.12	Am
41	200	50	0.12	Ib
42	31.821	50	0.12	Ib
43	200	50	0.12	Ib
44	100	30	0.04	Am
45	200	50	0.12	Am
46	200	50	0.12	Ib
47	200	50	0.12	Ib
48	300	70	0.04	Ib
49	300	30	0.04	Ib
50	200	50	0.12	Am
51	200	50	0.12	Ib
52	200	50	0.12	Am

3.5Adsorption Isotherms

The fitness of the experimental data was tested into Langmuir, Freundlich, Temkin andDubinin-Radushkevich (R-D) adsorption isotherm models:

3.5.1 Langmuir Model

This model assumes monolayer adsorption at active sites of the adsorbent with no interaction between molecules of adsorbed metals (Hussein et al., 2019). According to Foo and Hameed (2010), Langmuir isotherm can be expressed as:

$$q_e = \frac{QklCe}{1+ klCe} \quad (3.11)$$

Equation 5 when linearized becomes:

$$\frac{Ce}{qe} = \frac{1}{Qkl} + \frac{Ce}{Q} \quad (3.12)$$

Where qe = equilibrium adsorption capacity, which is the amount of API adsorbed per unit mass of the adsorbent (mg/g), Q = maximum monolayer adsorption capacity (mg/g), and kl = Langmuir adsorption constant (L/mg), which relates to the energy of adsorption (l/mg) respectively; Ce is the equilibrium API concentration (mg/l), kl and q are obtained from the intercept and slope of the graph of Ce/q_e against Ce.

The nature of the adsorption process is reflected in Langmuir model by a dimensionless quantity called separation factor R_L. Mathematically, it can be expressed as:

$$R_L = \frac{1}{1+ klCo} \quad (3.13)$$

Where Co is the initial concentration of the adsorbate.

Adsorption process is not reversible if the value of $R_L = 0$, it is favorable if $0< R_L<1$, linear if $R_L = 1$ and unfavorable if $R_L >1$ (Folasegun and Kovo, 2014, Anirudan and Radhakrishnan, 2008).

3.5.2 Freundlich Model

In linearized form, this model is presented thus (Freundlich, 1906):

$$\log q_e = \log kf + \frac{1}{n}\log Ce \quad (3.14)$$

Where qe = equilibrium adsorption capacity or the amount of API adsorbed per unit mass of the adsorbent (mg/g), Ce is the equilibrium API concentration (mg/l), kf = Freundlich adsorption constant in mg/g; n = adsorption index reflecting the adsorption intensity.

3.5.3 Temkin Model

This modelconsiders the interaction between the adsorbents and the API as a function of the surface coverage. Mathematically, Temkin's model is given as:

$$qe = B\ln K_T + B\ln Ce \quad (3.15)$$

$$\text{Where } B = \frac{RT}{b} \quad (3.16)$$

Where K_T (L/mol) is Tempkin binding constant at equilibrium relating to the maximum binding energy; B (RT/b) is a constant related to the adsorption heat, b (Jg/Lmol) is the adsorption constant, R (8.314 J/mol K) is the gas constant and T (K) is the absolute temperature.

3.5.4 Dubinin-Radushkevich (R-D) Model

This isotherm in empirical form:

$$\ln q_e = \ln q_n - \beta\varepsilon^2 \quad (3.17)$$

Where β is a coefficient related to the mean free energy of adsorption per mol of the API (mol^2/J^2), $q_n$is the theoretical saturation capacity (mg/g) and ε is the Polanyi potential mathematically explained as:

$\varepsilon = RT\ln(1 + \frac{1}{Ce})$. Ce and qe are the API equilibrium concentration (mg/l) and equilibrium adsorption capacity (mg/g).

3.6Thermodynamics of the Adsorption Process

Change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) are thermodynamic parameters used to further elucidate the adsorption of API by the synthesized adsorbent. According to (Guerra et al., 2006), they can be calculated using the following formulas:

$$\Delta G = -RT\ln K \quad (3.18)$$

where K is the equilibrium constant obtained from each adsorption model, T the absolute temperature (K) and the universal gas constant $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}. K could also be calculated from the relation:

$$K = \frac{Ca}{Ce} = \frac{Co-Ce}{Ce} \quad (3.19)$$

K, ΔG, ΔH and ΔS are related according to Van't Hoff correlation (Yildiz et al., 2004) as follows:

$$\ln K = \frac{\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (3.20)$$

Thus when lnK is plotted against $\frac{1}{T}$, a straight line is obtained and the slope is equal to $\frac{-\Delta H}{R}$ while the intercept is equal to $\frac{\Delta S}{R}$. The enthalpy and entropy can then be calculated accordingly.

3.7Kinetics of the removal of the APIs by the activated plantain peel

Here, 50ml of the collected pharmaceutical wastewater was mixed with 0.1g of the adsorbent at constant temperature and neutral pH, for a contact time of 100, 150, 200, 250 and 300 minutes respectively. The decrease in the API concentration at the different stirring times was used in obtaining the data for the kinetic studies, according to equation 3.8. The fitness of the data obtained was tested into the following kinetic models in order to analyze the removal of removal of the APIs by the adsorbent.

3.7.1 First order kinetic model

First order kinetic model could be represented in linear form as $\ln C_t = \ln C_o - K_1 t$; which can be further simplified as:

$$\ln\frac{Ct}{Co} = -K_1 t \qquad (3.21)$$

Where C_t= Concentration of API at time, t, C_o= initial amount of API, t = stirring time (min) and K_1 = first order adsorption rate constant.

3.7.2 Pseudo-second order kinetic model

The linearized form of pseudo-second order model is presented in equation in equation 3.22:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \qquad (3.22)$$

Where q_e= equilibrium adsorption capacity (mg/g), q_t= instantaneous adsorption capacity (mg/g), t = stirring time in minutesand K_2= pseudo-second order adsorption constant (g/mgmin).

Parameters q_e and K_2 are obtained from the slope and intercept of the plot of $\frac{t}{qt}$ against t. Equation 3.22 shows that the rate of adsorption varies directly as the square of the number of empty positions (Hussein et al., 2019).

3.7.3 Elovich kinetic model

Initially, this model was specifically designed for gas adsorption on solid surfaces. However, it also provides a good fit for adsorption in solid-liquid phase or solid-solid adsorption (Folasegun and Kovo, 2014). Therefore, it is a unique second order kinetic model that studies adsorption in heterogeneous surfaces (Hussein et al., 2019). In straight line equation form, this model is expressed as (Wu et al., 2009):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (3.23)$$

Where α = initial adsorption rate constant (mg/min) at t = 0 while β is the extent of surface coverage and the activated energy.

3.7.4 Webber Morris kinetic model

This is also known as intra-particle diffusion kinetic model and it is often used in adsorption study (Das and Mondal, 2011). This model assumes that the intra-particle diffusion assay takes place as the solubized ions move from aqueous solutions to the adsorbent materials (Demiral and Gündözoğlu, 2010). The model can be presented in linear form as follows:

$$q_t = K_d t^{1/2} + l \qquad (3.24)$$

where K_d = intraparticle diffusion rate constant (mg/gmin$^{1/2}$), l = boundary layer effect mg/g, which is the intercept of the plot of $q_t$against $t^{1/2}$

IV. RESULTS AND DISCUSSION

4.1: Characterization of the plantain peel

Table 4.1: Proximate analysis of the raw and activated oil palm bunch

Parameters	Raw plantain peel	Activated plantain peel
Moisture content (%)	12.263	1.035
Volatile content	40.992	23.526
Ash content (%)	7.054	10.983
Fixed carbon	39.691	47.52
Lignin	10.869	26.645
Iodine content	20.533	42.216
pH	6.57	6.41

Table 4.1 is theresult of the proximate analysis carried out on the raw and activated plantain peel. A contrast analysis of raw and activated plantain peel using Table 4.1 shows a significant rise in fixed carbon content, lignin constituent, iodine value, ash content while properties such as moisture content and volatile matter decrease remarkably after chemical activation using the acetic acid. The significant increase in fixed carbon and lignin contents is a portent evidence of high adsorptive capacity of plantain peel(Thoe et al., 2019; Nick et al., 2021).The pH, which is in acidic range slightly changed. This result is in agreement with the outcomes of literatures on carbonization and acid activation of waste biomass.Moreover, the decline in volatile matter due to the thermal activation of the agro-based biomass causes an upset in the molecular structure of the biomass leading increases in surface pores and fixed carbon content(Omar, 2012). Thus, at high temperatures of the carbonization and activation process, some of the volatile particles must have escaped from the treated plantain peel, causing a significant decrease in volatile matter. High iodine value means high degree of unsaturation, which is a lucid suggestion of an improve in chemical reactivity.

4.2 AAS Characterization Results

Table 4.2: AAS analysis ofthe APIs in the pharmaceutical wastewater

APIs	Am(ppm)	Ib(ppm)	Ac(ppm)	Par(ppm)
Amount	501.2	515.6	189.5	209.1
% Composition	35.4	36.4	13.4	14.8

AAS is a very sensitive analytical technique, which could detect tiny quantities up to parts per billion. The different APIs present in the collected pharmaceutical wastewater sample were revealed by the Atomic Absorption Spectrometry (AAS). The most prominent APIs revealed by Table 4.1 are Amoxicillin and Ibuprofen. Hence the need to mitigate them before discarding the pharmaceutical wastewater sample to avoid possible land and water pollution.Accumulation of these two common APIs in Nigeria through the pharmaceutical discharges containing them poses serious ill-health both land and aquatic organisms.

4.3 Fourier Transform Infra-Red Spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy was carried out on raw and activated plantain peels. The plots obtained areFigures 4.1 and 4.2.The spectra in Figures 4.1 and 4.2 are interpreted in Tables A1 andA2 in the appendix A.

4.3.1 FTIR spectrum of raw plantain peel

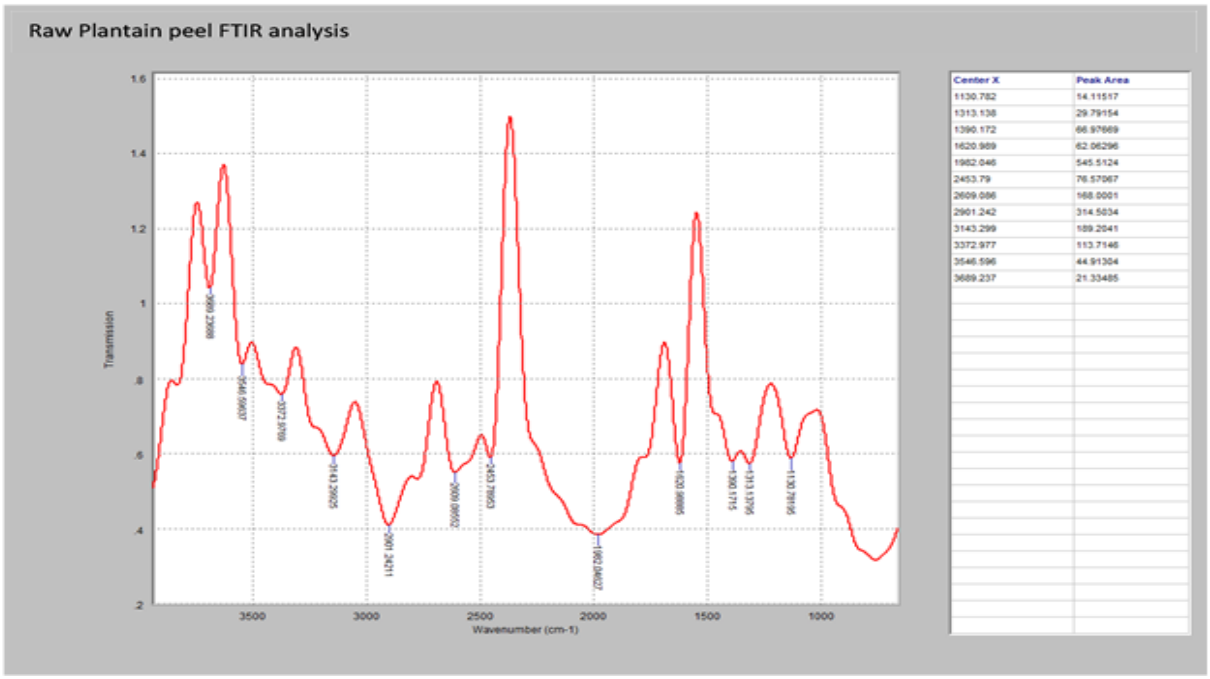

Figure 4.1: FTIR of raw plantain peel

4.3.2 FTIR spectrum of activated plantain peel

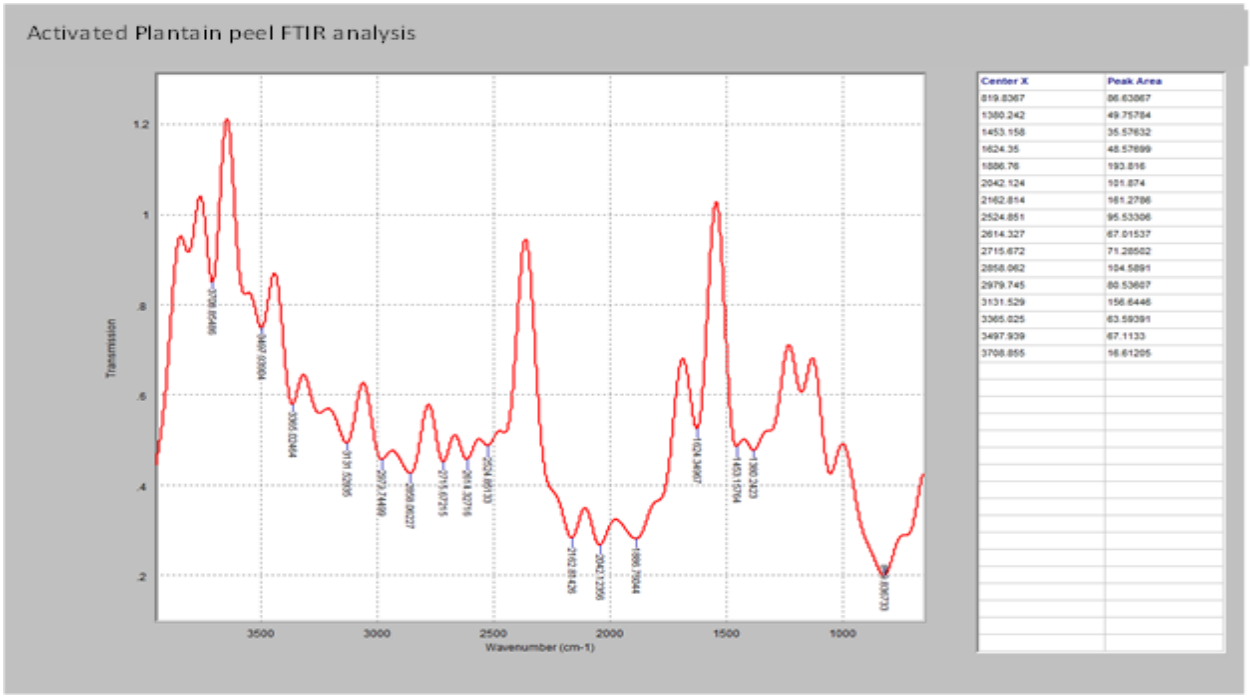

Figure 4.2: FTIR of activated plantain peel

In both Figures 4.1 and 4.2, the single bond areas are contained in peaks 2500-4000 cm^{-1}, while the sharp bond at about 3500cm^{-1}, suggested the presence of oxygen-related bonding. The narrow band at less than 3000cm^{-1}in Figure 4.1 corresponds to C-C bond, however the weak band at less than 3000cm^{-1}in Figure 4.2 represents the O-H bond. Also in Figure 4.1, no specific peak for aldehyde was found between 2700 and 2800 cm^{-1}. Further explanation using Tables A1 and A2 in the appendix A revealed high degree of unsaturation in the activated sample. Thus, the tendency to react with the adsorbate increases after chemical activation.

4.5 Effect of Process Conditions on the Adsorption Process

The influence of changes in process conditions such asstirring time, temperature and adsorbentdosage on the removal efficiency and adsorption capacity of the activated plantain peel was investigated. The adsorption capacity was determined using equation 3.7while equation 3.10 was responsible for determining the removal efficiency.

4.5.1: Effect of stirringtime on adsorption capacity and removal efficiency

Howagitation time affects the rate of removal of the unwanted pharmaceutical particles from the sample wastewater under study was determined by intermittent checking of the agitation time of the mixture of the wastewater sample and the activated plantain peel at 15mins interval as shown in Tables B1 and B2 in appendix B. Figures 4.3 and 4.4 have more to enlighten:

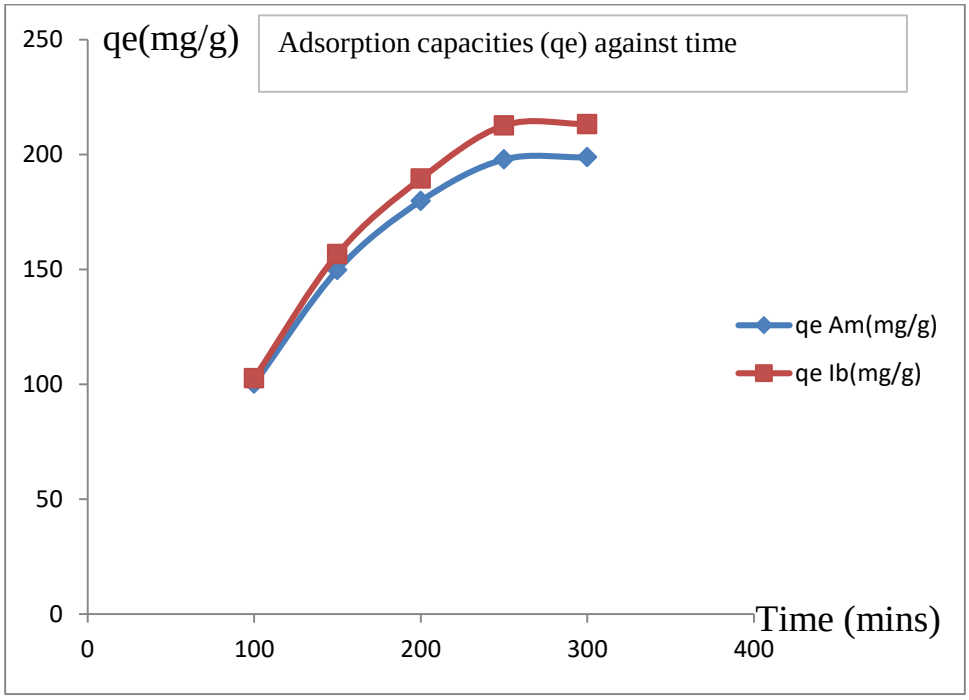

Fig 4.3: Adsorption capacity against stirring time during APIs removal

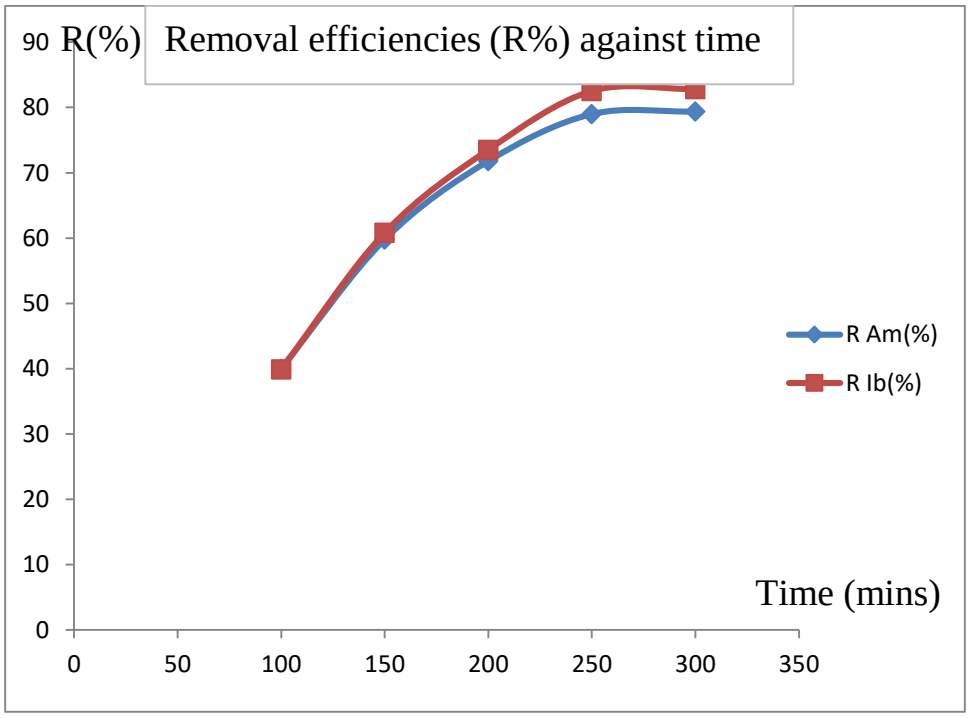

Fig 4.4: Removal efficiency against stirring time during APIs removal

Figures 4.3 and 4.4 represent the adsorption capacity and removal efficiency of the prepared biomass adsorbent during APIs purging. The red curves represent Ibuprofen removal while the Amoxicillin removal is represented by the blue curves. It can be visibly seen from the Figures that the impact of time on the adsorption capacity and removal efficiency of the adsorbent is very positive. Eachof the curves in the above diagrams rises with time. When the mixture of the pharmaceutical wastewater sample and the synthesized adsorbent has sufficient time to mix, the adsorption capacity and hence the removal efficiency will increase because sufficient time is allotted for the diffusion of the unwanted active pharmaceutical materials into the vacant pores of the activated plantain peel sample. However, equilibrium was attained after 250minutes; hence the curves became somewhat flat and afterward started bending inwards slowly. Equilibrium is attained after 250minutes because almost all the void pores have been occupied by the adsorbed impurities. In comparison of the rate of removal of the Amoxicillin with the rate of removal of Ibuprofen, it could be inferred that Ibuprofen removal, represented by the red curve has higher purge rateas evidenced by the higher curve in both the adsorption capacity and removal efficiency plots. The higher purge rate of Ibuprofen by the activated biomass could signify its affinity with the adsorbent is higher. Another factor contributing to the higher intake of the Ibuprofen particles by the adsorbent could be traced to the fact that its initial amount (C_o) is higher.

4.5.2 Effect of temperature on adsorption capacity and removal efficiency

The increase in the average kinetic energy of the participating particles at elevated temperatures is the reason behind its positive effect on reaction rate of most reactions.

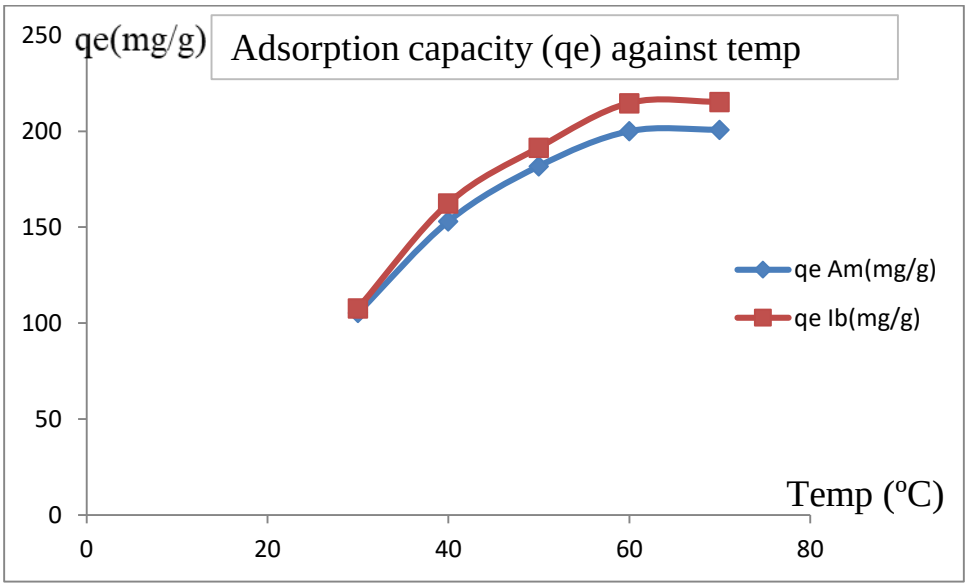

Fig 4.5: Adsorption capacity against temperature during APIs removal

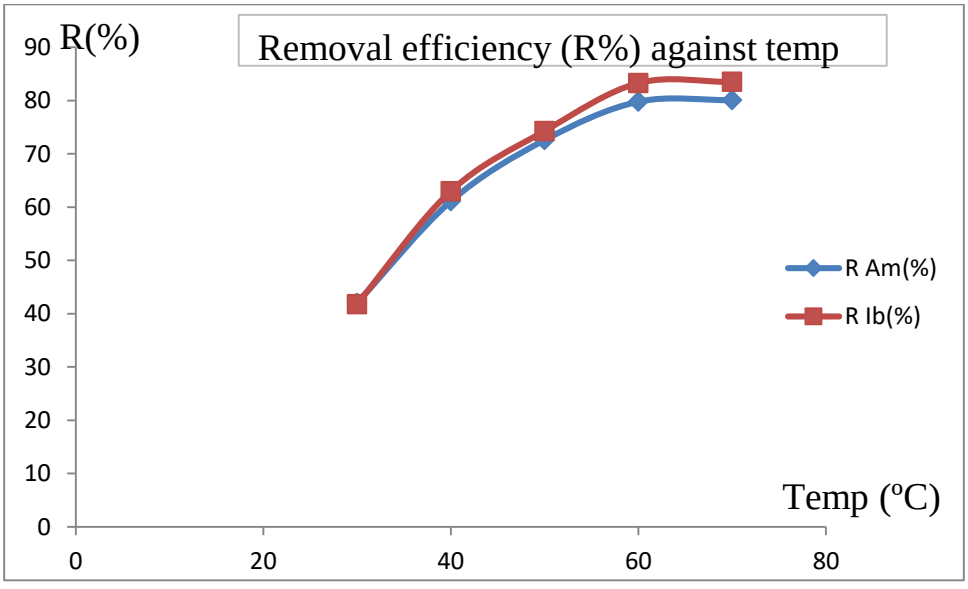

Fig 4.6: Removal efficiency against temperature during APIs removal

The notion that most reactionstake place spontaneously at elevated temperatures is evidenced inFigures 4.5 and 4.6. The removal of APIs impurities (Amoxicillin and Ibuprofen) occurs faster at high temperatures because of the increase in the spontaneity of mixing between the adsorbate (APIs impurities) and adsorbent particles, thereby causing more molecules of the adsorbate to diffuse quickly and fill up the void spaces in the adsorbent surface. According to Mnasri-Ghnimi and Frini-Srasra (2019), the number of pores in the adsorbent could be increased by elevating temperature. Diffusion rate increases when the temperature of the reaction increases because even the less energetic molecules acquire sufficient to participate in the reaction. And as the mixing of target impurities and the activated plantain peel particles occur faster, then the tendency for the impurities to penetrate the available micro and macro pores of the adsorbate increases. Thus, speeding up the rate of adsorption of the impurities by the activated plantain peels.Similar observation was made in the removal of oil layer from surface water using plantain pseudo stem fiber by Asadu et al. (2022).

The plots also revealed that the adsorption of Ibuprofen (represented by in red) is faster than the removal of the Amoxicillin by the same adsorbent at the same conditions. Again, the reason could be same as given in section 4.5.1.

4.5.3 Effect of dosage on adsorption capacity and removal efficiency

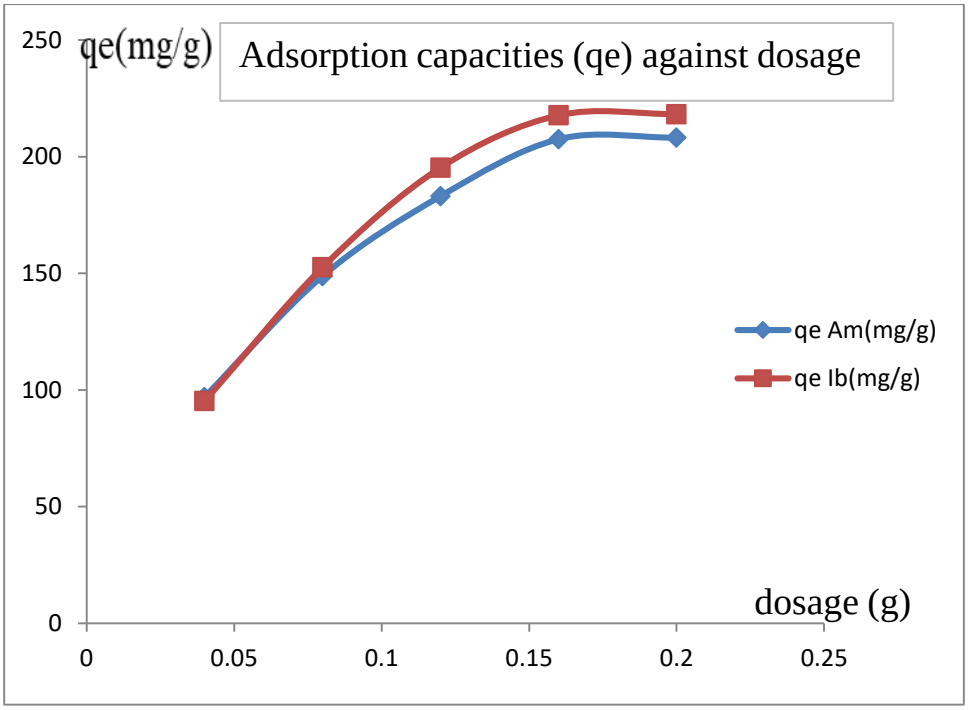

Fig 4.7: Adsorption capacity against adsorbent dosage during APIs removal

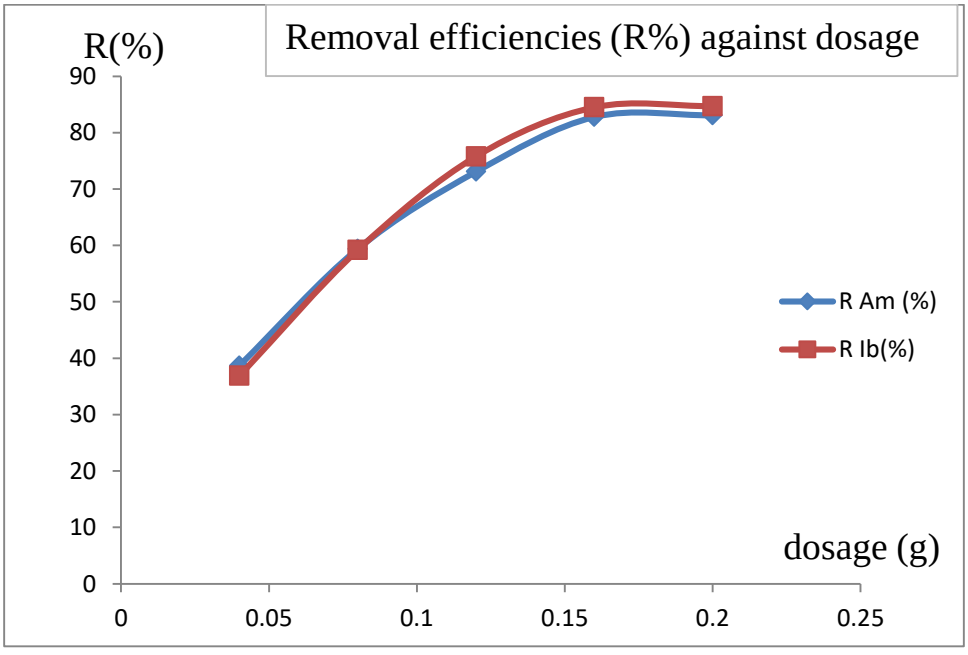

Fig 4.8: Removal efficiency against adsorbent dosage during APIs removal

The effect of adsorbent dosage on the adsorption capacity of the adsorbent is represented in Figure 4.7 while the impurity removal efficiency of the adsorbent is plotted against adsorbent dosage in Figure 4.8. In both plots, the adsorption capacity and the removal efficiency respond positively to increase in the adsorbent dosage. The removal of unwanted pharmaceutical ingredients is as a result of their accumulation on the vacant openings on the interstitial surface of the adsorbent.These interstitial surfaces are bound to increase as the amount of adsorbents available for the adsorption increases. Therefore, it could right to deduce that dosage of the adsorbent is the most pertinent factor since it determines the availability of sorption sites for the target impurity removal. Adequate temperature and stirring time enhances the reaction between adsorbent and the impurities to be removed. It is therefore important to maintain optimum temperature and agitation time to obtain the best result.The surge in the removal of APIs (Amoxicillin and Ibuprofen) at higher dosage of the activated plantain peel is because at sufficient dosage of the adsorbents, the target impurities easily accumulate on the vacant pores of the adsorbent for easy removal (Saeed et al., 2005) because of the availability of copious void spaces. It is evident from Figures 4.7 and 4.8 that Ibuprofen is easily adsorbed for removal than Amoxicillin.

4.6 ADSORPTION ISOTHERMS AND EQUILIBRIUM STUDIES

A sound knowledge of adsorption isotherm is crucial to formulating a good system (Rajeshkannan et al., 2011).The validity of the impurity removal using adsorption technology is tested by fitting the experiment into the under-listed models:

4.6.1 The Langmuir Isotherm Model:

Equation 3.12 was used to model the adsorption experiment into the Langmuir model. Tables D1 and D2 in the appendix D are the parameters used to plot Langmuir model plots (Figures 4.22 and 4.23) for the removal of Amoxicillin and Ibuprofen respectively.

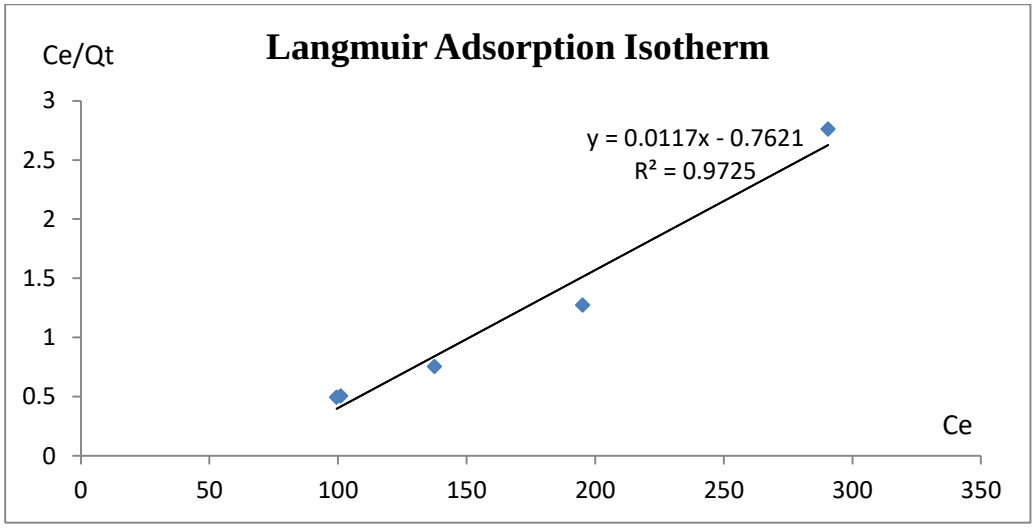

Fig 4.22: Langmuir isotherm for Amoxicillin adsorption

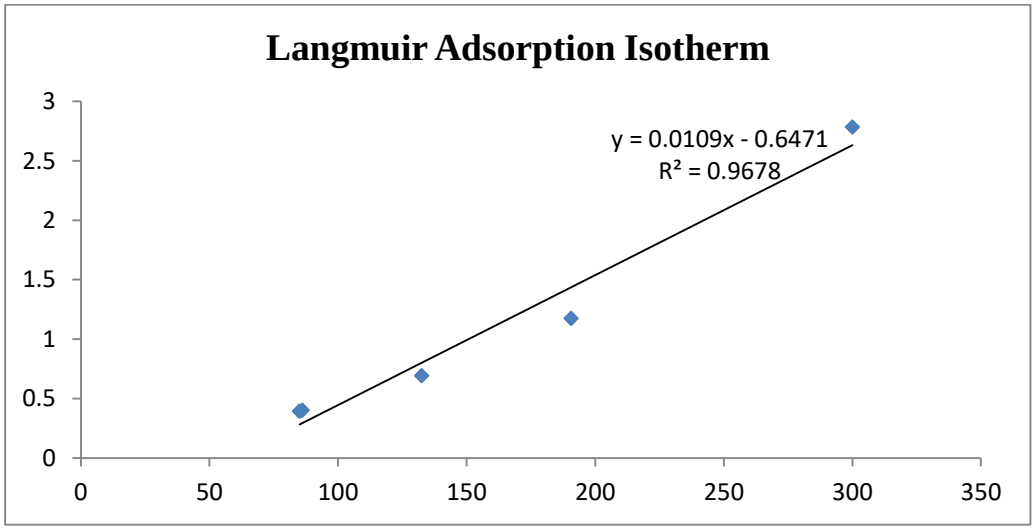

Fig 4.23: Langmuir isotherm for Ibuprofen adsorption

Plots obtained in Figures 4.22 and 4.23 are linear and the R^2 values of 0.9725 and 0.9678 for the removal of Amoxicillin and Ibuprofen using the activated plantain peel biomass are still close to unity. These are acceptable signs of fitness of the experiment into standard Langmuir empirical model. Equation 3.13 was used to calculate the separation factor (R_L); the values obtained indicate favourable adsorption because they are greater than zero ($R_L > 0$). The calculated parameters includingLangmuir equilibrium constant (K_{ads}) are presented in Table 4.8.

4.6.2 The Freundlich Isotherm Model

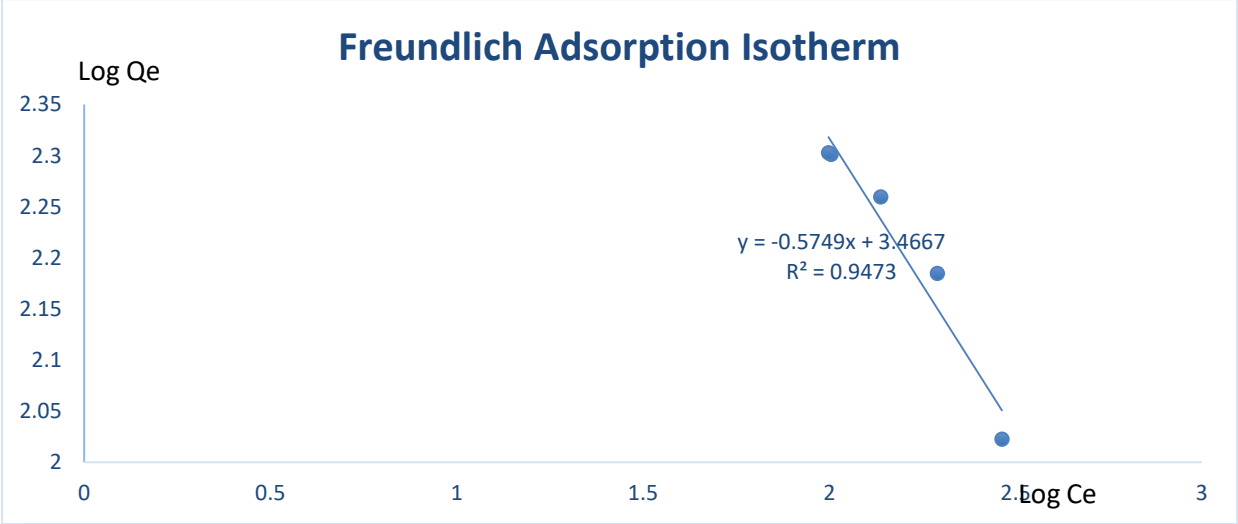

Fig 4.24: Freundlich isotherm for Amoxicillin adsorption

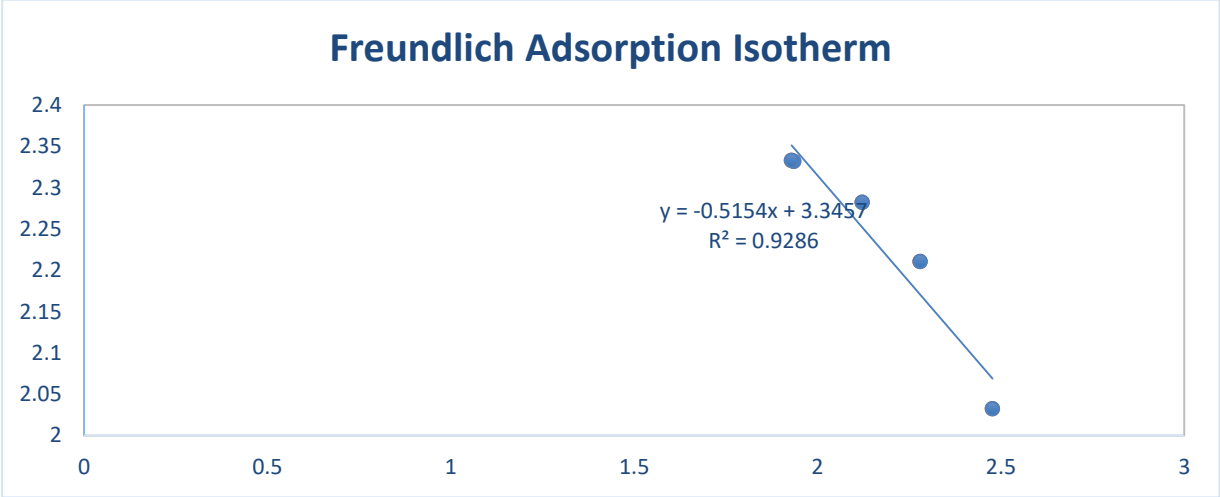

Fig 4.25:Freundlich isotherm for Ibuprofen adsorption

Figures 4.24 and 4.25 are the Freundlich isotherm plots obtained using equation 3.14 for the removal of Amoxicillin and Ibuprofen respectively. The data for plotting the diagrams are found in Tables D3 and D4 in appendix D while the important parameters from the graphs, such as Freundlich constant, K_f, n and R^2 are also tabulated in Table 4.8. Since n values greater than one but less than ten are desirable (Ladhe et al., 2011; Rabiu&MunjurHasan, 2014), it follows that n values of 1.74 and 1.94 for Amoxicillin and Ibuprofen removal by adsorptive measures are desirable. Furthermore, R^2 values (0.9473 and 0.9286) show congeniality of this study with this model.

4.6.3 The Temkin Isotherm Model

Equation 3.15 was used to model this experimental study into Temkin adsorption isotherm and the plots obtained are displayed in Figures 4.26 and 4.27 for Amoxicillin and Ibuprofen removal respectively.

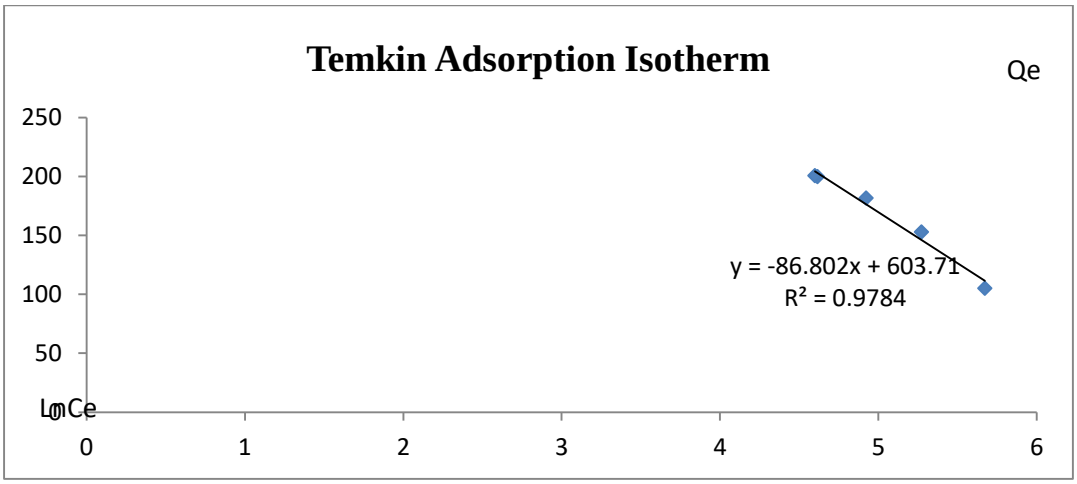

Fig 4.26: Temkin isotherm for Amoxicillin adsorption

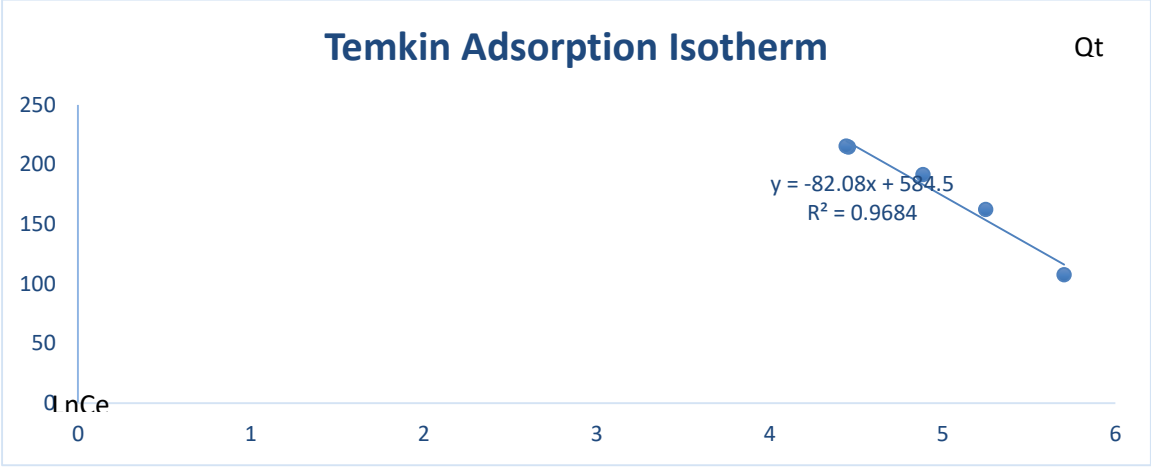

Fig 4.27: Temkin isotherm for Ibuprofen adsorption

The plots are linear and the R^2 values are close enough to one (1); suggesting fitness of the removal of the APIs by adsorption into Temkin model. Thus, Temkin equation model explicably described the process. R^2 values and other important parameters obtained from Temkin's graphs could be found in Table 4.8.

4.6.4 The Dubinin-Radushkevich (R-D) Isotherm Model

The experimental study was modelled into Dubinin-Radushkevich model using equation 3.17. Figures 428 and 4.29 are the plots obtained from Table D7 and D8 in the appendix D.

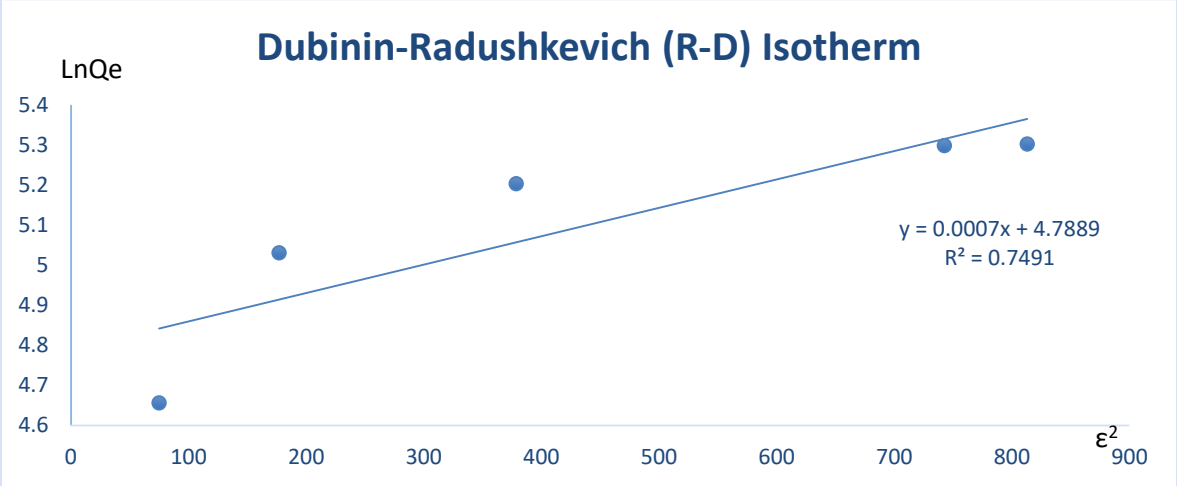

Fig 4.28: Dubinin-Radushkevich (R-D) isotherm for Amoxicillin adsorption

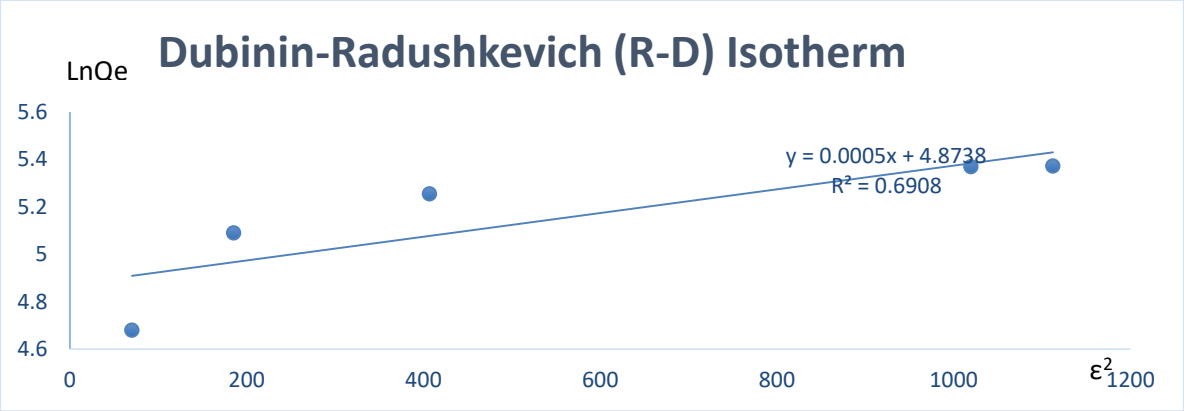

Fig 4.29: Dubinin-Radushkevich (R-D) isotherm for Ibuprofen adsorption

The low R^2 values of 0.7491 and 0.6908 for Amoxicillin and Ibuprofen adsorption by the activated plantain peel suggest that this model is the least fitting adsorption model amongst others for this experimental process. The values of the coefficient of determination and other important parameters from this model graphs are found in Table 4.

Table 4.8: Adsorption isotherm parameters

Langmuir Isotherms	Units	Am	Ib
Kl	l/mg	0.015	0.017
Q	mg/g	85.5	91.7
R^2		0.9725	0.9678
R_L		0.12	0.10
Freundlich			
K_f		2929	2217
n		1.74	1.94
R^2		0.9473	0.9286
Temkin			

B		-86.80	-82.08
K_T		0.00095	0.0008
R^2		0.9784	0.9684
Dubinin-Radushkevich			
B		-0.0007	-0.0005
q_n		120.2	130.8
R^2		0.7491	0.6908

According to data available in Table 4.8, it could be glanced that based on regression coefficients (R^2 values), Temkin's model is the most fitting for describing the removal of the target APIs impurities using activated plantain peel biomass. Langmuir model followed then Freundlich and finally Dubinin-Radushkevich, which is the least fitting model. The closer R^2 values of any given model are to unity, the more likely the model is useful in describing the experimental study. Thus the criteria for choosing Temkin model as the best model is because it has the highest R^2 values for both Amoxicillin removal and Ibuprofen removal.

4.7. Adsorption Kinetics

The efficiency of adsorption could be determined by adsorption kinetics (Arivori et al., 2009). Equations 3.21 to 3.24, which are the equations for four different kinetic models, wereemployed to generate Figures 4.32 to 4.39. Table 4.12 contains the kinetic constants, R^2 values and other important parameters from the plots.

4.7.1 First Order Kinetic Model

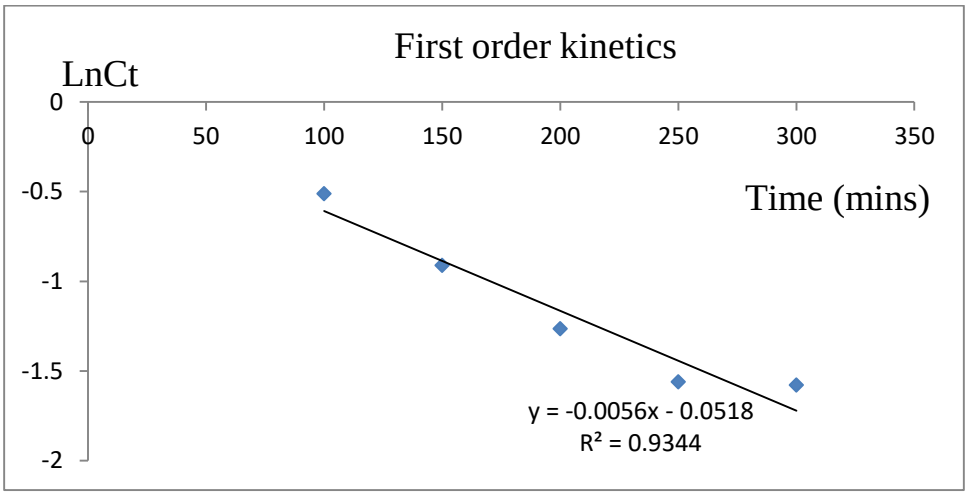

Figure 4.32: First order kinetics for Amoxicillin adsorption

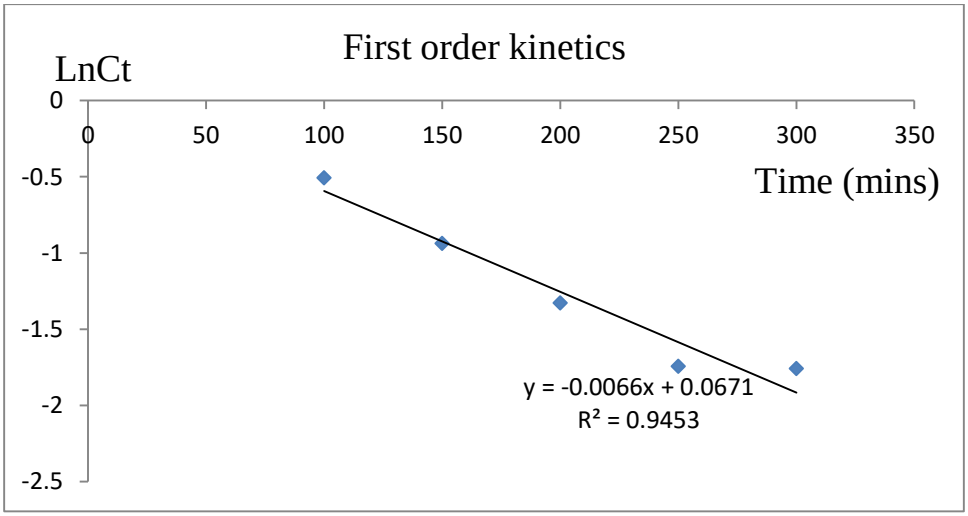

Figure 4.33: First order kinetics for Ibuprofen adsorption

R^2 values of the first order empirical model graphs shown above are desirable and evidences of good fit in describing the purging of the Amoxicillin and Ibuprofen from the pharmaceutical wastewater, because of their proximity to one. The first order rate constants, calculated from the slope of the plots, alongside R^2 values are presented in Table 4.12

4.7.2 Pseudo-second Order Kinetic Model

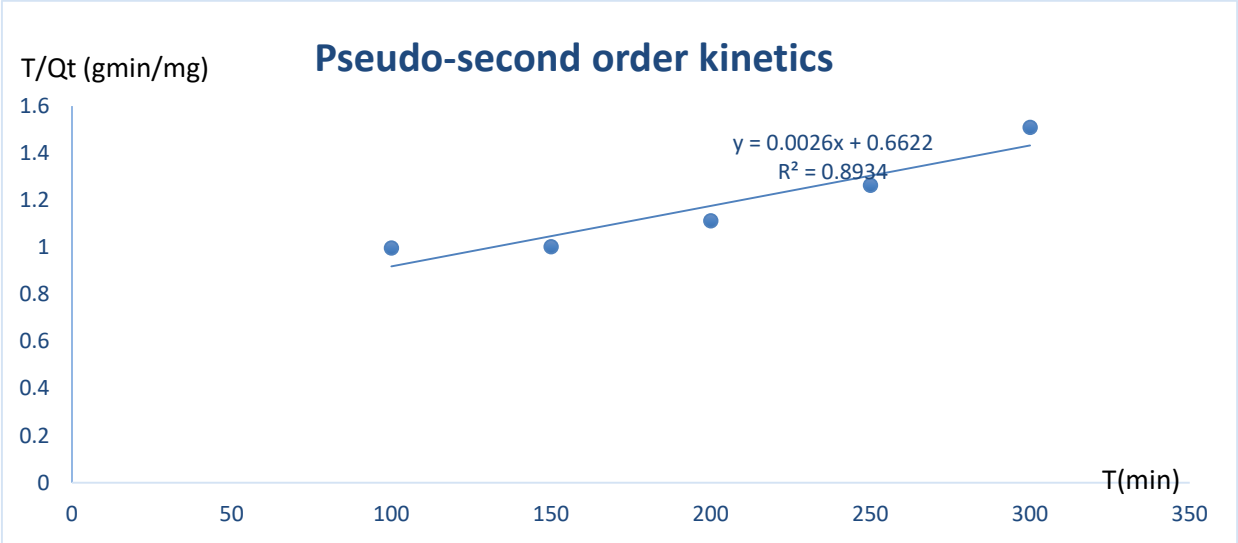

Figure 4.34: Pseudo-second order kinetics for Amoxicillin adsorption

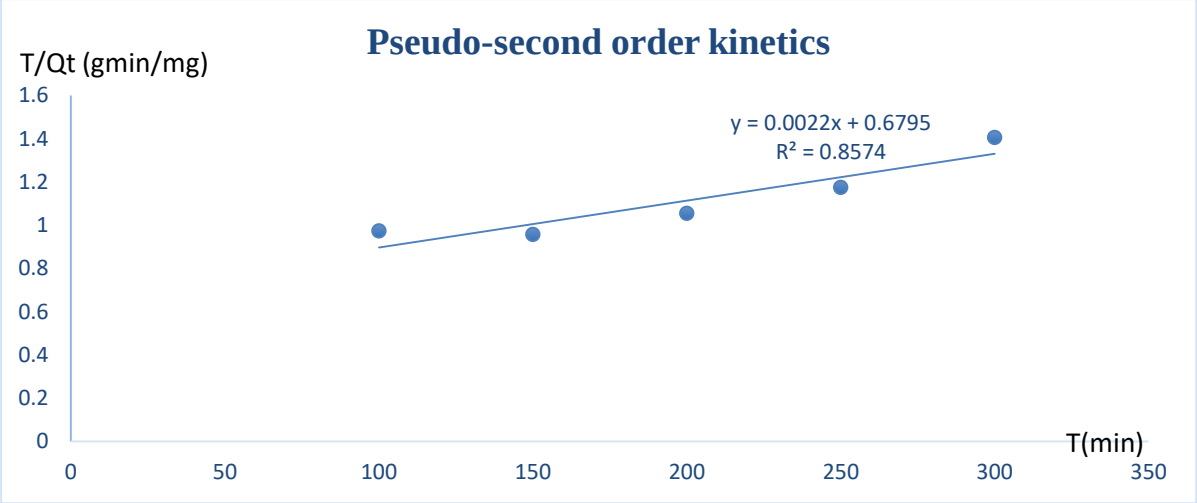

Figure 4.35: Pseudo-second order kinetics for Ibuprofen adsorption

Figures 4.34 and 4.35 represent the pseudo-second order kinetic model for describing the removal of Amoxicillin and Ibuprofen molecules from the wastewater sample using activated plantain peel. The values of the R^2 also reveal that the adsorption process fits into this kinetic model. The equilibrium adsorption capacity calculated is high. The calculated adsorption capacity, the pseudo-second orderrate constant and R^2 values can be found in Table 4.12.

4.7.3 Elovich Kinetic Model

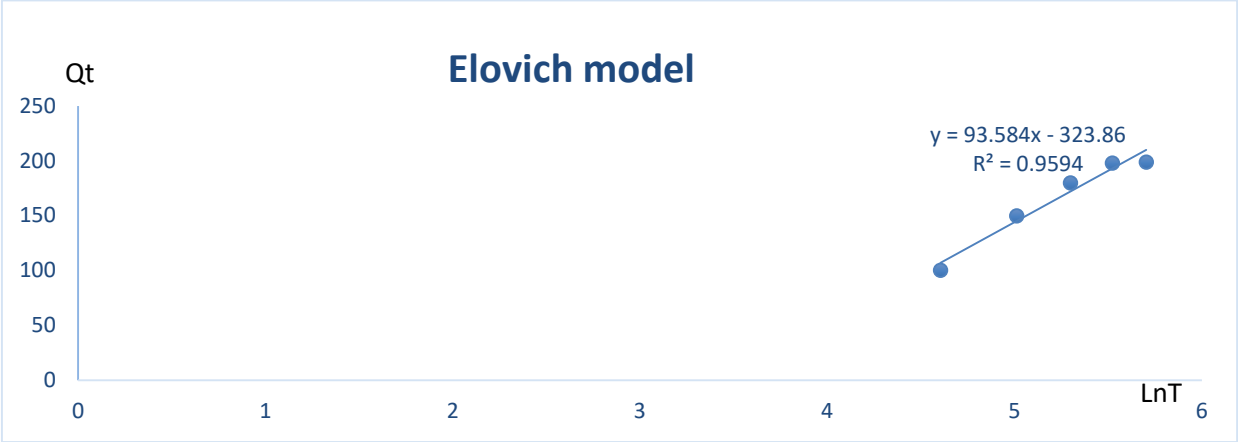

Figure 4.36: Elovich model for Amoxicillin adsorption

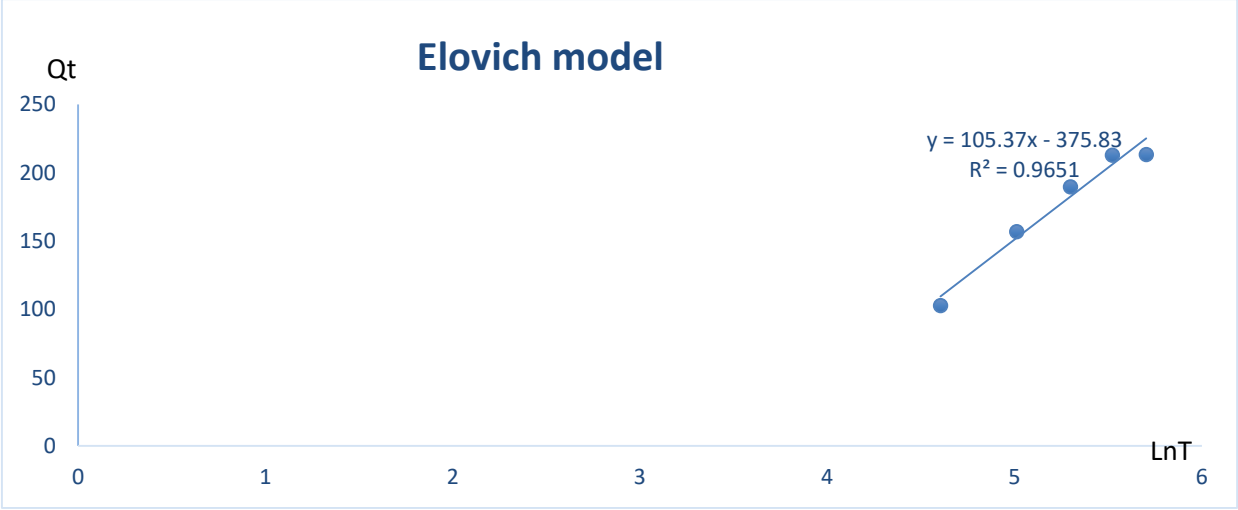

Figure 4.37: Elovich model for Ibuprofen adsorption

The high values of the regression coefficient (R^2) values portray the degree of fitness of this experiment into this adsorption kinetic. The fitness of this model in describing the adsorption experiment is also an indication that the adsorption process can occur in heterogeneous surface since this model is unique for describing adsorption studies in a heterogeneous surface (Hussein et al., 2019).

The R^2values as well as other pertinentElovich model constants, such as α, β, calculated from the slope and intercept of each graph are also found in Table 4.12.

4.7.4 Webber Morris Kinetic Model

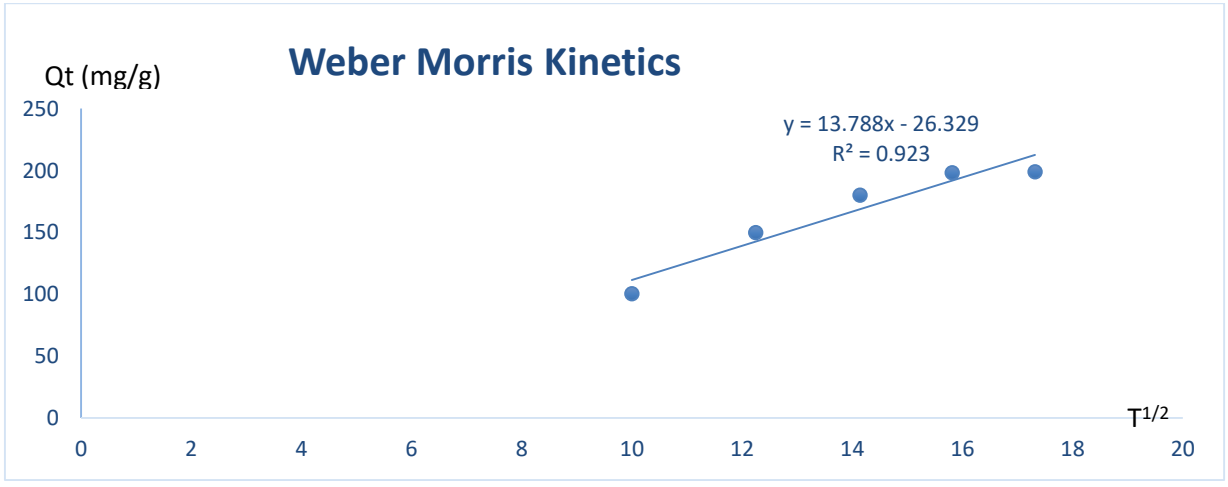

Figure 4.38: Weber Morris Kinetics for Amoxicillin adsorption

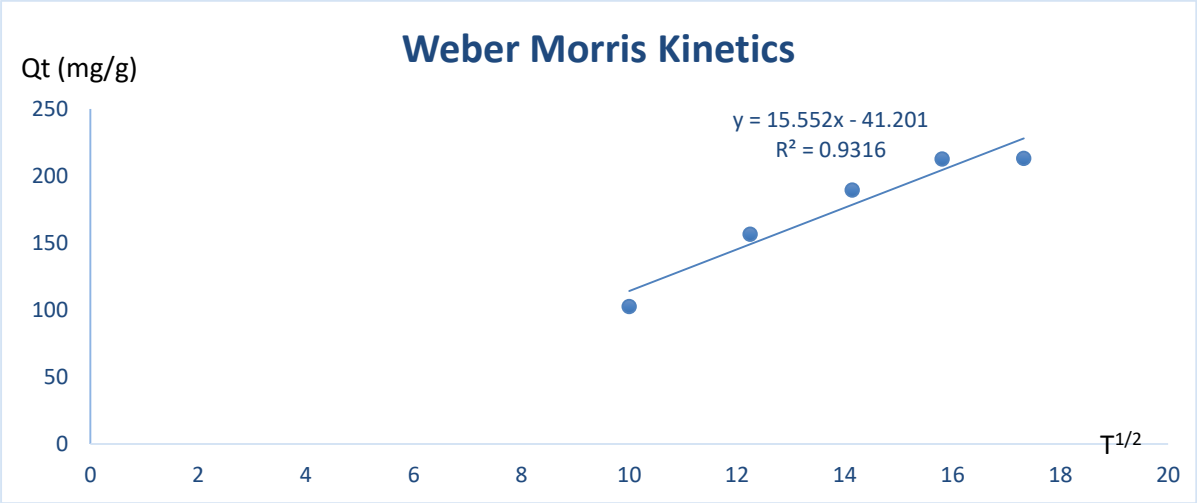

Figure 4.39: Weber Morris Kinetics for Ibuprofen adsorption

Another nomenclature for this kinetic model is intra-particle diffusion kinetic model .This model has higher regression coefficient (R^2) values than pseudo-second order kinetic models, suggesting it is very suitable for describing the removal of the APIs by adsorption.

Table 4.12: Adsorption kinetics parameters

First order	Units	Am	Ib
K_1	Min^{-1}	0.0056	0.0066
R^2		0.9344	0.9453
Pseudo-second order			
K_2	g/mgmin	0.0000102	0.0000071
$q_{e\ calculated}$	mg/g	384.6	454.5
R^2		0.8934	0.8574
Elovich model			
A	Mg/gmin	2.935	2.973
B	gmin/mg	0.0107	0.0095
R^2		0.9594	0.9651
Weber Morris model			
K_d	$mg/gmin^{1/2}$	13.788	15.552
L	mg/g	-26.329	-41.201
R^2		0.923	0.9316

It could be inferred from the data in Table 4.12 that based on R^2 values, Elovich is the most fitting model, followed by first order and Weber morris kinetic models.

V. CONCLUSIONS, RECOMMENDATIONS AND CONTRIBUTIONS TO KNOWLEDGE

5.1 Conclusions

Activated plantain peel has good adsorbent potential for removal of active pharmaceutical particles based on the proximate analysis carried out.

Thesurface morphological study of raw and activated plantain peel revealed significant surge in the number of interstitial pores after chemical activated with acetic acid. The high number of vacant openings enables easy removal of the carcinogenic ingredients because of available spaces for the accumulation of the impurities.

While the removal of the APIs with the activated plantain peels using adsorption measures followed the four adsorption isotherms discussed in this review, Temkin followed by Langmuir proved to be the most fits. Furthermore, the adsorption kinetics studied by modeling into four different kinetic models revealed that Elovichmodel is the most fitting kinetic model.

The effects of the process parameters analyzed revealed that positive increase in any of the factors leads to corresponding increase in the rate of removal of the impurities until equilibrium is reached. The optimization of the process conditions using RSM revealed buttressed their significance to the response of the experiment, that is, the removal efficiency of the adsorbent. The predicted removal efficiencies showed excellent relationship with the actual removal efficiencies obtained at the same suggested probable conditions.

5.2 Recommendations

Though active pharmaceutical ingredients are the most important substances in every drug, their presence in wastewater is not welcome because of plausible environmental hazard. Many important analyses were successfully carried out in this study to prove that activated plantain peels have good adsorbent properties to remove Amoxicillin and Ibuprofen from pharmaceutical wastewater. However, there are certain areas the researcher thinks serious work must be done in the future to improve the overall standard of the process. They include:

1) Development of more effective technologies to recover tiny particles of the used adsorbent after treatment. It is observed that filtration process carried at the end of the treatment process is not enough to remove all the adsorbent particles because some are very minute.
2) Nigeria government ought to develop proper wastewater management techniques and teams, which should be proactive in carrying out their duties. Strict guidelines must be laid out for every pharmaceutical industry before giving them license to operate and commensurate penalties must be meted out for failures.

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